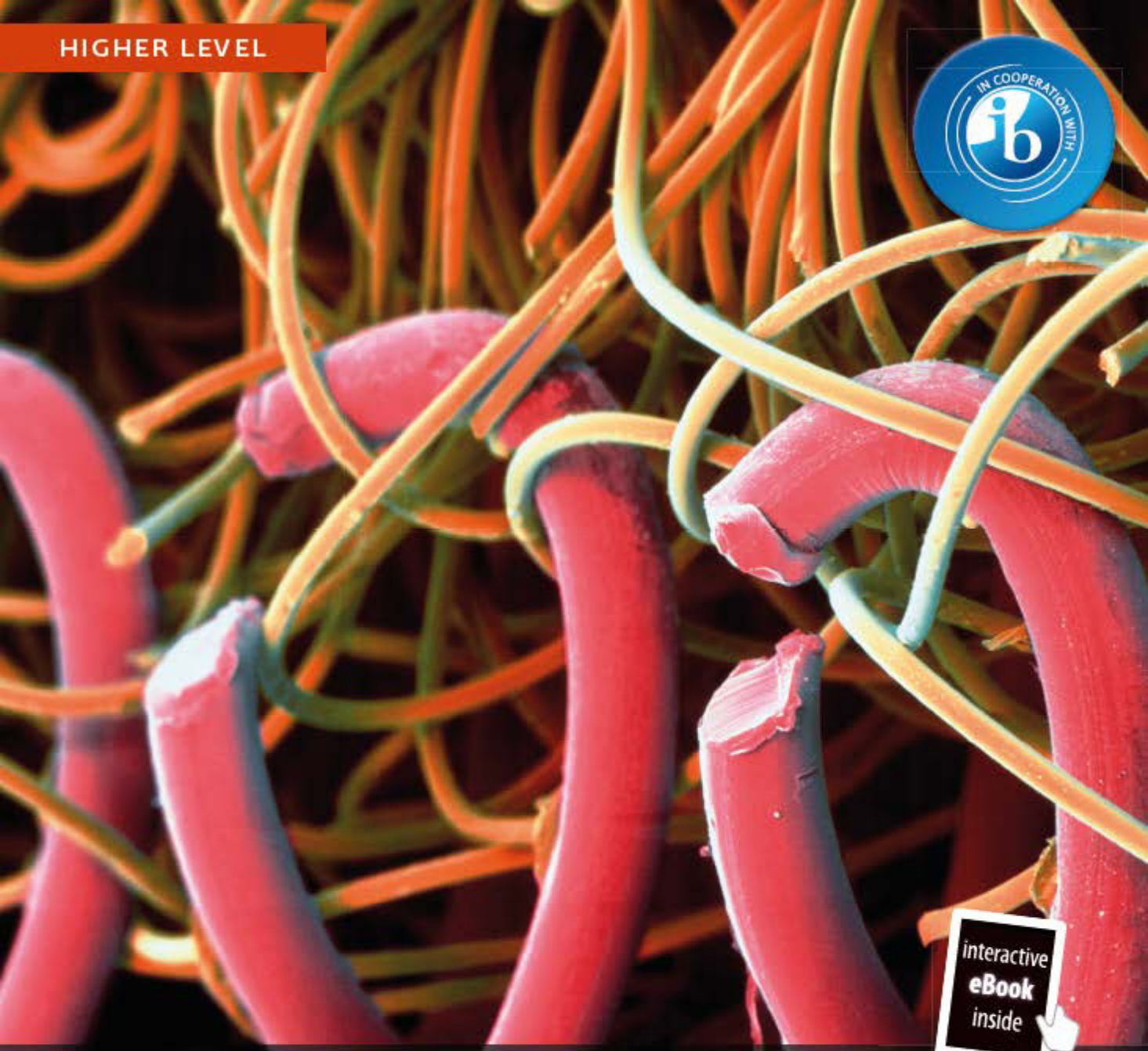
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Chemistry

for the IB Diploma Programme

3rd Edition

CATRIN BROWN
MIKE FORD
OLIVER CANNING
ANDREAS ECONOMOU
GARTH IRWIN

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eBook code inside back cover

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.01						Atomic number Element Relative atomic mass											2 He 4.00
2	3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.96	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
6	55 Cs 132.91	56 Ba 137.33	57 La † 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.20	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89 Ac ‡ (227)	104 Rf (267)	105 Db (268)	106 Sg (269)	107 Bh (270)	108 Hs (269)	109 Mt (278)	110 Ds (281)	111 Rg (281)	112 Cn (285)	113 Nh (286)	114 Fl (289)	115 Mc (288)	116 Lv (293)	117 Ts (294)	118 Og (294)

†	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97
‡	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

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Chemistry

for the IB Diploma Programme

Catrin Brown, Mike Ford,
Oliver Canning, Andreas Economou and Garth Irwin

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Syllabus roadmap

The aim of the syllabus is to integrate concepts, topic content and the Nature of Science through inquiry. Students and teachers are encouraged to personalize their approach to the syllabus according to their circumstances and interests.

Skills in the study of chemistry			
Structure **Structure refers to the nature of matter from simple to more complex forms**		**Reactivity** **Reactivity refers to how and why chemical reactions occur**	
Structure determines reactivity, which in turn transforms structure			
Structure 1 **Models of the particulate nature of matter**	Structure 1.1 – Introduction to the particulate nature of matter	**Reactivity 1** **What drives chemical reactions?**	Reactivity 1.1 – Measuring enthalpy changes
	Structure 1.2 – The nuclear atom		Reactivity 1.2 – Energy cycles in reactions
	Structure 1.3 – Electron configurations		Reactivity 1.3 – Energy from fuels
	Structure 1.4 – Counting particles by mass: The mole		Reactivity 1.4 – Entropy and spontaneity (Additional higher level)
	Structure 1.5 – Ideal gases		
Structure 2 **Models of bonding and structure**	Structure 2.1 – The ionic model	**Reactivity 2** **How much, how fast and how far?**	Reactivity 2.1 – How much? The amount of chemical change
	Structure 2.2 – The covalent model		Reactivity 2.2 – How fast? The rate of chemical change
	Structure 2.3 – The metallic model		Reactivity 2.3 – How far? The extent of chemical change
	Structure 2.4 – From models to materials		
Structure 3 **Classification of matter**	Structure 3.1 – The periodic table: Classification of elements	**Reactivity 3** **What are the mechanisms of chemical change?**	Reactivity 3.1 – Proton transfer reactions
	Structure 3.2 – Functional groups: Classification of organic compounds		Reactivity 3.2 – Electron transfer reactions
			Reactivity 3.3 – Electron sharing reactions
			Reactivity 3.4 – Electron-pair sharing reactions

Authors' introduction to the third edition

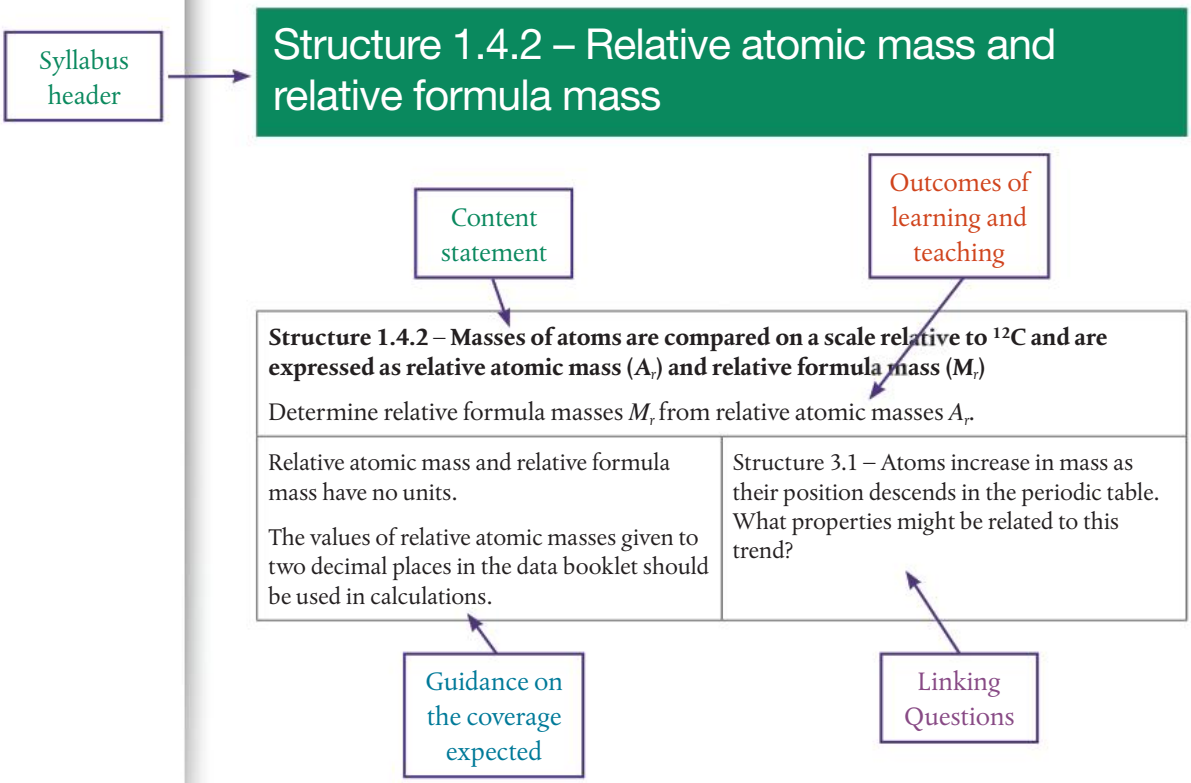
Welcome to your study of IB Diploma Programme chemistry. This is the third edition of Pearson's highly successful Higher Level (HL) chemistry book, first published in 2009. It has been completely rewritten to match the specifications of the new IB chemistry curriculum for first assessments in 2025 and gives thorough coverage of the entire course content. While there is much new and updated material, we have kept and refined the features that made the previous editions so successful. We are delighted to share our enthusiasm for learning chemistry in the IB programme with you!

Content

This book covers the entire HL course. It is divided into the two main themes, **Structure** and **Reactivity**, which in turn are divided into six topics, Structure 1–3 and Reactivity 1–3. Separate chapters cover each sub-topic within each topic. For example, the Structure 1.1 chapter deals with 'Introduction to the particulate nature of matter'.

The syllabus is presented as a sequence of numbered Understandings, which are shown as three-part boxes. We have given the relevant Understanding from the subject guide at the start of each section within a chapter under a brief header. The Table of Contents shows the full list of these Understanding headers, so you can see what is covered in each chapter.

For example:



The Understandings are presented in the same sequence as in the subject guide, so that common Standard Level (SL) and HL content is covered first, followed by HL only material. The transition from SL to HL content is shown by icons as follows.

HL

Individual icons to identify HL material such as exercises and practice questions can also be found throughout the book.

The text covers the course content using plain language, with all scientific terms explained and shown in bold as they are first introduced. It follows SI notation, and IUPAC nomenclature and definitions throughout. We have been careful also to apply the same terminology you will see in IB examinations in all worked examples and questions.

Conceptual approach

The syllabus emphasizes a conceptual approach, where the two main themes of chemistry, Structure and Reactivity, are shown to be interdependent. There is no suggested sequence for the coverage of the topics, and many different routes through the syllabus are possible. What is important though, is that the relationships between the different topics are recognized, which leads to an increasing depth of understanding.

There are two features, **Guiding Questions** and **Linking Questions**, which are incorporated into each topic in the syllabus. These are designed to help promote the conceptual approach, and we have emphasized them in the text as follows.

Guiding Question



Guiding Question

How do the nuclei of atoms differ?

Each chapter starts with the Guiding Question for the sub-topic from the IB chemistry subject guide. This is followed by a brief consideration of the question itself, which sets the context for the topic and how it relates to your previous knowledge. It is expected that by the end of the chapter you will be able to answer the Guiding Question more fully.

Guiding Question revisited



Guiding Question revisited

How do we quantify matter on the atomic scale?

At the end of each chapter, the Guiding Question is revisited, and can now be answered with significantly more detail and understanding. It is presented as a bulleted list of the material covered, that may help serve as a checklist of your learning at the end of each chapter. The Guiding Question revisited bulleted lists are available as downloadable PDFs from the eBook to help you with revision.

Reactivity 3.2 – How can oxidation states be used to analyze redox reactions?

Linking Questions

Linking Questions are given in many of the Understandings. Linking Questions have a number which indicates a link from the current chapter to another sub-topic, to Tools or to the Nature of Science (NOS). These questions are designed as prompts to help you build a grasp of unifying concepts and to stimulate further learning. Linking Question boxes can be found in the margin next to the content they link to (see example on the left).

By their very nature, the Linking Questions make reference to different parts of the course, some of which you may not have studied yet. As the questions can be asked in either direction, you may choose to consider them as part of the study of either or both of the linked topics. You will again find that you are able to answer the question more fully as your knowledge and understanding increase.

The Linking Questions are designed to lead to a thoughtful response. For this reason, we have given brief answers alongside the questions in the text, and hope these stimulate further consideration of the question.

The Nature of Science

Throughout the course you are encouraged to think about the nature of scientific knowledge and the scientific process as it applies to chemistry. Examples are given of the evolution of chemical theories as new information is gained, the use of models to conceptualize our understanding, and the ways in which experimental work is enhanced by modern technologies. Ethical considerations, environmental impacts, the importance of objectivity, and the responsibilities regarding scientists' code of conduct are also considered here. The emphasis is not on learning any of these examples, but on appreciating the broader conceptual themes in context. We have included several NOS examples in each chapter, and hope you will come up with your own as you keep these ideas at the forefront of your learning.

Key to feature boxes

You will find different coloured feature boxes interspersed throughout each chapter. These are used to enhance your learning and how it applies to real world examples, as explained below.

Nature of Science

As mentioned this is an overarching theme in the course. Throughout the book you will find NOS themes and questions emerging across different topics. We hope they help you to develop your skills in scientific literacy.

Nature of Science

Magnetism was used in navigation long before it was explained scientifically. Historically, technology emerged before science. Materials were often used practically long before there was an understanding of why they possessed their properties.

In today's world, the reverse is often the case, with scientific understanding leading to technological developments, which in turn drive further developments in scientific ideas.

Global context

The impact of the study of chemistry is global, and includes environmental, political and socio-economic considerations. Examples of this are given to help you to see the importance of chemistry in an international context. These examples also illustrate some of the innovative and cutting-edge aspects of research in chemistry.

A different unit of concentration is known as **ppm**, parts per million. It denotes one part per 10^6 parts of the whole solution, and is useful in describing very low concentrations. This unit is widely used in reporting levels of pollutants in air, water, soil and food. For example, in the USA the FDA has set a maximum permissible level of 1 part of methylmercury in a million parts of seafood (1 ppm).

Skills in the study of chemistry

These boxes indicate links to the Skills section of the course, including ideas for lab work and experiments that will support your learning and help you prepare for the Internal Assessment. These link to further resources in the eBook (look out for the grey icon).

Using spectra to confirm the structure of a compound. Full details of how to carry out this experiment with a worksheet are available in the eBook.

Theory of Knowledge

These questions, which are mostly from the Theory of Knowledge (TOK) guide, stimulate thought and consideration of knowledge issues as they arise in context. The questions are open-ended and will help trigger critical thinking and discussion.

How might developments in scientific knowledge trigger political controversies or controversies in other areas of knowledge?

Key fact

These key facts are drawn out of the main text and highlighted in bold. These boxes will help you to identify the core learning points within each section. They also act as a quick summary for review.

At equilibrium the rate of the forward reaction is equal to the rate of the backward reaction.

Hint for success

These give hints on how to approach questions, and suggest approaches that examiners like to see. They also identify common pitfalls in understanding, and omissions made in answering questions.

Note the definition of bond enthalpy indicates that all the species have to be in the gaseous state.

Challenge yourself

These boxes contain probing questions that encourage you to think about the topic in more depth, and may take you beyond the syllabus content. They are designed to be challenging and to make you think.

Challenge yourself

1. The components of a mixture can usually be separated by physical means. What might be the challenges of trying to separate the metals from an alloy?

Interesting fact

These give background information that will add to your wider knowledge of the topic and make links with other topics and subjects. Aspects such as historic notes on the life of scientists and origins of names are included here.

Gilbert Lewis (1875–1946), responsible for the electron-pair theory of the covalent bond, was nominated 41 times for the Nobel Prize in Chemistry without winning. In 1946, he was found dead in his laboratory where he had been working with the toxic compound hydrogen cyanide.

Towards the end of the book, there are chapters on Green Chemistry, TOK as it relates to chemistry, the Internal Assessment, the Extended Essay and Strategies for success in IB chemistry.

Questions

There are three types of question in this book.

1. Worked examples with solutions

Worked examples appear at intervals in the text and are used to illustrate the concepts covered.

They are followed by the solution, which shows the thinking and the steps used in solving the problem.

Worked example

Identify the species with 19 protons, 20 neutrons and 18 electrons.

Solution

- the number of protons tells us the atomic number, $Z = 19$, and so the element is potassium, K
- the mass number = p + n = 19 + 20 = 39: $^{39}_{19}K$
- the charge = p – e = 19 – 18 = +1 as there is one extra proton: $^{39}_{19}K^{+}$

2. Exercises

These questions are found throughout the text, usually at the end of each Understanding. They allow you to apply your knowledge and test your understanding of what you have just been reading. The answers to these, together with worked solutions, are accessed via icons on the first page of each chapter in the eBook. Exercise answers can also be found at the back of the eBook.

Exercise

Q1. Explain why the relative atomic mass of tellurium is greater than the relative atomic mass of iodine, even though iodine has a greater atomic number.

3. Practice questions

These questions are found at the end of each chapter. They are mostly taken from previous years' IB exam papers. The markschemes used by examiners when marking these questions are accessed via icons in the eBook on the first page of each chapter. Questions which are based on the Understandings for SL are given first, followed by questions which include HL only material. HL questions are clearly marked.

Practice questions

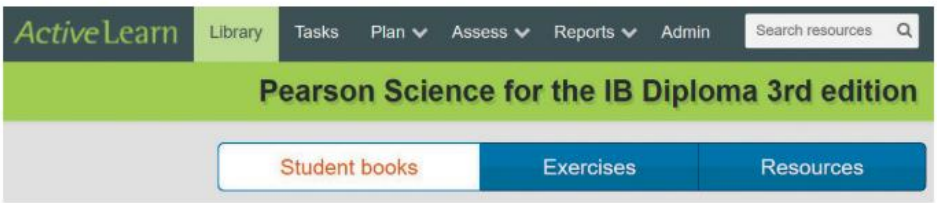
7. HL The transition element gold, Au, is used in electrical circuits due to its high electrical conductivity.

   Explain why transition elements are generally better electrical conductors than s and p block metals. (2)

   (Total 2 marks)

eBook

In your eBook you will find more information on the Skills section of the course including detailed suggestions for lab work. You will also find links to videos. In addition, there are auto-marked quizzes in the Exercises tab of your eBook account (see screenshot below).



We hope you enjoy your study of IB chemistry from this textbook.

Catrin Brown, Mike Ford, Oliver Canning, Andreas Economou and Garth Irwin

Introduction to skills in the study of chemistry

"I hear and I forget, I see and I remember, I do and I understand"

Chemistry is an experimental science and its progress continues to be based on the scientific method. The study of chemistry in the IB programme reflects this in the emphasis it places on laboratory work. This approach will help you to understand concepts, learn some practical skills and give you opportunities to explore further through investigations. It is also often the best part about studying chemistry!

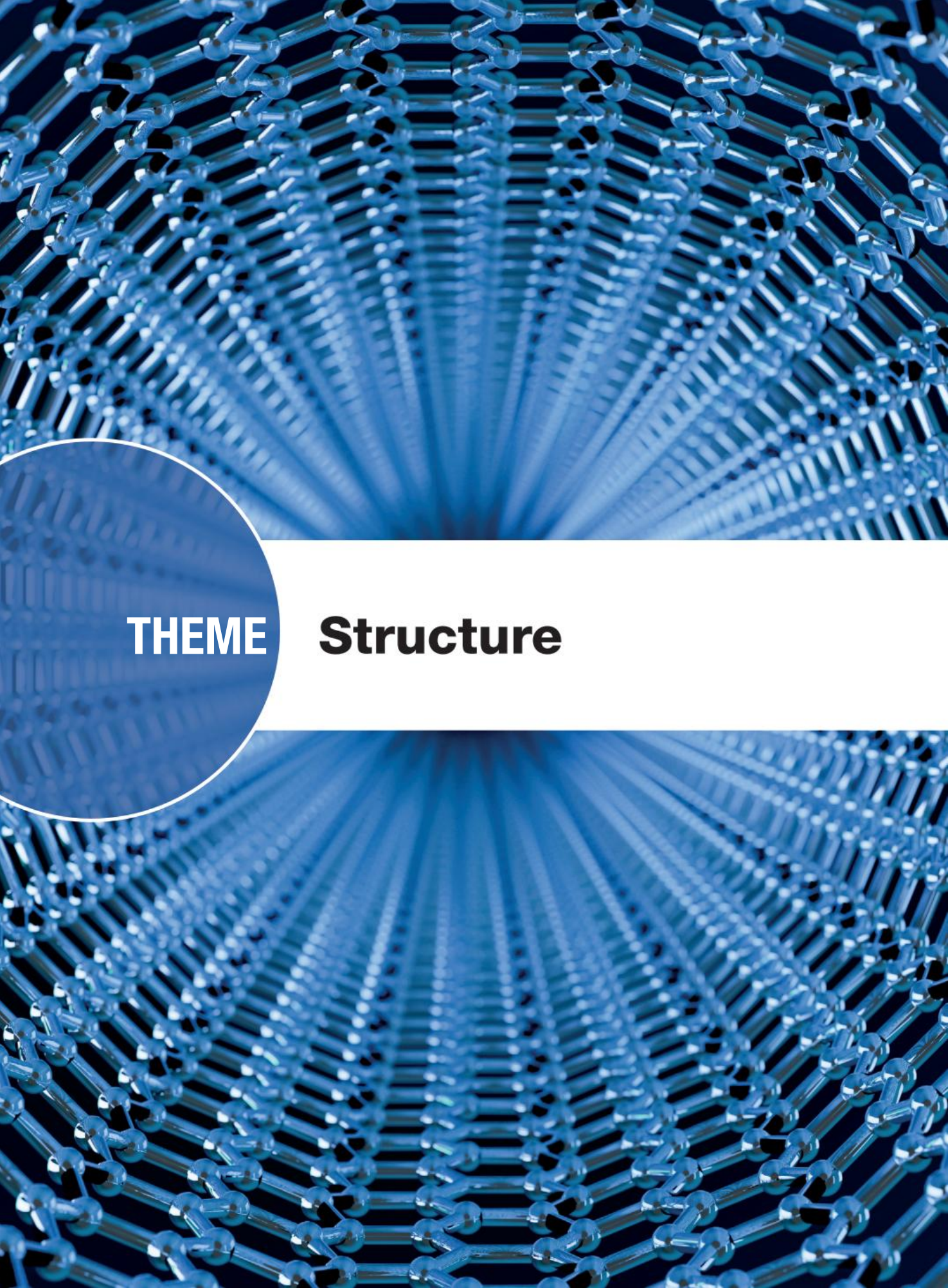
The syllabus roadmap on page vii has 'Skills in the study of chemistry' at the top. This unit is a summary of experimental skills and techniques that should be experienced during the course, including the application of technology and mathematics. It is not intended that these 'Tools' are covered as separate content, but should be integrated into the study of all topics. The 'Skills in the study of chemistry' chapter towards the back of this book includes tables that summarize the details of this unit with references to where in the syllabus content the Tools may be suitably included. There are also many links to experimental work and resources available in the ebook.

Nature of Science

The scientific method consists of systematic observation, the formulation and testing of hypotheses, and the collection of data for analysis and evaluation. Central to this process is a consideration of the limits of the usefulness of the data obtained. The interpretation of results must take into account the precision and accuracy of the measurements, the amount and limitations of data collected and the reproducibility of the results. Effective communication of the results must include this information.



The choice of apparatus for measurement in the laboratory determines the precision of the data collected. Here a pipette is used to deliver a single drop of liquid.



THEME Structure



View of graphene with 3D rendering. Graphene is a relatively modern structure, usually composed of a single layer of carbon atoms. It is considered to be the world's thinnest, strongest and most conductive material, of both electricity and heat. Understanding the structure of graphene has helped develop its applications in many fields such as energy generation, sensors, medical equipment and composite materials.

Structure

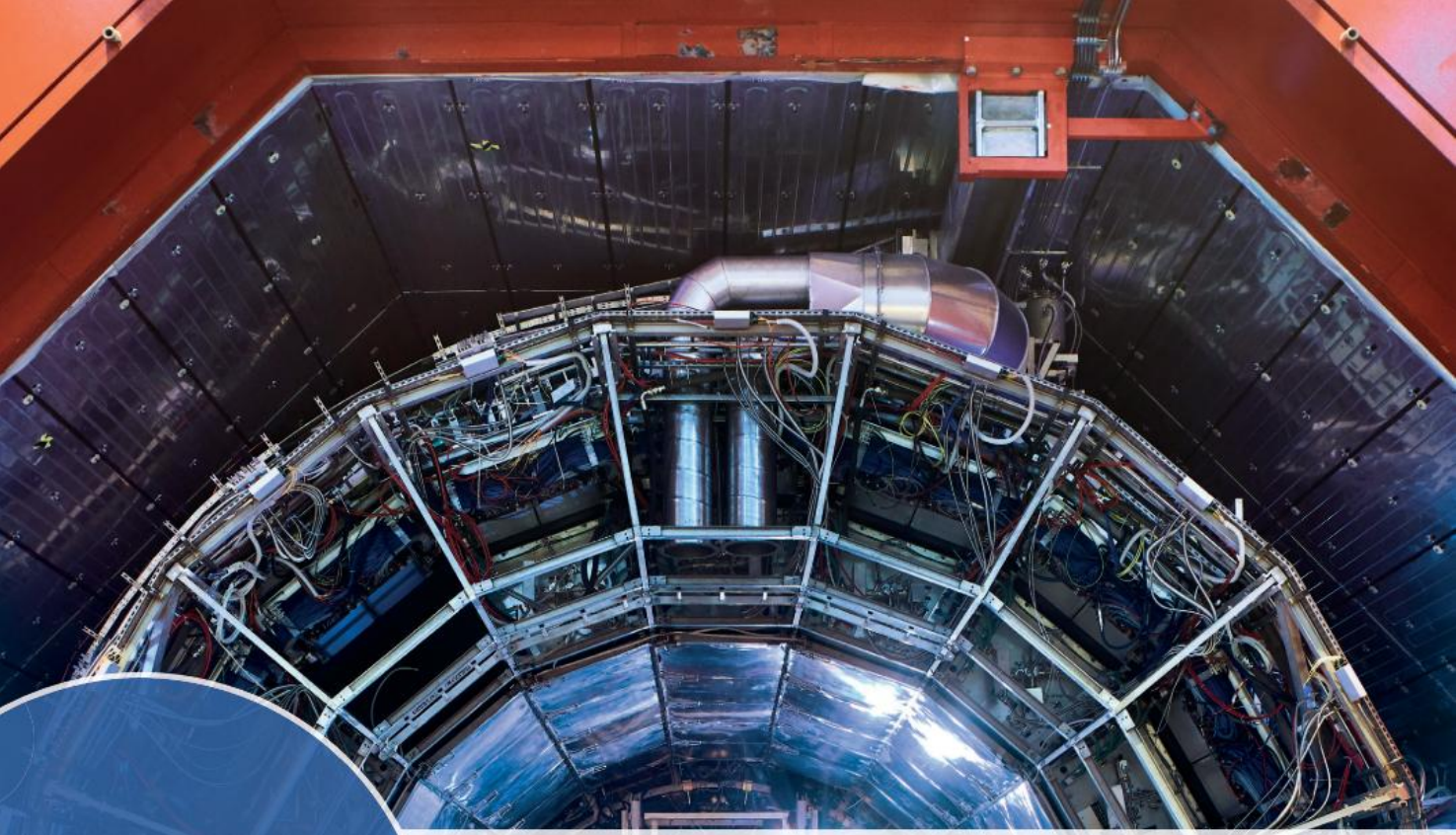
Structure refers to the nature of matter. Chemists seek to understand the way in which fundamental particles, the building blocks of all chemical structure, combine to form every chemical structure that exists – from single atoms to the most complex compounds. An understanding of structure leads to the ability to explain and predict chemical properties, as studied in our second theme, *Reactivity*.

A major challenge in the study of structure is that the fundamental particles are too small for us to observe directly. Even the most advanced technology gives us only limited information on the nature and behaviour of these particles. As a result, since the early days of chemical exploration, scientists have used models to help explain and predict the nature of matter. Over time, these models have developed and changed in the light of increasingly detailed observations and new evidence. As we explore the applications of these models, we must also consider their limitations and how they may continue to evolve.

In Structure 1 we consider evidence for the particulate nature of matter. From an exploration of the properties of sub-atomic particles, we build an understanding of the structure of atoms and how they characterize the unique properties of each element. The problem of scale, how we quantify what we cannot observe directly, is addressed through an introduction to the mole as the unit of amount in chemistry. A detailed study of electron configurations helps us to recognize why atoms of different elements differ in their tendency to attract electrons. This leads to descriptions of the models of different chemical bonds – ionic, covalent and metallic – in Structure 2. The organization of elements in the periodic table, as studied in Structure 3, suggests patterns in elements' properties. This gives predictive power to the types of bonds that they will form. As atoms associate through bond formation, the products have different properties, giving rise to an infinite variety of structures. Chemists have developed clear terminology to communicate about chemical structure, and in Structure 3 we are introduced to the IUPAC (International Union of Pure and Applied Chemistry) system of nomenclature, and learn how compounds are given unambiguous and internationally agreed names.

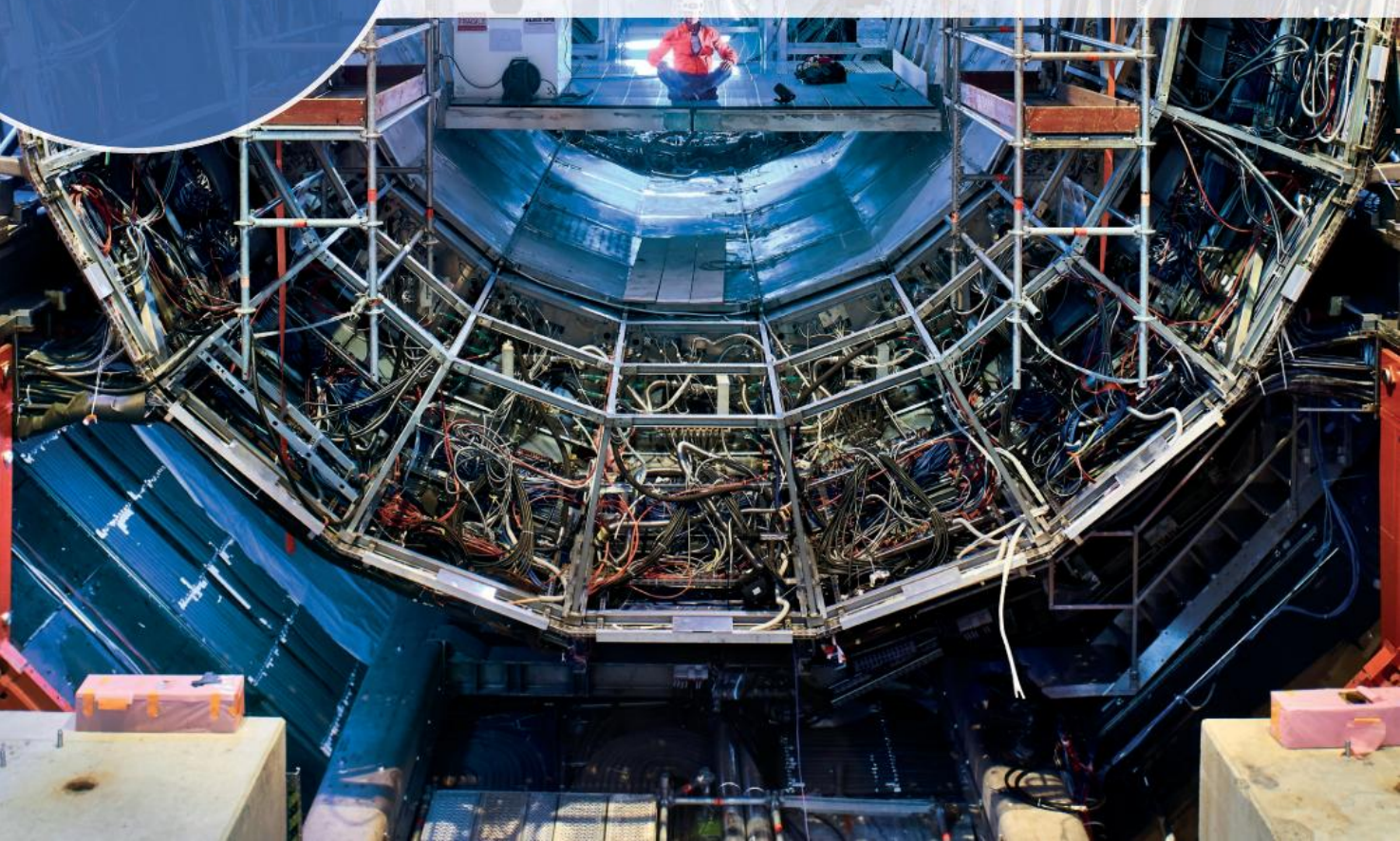
Our understanding of structure has developed alongside advances in technology and has led to many innovations in materials science. Many modern materials, such as breathable fabrics and biodegradable plastics, and compounds such as therapeutic drugs, are designed for specific functions. You need look no further than your smart phone or clothing to realize how much our lives are influenced by these products. And yet, despite their extraordinary variety and complexity, every chemical structure is based on associations between a relatively small number of different atoms.

Structure determines reactivity, which in turn transforms structure.



STRUCTURE 1

Models of the particulate nature of matter

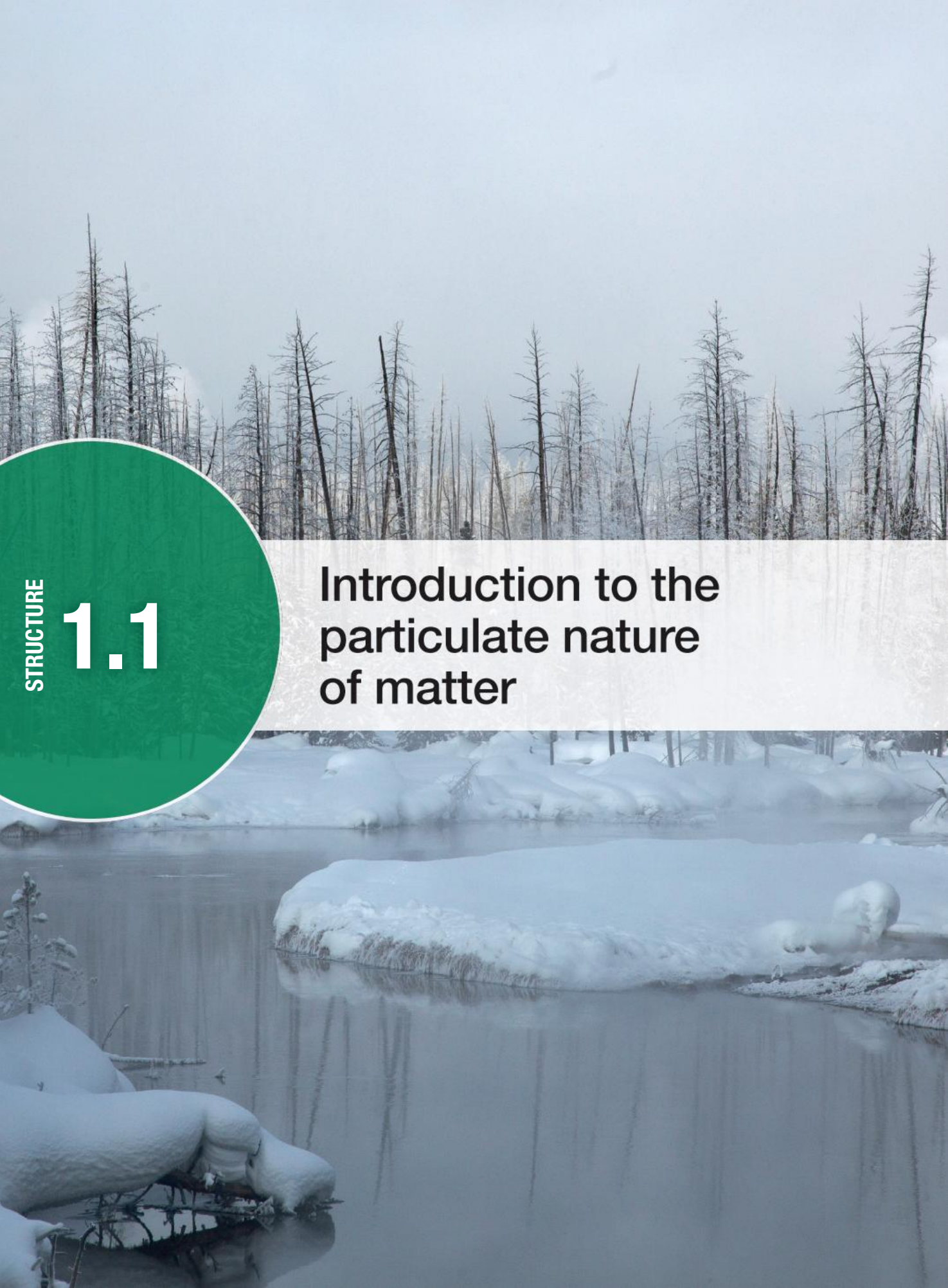


Inside the empty skeleton of the ALICE detector at CERN (the European particle physics laboratory) near Geneva, Switzerland. ALICE (A Large Ion Collider Experiment) is a detector built around the Large Hadron Collider (LHC). The LHC is the world's largest and most powerful particle collider. Beams of ions are accelerated to collide head-on. The collision energy creates new particles that decay into other particles. The LHC energies have allowed the study of exotic materials like quark-gluon plasma, a form of quark matter. CERN announced the Higgs boson discovery on 4 July 2012.

Nature of Science

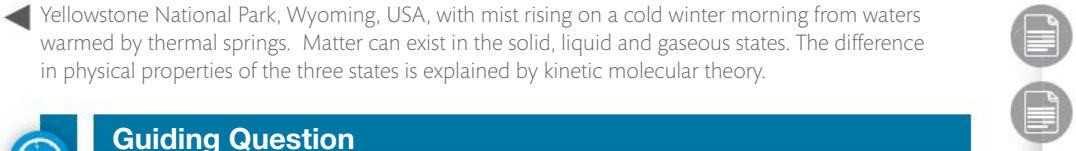
Progress in science often follows technological developments. The discovery of the Higgs boson was due to the use of particle accelerators, detectors and sophisticated computers. Such technological advances are only possible with international collaboration between scientists. Scientists communicate and collaborate throughout the world. CERN is run by over 20 member states, and many non-European countries are involved in different ways.

One of the earliest questions philosophers asked concerned the divisibility of matter. Could a piece of material be divided again and again continually into smaller and smaller pieces as Aristotle proposed, or would a limit be reached, a single particle, as Democritus argued? The latter idea has generally stood the test of time. This particulate model of matter enables us to explain many aspects of the behaviour of matter despite these particles being not directly visible. We have no proof that matter is not infinitely divisible, but we do have evidence that it becomes increasingly more difficult to divide it into smaller pieces. The limiting factor is the energy required to divide a particle. Experimental evidence for this has come from work with particle accelerators, such as at CERN, referenced in the photo at the start of the chapter, where beams of ions undergo high-energy collisions, which produce new particles. We are still learning about how the world is made up of fundamental particles. The Higgs boson, a key elementary particle, was only discovered as recently as 2012 although its existence had been predicted by scientific models in 1964.



STRUCTURE

1.1 Introduction to the particulate nature of matter



Yellowstone National Park, Wyoming, USA, with mist rising on a cold winter morning from waters warmed by thermal springs. Matter can exist in the solid, liquid and gaseous states. The difference in physical properties of the three states is explained by kinetic molecular theory.

Guiding Question

How can we model the particulate nature of matter?

All things are made from atoms. This is one of the most important ideas that the human race has learned about the universe. Atoms are everywhere and they make up everything. You are surrounded by atoms – they make up the foods you eat, the liquids you drink and the fragrances you smell. Atoms make up you! To understand the world and how it changes, you need to understand atoms.

Atoms are the smallest particle of an element and so are fundamental to chemistry. As they are too small ever to be seen directly by a human eye, scientists have developed a series of models to explain the physical and chemical properties of materials. We can understand many aspects of the world simply by considering how these particles move and interact with each other. This particulate model of matter, which includes atoms, molecules and ions, provides a very strong foundation for our chemical understanding and is a good place to start our explorations.

Nature of Science

Scientists construct models as artificial representations of natural phenomena. All models have limitations that need to be considered in their application.

Structure 1.1.1 – Elements, compounds and mixtures

Structure 1.1.1 – Elements are the primary constituents of matter, which cannot be chemically broken down into simpler substances.

Compounds consist of atoms of different elements chemically bonded together in a fixed ratio.

Mixtures contain more than one element or compound in no fixed ratio, which are not chemically bonded and so can be separated by physical methods.

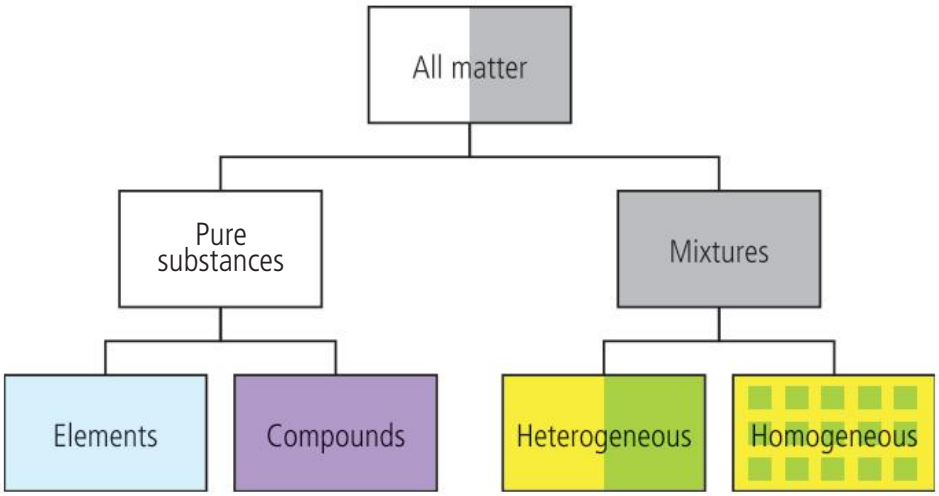
Distinguish between the properties of elements, compounds and mixtures.

Solvation, filtration, recrystallization, evaporation, distillation and paper chromatography should be covered. The differences between homogeneous and heterogeneous mixtures should be understood.	Tool 1 – What factors are considered in choosing a method to separate the components of a mixture? Tool 1 – How can the products of a reaction be purified? Structure 2.2 – How do intermolecular forces influence the type of mixture that forms between two substances? Structure 2.3 – Why are alloys generally considered to be mixtures, even though they often contain metallic bonding?

Matter can be classified into elements, compounds and mixtures

Classifying matter

Matter is present in an infinite number of different forms. The first step to understanding the chemistry of all these substances is an effective classification system. We start with a basic chemical distinction: some matter is made of pure substances, and some is made from mixtures. The chapter will follow the classification outlined in Figure 1.



S1.1 Figure 1 Matter can be classified into pure substances and mixtures. Pure substances can be elements or compounds. Mixtures can be homogeneous or heterogeneous.

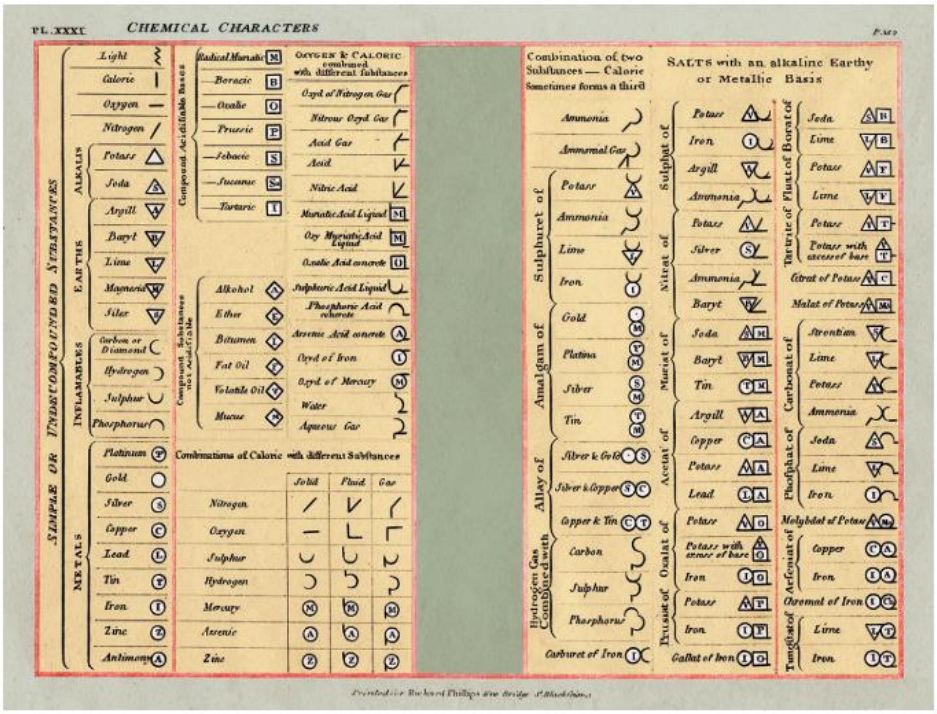
Elements are the primary constituents of matter, which cannot be chemically broken down into simpler substances

An element is a pure chemical substance composed of atoms with the same number of protons in the atomic nucleus.

All languages are based on an alphabet of a limited number of characters. The 26 letters of the English alphabet, for example, can be combined in different ways to form the estimated 600 000 words in the language. In a similar way, the substances known as chemical elements can combine to form the material of our universe. Elements are the primary constituents of matter. They cannot be chemically broken down into simpler substances. The near infinite number of different chemical substances in our world are made from only about 100 known elements.

An atom is the smallest particle of an element to show the characteristic properties of that element.

In Structure 2.1 we will learn about atomic structure, and how each element is made up of a particular type of atom. Atoms of the same element all have the same number of protons in the atomic nucleus and the same number of electrons. The distinct make-up of an element's atoms gives each element its individual properties. An atom is the smallest particle of an element to show the characteristic properties of that element.



Pictographic symbols used at the beginning of the 18th century to represent chemical elements and compounds. They are similar to those of the ancient alchemists. As more elements were discovered during the 18th century, attempts to devise a chemical nomenclature led to the modern alphabetic notational system. This system was devised by the Swedish chemist Berzelius and introduced in 1814.

Each element is denoted by a **chemical symbol** and some examples are given below.

Name of element	Symbol
carbon	C
fluorine	F
potassium	K
calcium	Ca
mercury	Hg
tungsten	W

You will notice that often the letter or letters used to represent the elements are derived from its English name, but in some cases, they derive from other languages. For example, Hg for mercury comes from Latin, whereas W for tungsten has its origin in European dialects. These symbols are all accepted and used internationally, which allows for effective global communication between chemists. A complete list of the names of the elements and their symbols is given in Section 6 of the data booklet.

The number of elements is open to change as new ones can be invented or discovered. It takes time for an element's existence to be confirmed by IUPAC so in the interim, a provisional systematic three-letter symbol is used. Latin abbreviations represent the atomic number. The letters u (un) = 1, b (bi) = 2, t (tri) = 3 and so on are used. The element of atomic number 118 now known as oganesson (Og) was previously known as ununoctium or uuo.

Chemistry is a very exact subject, and it is important to be careful in distinguishing between upper and lower case letters. Cobalt (Co) is a metallic element whereas carbon monoxide (CO) is a poisonous gas.

Compounds consist of atoms of different elements chemically bonded together in a fixed ratio

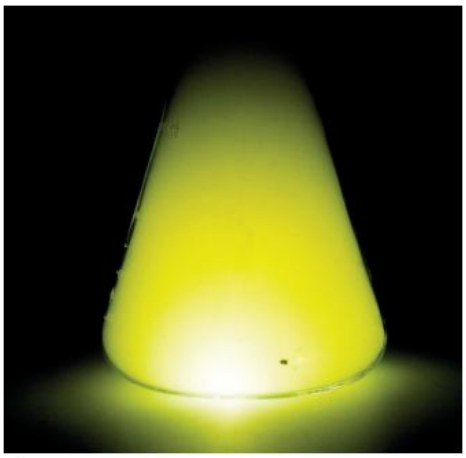
Some elements, such as nitrogen and gold, are found in **native** form, uncombined with other elements in nature. But more commonly, elements exist in chemical combinations with other elements, as **chemical compounds**. Compounds consist of atoms of different elements chemically bonded together in a fixed ratio. The physical and chemical properties of compounds are completely different from those of their component elements.

Sodium chloride, for example, is a white crystalline solid that is added to improve the taste of food, whereas sodium is a dangerously reactive metal that reacts violently with water, and chlorine is a toxic gas.

The **chemical formula** of a compound uses a combination of chemical symbols of its constituent elements. A subscript is used to show the number of atoms of each element in a unit of the compound. Some examples are given below. (The reasons for the different ratios of elements in compounds will become clearer after we have studied atomic structure and bonding in Structure 2.)



Assorted minerals, including elements such as sulfur and silver, and compounds such as Al_2O_3 (sapphire) and CaF_2 (fluorite). Most minerals are impure and exist as mixtures of different elements and compounds.



Sodium, Na, reacts violently with chlorine, Cl_2, to produce white crystals of the compound sodium chloride, NaCl.

$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$

The properties of the compound are completely different from those of its component elements.

A compound is a substance made by chemically combining two or more elements in a fixed ratio of atoms. The physical and chemical properties of a compound are different from those of its constituent elements.

Name of compound	Chemical formula	Name of compound	Chemical formula
sodium chloride	NaCl	methane	CH_4
magnesium hydroxide	$Mg(OH)_2$	ammonia	NH_3
copper sulfate	$CuSO_4$	glucose	$C_6H_{12}O_6$
water	H_2O	sulfuric acid	H_2SO_4

Mixtures contain more than one element or compound in no fixed ratio

Chemistry is primarily concerned with understanding the structure and reactivities of pure substances but dealing with mixtures is a practical reality. Although there are a countable number of pure substances, the elements and compounds, which all have distinctive names, there is an infinite number of mixtures. The composition of any one mixture can vary continuously – the relative amounts of ice cream, milk and flavourings in a milkshake can vary depending on the taste of the person preparing the drink. Names for all the mixtures we could make do not exist.

Air is described as a **mixture** of gases because the separate components – different elements and compounds – are interspersed with each other, but not chemically combined. The gases nitrogen and oxygen when mixed in air, for example, have the same properties as they do when they are in pure samples. Substances burn in air because they react with the oxygen in the same way that they react with pure oxygen. As substances can be mixed in any proportion, mixtures, in contrast to compounds, do not have a fixed composition and cannot be represented by a chemical formula. The composition of air for example varies widely around the world due to the presence of different pollutants.

Air is an example of a **homogeneous mixture**, as it has uniform composition and properties throughout. A solution of salt in water and a metal alloy such as bronze, which is a mixture of copper and tin, are also homogeneous. To form a homogeneous mixture, the inter-particle attraction within the different components must be similar in nature to those between the components in the mixture. Explanations of the different particle interactions are given in Structure 2.2.

Mixture	Component 1	Particle interaction 1	Component 2	Particle interaction 2	Interaction in mixture
air	N_2	dispersion forces	O_2	dispersion forces	dispersion forces
bronze	Cu	metallic bonding	Sn	metallic bonding	metallic bonding
salt water	NaCl	ionic	H_2O	hydrogen bonding	ion-dipole



Making alloys at a steel mill. Alloys are formed by mixing two molten metals that can then form a mixture of uniform composition. There is no chemical reaction between the metallic elements as the metallic bonding present in the individual metals and the alloys is non-directional and not significantly disrupted by the mixing process. Metallic bonding is explored more fully in Structure 2.3.

TOK

Our classification systems are embedded in the language we use. To what extent do the classification systems we use affect the knowledge we obtain? To what extent do the names and labels that we use help or hinder the acquisition of knowledge?

A mixture contains more than one element or compound in no fixed ratio, which are not chemically bonded. The components of a mixture can be separated by physical methods.

Structure 2.3 – Why are alloys generally considered to be mixtures, even though they often contain metallic bonding?

Challenge yourself

1. If you add 10 cm^3 of water to 10 cm^3 of water, you get 20 cm^3 of water. Similarly, if you add 10 cm^3 of ethanol to 10 cm^3 of ethanol you get 20 cm^3 of ethanol. Explain why the volume of the solution formed between 10 cm^3 of water and 10 cm^3 ethanol is less than 20 cm^3.

Structure 2.2 – How do intermolecular forces influence the type of mixture that forms between two substances?

A **heterogeneous mixture**, by contrast, such as water and oil, has a non-uniform composition, and its properties are not the same throughout. The interactions between the components of a heterogeneous mixture are different in nature. The water molecules interact by hydrogen bonding and the oil molecules by dispersion forces, as discussed in Structure 2.2.

It is usually possible to see the separate components in a heterogeneous mixture but not in a homogeneous mixture.

Ocean oil spills can occur when oil is extracted or transported. They cause widespread damage to the environment and can have a major impact on local industries such as fishing and tourism. Efforts to reduce the impact of the spill include the use of dispersants, which break up the oil into smaller droplets, allowing it to mix better with water.



Smoke from a controlled burn of the oil spill caused by the explosion of the Deepwater Horizon oil rig, 20th April 2010. Five thousand barrels of oil a day leaked into the Gulf of Mexico, harming local wildlife and fishing industries.

Challenge yourself

2. Does a mixture have the same classification at all scales?

The components in a mixture can be relatively easy to separate if they have a distinct physical property. The technique chosen will depend on this distinct property.

Mixture	Difference in property of components	Technique used
sand and salt	solubility in water	solution and filtration
salt and water	boiling point	distillation
iron and sulfur	magnetism	response to a magnet
pigments in food colouring	adsorption to solid phase	paper chromatography

SKILLS

The required product of a chemical reaction similarly needs to be separated from the reaction mixture, which also contains unreacted reactants and other unwanted products. It is a practical challenge to both maximize the yield and the purity, as some product can be removed with the impurities during the purification process.

Filtration is the process where a solid is separated from a liquid or gas using a membrane. The solid is collected on the membrane as the residue, and the filtrate containing the solute passes through. Sand and salt have different solubilities in water so can be separated by adding water which dissolves the salt – an example of **solvation**. The resulting mixture can be filtered with the insoluble sand removed as the **residue** leaving the salt water solution as the **filtrate**. The water can be separated from the salt by evaporation, which allows the salt crystals to form (**crystallization**).



Filtration apparatus

Tool 1 – What factors are considered in choosing a method to separate the components of a mixture?

Tool 1 – How can the products of a reaction be purified?

SKILLS

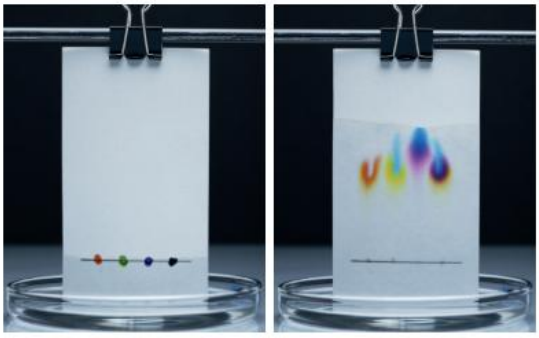
Preparation of AgI precipitate from aqueous solutions. Full details of how to carry out this experiment with a worksheet are available in the eBook.

Distillation is used to separate a solvent from a solute. The solvent has a lower boiling point than the solute and so is collected as a gas and passes into the condensing tube, which is surrounded by cold flowing water. The gas is condensed into the pure solvent collected in the beaker at the bottom. This method can be used to separate water from seawater, for example.



Distillation apparatus

In **paper chromatography**, small spots of solutions containing the samples being tested are placed on the baseline. The paper is suspended to ensure that it is saturated **(a)**. The different components have different affinities for the water in the paper (the solvent) and so separate as the solvent moves up the paper **(b)**. This method can be used to investigate the different pigments in food colouring.



(a) **(b)**

Paper chromatography apparatus

Exercise

Q1. Identify the homogeneous mixture.

A water and oil **B** sand and water

C salt and water **D** sand and salt

Q2. Identify the correct descriptions about mixtures.

I. The components can be elements or compounds.

II. All components must be in the same state.

III. The components retain their individual properties.

A I and II only **B** I and III only

C II and III only **D** I, II and III

Q3. Identify the homogeneous mixtures.

I. gold

II. bronze

III. steel

A I and II only **B** I and III only

C II and III only **D** I, II and III

Q4. **(a)** River water needs to be purified to make it safe to drink. The water passes through a grid and is then left in a tank where other impurities are removed as they fall to the bottom in a process known as sedimentation. Suggest why pollutants such as fertilizers are not removed in this process.

(b) Drinking water can be obtained from seawater by distillation. Explain the disadvantages of using distillation to obtain large amounts of drinking water.

Q5. A layer of oil paint is left to dry in the air and it hardens. Suggest what causes the oil to harden.

Q6. Metal coins are made from different metals. The composition of a 20-cent and a 50-cent euro coin is given below.

	Mass/g			
Coin	**Copper**	**Aluminium**	**Zinc**	**Tin**
20 cent	5.11	0.287	0.287	0.057
50 cent	6.94	0.39	0.39	0.080

Compare the chemical compositions of the two coins.

Structure 1.1.2 – The kinetic molecular theory

Structure 1.1.2 – The kinetic molecular theory is a model to explain physical properties of matter (solids, liquids and gases) and changes of state.	
Distinguish the different states of matter.	
Use state symbols (s, l, g and aq) in chemical equations.	
Names of the changes of state should be covered: melting, freezing, vaporization (evaporation and boiling), condensation, sublimation and deposition.	Structure 2.4 – Why are some substances solid while others are fluid under standard conditions? Structure 2 (all), Reactivity 1.2 – Why are some changes of state endothermic and some exothermic?

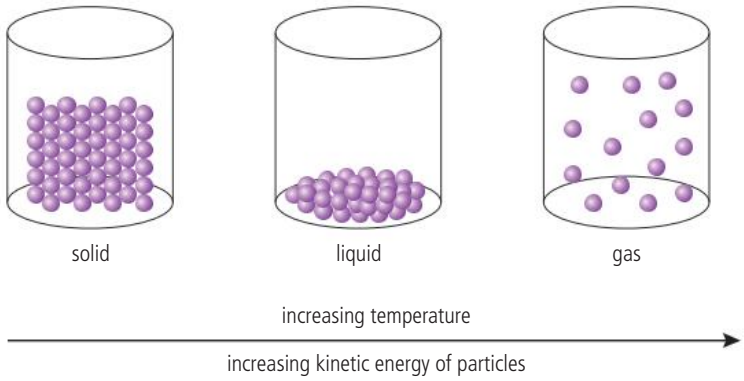
The kinetic molecular theory explains physical properties

If you were hit with a bucket of solid water (ice), you could be seriously injured, but the same mass of liquid water would only be annoying. Gaseous water (steam) could

also be harmful but for different reasons. These three samples are all made from the same particles: water molecules, H_2O. The difference in physical properties of the three states is explained by **kinetic molecular theory**.

Matter exists in different states as determined by the temperature and the pressure

From our common experience, we know that all matter (elements, compounds, and mixtures) can exist in different forms depending on the temperature and pressure. Liquid water changes into a solid form, such as ice, hail, or snow, as the temperature drops, and it becomes a gas, steam, at higher temperatures. These different forms are known as the **states of matter** and are characterized by the different energies of the particles.



S1.1 Figure 2 Representation of the arrangement of the particles of the same substance in the solid, liquid, and gas states.

Solid	Liquid	Gas
• particles closely packed	• particles more spaced	• particles fully spread out
• inter-particle forces strong, particles vibrate in position	• inter-particle forces weaker, particles can slide over each other	• inter-particle forces negligible, particles move freely
• fixed shape	• no fixed shape	• no fixed shape
• fixed volume	• fixed volume	• no fixed volume

This is known as the kinetic molecular theory of matter as the three states are distinguished by the way the particles move. The temperature of the system is directly related to the average kinetic energy of the particles and the state of matter at a given temperature and pressure is determined by the strength of **inter-particle forces** that exist between the particles relative to this average kinetic energy. If the inter-particle forces are sufficiently strong to keep the particles in position at a given temperature and pressure, the substance will be a solid. If not, it will be a liquid or a gas. The different inter-particle forces are explored more fully in Structure 2.

Challenge yourself

3. What evidence based on simple observations can you think of that supports the idea that water is made from discrete particles?

A fourth state of matter, plasma, exists only at conditions of very high temperatures and pressures, such as those commonly found in stars such as our Sun.

Depending on the chemical nature of the substance, matter may exist as atoms such as Ar(g), as molecules such as $H_2O(l)$, or as ions such as Na^+ and Cl^- in aqueous solution NaCl(aq). The term **particle** is therefore used as an inclusive term that is applied in this text to any or all of these entities of matter.

Temperature is a measure of the average kinetic energy of the particles of a substance.

Structure 2.4 – Why are some substances solid while others are fluid under standard conditions?

Worked example

Which of the following has the highest average kinetic energy?

A He at 100 °C **B** H_2 at 200 °C **C** O_2 at 300 °C **D** H_2O at 400 °C

Solution

D The substance at the highest temperature has the highest average kinetic energy.

Liquids and gases are both referred to as **fluids**, as they have the ability to flow. In the case of liquids, it means that they take the shape of their container. **Diffusion**, the process by which the particles of a substance spread out more evenly, occurs as a result of their random movements. It occurs predominantly in these two fluid states.

Kinetic energy (E_k) refers to the energy associated with movement or motion. It is determined by the mass (m) and speed or velocity (v) of a substance, according to the relationship:

$$E_k = \frac{1}{2}mv^2$$

As the average kinetic energy of all particles at the same temperature is the same, there is an inverse relationship between mass and velocity:

$$E_k = \frac{1}{2}m_1v_1^2 = \frac{1}{2}m_2v_2^2$$

$$\frac{m_1}{m_2} = \frac{v_2^2}{v_1^2}$$

Particles with smaller mass therefore diffuse more quickly than those with greater mass, at the same temperature.



▲ Bromine liquid, $Br_2(l)$, has been placed in the lower gas jar only, and its vapour has diffused to fill both jars. Bromine vaporizes readily at room temperature and its distinctive colour allows the diffusion to be observed.

State symbols are used to show the states of the reactants and products taking part in a reaction. These are abbreviations, which are given in parenthesis after each term in an equation, as shown below.

State	Symbol	Example
solid	(s)	Fe(s)
liquid	(l)	$Br_2(l)$
gas	(g)	$O_2(g)$
aqueous	(aq)	$H_2SO_4(aq)$

For example:

$$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$$

Sodium hydroxide, NaOH, is produced during this reaction in **aqueous solution**.

It is good practice to show state symbols in all equations, even when they are not specifically requested.

Solutions more generally are mixtures of two components. The less abundant component is the **solute** and the more abundant is the **solvent**. The solute can be solid, liquid or gas but the solvent is generally a liquid. Solutions in water are particularly important and are given the state symbol (aq).

Matter changes state reversibly

As the movement or kinetic energy of the particles increases with temperature, they will overcome the inter-particle forces and change state. This occurs at a fixed temperature and pressure for each substance. A solid (X(s)) changes to a liquid at a defined **melting point** and a liquid (Y(l)) changes to a gas at its **boiling point**.

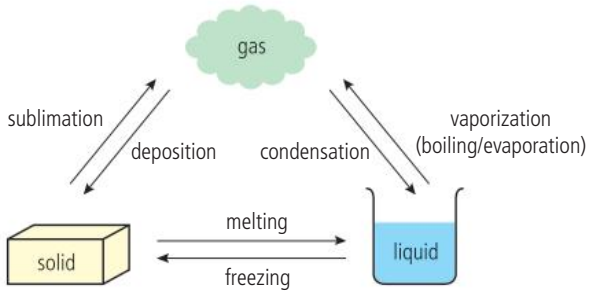
These changes can be reversed when the substance is cooled: a liquid freezes and becomes solid at the same temperature as the solid melts.

A gas or vapour condenses at the same temperature as the liquid boils.

The reversibility of these changes can be represented by reversible arrows as shown in the table.

Change of state		Change of state		Reversible equation
melting	$X(s) \rightarrow X(l)$	freezing	$X(l) \rightarrow X(s)$	$X(s) \rightleftharpoons X(l)$
boiling	$Y(l) \rightarrow Y(g)$	condensing	$Y(g) \rightarrow Y(l)$	$Y(l) \rightleftharpoons Y(g)$

Some substances can also change directly between the solid and gaseous states.



S1.1 Figure 3 The different state changes between the solid, liquid and gaseous states.

Sublimation is the direct inter-conversion of a solid to a gas without going through the liquid state. It is characteristic of some substances such as iodine, carbon dioxide and ammonium chloride.

Deposition is the reverse of sublimation and occurs when a gas changes directly to a solid. It occurs when snow and frost are formed.



Ice crystals, known as hair ice, formed by deposition on dead wood in a forest on Vancouver Island, Canada.

The temperature of a state change can be presented from both perspectives:
melting point = freezing point;
boiling point = condensation point.

SKILLS

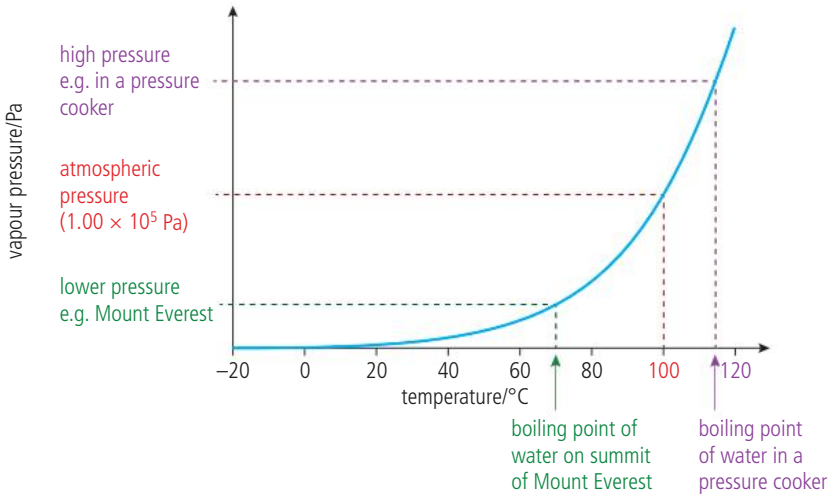
Sublimation of iron and iodine. Full details of how to carry out this experiment with a worksheet are available in the eBook.

A liquid can change to gas by two processes: **evaporation** and **boiling**. Boiling occurs at a fixed temperature for a given pressure, when bubbles of gas form throughout the liquid. Evaporation, by contrast, occurs only at the surface and takes place over a range of temperatures below the boiling point.



The heat of the Sun enables all the water to evaporate from the clothes.

More precisely, the boiling point is the temperature at which the vapour pressure is equal to the external pressure. As a liquid is heated, more particles enter the vapour state and the vapour pressure increases. When the vapour pressure reaches the external atmospheric pressure the liquid boils. When the external pressure is lower, the vapour pressure needed to boil is reduced and so boiling occurs at a lower temperature.
The relationship between temperature and vapour pressure and the influence of external pressure on the boiling point is demonstrated in Figure 4.



S1.1 Figure 4 Graph showing the boiling point of water at three different pressures.

A pressure cooker is a sealed container in which a high pressure can be generated. This raises the boiling point of water, allowing cooking time to decrease. Conversely, at altitude, where the atmospheric pressure is lower, the boiling point of water is reduced so it takes much longer to cook food.



A butane gas camping stove. Butane, C_4H_{10}, is stored as a liquid because the high pressure in the canister raises its boiling point. When the valve is opened the release of pressure causes the butane to boil, releasing a gas that can be burned.

Challenge yourself

4. Propane (C_3H_8) and butane (C_4H_{10}) are both commonly used in portable heating devices. Their boiling points are butane –1 °C and propane –42 °C. Suggest why butane is less suitable for use in very cold climates.



Macrophotograph of freeze-dried instant coffee granules.

Freeze-drying is used to preserve food and some pharmaceuticals. It differs from standard methods of dehydration as the energy needed to evaporate water is produced by the sublimation of ice. The substance to be preserved is first frozen, and then warmed gently at very low pressure which causes the ice to change directly to water vapour. The process is slow but has the significant advantage that the composition of the material, and so also its flavour, are largely conserved. The freeze-dried product is stored in a moisture-free package that excludes oxygen, and can be reconstituted by the addition of water.

At night, as the temperature is lowered, the rate of condensation increases. As the air temperature drops below its saturation point, known as the **dew point**, condensed water called **dew** forms. The temperature of the dew point depends on the atmospheric pressure and the water content of the air – that is, the relative humidity.

Exercise

Q7. A mixture of two gases, X and Y, which both have strong but distinct smells, is released. From across the room the smell of X is detected more quickly than the smell of Y. What can you deduce about X and Y?

Q8. Use the kinetic theory to explain whether you would expect the rate of diffusion in a liquid to increase or decrease as the temperature is increased.

Q9. Which is the correct descriptor for the movement of particles in the solid, liquid and gaseous states?

	Solid	Liquid	Gas
A	vibrational movement in one dimension	vibrational movement in two dimensions	vibrational movement in three dimensions
B	no movement, fixed in position	only vibrational movement	free movement in all dimensions
C	free movement in all dimensions	free movement in all dimensions	free movement in all dimensions
D	vibrational movement	limited movement in all dimensions	free movement in all dimensions

Q10. A closed flask contains a pure substance, a brown liquid that is at its boiling point.

(a) Explain what you are likely to observe in the flask.

(b) Distinguish between the inter-particle distances and the average speeds of the particles in the two states present.

Q11. A beaker containing solid carbon dioxide is placed in a fume cupboard at room temperature. The carbon dioxide becomes gaseous. Which process describes this change of state?

A boiling **B** condensation **C** evaporation **D** sublimation

Q12. Water exists in three states: ice, liquid water or steam. Which transition can occur over a range of temperatures at constant pressure?

A freezing **B** melting **C** evaporation **D** boiling

Q13. A liquid is placed in an open dish. Which change increases the rate of evaporation?

I. increased temperature of the liquid

II. increased depth of the liquid

III. increased surface area of the liquid

A I and II **B** I and III **C** II and III **D** I, II and III

Q14. During very cold weather, snow often gradually disappears without melting. Explain how this is possible.

Structure 1.1.3 – Kinetic energy and temperature

Structure 1.1.3 – Temperature (T) in kelvin (K) is a measure of average kinetic energy (E_k) of particles.	
Interpret observable changes in physical properties and temperature during changes of state. Convert between values in the Celsius and Kelvin scales.	
The kelvin (K) is the SI unit of temperature and has the same incremental value as the Celsius degree (°C).	Reactivity 2.2 – What is the graphical distribution of kinetic energy values of particles in a sample at a fixed temperature? Reactivity 2.2 – What must happen to particles for a chemical reaction to occur?

The heat curve of water. Full details of how to carry out this experiment with a worksheet are available in the eBook.

SKILLS

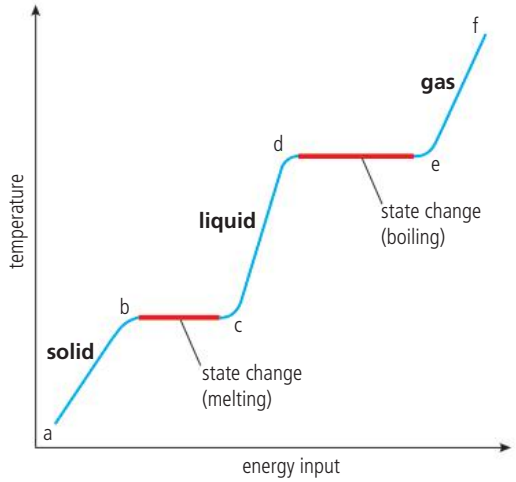
Temperature is constant during changes of state

Matter changes state when it is heated

Simple experiments can be done to monitor the temperature change while a substance is heated and changes state. Figure 5 shows a typical result.



Ice cubes melting in a beaker of water. Heat from the surroundings breaks some inter-particle forces between the water molecules in the ice. In Structure 2.2.8, we will see that the inter-particle forces in ice are hydrogen bonds.



S1.1 Figure 5 Temperature change versus energy input at fixed pressure as a solid substance is heated. The flat regions shown in red are where a change of state is occurring. Heat energy is used to overcome the inter-particle forces.

The graph can be interpreted as follows:

a–b As the solid is heated, the vibrational energy of its particles increases and so the temperature increases.

b–c This is the melting point. The vibrations are sufficiently energetic for the particles to move away from their fixed positions and form a liquid. Energy added during this stage is used to break the inter-particle forces, not to raise the kinetic energy, so the temperature remains constant.

c–d As the liquid is heated, the particles gain kinetic energy and so the temperature increases.

d–e This is the boiling point. There is now sufficient energy to break all of the inter-particle forces and form a gas. Note that this state change needs more energy than melting, as all the inter-particle forces must be broken. The temperature remains constant as the kinetic energy does not increase during this stage. Bubbles of gas are visible through the volume of the liquid.

e–f As the gas is heated under pressure, the kinetic energy of its particles continues to rise, as does the temperature.



Geothermal hot spring, Hveragerdi, Iceland. The geothermal spring provides sufficient energy to separate the water molecules and turn water into steam.

Melting (b to c) and boiling (d to e) are endothermic processes as energy is needed to separate the particles. The reverse processes, freezing (c to b) and condensation (e to d), are exothermic. Energy is given out as the inter-particle forces bring the particles closer together. Energy changes are explored in Reactivity 1.2.

Structure 2 (all), Reactivity 1.2 – Why are some changes of state endothermic and some exothermic?

Challenge yourself

5. Which physical properties determine the gradient of the lines for the different states in Figure 5?

Nature of Science

Scientists analyse their observations looking for patterns, trends or discrepancies. You may have noticed that the volume decreases as ice melts and its density increases. This is unusual as density generally decreases as a solid melts. This discrepancy is explained in Structure 2.2.8.

Temperature in kelvin is known as the absolute temperature

The movement or kinetic energy of the particles of a substance depends on the temperature. If the temperature of a substance is decreased, the average kinetic energy of the particles also decreases. Absolute zero (–273 °C) is the lowest possible temperature attainable as this is the temperature at which all movement stops.

The kelvin is the SI unit of temperature. The absolute temperature is directly proportional to the average kinetic energy of its particles. A temperature increase of 1 °C is also an increase of 1 K. This facilitates conversions between the two scales.

The Celsius scale of temperature is defined relative to the boiling and freezing points of water. The original scale, developed by the Swedish astronomer Anders Celsius, made the boiling point of water zero and the freezing point 100. The modern scale reverses this with the boiling point of water 100 °C and the melting point of ice as 0 °C. The original scale may now seem absurd, but the modern scale is just as arbitrary.

An increase of temperature $\Delta T = 1\ K = 1\ °C$.

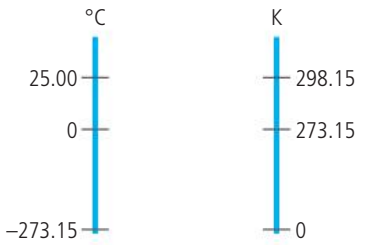
More generally $T(K) = T(°C) + 273.15$

The kelvin is the SI unit of temperature.

Temperature can be converted from Celsius to the Kelvin scale by the relation:

$$T(K) = T(°C) + 273.15 \text{ therefore } T(°C) = T(K) - 273.15$$

temperature (K) = temperature (°C) + 273.15



S1.1 Figure 6 The Celsius and Kelvin scales of temperature.

William Thomson (1824–1907), who became known as Lord Kelvin later in life, completed most of his work at the University of Glasgow, Scotland. His concept of the absolute temperature scale followed from his recognition of the relationship between heat energy and the ability to do work. The existence of a minimum possible temperature at which no heat can be extracted from the system and so no work done, led him to the definition of absolute zero in 1848. This in turn led to the formulation of the laws of thermodynamics. Kelvin is considered one of the great scientists of the 19th century, and is buried next to Isaac Newton in London.

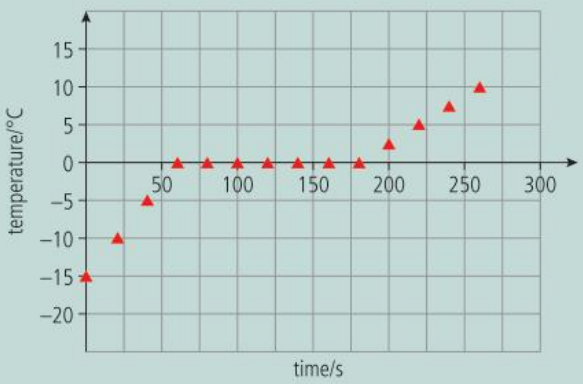
Although we can only relate the average kinetic energy to the temperature, there are many particles in a sample each with a different kinetic energy. The total kinetic energy is conserved in particle collisions, but the kinetic energy of individual particles changes upon each collision. We can however predict the statistical distribution of energies in a sample at a particular temperature, known as the Maxwell–Boltzmann distribution. This distribution will also help us understand the effect of temperature on rates of reaction. To react, particles must collide with sufficient kinetic energy known as the activation energy. Both these points are explored in Reactivity 2.2.

Reactivity 2.2 – What is the graphical distribution of kinetic energy values of particles in a sample at a fixed temperature?

Reactivity 2.2 – What must happen to particles for a chemical reaction to occur?

Exercise

Q15. A solid is heated and the temperature is measured every 20 seconds.



(a) Identify the solid.

(b) Describe how the particles in the solid are moving in the interval 0–60 s.

(c) Describe how the particles are moving in the interval after 180 s.

(d) Explain why the temperature does not change in the interval 60–180 s.

(e) Use the graph to predict the temperature after the material has been heated for 600 s.

(f) Use the graph to predict the temperature after 1200 s. Comment on the validity of your prediction.

Q16. Which of the following shows the correct Celsius temperature for the given kelvin temperature?

	Kelvin scale	Celsius scale
A	0	273
B	50	323
C	283	110
D	323	50

Q17. Which of the following occurs at the freezing point when a liquid is converted to a solid?

I. kinetic energy of the particles decreases

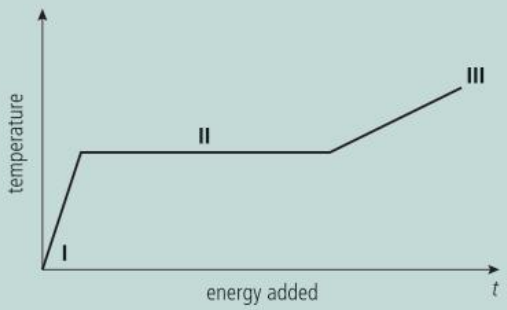
II. separation between the particles decreases

A I only **B** II only **C** I and II **D** neither I nor II

Q18. Two objects made from different masses of iron have the same temperature. Which of the following is the correct comparison of the average kinetic energy and the total energy of the atoms in the objects?

	Average kinetic energy of the atoms	Total energy of the atoms
A	greater in an object of larger mass	same
B	less in an object of larger mass	same
C	same	greater in an object of larger mass
D	same	less in an object of larger mass

Q19. A substance is heated. The graph shows how the temperature changes with the heat energy added.



In which region of the graph must the solid state be present?

A I **B** II **C** III **D** None

Q20. Explain why a burn to the skin caused by boiling water is less harmful than a burn caused by the same amount of steam produced as the water boils.

Guiding Question revisited

How can we model the particulate nature of matter?

In this chapter we have used a particulate model to show:

- All matter is made up from small particles.
- An element is a pure chemical substance composed of the same type of atoms.
- Compounds consist of atoms of different elements chemically bonded together in a fixed ratio.
- Mixtures are made from particles of one substance interspersed between particles of at least one other substance. If this mixing is uniform, it is a homogeneous mixture. If it is not uniform, it is heterogeneous.
- The different states of matter are characterized by the movement and arrangement of the particles.
- Changes of state require energy changes as energy is needed to separate particles and is given out when particles come together.

Practice questions

1. Which statements are correct?

I. Solids have a fixed shape because the particles can only vibrate about a fixed point.

II. Liquids can flow because the particles can move freely.

III. Gases are less dense because the interactions between the particles are very weak.

A I and II **B** I and III **C** II and III **D** I, II and III

2. The temperature of a gas is reduced. Which of the following statements is true?

A The molecules collide with the walls of the container less frequently.

B The molecules collide with each other more frequently.

C The time of contact between the molecules and the wall is reduced.

D The time of contact between molecules is increased.

3. Which of the following occurs at the melting point when a solid is converted to a liquid?

I. kinetic energy of the particles increases

II. separation between the particles increases

A I only **B** II only **C** I and II **D** neither I nor II

4. Identify the change(s) that occur at the boiling point when a liquid is converted to a gas.

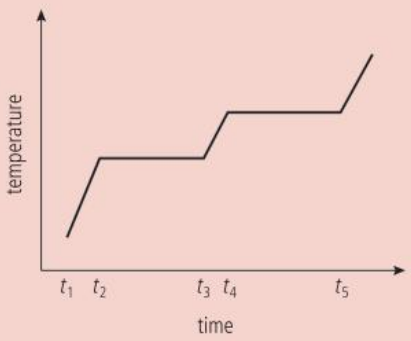
I. kinetic energy of the particles increases

II. separation between the particles increases

A I only **B** II only **C** I and II **D** neither I nor II

5. A substance is heated at a constant rate.

During which interval does the energy of the substance increase the most?



A t_1 to t_2

B t_2 to t_3

C t_3 to t_4

D t_4 to t_5

6. An ice cube of mass 10.0 g with a temperature of 0 °C is placed into a glass containing 90 cm^3 of water at 10 °C.

After 5 minutes some of the ice has melted. What is the temperature of the ice remaining?

A 0 °C **B** 0.5 °C **C** 2.0 °C **D** 5 °C

7. Identify the pair of substances that can form a homogeneous mixture.

A olive oil and vinegar **B** sand and water

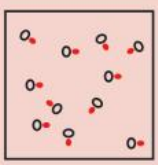
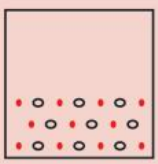
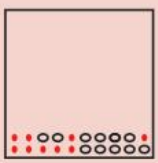
C carbon dioxide and water **D** salt and pepper

8. Identify the equation that represents sublimation.

A $I_2(g) \rightarrow 2I(g)$ **B** $I_2(s) \rightarrow I_2(g)$

C $I_2(s) + I^-(aq) \rightarrow I_3^-(aq)$ **D** $2Al(s) + 3I_2(s) \rightarrow 2AlI_3(s)$

9. Which descriptions are consistent with the diagram?

	Diagram	Description
I.		A compound in the gaseous state.
II.		A compound in the liquid state.
III.		A heterogeneous mixture in the solid state.

A I and II only **B** I and III only **C** II and III only **D** I, II and III

10. A mixture of ethanol and methanol can be separated by fractional distillation. This method of separation depends on the difference of which property of the two alcohols?

A melting point **B** boiling point **C** solubility **D** density

11. The solubilities of four different substances in water and ethanol are given.

	Solubility in water	**Solubility in ethanol**
P	insoluble	insoluble
Q	insoluble	soluble
R	soluble	insoluble
S	soluble	soluble

Some mixtures can be separated by solvation and filtration using water or ethanol as solvents.

Method I uses water as the solvent.

Method II uses ethanol as the solvent.

Which substances can be separated from each other using both methods?

A P and S **B** Q and S **C** R and S **D** Q and P

12. Classify the following mixtures as homogeneous or heterogeneous:

(a) smoke **(b)** sugar and water **(c)** steel (3)

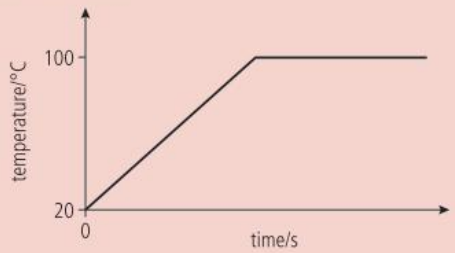
(Total 3 marks)

13. During very cold weather, snow often gradually disappears without melting. Explain how this is possible.

14. **(a)** Describe **two** differences, in terms of particle structure, between a gas and a liquid. (2)

(b) The temperature of a gas is a measure of the average kinetic energy of the gas particles. Suggest why the **average** kinetic energy is specified. (2)

(c) A sample of water was heated. The graph shows how the temperature of the water varied with time.



(i) State why the temperature initially increases. (1)

(ii) State why the temperature remains constant at 100 °C. (2)

(Total 7 marks)

15. (a) The physical properties of some halogens are shown in the table.

Element	Molecular formula	Melting point / °C	Boiling point / °C
fluorine	F_2	−220	−188
chlorine	Cl_2	−101	−35
bromine	Br_2		58.8
iodine	I_2	114	184

Predict the melting point of bromine. (1)

(b) Describe the trend in the boiling points of the halogens down the group. (1)

(c) Predict the physical state of iodine at 200 °C. (1)

(d) A simplified diagram of the structure for bromine is shown.



(i) Suggest the state of bromine with this structure and justify your answer. (2)

(ii) Describe the changes that occur to this arrangement when bromine is heated. (2)

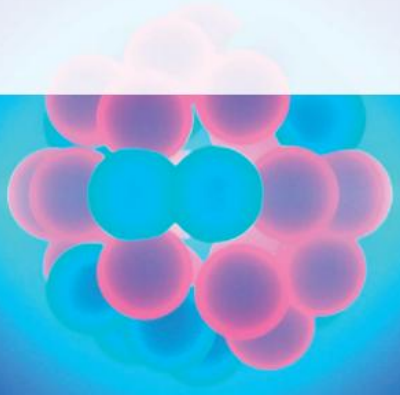
(iii) Describe the changes that occur when bromine reacts. (1)

(iv) Use the kinetic theory to explain the effect of an increase in temperature on the rate of diffusion of bromine. (1)

(Total 9 marks)

STRUCTURE

1.2 The nuclear atom




The atomic nucleus is at the centre of the atom. The number of protons in the nucleus gives the atom its identity.





Guiding Question

How do the nuclei of atoms differ?

We saw in Structure 1.1 that all matter is built from no more than about 100 elements. The smallest amount of an element that can exist is an atom, which is the smallest particle of an element to show the element's characteristic properties. It is amazing that particles as small as the atom can have such a huge impact on the universe. Almost all explanations in chemistry refer to the atom, either individually or in the groups we call molecules.

In this chapter we will explore the structure of atoms in more detail. Although the word 'atom' means uncuttable, the atom *can* be split into smaller subatomic particles. All atoms are made from the same basic ingredients: protons, neutrons and electrons, but differ in their composition. If you look at the periodic table, you will see that each element has an atomic number. This was originally used to give the relative position of the element in the table. For example, the first element, hydrogen, has an atomic number of 1. We now know that this number is more fundamental than just a ranking. The atomic number is the defining property of an element as it is the number of protons in the nucleus of the atom.

Although the nucleus is only a small part of the atom, you can think of it as the atom's control centre. As an atom has a neutral charge, the number of protons also determines the number of electrons. The number of protons gives an atom its identity and the number of electrons determines its chemical properties. The mass of an element's atoms can vary due to a difference in the number of neutrons in the nucleus, but this has little impact on the chemistry of the atom. The number of neutrons does, however, affect some physical properties, including the nuclear stability.



Richard Feynman: '... if all of scientific knowledge were to be destroyed, and only one sentence passed on to the next generation of creatures, what statement would contain the most information in the fewest words? I believe it is the atomic hypothesis... that *all things are made of atoms.*'
Are the models and theories that scientists create accurate descriptions of the natural world, or are they primarily useful interpretations for prediction, explanation, and control of the natural world?

Structure 1.2.1 – The atomic model

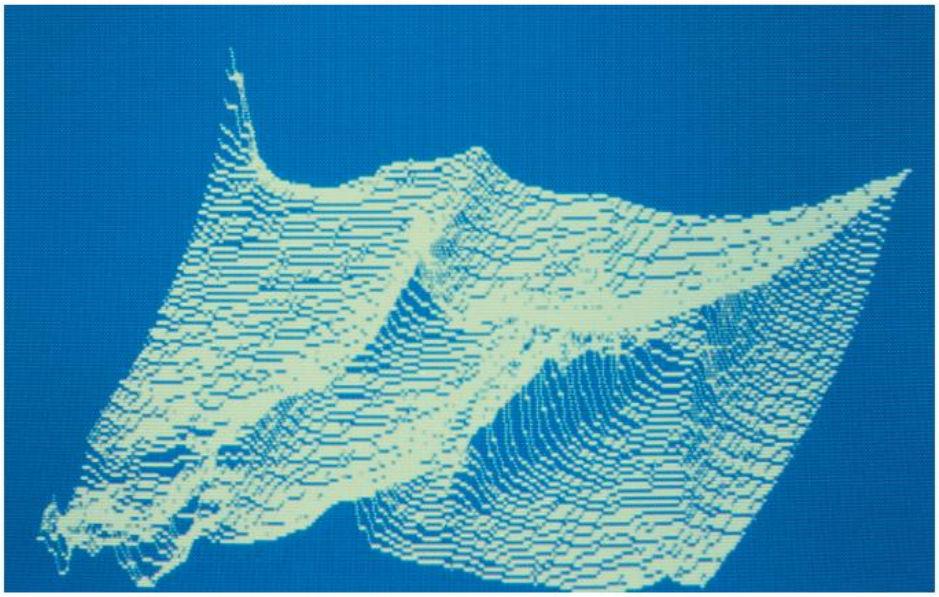
Structure 1.2.1 – Atoms contain a positively charged, dense nucleus composed of protons and neutrons (nucleons). Negatively charged electrons occupy the space outside the nucleus. Use the nuclear symbol ($^{A}_{Z}X$) to deduce the number of protons, neutrons and electrons in atoms and ions.	
Relative masses and charges of the subatomic particles should be known; actual values are given in the data booklet. The mass of the electron can be considered negligible.	Structure 1.3 – What determines the different chemical properties of atoms? Structure 3.1 – How does the atomic number relate to the position of an element in the periodic table?

Atoms contain a positively charged, dense nucleus

Dalton's model of the atom

One of the first great achievements of chemistry was to show that all matter is built from about 100 **elements.** As mentioned in Structure 1.1, the elements are substances which cannot be broken down into simpler components by chemical reactions. Different elements have different chemical properties but gold foil, for example, reacts in essentially the same way as a single piece of gold dust. Indeed, if the gold dust is cut into smaller and smaller pieces, the chemical properties would remain the same until we reached an **atom**. The atom is the smallest unit of an element. There are only 92 elements which occur naturally on Earth, and they are made up of only 92 different types of atom. (This statement will be qualified when isotopes are discussed later in the chapter.)

The word 'atom' comes from the Greek words for 'not able to be cut'.



Scanning tunnelling microscope (STM) image of the surface of pure gold. STM imaging records the surface structure at the level of the individual atoms. Gold exists in many forms, but all the forms contain the same type of atoms. The 'rolling hills' structure seen here is the result of changes in the surface energy as the gold cooled from its molten state.

Nature of Science

The idea that matter is made up of elements and atoms dates back to the 4th century BCE. This was speculative as there was little evidence to support the idea. Scientists adopt a sceptical attitude to claims and evaluate them using evidence. A significant development for chemistry came with the publication of Robert Boyle's *Sceptical Chymist* in 1661 which emphasized the need for scientific knowledge to be justified by evidence from practical investigations. Boyle was the first person to propose the modern concept of an element as a substance which cannot be changed into anything simpler.

The modern idea of the atom dates from the beginning of the 19th century. John Dalton noticed that the elements hydrogen and oxygen always combined in fixed proportions. To explain this observation, he proposed that:

- all matter is composed of tiny indivisible particles called atoms
- atoms cannot be created or destroyed
- atoms of the same element are alike in every way
- atoms of different elements are different
- atoms can combine together in small numbers to form **molecules**.

Using this model, we can understand how elements react together to make **compounds**. The compound water, for example, is formed when two hydrogen atoms combine with one oxygen atom to produce one water molecule. If we repeat the reaction on a larger scale with $2 \times 6.02 \times 10^{23}$ atoms of hydrogen and 6.02×10^{23} atoms of oxygen, then 6.02×10^{23} molecules of water will be formed. This leads to the conclusion (see Structure 1.4) that 2.02 g of hydrogen will react with 16.00 g of oxygen to form 18.02 g of water. This is one of the observations Dalton was trying to explain.

Nature of Science

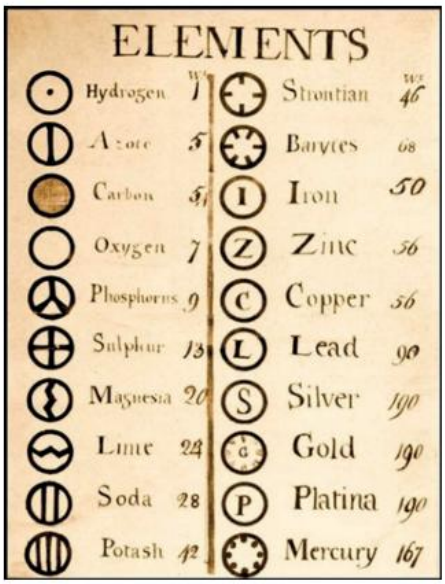
Dalton was a man of regular habits. 'For fifty-seven years… he measured the rainfall, the temperature… Of all that mass of data, nothing whatever came. But of the one searching, almost childlike, question about the weights that enter the construction of simple molecules – out of that came modern atomic theory. That is the essence of science: ask an impertinent question: and you are on the way to the pertinent answer.' (J. Bronowski).

TOK

'What we observe is not nature itself but nature exposed to our mode of questioning.' (Werner Heisenberg).

How does the knowledge we gain about the natural world depend on the questions we ask and the experiments we perform?

Dalton was the first person to assign chemical symbols to the different elements.



John Dalton's symbols for the elements.

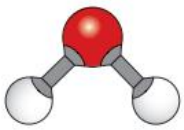
Challenge yourself

1. It is now known that some of these substances are not elements but compounds. Lime, for example, is a compound of calcium and oxygen. Find any other examples of compounds in this list, and explain why the component elements had not been extracted at this time.

Following Dalton's example, you can write the formation of water using modern notation:

$$2H + O \rightarrow H_2O$$

But what are atoms really like? It can be useful to think of them as hard spheres (Figure 1), but this tells us little about how the atoms of different elements differ. To understand this, it is necessary to probe deeper.



S1.2 Figure 1 A model of a water molecule made from two hydrogen atoms and one oxygen atom. Dalton's picture of the atom as a hard ball is the basis behind the molecular models we use today.

Nature of Science

Dalton's atomic theory was not accepted when it was first proposed. Many scientists considered it as nothing more than a useful fiction which should not be taken too seriously. Over time, as the supporting evidence grew, this changed to its widespread acceptance. These revolutions in understanding, or '**paradigm shifts**', are characteristic of the evolution of scientific thinking.

TOK

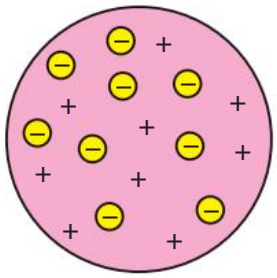
One of the barriers to the acceptance of Dalton's model of the atom was opposition from leading scientists such as Kelvin. In what ways can influential individuals help or hinder the development of scientific knowledge?

Atoms contain electrons

The first indication that atoms were destructible came at the end of the 19th century when the British scientist J. J. Thomson discovered that different metals produce a stream of negatively charged particles when a high voltage is applied across two electrodes. As these particles, which we now know as **electrons**, were the same regardless of the metal, he suggested that they are part of the make-up of all atoms.

Nature of Science

The properties of electrons, or cathode rays as they were first called, could only be investigated once powerful vacuum pumps had been invented – and once advances had been made in the use and understanding of electricity and magnetism. Improved instrumentation and new technology are often the drivers for new discoveries.



S1.2 Figure 2 Thomson's 'plum pudding' model of the atom. The negatively charged electrons (yellow) are positioned in a positively charged sponge-like substance (pink).

As Thomson knew that the atom had no net charge, he pictured the atom as a 'plum pudding', with the negatively charged electrons positioned in a positively charged sponge-like substance (Figure 2).

Atoms contain a nucleus

Ernest Rutherford (1871–1937) and his research team working at Manchester University in England, tested Thomson's model by firing alpha particles at a piece of gold foil. If Thomson's model was correct, the alpha particles should either pass straight through or get stuck in the positive 'sponge'. Most of the alpha particles did indeed pass straight through, but a very small number were repelled.

The large number of undeflected particles led Rutherford to the conclusion that the atom is mainly empty space. Large deflections occur when the positively charged alpha particles collide with, and are repelled by, a positively charged nucleus. The fact that only a small number of alpha particles bounce back suggests that the nucleus is very small.

TOK

When Rutherford's team reported that they had seen a small number of alpha particles deflected by small angles, he asked them to see if any of the alpha particles had bounced back. This was a very unusual suggestion to make at the time, with little logical justification. What is the role of intuition in the pursuit of scientific knowledge?

Nature of Science

Our knowledge of the nuclear atom came from Rutherford's experiments with the relatively newly discovered alpha particles. Progress in science often follows technological developments that allow new experimental techniques.

Nature of Science

Rutherford used his model of a positively charged nucleus to derive an equation for the scattering pattern of the alpha particles. His derivation assumed that only electrostatic repulsive forces acted between the positive gold nucleus and the positive alpha particles. All models have limitations which need to be considered in their application.

Challenge yourself

2. The derivation of the Rutherford formula is based on the assumption that only electrostatic forces need to be considered during the scattering process. Suggest why the experimental results deviate from this model for high-energy alpha particles.

Subatomic particles

A hundred years or so after Dalton first proposed his model, further experiments showed that the nucleus of an atom is made up of **protons** and **neutrons,** collectively called **nucleons.** Protons and neutrons have almost the same mass and together account for most of the mass of the atom. Electrons, which have a charge equal and opposite to that of the proton, have generally negligible mass and occupy the space in the atom outside of the nucleus.

The absolute masses and charges of these fundamental particles are given in Section 2 of the data booklet and this table gives their relative masses and charges. Note that relative quantities are ratios and so have no units.

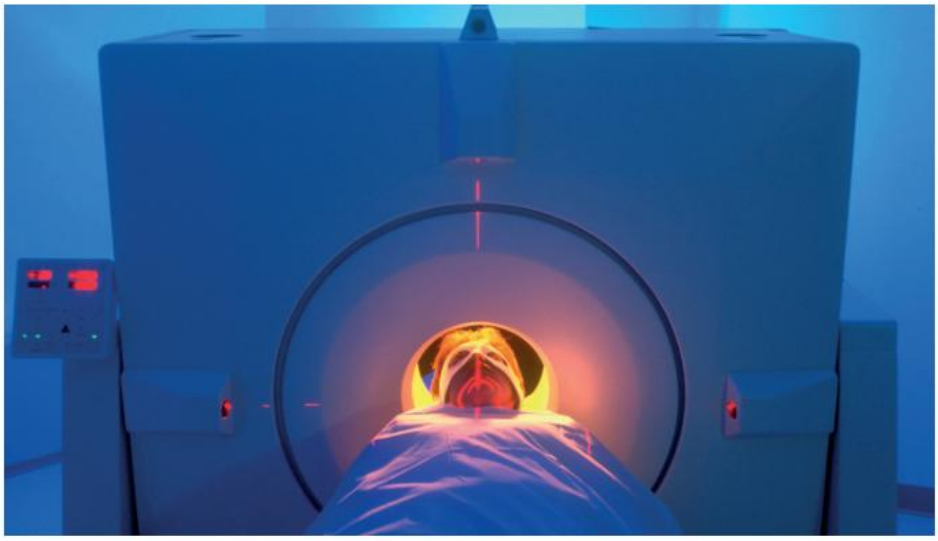
Subatomic particle	Relative mass	Relative charge
proton	1	+1
electron	0.0005	−1
neutron	1	0

You should know the relative masses and charges of the subatomic particles. Actual values are given in the data booklet. The mass of the electron can generally be considered to be negligible.

Nature of Science

The description of subatomic particles given here is sufficient to understand chemistry but it is incomplete. Although the electron is indeed a fundamental particle, we now know that protons and neutrons are both themselves made up of more fundamental particles called quarks. We also know that all particles have anti-particles. The positron is the anti-particle of an electron; it has the same mass but has an equal and opposite positive charge. When particles and anti-particles collide, they destroy each other and release energy in the form of high-energy **photons** called gamma rays. Our treatment of subatomic particles is in line with the principle of Occam's razor, which states that theories should be as simple as possible while maximizing explanatory power.

PET (positron-emission tomography) scanners give three-dimensional images of tracer concentration in the body, and can be used to detect cancers. The patient is injected with a tracer compound labelled with a positron-emitting isotope. The positrons collide with electrons after travelling a short distance (≈1 mm) within the body. Both particles are destroyed, and two photons are produced. The protons can be collected by the detectors surrounding the patient, and used to generate an image.



A patient undergoing a positron-emission tomography (PET) brain scan. A radioactive tracer is injected into the patient's bloodstream, which is then absorbed by active tissues of the brain. The PET scanner detects photons emitted by the tracer and produces 'slice' images.

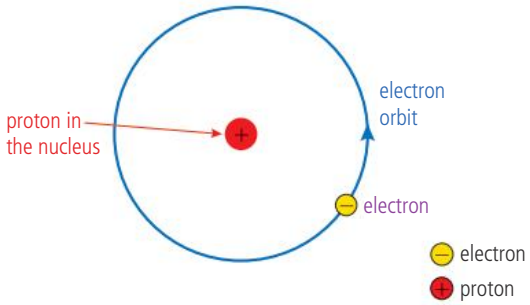
As you are made from atoms, you are also mainly empty space. The particles which make up your mass would occupy the same volume as a flea if they were all squashed together, but a flea with your mass. This gives you an idea of the density of the nucleus.

Challenge yourself

3. Construct an equation for the collision of an electron and a positron to give two photons and explain why it is balanced.

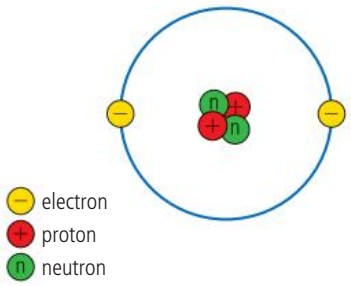
Bohr model of the hydrogen atom

The Danish physicist Niels Bohr pictured the hydrogen atom as a small 'solar system', with an electron moving in an orbit (energy level) around the positively charged nucleus of one proton (Figure 3). The electrostatic force of attraction between the oppositely charged subatomic particles prevents the electron from leaving the atom. The nuclear radius is 10^{-15} m and the atomic radius 10^{-10} m, so most of the volume of the atom is empty space.



S1.2 Figure 3 The Bohr model of the simplest atom. Only one proton and one electron make up the hydrogen atom. Most of the volume of the atom is empty – the only occupant is the single negatively charged electron. It is useful to think of the electron orbiting the nucleus in a similar way to the planets orbiting the Sun. The absence of a neutron is significant – it would be essentially redundant as there is only one proton.

The existence of neutrally charged neutrons is crucial for the stability of nuclei of elements that have more than one proton (Figure 4). Without the neutrons, the positively charged protons would mutually repel each other and the nucleus would fall apart.



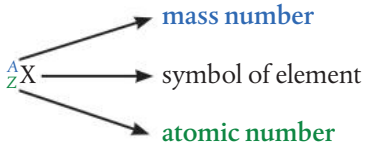
S1.2 Figure 4 The Bohr model of a helium atom. The two neutrons allow the two protons, which repel each other, to stay in the nucleus. A strong nuclear force acts between all the nucleons which is larger than the repulsive electrostatic forces that act between the protons.

Atomic number and mass number

We are now in a position to understand how the atoms of different elements differ. They are all made from the same basic ingredients, the subatomic particles. The only difference is the recipe – how many of each of these subatomic particles are present in the atoms of different elements. If you look at the periodic table, you will see that the elements are each given a number which describes their relative position in the table. This is their **atomic number**. We now know that the atomic number, represented by **Z**, is the defining property of an element as it tells us something about the structure of the atoms of the element. The atomic number is defined as the number of protons in the atom.

As an atom has no overall charge, the positive charge of the protons must be balanced by the negative charge of the electrons. Therefore the atomic number is also equal to the number of electrons in an atom.

The electron has such a very small mass that it is essentially ignored in mass calculations. The mass of an atom depends on the number of protons and neutrons only. The **mass number**, given the symbol **A**, is defined as the number of protons plus the number of neutrons in an atom. An atom is identified in the following way:

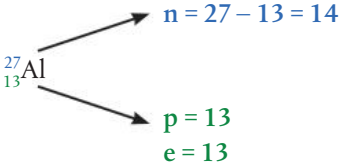


We can use these numbers to find the composition of any atom.

$$\text{number of protons (p)} = \text{number of electrons} = Z$$

$$\text{number of neutrons (n)} = \text{mass number} - \text{number of protons} = A - Z$$

Consider an atom of aluminium:



An aluminium atom has 13 protons and 13 electrons. An atom of gold on the other hand has 79 protons and 79 electrons. Can you find gold in the periodic table? The periodic table arranges the elements in order of their atomic number as discussed in Structure 3.1.

TOK

None of these subatomic particles can be (or ever will be) directly observed.

What assumptions are made when we interpret indirect evidence gained through the use of technology?

The atomic number is defined as the number of protons in the nucleus.

Make sure you have a precise understanding of the terms. The atomic number, for example, is defined in terms of the number of protons, not electrons.

The mass number (*A*) is the number of protons plus the number of neutrons in an atom. It is sometimes called the nucleon number.

SKILLS

Build an atom PhET activity. Full details on how to carry out this activity with a worksheet are available in the eBook.

Structure 3.1 – How does the atomic number relate to the position of an element in the periodic table?

Challenge yourself

4. Explain why the 13 protons in aluminium stay in the nucleus despite their mutual repulsion.

5. Experiments show the nuclear radius R depends on the mass number A according to the expression: $R = 1.2 \times 10^{-15} A^{\frac{1}{3}}$. Deduce an expression for the density of a nucleus and comment on your result.

Worked example

Identify the subatomic particles present in an atom of ^{226}Ra.

Solution

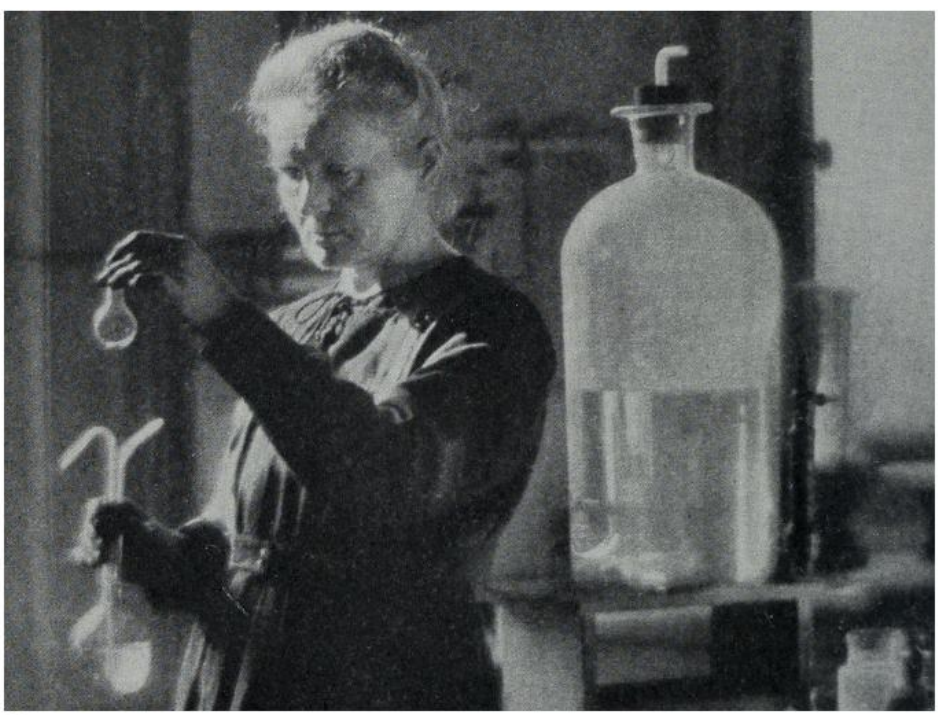
The number identifying the atom is the atomic number. We can find the atomic number from the data booklet (Section 6).

We have $Z = 88$ and $A = 226$

number of protons (p) = 88

number of electrons (e) = 88

number of neutrons (n) = 226 – 88 = 138



The element radium was first discovered by the Polish–French scientist Marie Curie. She is the only person to win Nobel Prizes in both Physics and Chemistry. The Curies were a remarkable family for scientific honours – Marie shared her first prize with her husband Pierre, and her daughter Irène shared hers with her husband Frédéric. All the Curies' prizes were for work on radioactivity.

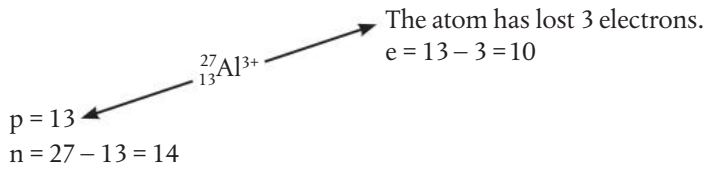
Ions

The atomic number is defined in terms of the number of protons because it is a fixed characteristic of the element. The number of protons identifies the element in the same way your fingerprints identify you. The number of protons and neutrons never changes during a chemical reaction. It is the electrons which are responsible for chemical change. Structure 2.1 examines how atoms can lose or gain electrons to form **ions**. When the number of protons in a particle is no longer balanced by the number of electrons, the particle has a non-zero charge. When an atom loses electrons, it forms a positive ion or **cation**, as the number of protons is now greater than the number of electrons. Negative ions or **anions** are formed when atoms gain electrons. The magnitude of the charge depends on the number of electrons lost or gained. The loss or gain of electrons makes a very big difference to the chemical properties. You swallow sodium ions, Na^+, every time you eat table salt, whereas (as covered in Structure 3.1) sodium atoms, Na, are dangerously reactive.

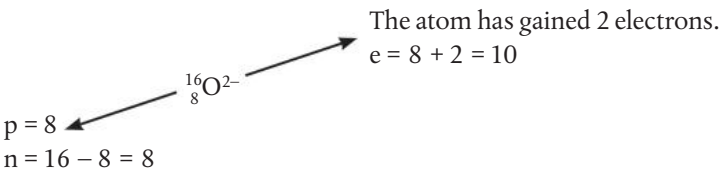
When an atom loses electrons, a positive ion is formed and when an atom gains electrons, a negative ion is formed. Positive ions are called cations and negative ions are called anions.

Structure 1.3 – What determines the different chemical properties of atoms?

An aluminium ion is formed when the atom loses three electrons. There is no change in the atomic or mass numbers of an ion because the number of protons and neutrons remains the same.



Oxygen forms the oxide ion when its atoms gain two electrons.



Worked example

Most nutrient elements in food are present in the form of ions. The calcium ion $^{40}Ca^{2+}$, for example, is essential for healthy teeth and bones. Identify the subatomic particles present in the ion.

Solution

We can find the atomic number from the data booklet (Section 6).
We have Z = 20 and A = 40:

- number of protons (p) = 20
- number of neutrons (n) = 40 – 20 = 20

As the ion has a positive charge of 2+ there are two more protons than electrons:

- number of electrons = 20 – 2 = 18

Worked example

Identify the species with 19 protons, 20 neutrons and 18 electrons.

Solution

- the number of protons tells us the atomic number, Z = 19, and so the element is potassium, K
- the mass number = p + n = 19 + 20 = 39: $^{39}_{19}K$
- the charge = p – e = 19 – 18 = +1 as there is one extra proton: $^{39}_{19}K^{+}$

Challenge yourself

6. We generally make the approximation that the mass of an ion is the same as that of the corresponding atom. To how many significant figures is this approximation valid for the H^{+} ion?

Exercise

Q1. Explain why the relative atomic mass of tellurium is greater than the relative atomic mass of iodine, even though iodine has a greater atomic number.

Q2. Use the periodic table to identify the subatomic particles present in the following species.

	Species	No. of protons	No. of neutrons	No. of electrons
(a)	^{7}Li			
(b)	^{1}H			
(c)	^{14}C			
(d)	$^{19}F^{-}$			
(e)	$^{56}Fe^{3+}$			

Q3. Isoelectronic species have the same number of electrons. Identify the following isoelectronic species by giving the correct symbol and charge. You will need a periodic table.

The first one has been done as an example.

	Species	No. of protons	No. of neutrons	No. of electrons
	$^{40}Ca^{2+}$	20	20	18
(a)		18	22	18
(b)		19	20	18
(c)		17	18	18

Q4. What is the difference between two neutral atoms represented by the symbols $^{14}_{6}C$ and $^{14}_{7}N$?

I. the number of neutrons II. the number of protons
III. the number of electrons

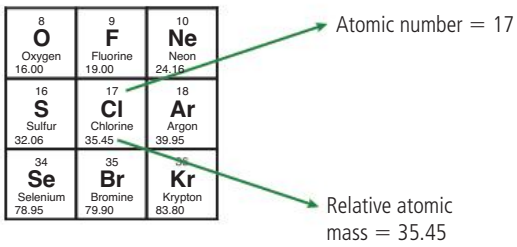
A I and II only **B** I and III only **C** II and III only **D** I, II and III

Structure 1.2.2 – Isotopes

Structure 1.2.2 – Isotopes are atoms of the same element with different numbers of neutrons. Perform calculations involving non-integer relative atomic masses and abundance of isotopes from given data.	
Differences in the physical properties of isotopes should be understood. Specific examples of isotopes need not be learned.	Nature of Science, Reactivity 3.4 – How can isotope tracers provide evidence for a reaction mechanism?

Isotopes are atoms of the same element with different numbers of neutrons

Find chlorine in the periodic table. There are two numbers associated with the element, as shown below.



How can an element have a fractional relative atomic mass if protons and neutrons each have a relative mass of 1? One reason is that atoms of the same element with different mass numbers exist, and the relative atomic mass given in the periodic table is an average value.

To have different mass numbers, the atoms must have different numbers of neutrons – all the atoms have the same number of protons as they are all chlorine atoms. Atoms of the same element with different numbers of neutrons are called **isotopes**.

The isotopes show the same chemical properties, as a difference in the number of neutrons makes no difference to how atoms react and so they occupy the same place in the periodic table.

Chlorine exists as two isotopes, $\boxed{^{35}_{17}\text{Cl}}$ and $\boxed{^{37}_{17}\text{Cl}}$. The average relative mass of the isotopes is, however, not 36, but 35.45. This value is closer to 35 as there are more $^{35}_{17}\text{Cl}$ atoms in nature – it is the more *abundant* isotope. In a sample of 1000 chlorine atoms, there are 775 atoms of $^{35}_{17}\text{Cl}$ and 225 atoms of the heavier isotope, $^{37}_{17}\text{Cl}$.

To work out the average mass of one atom, we first have to calculate the total mass of the thousand atoms:

$$\text{total mass} = (775 \times 35) + (225 \times 37) = 35450$$

$$\text{relative average mass} = \frac{(\text{total mass})}{(\text{number of atoms})} = \frac{35450}{1000} = 35.45$$

SKILLS

Modelling isotopic abundance. Full details on how to carry out this experiment with a worksheet are available in the eBook.

Isotopes are atoms of the same element with different mass numbers.

The word 'isotope' derives from the Greek for 'same place'. As isotopes are atoms of the same element, they occupy the same place in the periodic table.

A common error is to misunderstand the meaning of 'physical property'. A difference in the number of neutrons is not a different physical property. A physical property of a substance can be measured without changing the chemical composition of the substance. Density and boiling point are examples of physical properties.

The two isotopes are both atoms of chlorine with 17 protons and 17 electrons.

- $^{35}_{17}Cl$ number of neutrons = 35 – 17 = 18
- $^{37}_{17}Cl$ number of neutrons = 37 – 17 = 20

Although both isotopes essentially have the same chemical properties, the difference in mass does lead to different physical properties such as boiling and melting points. As explained in Structure 1.1, heavier particles move more slowly at a given temperature and these differences can be used to separate isotopes.

Uranium consists of two natural isotopes: mostly U-238 and less than 1% U-235. The fuel used in nuclear power stations is U-235; its content needs to be increased to around 3–5% of the overall mixture to make a controlled nuclear fission reaction feasible. The enrichment can be carried out by gas diffusion, by heating solid uranium hexafluoride (UF_6). The UF_6 molecules containing U-235 are lighter and diffuse faster through the pipelines and filters, producing a UF_6 gas that is enriched with U-235.



▲ Gas diffusion machinery in southern France used to enrich uranium for use in nuclear reactors.

Challenge yourself

7. Suggest why isotope nuclear enrichment plants based on gaseous diffusion are so large.

Nature of Science, Reactivity 3.4 – How can isotope tracers provide evidence for a reaction mechanism?

The stability of a nucleus depends on the balance between the number of protons and neutrons. A nucleus which contains either too many or too few neutrons to be stable is radioactive and changes to a more stable nucleus by giving out radiation. As these **radioisotopes** behave chemically in the same way as nonradioactive isotopes, they can be used as tracers to follow the movement of elements or compounds in complex processes such as living systems. The radioisotopes can be located because the radioactivity they emit can be detected. Radioactive isotopes can also provide evidence for the reaction mechanisms explored in Reactivity 3.4.

Human activities have caused increased atmospheric nitrogen pollution, mainly nitrogen oxides and ammonia. This nitrogen is eventually taken up by plants, increasing plant growth.

Evidence for this comes from experiments using tracer isotopes of nitrogen ($^{15}_{7}N$) to follow the nitrogen through the air and plants.



Evidence for increased nitrogen pollution comes from experiments using tracer isotopes of nitrogen ($^{15}_{7}N$) in plants.

Challenge yourself

8. Use the periodic table in the data booklet to identify an element with an atomic number of less than 80 which has no stable isotopes.

Exercise

Q5. State two physical properties other than boiling point and melting point that would differ for the two isotopes of chlorine.

Q6. Identify the particles which account for the existence of isotopes.

A electrons **B** nucleons **C** neutrons **D** protons

Q7. Which of the following species contains more electrons than neutrons?

A $^{2}_{1}H$ **B** $^{11}_{5}B$ **C** $^{16}_{8}O^{2-}$ **D** $^{19}_{9}F^{-}$

Q8. Which of the following gives the correct composition of the $^{71}Ga^{+}$ ion?

	Protons	Neutrons	Electrons
A	31	71	30
B	31	40	30
C	31	40	32
D	32	40	31

Q9. Chromium has an atomic number of 24. The mass numbers of its four stable isotopes are 50, 52, 53 and 54.

Identify the correct statements about the isotopes.

I. All the isotopes have the same chemical properties.

II. All the isotopes have nuclei containing 24 protons.

III. One of the isotopes has 54 neutrons.

A I and II only **B** I and III only **C** II and III only **D** I, II and III

Q10. Identify the atoms which are isotopes.

	Mass number	Atomic number
W	52	24
X	53	25
Y	53	24
Z	52	25

A W and Z **B** X and Y **C** W and Y **D** Y and Z

Q11. The relative atomic mass of silicon is 28.09. Comment on the claim that no atom of silicon exists with this relative mass.

Q12. Deduce the composition of a nucleus of boron-11, $^{11}_{5}B$.

	Protons	Neutrons
A	5	11
B	11	5
C	6	5
D	5	6

Q13. What is the same for an atom of phosphorus-26 and an atom of phosphorus-27?

A atomic number and mass number

B number of protons and electrons

C number of neutrons and electrons

D number of protons and neutrons

HL

Structure 1.2.3 – Mass spectra

Structure 1.2.3 – Mass spectra are used to determine the relative atomic masses of elements from their isotopic composition. Interpret mass spectra in terms of identity and relative abundance of isotopes.	
The operational details of the mass spectrometer will not be assessed.	Structure 3.2 – How does the fragmentation pattern of a compound in the mass spectrometer help in the determination of its structure?

Mass spectra are used to determine the relative atomic masses of elements from their isotopic composition

The mass spectrometer can measure the mass and abundance of isotopes

The masses of the different isotopes and their relative abundance can be measured using a mass spectrometer.

The element to be tested is first vaporized so that individual atoms can be analysed. The atoms are then ionized by high-energy electrons which knock out an electron to produce a positively charged ion:

$$X(g) + e^- \rightarrow X^+(g) + 2e^-$$

The positively charged ions are attracted to a negatively charged plate and deflected by a magnetic field placed at right angles to their path. The amount of deflection is inversely proportional to their **mass/charge** (m/z) ratio. This is equivalent to the mass when the ions have a single positive charge. Single-charge ions with smaller mass are deflected more than heavier ions with the same charge.

If a compound is analysed in a mass spectrometer, the electron collisions during the ionization step are so energetic that they can cause the molecule to break up into different fragments. The resulting **fragmentation pattern** provides useful evidence about the structure of the compound. A chemist pieces together the fragments to form a picture of the complete molecule, in the same way that archaeologists find clues about the past from the pieces of artefacts discovered in the ground. Fragmentation patterns are explored more fully in Structure 3.2.



Structure 3.2 – How does the fragmentation pattern of a compound in the mass spectrometer help in the determination of its structure?



You will not be assessed on the operational details of the mass spectrometer but you should include the positive charge when identifying the ions in a mass spectrum.

The relative atomic mass of an element

The mass of a hydrogen atom is 1.67×10^{-24} g and that of a carbon atom is 1.99×10^{-23} g. As the masses of all elements are in the range 10^{-24} to 10^{-22} g, and as these numbers are beyond our direct experience, it makes more sense to use relative values. The mass needs to be recorded relative to some agreed standard. As carbon is a very common element which is easy to transport and store because it is a solid, its isotope, ^{12}C, was chosen as the standard in 1961. This is discussed in Structure 1.4 and ^{12}C is given a relative mass of exactly 12, as shown below.

Element	Symbol	Relative atomic mass
carbon	C	12.011
chlorine	Cl	35.453
hydrogen	H	1.008
iron	Fe	55.845
Standard isotope	**Symbol**	**Relative atomic mass**
carbon-12	^{12}C	12.000



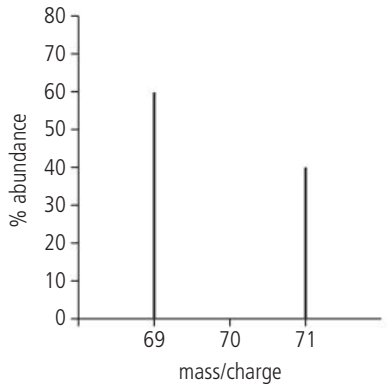
The relative atomic mass of an element (A_r) is the average mass of an atom of the element, taking into account all its isotopes and their relative abundance, compared to one atom of carbon-12.

Carbon-12 is the most abundant isotope of carbon but carbon-13 and carbon-14 also exist. This explains why the average value for the element is greater than 12.

Mass spectra

The results of the analysis by a mass spectrometer are presented in the form of a **mass spectrum**. As discussed earlier, the mass spectrometer measures the mass/charge ratio of the deflected particles and this is displayed on the horizontal axis using the carbon-12 scale. In most cases the charge of the ion is +1 so the horizontal axis generally also gives the mass. The relative abundance of the ions corresponding to different isotopes is shown on the vertical axis.

The mass spectrum of gallium in Figure 5 shows that in a sample of 100 atoms, 60 have a mass of 69 and 40 have a mass of 71. We can use this information to calculate the relative atomic mass of the element.



S1.2 Figure 5 Mass spectrum for gallium. The number of lines indicates the number of isotopes (two in this case), the value on the *x*-axis indicates their mass numbers (69 and 71) and the *y*-axis shows the percentage abundance.

$$\text{total mass of 100 atoms} = (60 \times 69) + (40 \times 71) = 6980$$

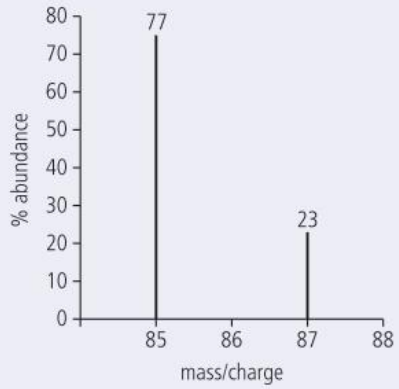
$$\text{relative average mass} = \frac{\text{total mass}}{\text{number of atoms}} = \frac{6980}{100} = 69.80$$

Challenge yourself

9. Suggest how the mass spectrum of gallium changes if the kinetic energy of the electrons used in ionizing the sample in a mass spectrometer is significantly increased.

Worked example

Deduce the relative atomic mass of the element rubidium from the data given in the graph.



Solution

Consider a sample of 100 atoms.

$$\text{total mass of 100 atoms} = (85 \times 77) + (87 \times 23) = 8546$$

$$\text{relative atomic mass} = \text{average mass of atom} = \frac{\text{total mass}}{\text{number of atoms}} = \frac{8546}{100} = 85.46$$

Worked example

Boron exists as two isotopes, ^{10}B and ^{11}B. ^{10}B is used as a control for nuclear reactors. Use your periodic table to find the abundances of the two isotopes.

Solution

Consider a sample of 100 atoms.

Let x atoms be ^{10}B atoms. The remaining atoms are ^{11}B.

number of ^{11}B atoms $= 100 - x$

total mass of 100 atoms $= [x \times 10] + [(100 - x) \times 11] = 10x + 1100 - 11x = 1100 - x$

$$\text{average mass} = \frac{\text{total mass}}{\text{number of atoms}} = \frac{1100 - x}{100}$$

From the periodic table, the relative atomic mass of boron = 10.81.

$$10.81 = \frac{1100 - x}{100}$$

$$1081 = 1100 - x$$

$$x = 1100 - 1081 = 19$$

The abundances are $^{10}B = 19\%$ and $^{11}B = (100 - 19) = 81\%$



A mass spectrometer used in radiocarbon dating. The ratio of radioactive ^{14}C to stable ^{12}C is related to the time since the death of the animal or plant being investigated.

Carbon-14 has eight neutrons, which is too many to be stable. It can reduce the neutron-to-proton ratio by radioactive decay. The relative abundance of carbon-14 present in living plants is constant as the carbon atoms are continually replenished from the carbon present in atmospheric carbon dioxide. When organisms die, however, no more carbon-14 is absorbed and the levels of carbon-14 fall as they decay. As this process occurs at a regular rate, it can be used to date carbon-containing materials.

Exercise

Q14. A sample of chromium has the following isotopic composition by mass.

Isotope	^{50}Cr	^{52}Cr	^{53}Cr	^{54}Cr
Relative abundance / %	4.31	83.76	9.55	2.38

Calculate the relative atomic mass of chromium based on these data, giving your answer to two decimal places.

Q15. Use the periodic table to find the percentage abundance of neon-20, if neon has only one other isotope, neon-22.

Q16. Magnesium has three stable isotopes: ^{24}Mg, ^{25}Mg, and ^{26}Mg. The lightest isotope has an abundance of 78.90%. Calculate the percentage abundance of the other isotopes.

Q17. The relative abundances of the two isotopes of chlorine are shown in this table:

Isotope	Relative abundance
^{35}Cl	75%
^{37}Cl	25%

Use this information to deduce the mass spectrum of chlorine gas, Cl_2.

i In 1911, a 40 kg meteorite fell in Egypt. Isotopic and chemical analyses of oxygen extracted from this meteorite showed a different relative atomic mass to that of oxygen normally found on Earth. The relative atomic mass value did however match measurements made of the Martian atmosphere by the Viking landing in 1976. This provides strong evidence that the meteorite had originated from Mars.

Challenge yourself

10. Oxygen atoms in water molecules from two different samples in an ice core were analysed.

	Sample 1		Sample 2	
isotope	^{16}O	^{18}O	^{16}O	^{18}O
relative abundance / %	99.759	0.241	99.757	0.243

Determine the relative mass of oxygen in the two samples and identify which sample originated from higher historic temperatures.

11. Bromine is a mixture of two isotopes with mass numbers 79 and 81. They are naturally present in equal amounts.

The relative abundances of the two isotopes of chlorine are ^{35}Cl (75%) and ^{37}Cl (25%).

Calculate the percentage of naturally occurring CH_2BrCl molecules with a relative molecular mass of 128.

You can assume that the carbon atoms have a mass number of 12 and the hydrogen atoms have a mass number of 1.

HL end

Guiding Question revisited

How do the nuclei of atoms differ?

In this chapter we explored the structure of the atom and how the nuclei of atoms differ.

- All atoms are made up of protons, neutrons and electrons.
- The protons and neutrons, which contribute most of the mass of the atom, are in a small dense nucleus surrounded by electrons which occupy most of the volume of the atom.
- The atomic number gives the atom its identity. This is the number of protons in the nucleus. In a neutral atom this is also the number of electrons.
- The mass number is the number of nucleons: the number of protons and neutrons in the nucleons.
- Evidence shows that most elements have more than one isotope: atoms with the same number of protons but a different number of neutrons.
- The relative atomic mass, which is the average mass of an atom, can be determined from the relative abundance of its isotopes.

HL

- The mass of individual atomic masses can be measured by a mass spectrometer.
- A mass spectrum shows the relative abundance of the different isotopes of an element.

HL end

Practice questions

1. Which statements about the isotopes of chlorine, $^{35}_{17}Cl$ and $^{37}_{17}Cl$, are correct?

I. They have the same chemical properties.

II. They have the same atomic number.

III. They have the same physical properties.

A I and II only **B** I and III only

C II and III only **D** I, II and III

2. Which statement about the numbers of protons, electrons and neutrons in an atom is always correct?

A The number of neutrons minus the number of electrons is zero.

B The number of protons plus the number of neutrons equals the number of electrons.

C The number of protons equals the number of electrons.

D The nu mber of neutrons equals the number of protons.

3. Which quantities are the same for all atoms of chlorine?

I. number of protons

II. number of neutrons

III. number of electrons

A I and II only **B** I and III only

C II and III only **D** I, II and III

4. How many electrons does the ion $^{31}_{15}P^{3-}$ contain?

A 12 **B** 15 **C** 16 **D** 18

4. Deduce the number of elementary particles present in the $^{55}_{25}Mn^{2+}$ ion. (3)

(Total 3 marks)

6. A sample of iron has the following isotopic composition by mass.

Isotope	^{54}Fe	^{56}Fe	^{57}Fe
Relative abundance / %	5.95	91.88	2.17

Calculate the relative atomic mass of iron based on these data, giving your answer to two decimal places. (2)

(Total 2 marks)

7. **(a)** Explain why the relative atomic mass of cobalt is greater than the relative atomic mass of nickel, even though the atomic number of nickel is greater than the atomic number of cobalt. (1)

(b) Deduce the numbers of protons and electrons in the Co^{2+} ion. (1)

(Total 2 marks)

8. The table below refers to a sample of silicon.

Mass number of isotope	28	29	30
Relative abundance / %	92.18	4.70	3.12

(a) Explain why atoms of an element can have different mass numbers. (1)

(b) Compare the chemical properties of the four isotopes and justify your answer. (1)

(c) HL Identify the instrument used to collect these data. (1)

(d) Calculate the relative atomic mass of this sample of silicon. (2)

(Total 5 marks)

HL

9. What is the relative atomic mass of an element with the following mass spectrum?



A 24 **B** 25 **C** 26 **D** 27

10. The mass spectrum of an element is shown below.



(a) Identify the element and justify your answer. (2)

(b) Estimate the percentage of the total mass of the element due to neutrons. (2)

(Total 4 marks)

HL end



STRUCTURE

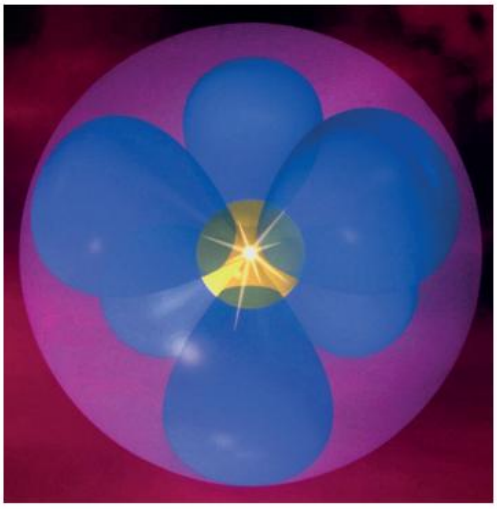
1.3 Electron configurations

The dazzling colours observed during a firework display are a result of electrons moving between different energy states.

Guiding Question

How can we model the energy states of electrons in atoms?

The chemical behaviour of an atom is determined by its electron configuration. As we cannot look inside the atom directly, we have to look elsewhere for evidence of how the electrons are arranged. The analysis of light emitted from an atom gives us valuable information about the electron configuration within it. It shows that an electron can exist only in certain discrete energy states. This cannot be understood with reference to our everyday experience and demands a new perspective. The notion of particles following fixed trajectories does not apply to the microscopic world of the atom. We can only give a probability description of electron behaviour and use quantum theory to adopt a wave description of the electron. The possible positions of an electron are spread out in space in the same way as a wave spreads through space. We will see how the energy states of electrons are best explained in terms of atomic orbitals. These are regions in space where an electron is likely to be found. Within one atom, there are an infinite number of orbitals of different shapes, sizes and energies. These ideas are revolutionary. As Niels Bohr, one of the principal scientists involved in the development of quantum theory said, 'Anyone who is not shocked by quantum theory has not understood it'.



Electrons occupy atomic orbitals of different energy states. The atomic orbitals in an atom of neon, Ne, are represented here. The nucleus is shown by a flash of light and the 1s orbital as a yellow sphere. The 2s orbital is shown as a pink sphere, and the 2p orbitals as blue lobes.

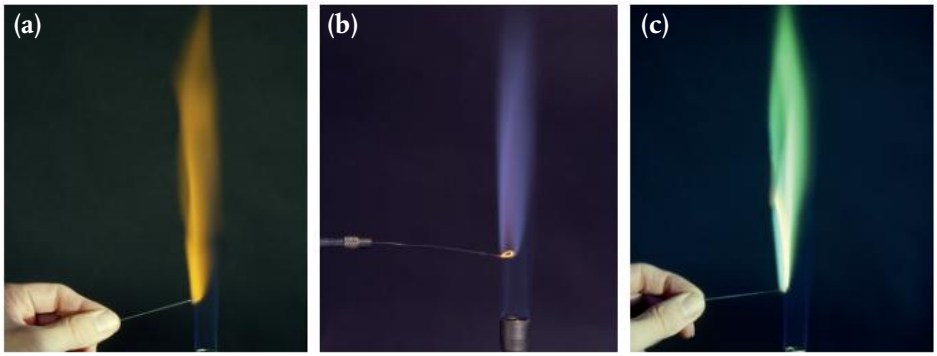
Structure 1.3.1 and 1.3.2 – Emission spectra

Structure 1.3.1 – Emission spectra are produced by atoms emitting photons when electrons in excited states return to lower energy levels.	
Qualitatively describe the relationship between colour, wavelength, frequency and energy across the electromagnetic spectrum. Distinguish between a continuous and a line spectrum.	
Details of the electromagnetic spectrum are given in the data booklet.	

Structure 1.3.2 – The line emission spectrum of hydrogen provides evidence for the existence of electrons in discrete energy levels, which converge at higher energies.	
Describe the emission spectrum of the hydrogen atom, including the relationships between the lines and energy transitions to the first, second and third energy levels.	
The names of the different series in the hydrogen emission spectrum will not be assessed.	Inquiry 2 – In the study of emission spectra from gaseous elements and from light, what qualitative and quantitative data can be collected from instruments such as gas discharge tubes and prisms? Nature of Science, Structure 1.2 – How do emission spectra provide evidence for the existence of different elements?

Atoms of different elements give out light of distinctive colours

Atoms of different elements give out light of a distinctive colour when an electric discharge is passed through a vapour of the element. Similarly, metals can be identified by the colour of the flame produced when their compounds are heated in a Bunsen burner. Analysis of the light emitted by different atoms gives us insights into the electron configurations within the atom.



Flame tests on the compounds of (a) sodium, (b) potassium and (c) copper.

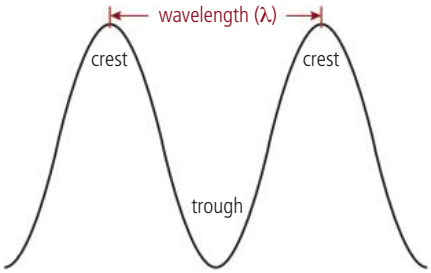
SKILLS

Flame colours can be used to identify unknown compounds. Full details of how to carry out a flame test experiment with a worksheet are available in the eBook.

To interpret these results, we must consider the nature of electromagnetic radiation.

Electromagnetic radiation is emitted in different forms of differing energies

Electromagnetic radiation comes in different forms of differing energy. The visible light we need to see the world is only a small part of the full spectrum, which ranges from low-energy radio waves to high-energy gamma (γ) rays. All electromagnetic waves travel at the same **speed (*c*)** but can be distinguished by their different **wavelengths (λ)** (Figure 1).



S1.3 Figure 1 Snapshot of a wave at a given instant. The distance between successive crests or peaks is called the wavelength (λ).

Different colours of visible light have different wavelengths; red light, for example, has a longer wavelength than blue light. The full electromagnetic spectrum is given in Section 5 of the data booklet.

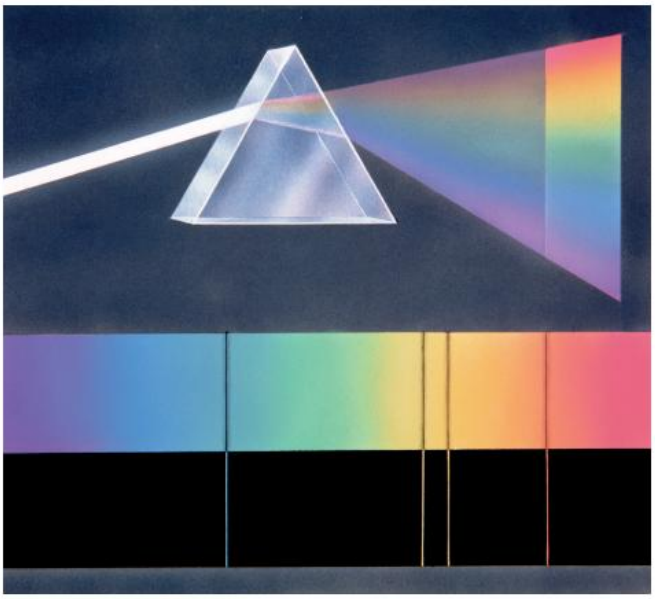
The number of waves that pass a particular point in 1 s is called the **frequency (*f*)**; the shorter the wavelength, the higher the frequency. Blue light has a higher frequency than red light.

The precise relation is:

$$c = f\lambda$$

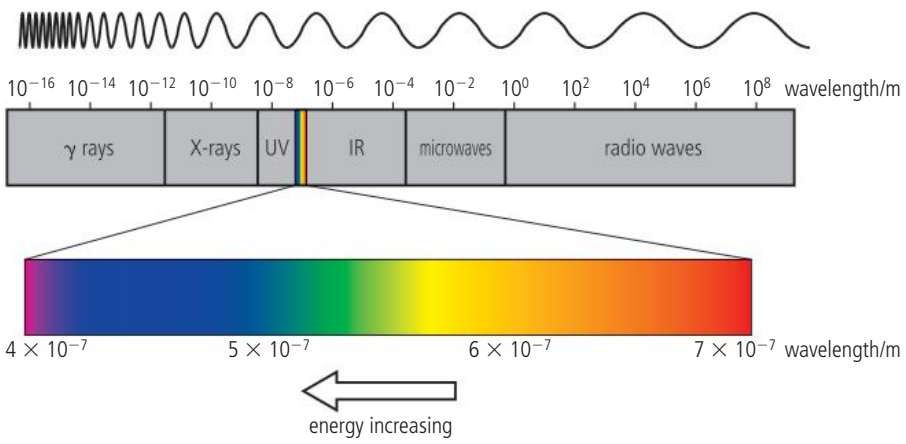
where c is the speed of light.

White light is a mixture of light waves of differing wavelengths or colours. We see this when sunlight passes through a prism to produce a **continuous spectrum** or when light is scattered through water droplets in the air.



A continuous spectrum is produced when white light is passed through a prism. The different **colours** merge smoothly into one another. The two spectra below the illustration of the prism show (top) a continuous spectrum with a series of discrete absorption lines, and (bottom) a line emission spectrum. Details of the absorption spectrum will not be assessed.

As well as visible light, atoms emit infrared (IR) radiation, which has a longer wavelength than red light, and ultraviolet radiation, which has a shorter wavelength than violet light. The complete electromagnetic spectrum is shown in Figure 2.



S1.3 Figure 2 The changing wavelength (in m) of electromagnetic radiation through the spectrum is shown by the trace across the top. At the short wavelength end (on the left) of the spectrum are gamma rays, X-rays, and ultraviolet light. In the centre of the spectrum are wavelengths that the human eye can see, known as visible light. Visible light comprises light of different wavelengths, energies, and colours. At the longer wavelength end of the spectrum (on the right) are infrared radiation, microwaves, and radio waves. The visible spectrum gives us only a small window to see the world.

All electromagnetic waves travel at the same speed, $c = 3.00 \times 10^8\ m\,s^{-1}$. This is the cosmic speed limit as, according to Einstein's Theory of Relativity, nothing in the universe can travel faster than this in a vacuum.

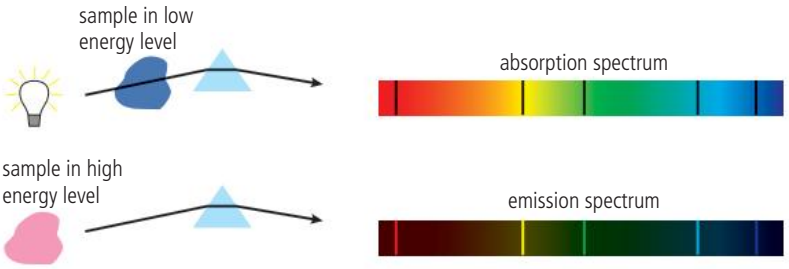
The distance between two successive crests (or troughs) is called the wavelength (λ). The frequency (f) of the wave is the number of waves that pass a point in one second. The wavelength and frequency are related by the equation $c = f\lambda$ where c is the speed of light.

Electromagnetic waves allow energy to be transferred across the universe. They also carry information. Low-energy radio waves are used in radar and television, for example, and higher energy gamma rays are used as medical tracers. The precision with which we view the world is limited by the wavelengths of the colours we can see. This is why we will never be able to see an atom directly; it is too small to interact with the relatively long waves of visible light. What are the implications of this for human knowledge?

TOK

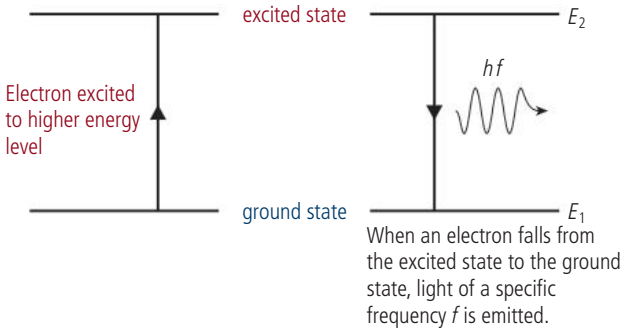
An emission spectrum is produced when an atom moves from a higher to a lower energy level

When electromagnetic radiation is passed through a collection of atoms, some of the radiation is absorbed and used to excite the atoms from a lower energy level to a higher energy level. A spectrometer analyses the transmitted radiation relative to the incident radiation and an absorption spectrum is produced (Figure 3).



S1.3 Figure 3 The origin of absorption and emission spectra. An absorption spectrum shows the radiation absorbed as atoms move from a lower to a higher energy level. An emission spectrum is produced when an atom moves from a higher to a lower level.

Gases produce a characteristic **emission line spectrum** when they are heated to a high temperature or if a high voltage is applied. Atoms are excited into a higher energy level, which is unstable, so the electron soon falls back to the **ground state**. The energy the electron gives out when it falls into lower levels is in the form of electromagnetic radiation. One packet of energy, a **photon,** is released for each electron transition (Figure 4). Photons of ultraviolet light have more energy than photons of infrared light. The energy of the photon is proportional to the frequency of the radiation.



S1.3 Figure 4 Emission spectra are the result of electrons falling from an excited state E_2 to a lower energy level E_1.

- **A continuous spectrum shows an unbroken sequence of frequencies, such as the spectrum of visible light.**
- **A line emission spectrum has only certain frequencies of light because it is produced by excited atoms and ions as they fall back to a lower energy level.**

The energy of the photon of light emitted (E_{photon}) is equal to the energy change of the electron in the atom ($\Delta E_{electron}$):

$$\Delta E_{electron} = E_{photon}$$

It is also related to the frequency of the radiation by the Planck equation:

$$E_{photon} = hf$$

This equation and the value of h (Planck's constant) are given in Sections 1 and 2 of the data booklet.

This leads to:

$$\Delta E_{electron} = hf$$

This is a very significant equation because it shows that line spectra allow us to glimpse inside the atom. The atoms emit photons of certain energies, which give lines of certain frequencies because the electron can only occupy certain energy levels. You can think of the energy levels as a staircase. The electron cannot change its energy in a continuous way, in the same way that you cannot stand between steps; it can only change its energy by discrete amounts. This energy of the atom is said to be **quantized**. The line spectrum is crucial evidence for quantization: if the energy were not quantized, the emission spectrum would be continuous.

Nature of Science

The idea that you can think of electromagnetic waves as a stream of photons, or quanta, is one aspect of quantum theory. The theory has implications for human knowledge and technology. The key idea is that energy can only be transferred in discrete amounts or quanta. Quantum theory shows us that our everyday experience cannot be transferred to the microscopic world of the atom. It has led to great technological breakthroughs such as the modern computer. It has been estimated that 30% of the gross national product of the USA depends on the application of quantum theory. Our scientific understanding has led to many technological developments. These new technologies in turn drive developments in science. The implications of quantum theory for the electron are discussed in more detail later (page 60). Note that 'discrete' has a different meaning to 'discreet'.

As different elements have different line spectra, they can be used like barcodes to identify unknown elements. They give us valuable information about the electron configurations of different atoms.

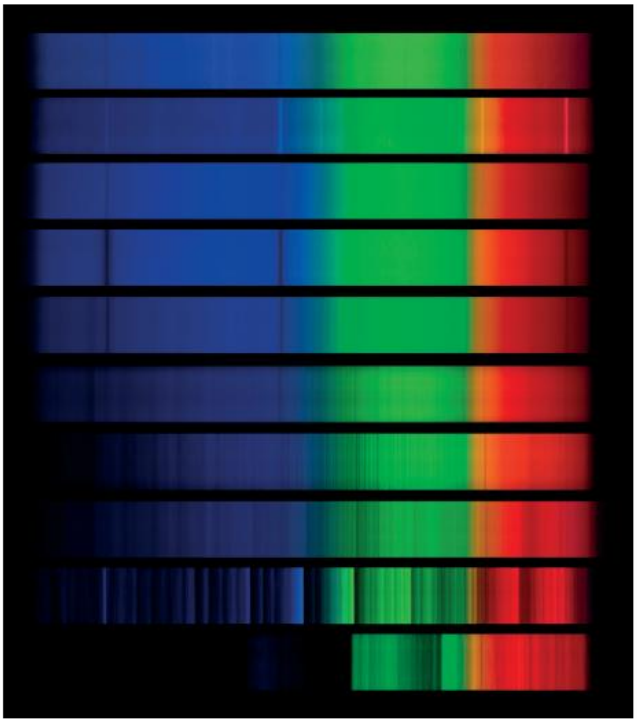


Diagram of the spectra of stars, showing a set of dark absorption lines, which indicate the presence of certain elements, such as hydrogen and helium, in the outer atmosphere of the star.

The words 'discrete' meaning 'separate', and 'discreet' meaning 'unobtrusive' both come from the Latin word 'discretus' for 'to keep separate'.

When asked to distinguish between a line spectrum and a continuous spectrum, references should be made to discrete or continuous energy levels and to specific colours, wavelengths or frequencies.

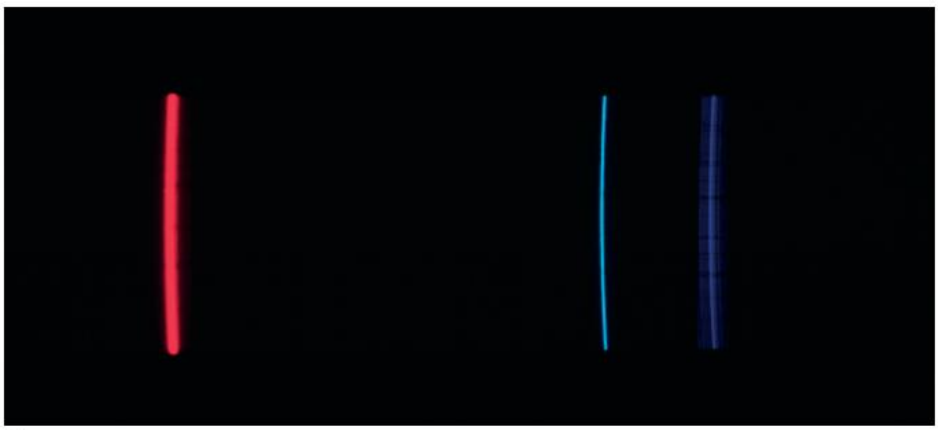
Elements discovered from their line spectra and named from their flame colours include rubidium (red), caesium (sky blue), thallium (green), and indium (indigo). Emission spectroscopy was a key tool in the discovery of new elements.

Nature of Science, Structure 1.2 – How do emission spectra provide evidence for the existence of different elements?

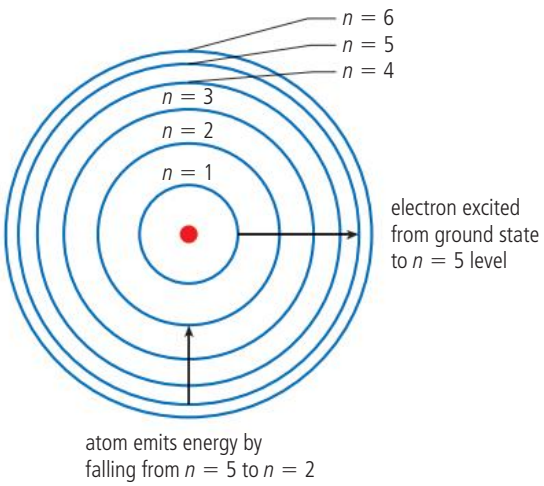
The elemental composition of stars can be determined by analysing their spectra. The gases that surround the center of a star absorb some wavelengths of the star's emitted radiation, producing dark absorption lines in the spectrum. These dark bands can be used to identify the elements present. The Sun's spectrum shows dark lines that represent absorbed radiation due to the presence of hydrogen and helium.

The line emission spectrum of hydrogen provides evidence for discrete energy levels

As discussed earlier, a line emission spectrum provides evidence for the electrons in an atom occupying discrete energy levels. A simple picture of the hydrogen atom was considered in Structure 1.2 with the electron orbiting the nucleus in a circular energy level. Niels Bohr proposed that an electron moves into an orbit further from the nucleus (a higher energy level) when an atom absorbs energy. This energy is given out in the form of electromagnetic radiation when the electron falls back from a higher to a lower energy level. In any sample of hydrogen many transitions can occur with each line corresponding to a particular transition. Visible light is produced when the electron falls to the second energy level ($n = 2$; see Figure 5).

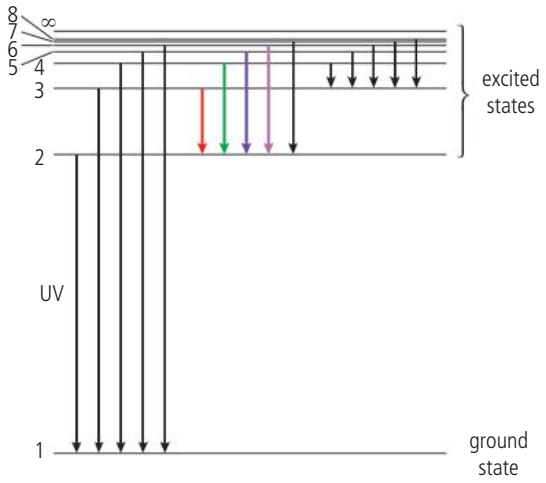


Visible emission spectrum of hydrogen. The energy of lines increases from left to right. They converge at higher energies. Similar series are found in the UV and IR regions.



S1.3 Figure 5 An electron is excited from the ground state to a higher energy level. If the unstable electron then falls to a lower $n = 2$ energy level, visible light is emitted.

The transitions to the first energy level ($n = 1$) correspond to the highest energy change and are in the ultraviolet region of the spectrum. Infrared radiation is produced when an electron falls to the third or higher energy levels (Figure 6).



S1.3 Figure 6 Energy levels of the hydrogen atom showing the transitions. The transition $1 \rightarrow \infty$ corresponds to ionization:

$$H(g) \rightarrow H^+(g) + e^-$$

HL This is discussed in more detail later.

The pattern of the lines in Figure 6 gives us a picture of the energy levels in the atom. The lines converge at higher energies because the energy levels inside the atoms are closer together. When an electron is at the highest energy $n = \infty$, it is no longer in the atom and the atom has been ionized. The energy needed to remove an electron from the ground state of one mole of gaseous atoms, ions, or molecules is called the **ionization energy**. Ionization energies can also be used to support this model of the atom (see page 74).

SKILLS Emission spectra can be observed using discharge tubes of different gases and a spectroscope. The colours and relative intensities of the lines should be observed. The wavelengths can be measured.

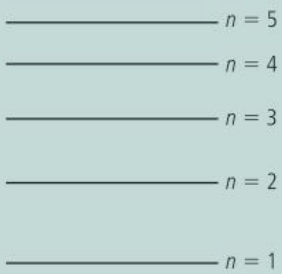
Inquiry 2 – In the study of emission spectra from gaseous elements and from light, what qualitative and quantitative data can be collected from instruments such as gas discharge tubes and prisms?

Exercise

Q1. Emission spectra provide evidence for:

A the existence of neutrons
B the existence of isotopes
C the existence of atomic energy levels
D the nuclear model of the atom

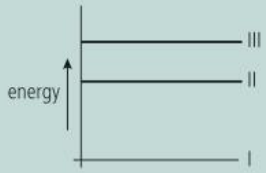
Q2. The diagram shows the lowest five electron energy levels in the hydrogen atom.



Deduce how many different frequencies in the visible emission spectrum of atomic hydrogen would arise as a result of electron transitions between these levels.

A 3 **B** 4 **C** 6 **D** 10

Q3. The diagram shows three energy levels of an atom.

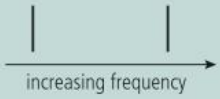


(a) Identify the transition that corresponds to the emission of light with the shortest wavelength.

A I → II **B** II → III **C** III → I **D** III → II

(b) Identify the emission line spectra that results from transitions between these energy levels.

A



B



C



D



Q4. The visible emission spectrum for hydrogen includes a red line with a wavelength of 657 nm corresponding to the transition 3 → 2. State if the transition from 4 → 2 corresponds to a higher or lower wavelength and justify your answer.

Challenge yourself

1. One of the wavelengths in the emission spectrum of helium occurs at 588 nm.

Some energy levels of the helium atom are shown. The energies of the levels are given in joules. Identify the transition that produces the line at 588 nm.



A I → III **B** III → I **C** II → IV **D** IV → II

Structure 1.3.3, 1.3.4 and 1.3.5 – Electron configuration

Structure 1.3.3 – The main energy level is given an integer number, *n*, and can hold a maximum of $2n^2$ electrons.	
Deduce the maximum number of electrons that can occupy each energy level.	
	Structure 3.1 – How does an element's highest main energy level relate to its period number in the periodic table?

Structure 1.3.4 – A more detailed model of the atom describes the division of the main energy level into s, p, d and f sublevels of successively higher energies. Recognize the shape and orientation of an s atomic orbital and the three p atomic orbitals.	
	Structure 3.1 – What is the relationship between energy sublevels and the block nature of the periodic table?

Structure 1.3.5 – Each orbital has a defined energy state for a given electron configuration and chemical environment, and can hold two electrons of opposite spin. **Sublevels contain a fixed number of orbitals, regions of space where there is a high probability of finding an electron.** Apply the Aufbau principle, Hund's rule and the Pauli exclusion principle to deduce electron configurations for atoms and ions up to Z = 36.	
Full electron configurations and condensed electron configurations using the noble gas core should be covered. Orbital diagrams, i.e. arrow-in-box diagrams, should be used to represent the filling and relative energy of orbitals. The electron configurations of Cr and Cu as exceptions should be covered.	

A more sophisticated model is needed for atoms with more than one electron

Wave and particle models of light and the electron

Although the Bohr model of the atom was able to predict the wavelengths of lines in the emission spectrum of hydrogen with great success, it failed to predict the spectral lines of atoms with more than one electron. The model is a simplification. To develop the model of the atom further, we need to reconsider the nature of light and matter.

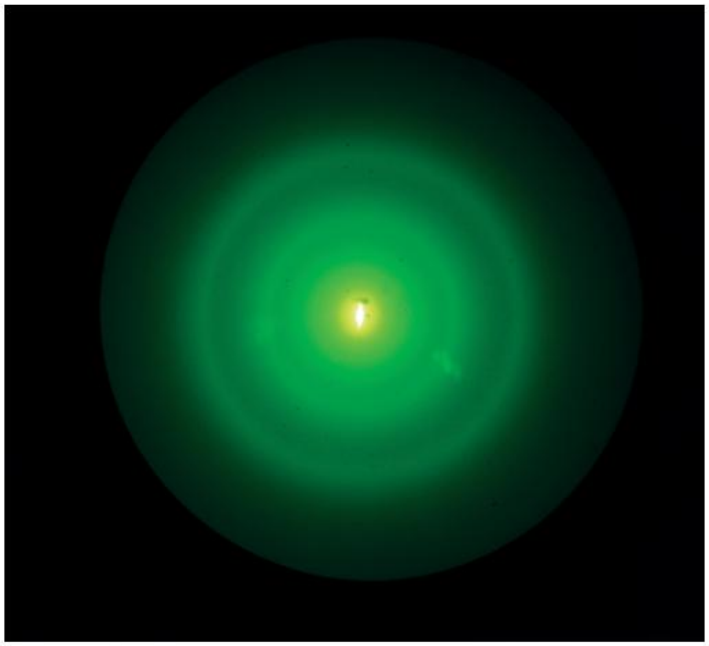
We saw earlier that light could either be described by its frequency, f, which is a wave property, or by the energy of individual particles, E (called photons, or quanta, of light), which make up a beam of light. The two properties are related by the Planck equation $E = hf$. Both wave and particle models have traditionally been used to explain scientific phenomena and you may be tempted to ask which model gives the 'true' description of light. We now realize that neither model gives a complete explanation of light's properties – both models are needed.

- The diffraction, or spreading out, of light that occurs when light passes through a small slit can only be explained by a wave model.
- The scattering of electrons that occurs when light is incident on a metal surface is best explained using a particle model of light.

TOK

We have outlined the plum pudding and Bohr models of the atom even though we now know they are incorrect. How can a model be useful even if it is obviously false?

In a similar way, quantum theory suggests that it is sometimes preferable to think of an electron (or indeed any particle) as having wave properties. The diffraction pattern produced when a beam of electrons is passed through a thin sheet of graphite demonstrates the wave properties of electrons. To understand the electron configurations of atoms, it is useful to consider a wave description of the electron.



Demonstration of wave–particle duality. An electron gun is fired at a thin sheet of graphite. The electrons pass through the graphite and hit a luminescent screen, producing the pattern of rings associated with diffraction. Diffraction occurs when a wave passes through an aperture similar in size to its wavelength. Quantum theory shows that electrons have wavelengths inversely proportional to their momentum (momentum is the product of their mass and velocity).

Nature of Science

Scientists use models to explain processes that may not be observable. The models can be simple or complex in nature but must match the experimental evidence if they are to be accepted. The power of the wave and particle models is that they are based on our everyday experience, but this is also their limitation. We should not be too surprised if this way of looking at the world breaks down when applied to the atomic scale, as this is beyond our experience. The model we use depends on the phenomena we are trying to explain.

When differences occur between the theoretical predictions and experimental data, the models must be modified or replaced. Bohr's model of the hydrogen atom was very successful in explaining the line spectra of the hydrogen atom but could not explain the spectra of more complex atoms, or the relative intensities of the lines in the hydrogen spectra. It also suffered from a fundamental weakness in that it was based on postulates, which combined ideas from classical and quantum physics in an ad hoc manner, with little experimental justification. Ideally, models should be consistent with the assumptions and premises of other theories. A modification of Bohr's model could only be achieved at the expense of changing our model of the electron as a particle. Dalton's atomic model and quantum theory are both examples of such radical changes of understanding, often called **paradigm shifts**.

TOK

What role do paradigm shifts play in the progression of scientific knowledge? Do they play a similar role in other areas of knowledge?

The electron's trajectory cannot be precisely described

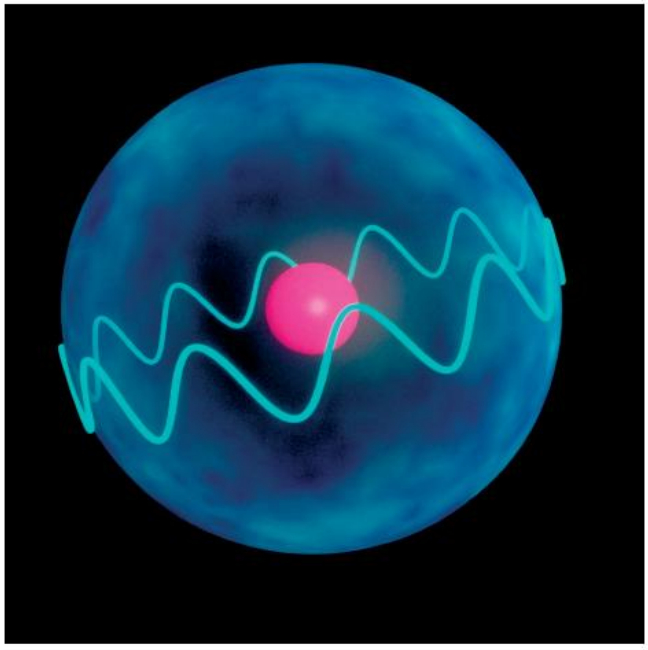
Another fundamental problem with the Bohr model is that it assumes the electron's trajectory can be precisely described. This is now known to be impossible, as any attempt to measure an electron's position will disturb its motion. The act of focusing radiation to locate the electron sends it hurtling off in a random direction.

According to Heisenberg's **Uncertainty Principle** we cannot know where an electron is at any given moment in time – the best we can hope for is a probability picture of where the electron is *likely* to be. The possible positions of an electron are spread out in space in the same way as a wave is spread across a water surface.

Electrons occupy atomic orbitals

Schrödinger model of the hydrogen atom

We have seen that the electron can be considered to have wave properties and that only a probability description of its location is possible at a given time. Both of these ideas are encapsulated in the Schrödinger model of the hydrogen atom. Erwin Schrödinger (1887–1961) proposed that a wave equation could be used to describe the behaviour of an electron in the same way that a wave equation could be used to describe the behaviour of light. The equation can be applied to multi-electron systems and its solutions are known as **atomic orbitals**. An atomic orbital is a region around an atomic nucleus in which there is a 90% probability of finding the electron. The shape of the orbitals will depend on the energy of the electron. When an electron is in an orbital of higher energy, it will have a higher probability of being found further from the nucleus.



The hydrogen atom shown as a nucleus (a central proton, pink), and an electron orbiting in a wavy path (light blue). It is necessary to consider the wave properties of the electron to understand atomic structure in detail. According to Heisenberg's Uncertainty Principle, the exact position of an electron cannot be defined; atomic orbitals represent regions where there is a high probability of finding an electron.

Challenge yourself

2. State **two** ways in which the Schrödinger model of the hydrogen atom differs from that of the Bohr model.

TOK

The Uncertainty Principle states that it is impossible to make an exact and simultaneous measurement of both the position and momentum of any given body. It can be thought of as an extreme example of the observer effect discussed on page 887. The significance of the Uncertainty Principle is that it shows the effect cannot be decreased indefinitely by improving the apparatus. There is an inherent uncertainty in our measurements. What are the implications of this for the limits of human knowledge?

i

The progressive nature of scientific knowledge about the atom is illustrated by the Nobel Prizes awarded between 1922 and 1933 to Bohr, Heisenberg and Schrödinger.

Our model of the atom owes a great deal to the work of Niels Bohr and Werner Heisenberg, who worked together in the early years of quantum theory before World War II. But they found themselves on different sides when war broke out. The award-winning play and film *Copenhagen* is based on their meeting in the city in 1941 and explores their relationship, the uncertainty of the past, and the moral responsibilities of the scientist.

An orbital can hold two electrons of opposite spin

The Schrödinger model of the hydrogen spectrum does not fully explain the fine details of the hydrogen spectrum. The model needs to be further refined: in addition to moving around the nucleus, electrons can also be thought to **spin** on their own axis. They can spin in either a clockwise direction, represented by an upward arrow, or an anti-clockwise direction, represented by a downward arrow. Spin is an important factor in electron–electron interactions. Electrons can occupy the same region of space despite their mutual repulsion if they spin in opposite directions. This leads to the **Pauli exclusion principle**, which states that an orbital can hold only two electrons of opposite spin.

The Pauli exclusion principle states that no more than two electrons can occupy any one orbital, and if two electrons are in the same orbital, they must spin in opposite directions.

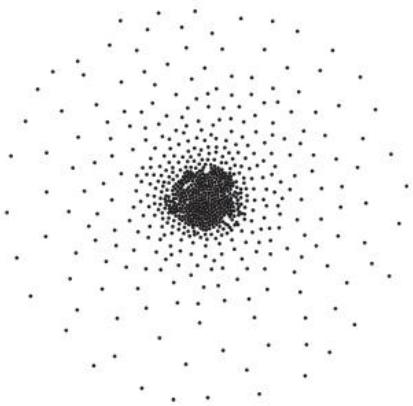
Atomic orbitals have different shapes and sizes

The first energy level has one 1s orbital

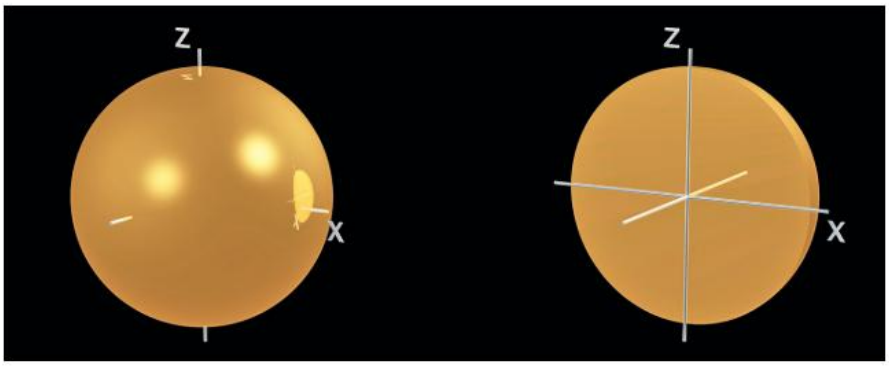
We saw that the electron in hydrogen occupies the first energy level in the ground state. This energy level can hold a maximum of two electrons. To highlight the distinction between this wave description of the electron provided by the Schrödinger model and the circular orbits of the Bohr atom, we say the electron occupies a 1s orbital.

An electron is uniquely characterized by its atomic orbital and spin. If two electrons occupied the same orbital spinning in the same direction, they would be the same electron – which is impossible!

The dots in Figure 7 represent locations where the electron is most likely to be found. The denser the arrangement of dots, the higher the probability that the electron occupies this region of space. The electron can be found anywhere within a spherical space surrounding the nucleus.



S1.3 Figure 7 An electron in a 1s atomic orbital. The density of the dots gives a measure of the probability of finding the electron in this region.



The first energy level consists of a 1s atomic orbital, which is spherical in shape.

An orbital shows the volume of space in which the electron is likely to be found.

The second energy level has a 2s and 2p sublevel

The second energy level of the Bohr model is split into two **sublevels** in the Schrödinger model. Further evidence of sublevels comes from a consideration of patterns in first ionization energies, which is discussed on page 74. The 2s sublevel is one 2s orbital and can hold a maximum of two electrons, and the 2p sublevel is three 2p orbitals and can hold six electrons. The 2s orbital has the same symmetry as a 1s orbital but extends over a larger volume. An electron in a 2s orbital is, on average, further from the nucleus than an electron in a 1s orbital and has higher energy.

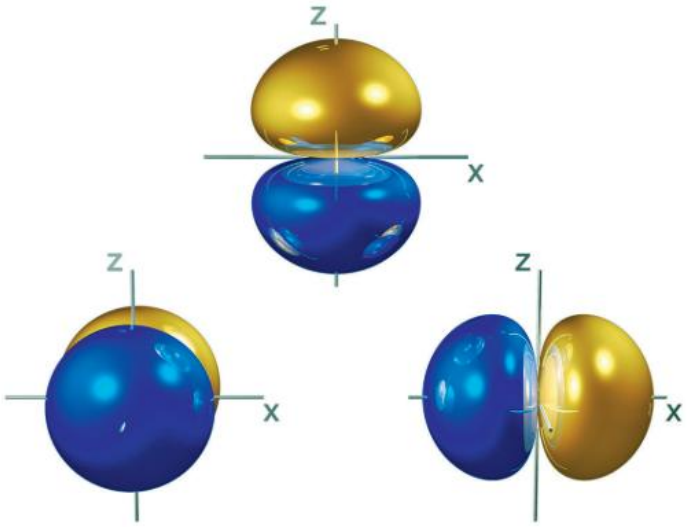


The 2s electron orbital. Just as a water wave can have crests and troughs, an orbital can have positive and negative areas. The blue area shows positive values, and the gold area negative. As it is the magnitude of the wave, not the sign, which determines the probability of finding an electron at particular positions, the sign is often not shown.

The three 2p atomic orbitals in the 2p sublevel have equal energy and are said to be **degenerate**. They all have the same dumbbell shape; the only difference is their orientation in space. They are arranged at right angles to each other with the nucleus at the centre.

SKILLS

Investigating orbital shapes with modelling clay. Full details of how to carry out this experiment with a worksheet are available in the eBook.

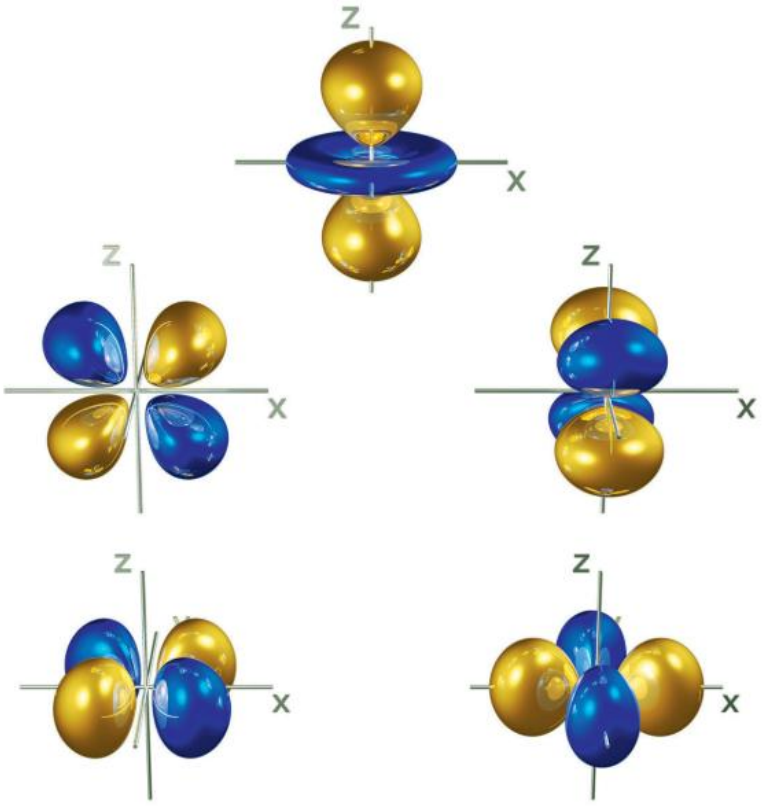


From left to right, the p_y, p_z, and p_x atomic orbitals, localized along the *y*, *z*, and *x*-axes respectively (the *y*-axis comes out of the page). As they have the same energy, they are said to be degenerate. They form the 2p sublevel.

d and f orbitals

We have seen that the first energy level is made up of one sublevel and the second energy level is made up of two sublevels. This pattern can be generalized; the *n*th energy level of the atom is divided into *n* sublevels. The third energy level is made up of three sublevels: the 3s, 3p and 3d. The d sublevel is made up of five d atomic orbitals.

The five electron orbitals found in the 3d sublevel. Four of the orbitals are made up of four lobes, centred on the nucleus.



You are expected to know the shapes and names of the s and p atomic orbitals, but not of the d atomic orbitals.

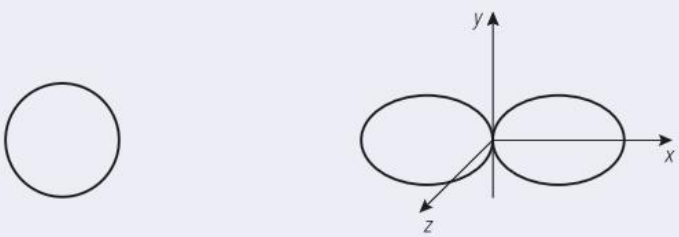
The labels s, p, d and f relate to the nature of the spectral lines the model was attempting to explain. The corresponding spectroscopic terms are *sharp*, *principal*, *diffuse* and *fine*.

The letters **s**, **p**, **d**, and **f** are used to identify different sublevels and the atomic orbitals that comprise them. The fourth level ($n = 4$) is similarly made up from four sublevels. The 4f sublevels are made up of seven f atomic orbitals, but you are not required to know the shapes of these orbitals.

Worked example

Draw the shapes of a 1s orbital and a $2p_x$ orbital.

Solution



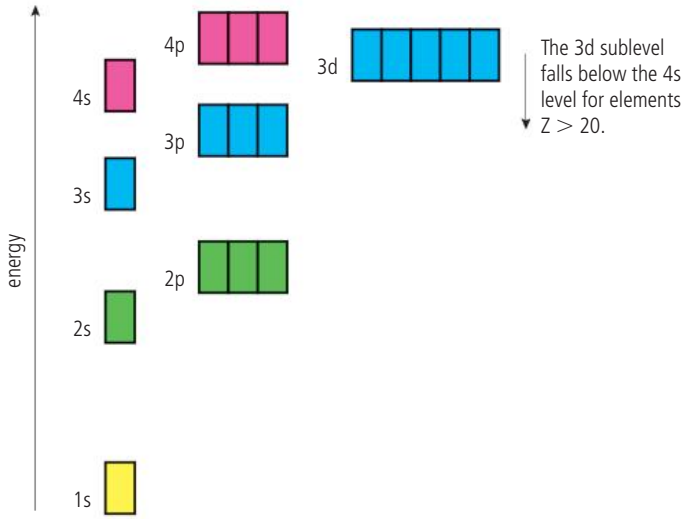
1s orbital

$2p_x$ orbital

The shapes of a 1s orbital and a $2p_x$ orbital. A simple two-dimensional drawing is sufficient.

Each main energy level is divided into sublevels

The atomic orbitals associated with the different energy levels are shown in Figure 8. This diagram is a simplification, as the relative energy of the orbitals depends on the atomic number. The relative energies of the 4s and 3d atomic orbitals are particularly significant and will be discussed in more detail later.



S1.3 Figure 8 The relative energies of the atomic orbitals up to the 4p sublevel. The 3d sublevel falls below the 4s level for elements $Z > 20$.

Degenerate orbitals of the same energy form a sublevel; three p orbitals form a p sublevel, five d orbitals form a d sublevel and seven f orbitals form an f sublevel. A single s orbital makes up an s sublevel.

The number of electrons in the sublevels of the first four energy levels are shown in the table.

Level	Sublevel	Maximum number of electrons in sublevel	Maximum number of electrons in level
$n = 1$	1s	2	2
$n = 2$	2s	2	8
	2p	6	
$n = 3$	3s	2	18
	3p	6	
	3d	10	
$n = 4$	4s	2	32
	4p	6	
	4d	10	
	4f	14	

We can see the following from the table:

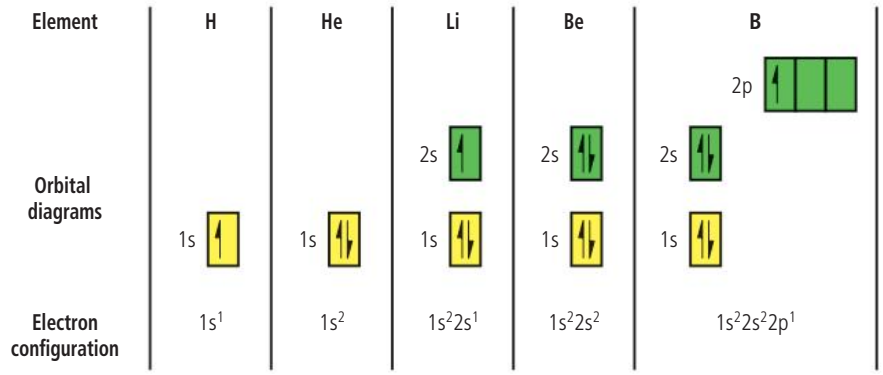
- The nth energy level of the atom is divided into n sublevels. For example, the fourth level ($n = 4$) is made up of four sublevels.
- Each main level can hold a maximum of $2n^2$ electrons. The 3rd energy level, for example, can hold a maximum of 18 electrons ($2 \times 3^2 = 18$).
- s sublevels can hold a maximum of 2 electrons.
- p sublevels can hold a maximum of 6 electrons.
- d sublevels can hold a maximum of 10 electrons.
- f sublevels can hold a maximum of 14 electrons.

Models are simplifications of complex systems. Details of the historic atomic models of Dalton, Bohr, Schrödinger and Heisenberg will not be assessed.

The Aufbau principle: constructing arrow-in-box diagrams

Aufbau means 'building up' in German.

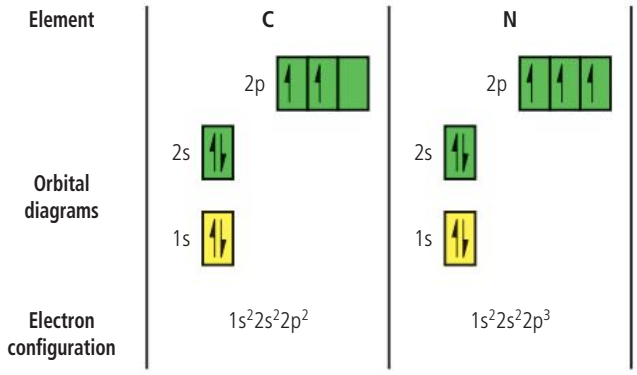
The electron configuration of the ground state of an atom of an element can be determined using the **Aufbau principle**, which states that electrons are placed into orbitals of lowest energy first. Boxes can be used to represent the atomic orbitals, with single-headed arrows to represent the spinning electrons. The **electron configurations** of the first five elements are shown in Figure 9. The number of electrons in each sublevel is given as a superscript.



S1.3 Figure 9 The electron configuration of the first five elements.

The next element in the periodic table is carbon. It has two electrons in the 2p sublevel. These could either pair up, and occupy the same p orbital, or occupy separate p orbitals. Following **Hund's third rule**, we place the two electrons in separate orbitals because this configuration minimizes the mutual repulsion between them. As the 2p orbitals are perpendicular to each other and do not overlap, the two 2p electrons are unlikely to approach each other too closely. The electrons in the different 2p orbitals have parallel spins, as this leads to lower energy. The electron configurations of carbon and nitrogen are shown in Figure 10.

Hund's rule: If more than one orbital in a sublevel is available, electrons occupy different orbitals with parallel spins.



S1.3 Figure 10 Electron configurations of carbon and nitrogen.

The 2p electrons begin to pair up for oxygen ($1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$) and fluorine ($1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$). The 2p sub-shell is completed for neon ($1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$).

Worked example

Deduce the electron configuration of sulfur.

Solution

Sulfur has an atomic number of 16. Therefore it has 16 electrons.

Two electrons occupy the 1s: $1s^2$

Two electrons occupy the 2s: $2s^2$

Six electrons occupy the 2p: $2p^6$

Two electrons occupy the 3s: $3s^2$

Four electrons occupy the 3p: $3p^4$

So the electron configuration is $1s^2\ 2s^2 2p^6\ 3s^2\ 3p^4$

Exercise

Q5. List the 4d, 4f, 4p, and 4s atomic orbitals in order of increasing energy.

Q6. State the number of 4d, 4f, 4p, and 4s atomic orbitals.

Q7. Apply the *orbital diagram* method to determine the electron configuration of calcium.

Q8. Deduce the number of unpaired electrons present in a phosphorus atom.

Q9. Deduce the number of orbitals in the $n = 4$ level and explain your answer.

Challenge yourself

3. Which of the following provide evidence to support the Bohr model of the hydrogen atom?

I. The energy of the lines in the emission spectra of atomic hydrogen.

II. The relative intensity of the different spectral lines in the emission spectrum of atomic hydrogen.

A I only **B** II only **C** I and II **D** Neither I nor II



S1.3 Figure 11 Order of filling sublevels: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p.

Can you think of a mnemonic for the order of filling orbitals? Figure 11 shows orbitals filled to sublevel 7s. Follow the arrows to see the order in which the sublevels are filled.

The mathematical nature of the orbital description is illustrated by some simple relationships:

- number of sublevels at *n*th main energy level = n
- number of orbitals at *n*th energy level = n^2
- number of electrons at *n*th energy level = $2n^2$
- number of orbitals at *l*th sublevel = $(2l + 1)$ where n and l are sometimes known as quantum numbers.

Sublevel	s	p	d	f
l	0	1	2	3

TOK

The abstract language of mathematics provides a powerful tool for describing the behaviour of electrons in the atom. The shapes and equations it generates have elegance and symmetry. What do such results tell us about the relationship between the natural sciences, mathematics, and the natural world? Why are many of the laws in the natural sciences stated using the language of mathematics?

The relative energy of the orbitals depends on the atomic number

The energy of an orbital depends on the attraction between the electrons and the nucleus and inter-electron repulsions. As these interactions change with the nuclear charge and the number of electrons – that is, the atomic number – so does the relative energy of the orbitals. All the sublevels in the third energy level (3s, 3p, and 3d), for example, have the same energy for the hydrogen atom and only become separated as extra protons and electrons are added. The situation is particularly complicated when we reach the d block elements. The 3d and 4s levels are very close in energy and their relative separation is very sensitive to inter-electron repulsion. For the elements potassium and calcium, the 4s orbitals are filled before the 3d sublevel. Electrons are, however, first lost from the 4s sublevel when transition metals form their ions, as once the 3d sublevel is occupied the 3d electrons push the 4s electrons to higher energy.

When the transition metal atoms form ions they lose electrons from the 4s sublevel before the 3d sublevel.

Worked example

State the full electron configuration of vanadium and deduce the number of unpaired electrons.

Solution

The atomic number of vanadium gives the number of electrons: Z = 23.

So the electron configuration is: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$. Note: the 3d sublevel is filled *after* the 4s sub level.

It is useful, however, to write the electron configuration with the 3d sub-shell before the 4s: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$ as the 3d sublevel falls below the 4s orbital once the 4s orbital is occupied (i.e. for elements after Ca).

The three 3d orbitals each have an unpaired electron. Number of unpaired electrons = 3.

The worked example asked for the full electron configuration. Sometimes it is convenient to use an abbreviated form, where only the outer electrons are explicitly shown. The inner electrons are represented as a noble gas core. Using this notation, the electron configuration of vanadium is written [Ar] $3d^3 4s^2$, where [Ar] represents the electron configuration of Ar, which is $1s^2 2s^2 2p^6 3s^2 3p^6$.

The electron configurations of the first 30 elements are shown in the table.

Element	Electron configuration	Element	Electron configuration
$_{1}H$	$1s^1$	$_{16}S$	$1s^22s^22p^63s^23p^4$
$_{2}He$	$1s^2$	$_{17}Cl$	$1s^22s^22p^63s^23p^5$
$_{3}Li$	$1s^22s^1$	$_{18}Ar$	$1s^22s^22p^63s^23p^6$
$_{4}Be$	$1s^22s^2$	$_{19}K$	$1s^22s^22p^63s^23p^64s^1$
$_{5}B$	$1s^22s^22p^1$	$_{20}Ca$	$1s^22s^22p^63s^23p^64s^2$
$_{6}C$	$1s^22s^22p^2$	$_{21}Sc$	[Ar] $3d^14s^2$
$_{7}N$	$1s^22s^22p^3$	$_{22}Ti$	[Ar] $3d^24s^2$
$_{8}O$	$1s^22s^22p^4$	$_{23}V$	[Ar] $3d^34s^2$
$_{9}F$	$1s^22s^22p^5$	$_{24}Cr$	[Ar] $3d^54s^1$
$_{10}Ne$	$1s^22s^22p^6$	$_{25}Mn$	[Ar] $3d^54s^2$
$_{11}Na$	$1s^22s^22p^63s^1$	$_{26}Fe$	[Ar] $3d^64s^2$
$_{12}Mg$	$1s^22s^22p^63s^2$	$_{27}Co$	[Ar] $3d^74s^2$
$_{13}Al$	$1s^22s^22p^63s^23p^1$	$_{28}Ni$	[Ar] $3d^84s^2$
$_{14}Si$	$1s^22s^22p^63s^23p^2$	$_{29}Cu$	[Ar] $3d^{10}4s^1$
$_{15}P$	$1s^22s^22p^63s^23p^3$	$_{30}Zn$	[Ar] $3d^{10}4s^2$

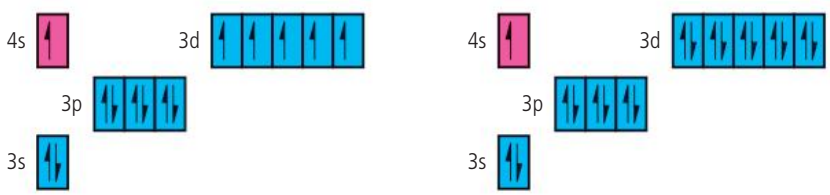
The electrons in the outer energy level are mainly responsible for compound formation and are called **valence electrons**. Lithium has one valence electron in the outer second energy level ($2s^1$), beryllium has two ($2s^2$), boron has three ($2s^2p^1$), and so on. The number of valence electrons follows a periodic pattern, which is discussed fully in Structure 3.1. Atoms can have many other electron configurations when in an excited state. Unless otherwise instructed, assume that you are being asked about ground-state configurations.

The term 'valence' is derived from the Latin word for 'strength'.

For the d block elements, three points should be noted:

- the 3d sublevel is written with the other $n = 3$ sublevels because it falls below the 4s orbital once the 4s orbital is occupied (i.e. for elements after Ca), as discussed earlier
- chromium has the electron configuration [Ar] $3d^54s^1$
- copper has the electron configuration [Ar] $3d^{10}4s^1$.

To understand the electron configurations of copper and chromium, it is helpful to consider the electrons-in-boxes arrangements in Figure 12. As the 4s and 3d orbitals are close in energy, the electron configuration for chromium, with a half-full d sublevel, is relatively stable as it minimizes electrostatic repulsion, with six singly occupied atomic orbitals. This would be the expected configuration using Hund's rule if the 4s and 3d orbitals had exactly the same energy. Half-filled and filled sublevels seem to be particularly stable: the configuration for copper is similarly due to the stability of the full d sublevel.



chromium: [Ar]$3d^54s^1$ copper: [Ar]$3d^{10}4s^1$

S1.3 Figure 12 The electron configurations of the 3rd and 4th energy levels for chromium and copper.

Exercise

Q10. Identify the sublevel that does not exist.

A 5d **B** 4d **C** 3f **D** 2p

Q11. Which is the correct order of orbital filling according to the Aufbau principle?

A 4s 4p 4d 4f **B** 4p 4d 5s 4f

C 4s 3d 4p 5s **D** 4d 4f 5s 5p

Q12. State the full ground-state electron configuration of the following elements.

(a) V **(b)** K **(c)** Se **(d)** Sr

Q13. Determine the total number of electrons in d orbitals in a single iodine atom.

A 5 **B** 10 **C** 15 **D** 20

Q14. Identify the excited state (i.e. not a ground state) in the following electron configurations.

A [Ne] $3s^2 3p^3$ **B** [Ne] $3s^2 3p^3 4s^1$

C [Ne] $3s^2 3p^6 4s^1$ **D** [Ne] $3s^2 3p^6 3d^1 4s^2$

Q15. Deduce the number of unpaired electrons present in the ground state of a titanium atom.

A 1 **B** 2 **C** 3 **D** 4

Q16. Identify the atom that possesses the most unpaired electrons.

A O **B** Mg **C** Ti **D** Fe

Electron configuration of ions

As discussed earlier, positive ions are formed by the loss of electrons. These electrons are lost from the outer sublevels. For example, the electron configurations of the different aluminium ions formed when electrons are successively removed are as follows:

- Al^+ is $1s^2 2s^2 2p^6 3s^2$
- Al^{2+} is $1s^2 2s^2 2p^6 3s^1$
- Al^{3+} is $1s^2 2s^2 2p^6$, etc.

When positive ions are formed for transition metals, the outer 4s electrons are removed before the 3d electrons, as discussed earlier.

For example, Cr is [Ar] $3d^5 4s^1$ and Cr^{3+} is [Ar] $3d^3$

The electron configurations of negative ions are determined by adding the electrons into the next available electron orbital:

S is $1s^2 2s^2 2p^6 3s^2 3p^4$ and S^{2-} is $1s^2 2s^2 2p^6 3s^2 3p^6$

Worked example

Deduce the ground-state electron configuration of the Fe^{3+} ion.

Solution

First find the electron configuration of the atom. Fe has 26 electrons:
$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

As the 3d sublevel is below the 4s level for elements after calcium, we write this as
$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

Now remove the two electrons from the 4s sublevel and one electron from the 3d sublevel.

Electron configuration of Fe^{3+} is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$



Note the abbreviated electron configuration using the noble gas core is not acceptable when asked for the *full* electron configuration.

Exercise

Q17. State the full ground-state electron configuration of the following ions.

(a) O^{2-} **(b)** Cl^- **(c)** Ti^{3+} **(d)** Cu^{2+}

Q18. State the electron configuration of the following transition metal ions by filling in the boxes below. Use arrows to represent the electron spin.

	Ion	3d					4s
(a)	Ti^{2+}						
(b)	Fe^{2+}						
(c)	Ni^{2+}						
(d)	Zn^{2+}						

Q19. **(a)** State the full electron configuration for neon.

(b) State the formulas of two oppositely charged ions which have the same electron configuration as neon.

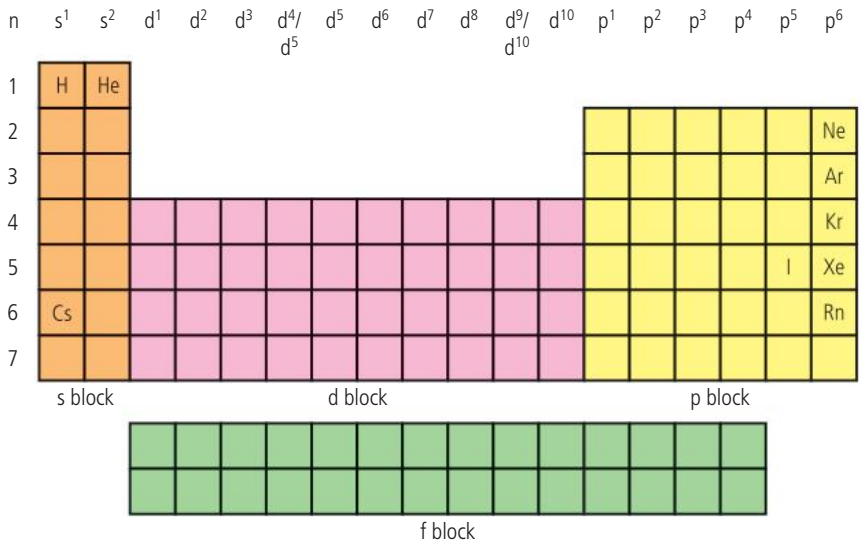
Q20. State the abbreviated electron configuration using the previous noble gas core for:

(a) Ni^{2+} **(b)** Pb^{2+} **(c)** S^{2-} **(d)** Si^{4+}

Electron configuration and the periodic table

We are now in a position to understand the structure of the periodic table (Figure 13):

- elements whose valence electrons occupy an s sublevel make up the s block
- elements with valence electrons in p orbitals make up the p block
- the d block and the f block are similarly made up of elements with outer electrons in d and f orbitals.



S1.3 Figure 13 The block structure of the periodic table is based on the sublevels of the atom. H and He are difficult elements to classify. Although they have electron configurations that place them in the s block, their chemistry is not typical of group 1 or group 2 elements.

Structure 3.1 – What is the relationship between energy sublevels and the block nature of the periodic table?

The *ns* and *np* sublevels are filled for elements in period *n*. However the (*n* – 1)d sublevel is filled for elements in period *n*.

The position of an element in the periodic table is based on the occupied sublevel of highest energy in the ground-state atom. Conversely, the electron configuration of an element can be deduced directly from its position in the periodic table.

Here are some examples.

- Caesium is in group 1 and period 6 and has the electron configuration: [Xe] $6s^1$.
- Iodine is in group 17 and in period 5 and has the configuration: [Kr] $5s^2 4d^{10} 5p^5$. Placing the 4d sublevel before the 5s gives [Kr] $4d^{10} 5s^2 5p^5$. Iodine has 7 valence electrons, in agreement with the pattern discussed on page 69.

Structure 3.1 – How does an element's highest main energy level relate to its period number in the periodic table?

Some versions of the periodic table use the numbering 3–7 for groups 13–17. In this version, group 3 elements have three valence electrons and group 7 elements have seven valence electrons. Although this is simpler, in some respects it can lead to problems. After extensive discussions, the IUPAC concluded that the 1 to 18 numbering provides the clearest and most unambiguous labelling system.

Exercise

Q21. Use the periodic table to find the full ground-state electron configuration of the following elements.

(a) Cl **(b)** Nb **(c)** Ge **(d)** Sb

Q22. Identify the elements that have the following ground-state electron configurations.

(a) [Ne] $3s^2 3p^2$ **(b)** [Ar] $3d^5 4s^2$

(c) [Kr] $5s^2$ **(d)** $1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$

Q23. State the total number of p orbitals containing one or more electrons in tin.

Q24. How many electrons are there in all the d orbitals in an atom of barium?

Q25. State the electron configuration of the ion Cd^{2+}.

Q26. State the full electron configuration of U^{2+}.

Challenge yourself

4. State the electron configuration of thorium.

5. Only a few atoms of element 109, meitnerium, have ever been made. Isolation of an observable quantity of the element has never been achieved and may well never be. This is because meitnerium decays very rapidly.
   (a) Suggest the electron configuration of the ground-state atom of the element.
   (b) There is no g block in the periodic table as no elements with outer electrons in g orbitals exist in nature or have been made artificially. Suggest a minimum atomic number for such an element.

6. Consider how the shape of the periodic table is related to the three-dimensional world we live in.
   (a) How many 3p and 3d orbitals would there be if only the *x* and *y* dimensions existed?
   (b) How many groups in the p and d block would there be in such a two-dimensional world?

Nature of Science

We have seen how the model of the atom has changed over time. All these theories are still used today. Dalton's model adequately explains many properties of the states of matter, the Bohr model is used to explain chemical bonding, and the structure of the periodic table is explained by the wave description of the electron. In science, we often follow Occam's razor and use the simplest explanation that can account for the phenomena. As Einstein said 'Explanations should be made as simple as possible, but not simpler'.

TOK

Do atomic orbitals exist or are they primarily useful inventions to aid our understanding? What consequences might questions about the reality of scientific entities have for the public perception and understanding of the subject? If they are only inventions, how is it that they can yield such accurate predictions?

HL

Structure 1.3.6 and 1.3.7 – Ionization energies

Structure 1.3.6 – In an emission spectrum, the limit of convergence at higher frequency corresponds to ionization.

Explain the trends and discontinuities in first ionization energy (IE) across a period and down a group.

Calculate the value of the first IE from spectral data that gives the wavelength or frequency of the convergence limit.

The value of the Planck constant *h* and the equations $E = hf$ and $c = \lambda f$ are given in the data booklet.	Structure 3.1 – How does the trend in IE values across a period and down a group explain the trends in properties of metals and non-metals? Nature of Science, Tool 3, Reactivity 3.1 – Why are log scales useful when discussing $[H^+]$ and ionization energies?

Structure 1.3.7 – Successive ionization energy (IE) data for an element give information about its electron configuration.	
Deduce the group of an element from its successive ionization data.	
Databases are useful for compiling graphs of trends in IEs.	Structure 3.1 – How do patterns of successive IEs of transition elements help to explain the variable oxidation states of these elements?

In an emission spectrum, the limit of convergence at higher frequency corresponds to ionization

The first ionization energy of an element is the energy needed to remove one mole of electrons from the ground state of one mole of the gaseous atom. For hydrogen it corresponds to the following change, with the electron being removed from the 1s orbital:

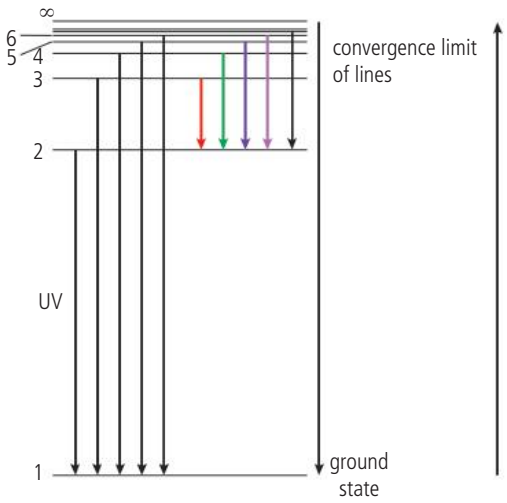
$$H(g) \rightarrow H^+(g) + e^-$$

Once removed from the atom, the electron is an infinite distance away from the nucleus and can be considered to be in the $n = \infty$ energy level.

The first ionization energy of an element is the minimum energy needed to remove one mole of electrons from one mole of gaseous atoms in their ground state.

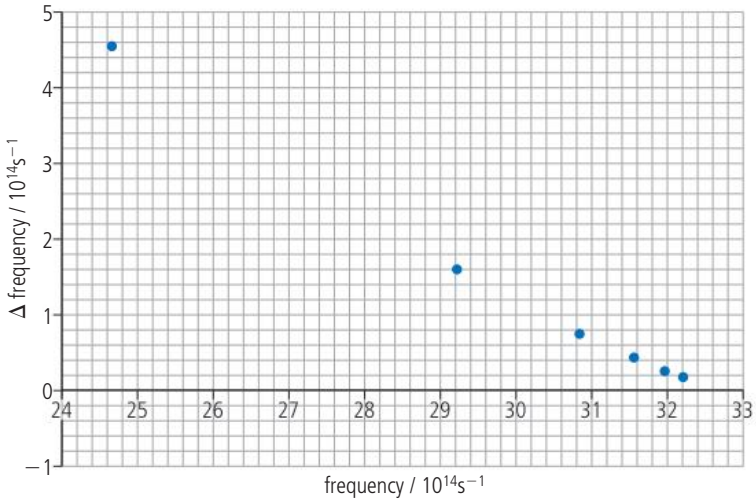
We saw earlier that the energy levels in hydrogen converge at higher energy. This allows us to calculate the ionization energy from the convergence limit at higher frequency.

The frequency at which convergence occurs can be obtained graphically. The frequencies of the lines where the transitions involve the electron falling from the excited levels with $n \geq 1$ to the $n = 1$ energy level are shown below. The difference between the frequencies in successive lines is given in the third column.



Excited energy level (n)	Frequency, f / × 10^{-14} s^{-1}	Δf / × 10^{-14} s^{-1}
2	24.66	4.57
3	29.23	1.60
4	30.83	0.74
5	31.57	0.40
6	31.97	0.24
7	32.21	0.16
8	32.37	

A graph of f against Δf ($f_{n+1} - f_n$) gives an approximate best-fit straight line with the intercept on the x axis giving the frequency at which convergence occurs.



A graph showing the frequency of the line emitted against the difference in frequency between successive lines in the UV region of the hydrogen atom.

From the graph, convergence occurs when $\Delta f = 0$ at $f = 32.3 \times 10^{-14}\,s^{-1}$

Using the equation $E = h f$ we have the ionization energy for one atom:

$$E = 32.3 \times 10^{-14}\,s^{-1} \times 6.63 \times 10^{-34}\,J\,s$$

So for one mole, the ionization energy is given by:

$$IE = 32.3 \times 10^{-14}\,s^{-1} \times 6.63 \times 10^{-34}\,J\,s \times 6.02 \times 10^{23}\,mol^{-1}$$

$$= 1290\,kJ\,mol^{-1}$$

This is close to the value of $1312\,kJ\,mol^{-1}$ given in Section 9 of the data booklet.

Nature of Science

The best data for making accurate and precise descriptions are often quantitative as you can use this for mathematical analysis. The data can often be presented in a variety of formats that can be analysed. Scientists look for patterns in an attempt to discover relationships.

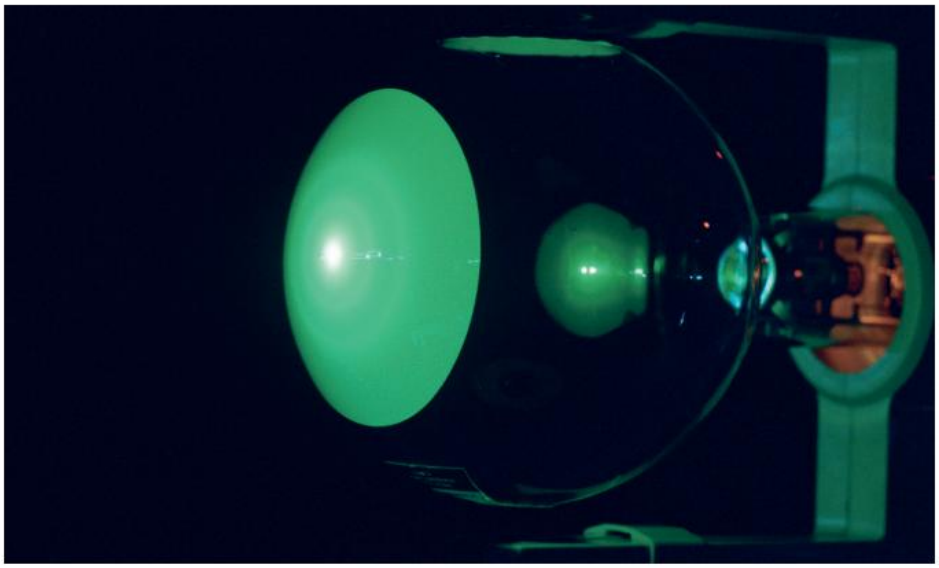
Challenge yourself

7. A more accurate value for the convergence limit can also be found by plotting a graph of the frequencies of the lines against $\frac{1}{n^2}$. Determine the ionization energy of hydrogen using this method and explain why this method is more accurate.

Nature of Science

The Bohr model of the hydrogen atom (1913) was able to explain the relationship between the frequency of the lines and the *n* values for the energy levels, but Bohr was unable to provide experimental evidence to support his postulates. They were inconsistent as they came from an unjustified mixture of classical and quantum theory. In general, scientists strive to develop hypotheses and theories that are compatible with accepted principles and that simplify and unify existing ideas. A deeper understanding needed the wave description of the electron suggested by de Broglie (1926).

Many scientific discoveries have come from speculation or simple curiosity about particular phenomena. De Broglie speculated on the wave properties of particles by combining results from Einstein's theory of relativity with Planck's quantum theory.



An electron diffraction tube. The electrons fired at a thin sheet of graphite produce the patterns of rings associated with diffraction. De Broglie (1892–1987) correctly deduced that the electrons would have wavelengths inversely proportional to their momentum ($\lambda = h/p$).

TOK

The de Broglie equation ($\lambda = h/p$) shows that macroscopic particles have too short a wavelength for their wave properties to be observed. Is it meaningful to talk of properties which can never be observed from sense perception?

Ionization energies can also be used to support this model of the atom.

Exercise

Q27. Sodium lamps used for street lighting emit a distinctive orange light with a wavelength of 590 nm. Calculate the energy produced by one mole of excited sodium atoms when they give out orange light of this wavelength.

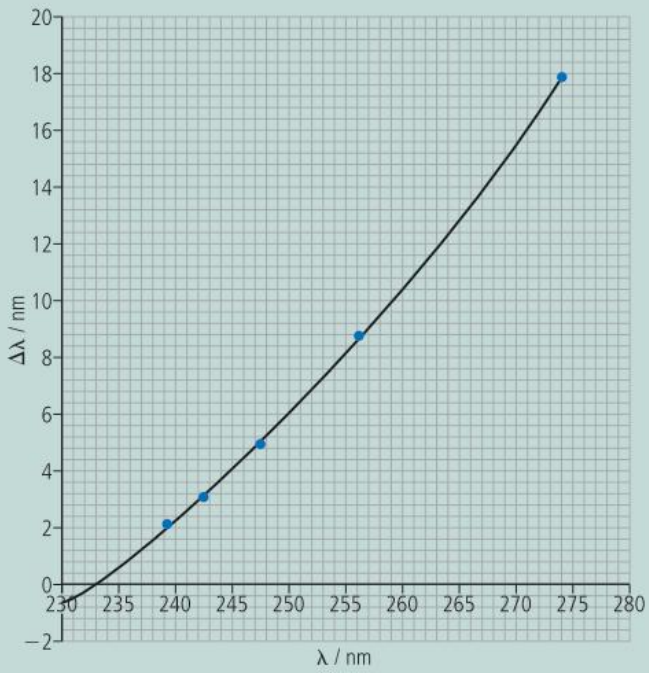
Q28. Some frequencies of the lines in the spectrum of He^+ ion are shown in the table. Determine the convergence limit and ionization energy of the He^+ ion.

Excited energy level (n)	Frequency, f / × 10^{-15} s^{-1}
2	9.87
3	11.72
4	12.36
5	12.66
6	12.82

Q29. The convergence limits in the spectra of two single electron ions are shown in the table. Use these values to calculate the ionization energy of the ions.

	Frequency of convergence limit/ s^{-1}
Li^{2+}	2.97×10^{16}
Be^{3+}	5.27×10^{16}

Q30. The emission spectrum of lithium includes a number of lines corresponding to the transitions involving the valence electron falling from excited states back to the 2s orbital. The graph shows the wavelength λ_n of a number of these lines in the spectrum, plotted against the difference in wavelength between consecutive lines ($\Delta\lambda = \lambda_n - \lambda_{n+1}$).



Determine the wavelength that corresponds to ionization of lithium and calculate the ionization energy.

Successive ionization energy (IE) data for an element give information about its electron configuration

Additional evidence for the electron configuration of an atom comes from looking at patterns of successive ionization energies. As discussed earlier for aluminium, the first ionization energy corresponds to the following process:

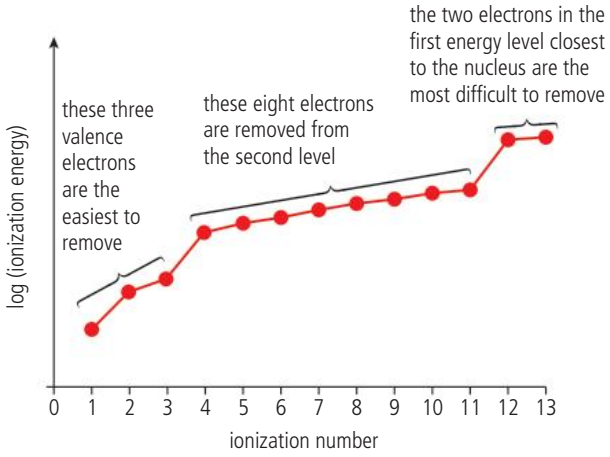
$$Al(g) \rightarrow Al^{+}(g) + e^{-}$$

The second ionization energy corresponds to the change:

$$Al^{+}(g) \rightarrow Al^{2+}(g) + e^{-}$$

and so on.

The ionization energies for aluminium are shown in Figure 14.



S1.3 Figure 14 Successive ionization energies for aluminium. Note the jumps between the 3rd and 4th and between the 11th and 12th ionization energies as electrons are removed from lower energy levels. As there is a wide range of values, they are best presented on a log scale.

TOK How does the method of data presentation influence how the data are interpreted? The use of scale can clarify important relationships but can also be used to manipulate data. How can you as a knower distinguish between the use and abuse of data presentation?

i Nature of Science, Tool 3, Reactivity 3.1 – Why are log scales useful when discussing $[H^+]$ and ionization energies?

TOK Which of Dalton's five proposals (page 30) do we now hold to be 'true'? How does scientific knowledge change with time? Are the models and theories of science accurate descriptions of the natural world, or just useful interpretations to help predict and explain the natural world?

The electron configurations of aluminium ions as electrons are successively removed are shown in the table.

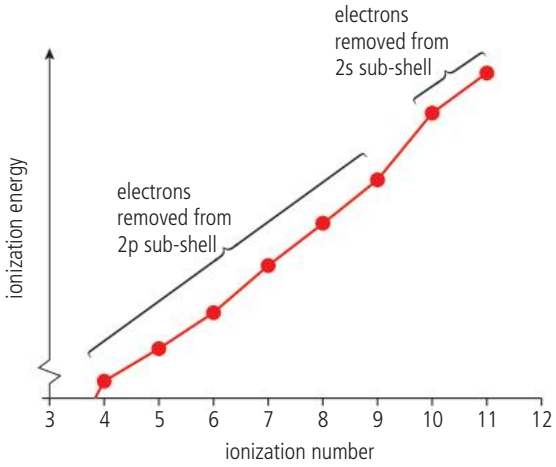
	Electron configuration		Electron configuration
Al	$1s^2 2s^2 2p^6 3s^2 3p^1$	Al^{6+}	$1s^2 2s^2 2p^3$
Al^+	$1s^2 2s^2 2p^6 3s^2$	Al^{7+}	$1s^2 2s^2 2p^2$
Al^{2+}	$1s^2 2s^2 2p^6 3s^1$	Al^{8+}	$1s^2 2s^2 2p^1$
Al^{3+}	$1s^2 2s^2 2p^6$	Al^{9+}	$1s^2 2s^2$
Al^{4+}	$1s^2 2s^2 2p^5$	Al^{10+}	$1s^2 2s^1$
Al^{5+}	$1s^2 2s^2 2p^4$	Al^{11+}	$1s^2$

Figure 14 shows two key points.

- There is an increase in successive ionization energies. The first ionization energy involves the separation of an electron from a singly charged ion and the second IE involves the separation of an electron from a doubly charged ion. The process becomes more difficult as there is increasing attraction between the higher charged positive ions and the oppositely charged electron.
- There are jumps when electrons are removed from levels closer to the nucleus. The first three ionization energies involve the removal of electrons from the third level. The 3p electron is removed first, followed by the electrons from the 3s orbital. An electron is removed from the second level for the fourth ionization energy. This electron is closer to the nucleus and is more exposed to the positive charge of the nucleus and so needs significantly more energy to be removed. There is similarly a large jump for the 12th ionization energy as it corresponds to an electron being removed from the 1s orbital.

A closer look at successive ionization energies gives evidence for sublevels in the atom

A closer look at the successive ionization energies shows evidence of the sublevels present with each level. The log graph of all 13 ionization energies showed a 2, 8, 3 pattern in successive ionization energies, which reflects the electron arrangement of the atom, with two electrons in the first level, eight electrons at the second energy level, and three valence electrons in the outer shell. Now we consider the fourth to eleventh ionization energies in more detail. These correspond to the removal of the eight electrons in the second energy level (Figure 15).



S1.3 Figure 15 Successive ionization energies for aluminium. The jump between the ninth and tenth ionization energies indicates that the second energy level is divided into sublevels. The smaller jump between the sixth and seventh ionization energies should also be noted and is discussed more fully in the text.

The jump between the ninth and tenth ionization energies shows that the eleventh electron is more difficult to remove than we would expect from the pattern of the six previous electrons. This suggests that the second energy level is divided into two sublevels.

This evidence confirms that the **2s sublevel** can hold a maximum of two electrons, and the **2p sublevel** can hold six electrons.

SKILLS

Successive ionization energies database investigation. Full details of how to carry out this activity with a worksheet are available in the eBook.

Worked example

A graph of some successive ionization energies of aluminium is shown in Figure 15.

(a) Explain why there is a large increase between the ninth and tenth ionization energies.

(b) Explain why the increase between the sixth and seventh values is greater than the increase between the fifth and sixth values.

Solution

(a) The ninth ionization energy corresponds to the change:

$$Al^{8+}(g) \rightarrow Al^{9+}(g) + e^-$$

Al^{8+} has the configuration $1s^2 2s^2 2p^1$. The electron is removed from a 2p orbital.

The tenth ionization energy corresponds to the change:

$$Al^{9+}(g) \rightarrow Al^{10+}(g) + e^-$$

Al^{9+} has the configuration $1s^2 2s^2$. The electron is removed from a 2s orbital.

Electrons in a 2s orbital are of lower energy than those is 2p orbitals. They are closer to the nucleus and experience a stronger force of electrostatic attraction and so are more difficult to remove.

(b) The sixth ionization energy corresponds to the change:

$$Al^{5+}(g) \rightarrow Al^{6+}(g) + e^-$$

Al^{5+} has the configuration $1s^2 2s^2 2p^4$ ($1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$). The electron is removed from a doubly occupied 2p orbital.

The seventh ionization energy corresponds to the change:

$$Al^{6+}(g) \rightarrow Al^{7+}(g) + e^-$$

The electron is removed from a singly occupied 2p orbital.

An electron in a doubly occupied orbital is repelled by its partner, and so is easier to remove than electrons in half-filled orbitals, which do not experience this force of repulsion.



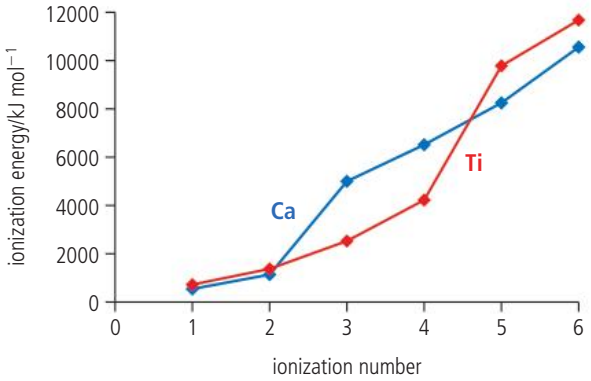
Al^{5+}: $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$ Al^{6+}: $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$

▲ The electron removed from the Al^{5+} ion is from a doubly occupied 2p orbital. This is easier to remove than an electron in a singly occupied orbital because it is repelled by its partner.

Successive ionization energies of transition elements

One of the key features of transition metal chemistry is the wide range of oxidation states that the metals display in their compounds. Calcium, for example, only shows the +2 state whereas titanium shows the +4 , +3, and +2 states. The difference in behaviour can be related to patterns in successive ionization energies (Figure 16).

Element	Electron configuration
Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
Ti	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$



S1.3 Figure 16 Successive ionization energies for Ca and Ti.

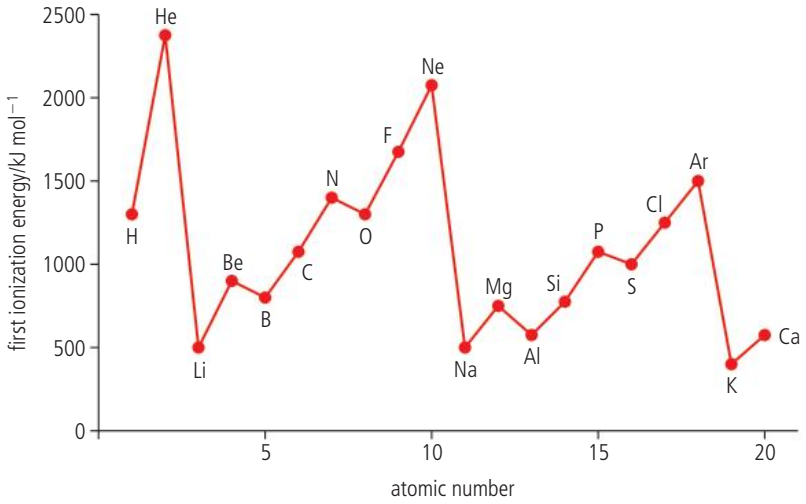
Structure 3.1 – How do patterns of successive IEs of transition elements help to explain the variable oxidation states of these elements?

The Ca^{3+} ion is energetically unstable because there is a large jump in ionization energy as the third electron is removed from the inner 3p orbital. The increase in successive energies for titanium is more gradual as the 3d and 4s orbitals are close in energy. Titanium shows the +2, +3, and +4 oxidation states. A large jump occurs between the fourth and fifth ionization energies, as the inner 3p electron is removed, so titanium does not form the +5 state.

Further evidence of sub-shells comes from a consideration of patterns in first ionization energies.

Trends in first ionization energy across periods account for the existence of main energy levels and sublevels in atoms

The periodic arrangement of the elements in the periodic table is also reflected by patterns in the first ionization energies.



The first ionization energies of the first 20 elements.

- Ionization energies generally increase from left to right across a period, as the nuclear charge increases. The electrons are removed from the same main energy level, but there is an increase in the force of electrostatic attraction between the nucleus and outer electrons.
- Ionization energy decreases down a group as a new energy level, which is further from the nucleus, is occupied. Less energy is required to remove outer electrons that are further from the attractive pull of the nucleus.
- There are regular discontinuities in the trend across a period, which are explored below. These provide further evidence for the existence of sub-shells.

The metals on the left of the periodic table have low ionization energies and generally form stable positive ions. The non-metals on the right of the periodic table have high ionization energies and do not lose electrons readily. They generally form negative ions. This is explored in more detail in Structure 3.1.

Structure 3.1 – How does the trend in IE values across a period and down a group explain the trends in properties of metals and non-metals?

Worked example

Further evidence for the existence of sub-shells comes from a study of first ionization energies.

(a) In period 2, there is a decrease in first ionization energies between Be and B, and in period 3, there is a decrease between Mg and Al. Explain this decrease in ionization energies between group 2 and group 13 elements.

(b) In period 2, there is a decrease in first ionization energies between N and O, and in period 3, there is a decrease between P and S. Explain the decrease in ionization energies between group 15 and group 16 elements.

Solution

(a) The group 2 elements have the electron configuration ns^2. The group 13 elements have the electron configuration ns^2np^1.

The electron removed when the group 13 elements are ionized is a p electron. The electron removed when the group 2 elements are ionized is an s electron. Electrons in p orbitals are of higher energy and further away from the nucleus than s electrons and so are easier to remove.

(b) Group 15 elements have the configuration $ns^2np_x^1np_y^1np_z^1$. Group 16 elements have the configuration $ns^2np_x^2np_y^1np_z^1$. For group 16 elements, the electron is removed from a doubly occupied p orbital. An electron in a doubly occupied orbital is repelled by its partner and so is easier to remove than an electron in a half-filled orbital.

SKILLS

Databases can be used for compiling graphs of trends in ionization energies.

Exercise

Q31. The first four ionization energies for a particular element are 738, 1450, 7730, and 10 550 kJ mol^{-1} respectively. Deduce the group number of the element.

A 1 **B** 2 **C** 3 **D** 4

Q32. Successive ionization energies for an unknown element are given in the table.

First ionization energy / kJ mol^{-1}	Second ionization energy / kJ mol^{-1}	Third ionization energy / kJ mol^{-1}	Fourth ionization energy / kJ mol^{-1}
590	1145	4912	6491

Identify the element.

A K **B** Ca **C** S **D** Cl

Q33. The successive ionization energies (in kJ mol^{-1}) for carbon are shown in the table.

1st	2nd	3rd	4th	5th	6th
1086	2352	4619	6220	37820	47280

(a) Explain why there is a large increase between the fourth and fifth values.

(b) Explain why there is an increase between the second and third values.

Q34. Sketch a graph to show the expected pattern for the first seven ionization energies of fluorine.

Q35. The first ionization energies of the period 3 elements Na to Ar are given in Section 9 of the data booklet.

(a) Explain the general increase in ionization energy across the period.

(b) Explain why the first ionization energy of magnesium is greater than that of aluminium.

(c) Explain why the first ionization energy of sulfur is less than that of phosphorus.

Nature of Science

This chapter has highlighted the need for experimental evidence to support our scientific theories.

Scientific ideas often start as speculations which are only later confirmed experimentally. The existence of the Higgs' boson was, for example, first suggested by the physicist Peter Higgs in 1964. It was, however, only detected in 2012 when two separate international teams working at the Large Hadron Collider at CERN independently announced that they had collected evidence to support its existence.

HL end

TOK

The discovery of the Higgs boson was greatly facilitated by growth in computing power and sensor technology. Experiments in CERN's Large Hadron Collider regularly produce 23 petabytes of data per second, equivalent to 13.3 years of high-definition TV content per second. How does computation help people to process data to gain knowledge?

Guiding Question revisited

How can we model the energy states of electrons in atoms?

In this chapter we have developed models of the energy states of electrons in atoms to explain atomic emission line spectra and patterns in successive ionization energies of an element, and first ionizations.

- Electromagnetic radiation can be described using a wave model or a particle model. The speed of the wave (c) is related to the frequency (f) and wavelength (λ) by the expression: $c = f\lambda$
- The existence of lines in an emission spectrum indicates that the electron can only exist in discrete energy levels. The lines in the spectra converge at high energies because the gaps between energy levels in the atom decrease at higher energies.
- In the Bohr model of the hydrogen atom, the electron travels in orbits of discrete radii around the nucleus. This model correctly predicts the frequencies and wavelengths of the line spectra but does not apply to more complex systems with more than one electron.
- According to the quantum theory, an electron's trajectory can only be described in terms of probabilities and a wave model of the electron is needed.
- Electrons in the atom occupy atomic orbitals, which are regions in which the electron is most likely to be found. Two electrons of opposite spin can occupy one orbital.
- Atomic orbitals have different shapes, sizes and energies. Orbitals of the same energy form sublevels. The first energy level is made up of one sublevel, the second has two sublevels and so on.
- The ground state configuration of an atom is obtained using the Aufbau principle, with electrons occupying the available orbitals of lowest energy.
- The periodic table reflects the periodicity of the electron configuration. Elements with valence electrons in s orbitals are in the s block, elements with valence electrons in p orbitals are in the p block, and so on.
- The energy of a photon (E_{photon}) depends on the frequency (f) according to Planck's equation: $E_{photon} = hf$.
- When an excited electron in an atom loses energy, the energy is given out as a photon. $\Delta E_{atom} = E_{photon}$

Practice questions

1. What is the electron configuration of the Cr^{2+} ion?

A [Ar] $3d^5 4s^1$ **B** [Ar] $3d^3 4s^1$

C [Ar] $3d^6 4s^1$ **D** [Ar] $3d^4 4s^0$

2. Which is correct for the following regions of the electromagnetic spectrum?

	Ultraviolet (UV)		Infrared (IR)	
A	high energy	short wavelength	low energy	low frequency
B	high energy	low frequency	low energy	long wavelength
C	high frequency	short wavelength	high energy	long wavelength
D	high frequency	long wavelength	low frequency	low energy

3. An ion has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$. Which ion could it be?

A Ni^{2+} **B** Cu^+ **C** Cu^{2+} **D** Co^{3+}

4. In the emission spectrum of hydrogen, which electron transition would produce a line in the visible region of the electromagnetic spectrum?

A $n = 2 \rightarrow n = 1$ **B** $n = 3 \rightarrow n = 2$

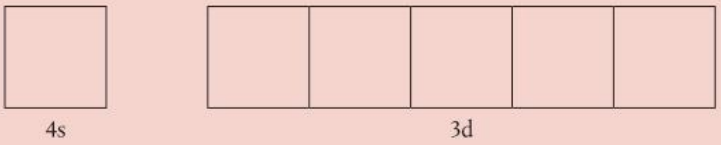
C $n = 2 \rightarrow n = 3$ **D** $n = \infty \rightarrow n = 1$

5. The electron configuration of chromium can be expressed as $[Ar]4s^x3d^y$.

(a) Explain what the square brackets around argon, [Ar], represent. (1)

(b) State the values of x and y. (1)

(c) Annotate the diagram below to show the 4s and 3d orbitals for a chromium atom. Use an arrow, ↑ and ↓, to represent a spinning electron.



(1)

(Total 3 marks)

6. **(a)** List the following types of electromagnetic radiation in order of increasing wavelength (shortest first).

I. Yellow light II. Red light

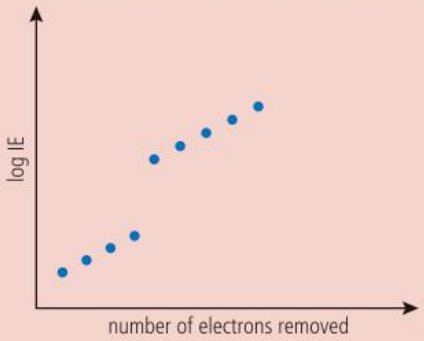
III. Infrared radiation IV. Ultraviolet radiation (1)

(b) Distinguish between a continuous spectrum and a line spectrum. (1)

(Total 2 marks)

HL

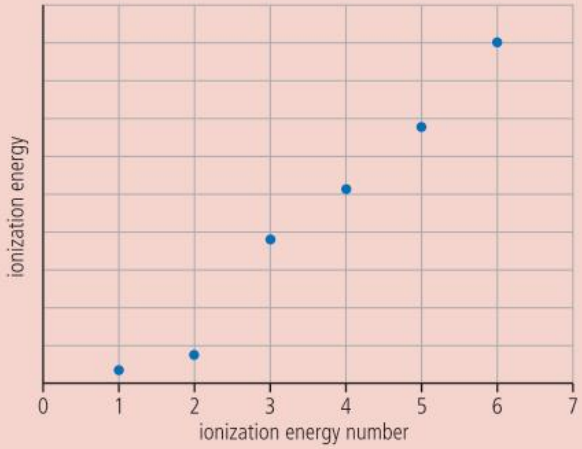
7. The graph represents the energy needed to remove nine electrons, one at a time, from an atom of an element. Not all of the electrons have been removed.



Which element could this be?

A C **B** Si **C** P **D** S

8. The graph gives the successive ionization energies for an element X.



Deduce the charge of the most stable ion formed by X.

A X^+ **B** X^{2+} **C** X^{3+} **D** X^{4+}

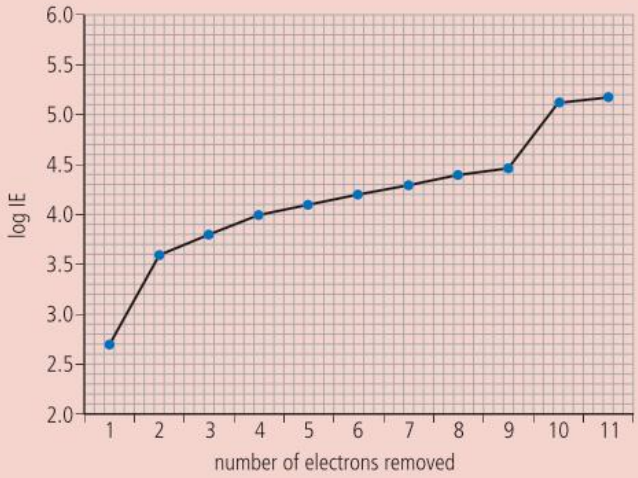
9. The successive ionization energies of an element, Y, are shown in the table.

	1st	2nd	3rd	4th	5th	6th	7th
Ionization energy / kJ mol^{-1}	788	1577	3232	4356	16091	19805	23780

Identify the type of orbital from which the first electron is removed when the first ionization energy is determined.

A s orbital **B** p orbital **C** d orbital **D** f orbital

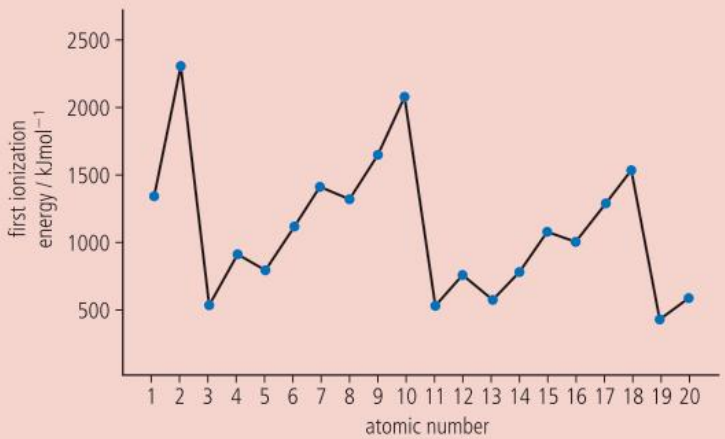
10. The graph represents the successive ionization energies of sodium. The vertical axis plots log(ionization energy) instead of ionization energy to allow the data to be represented without using an unreasonably long vertical axis.



State the full electron configuration of sodium and explain how the successive ionization energy data for sodium are related to its electron configuration. (4)

(Total 4 marks)

11. The graph of the first ionization energy plotted against atomic number for the first 20 elements shows periodicity.

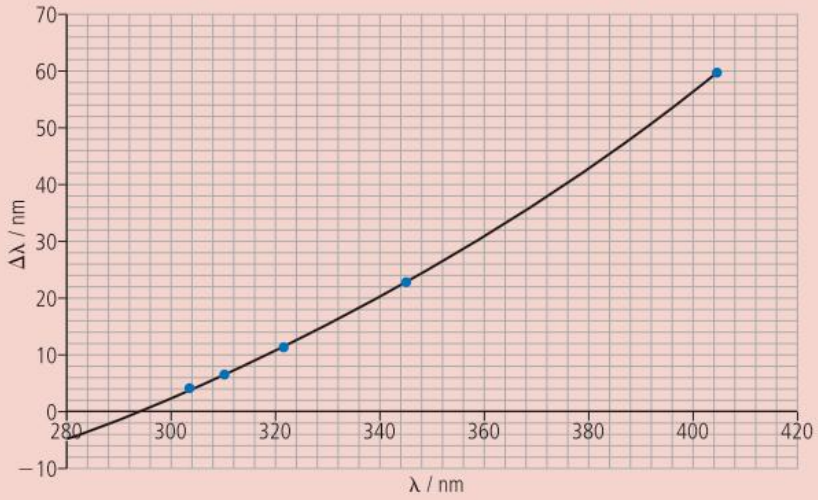


(a) Explain how information from this graph provides evidence for the existence of main energy levels and sublevels within atoms. (4)

(b) State what is meant by the term *second ionization energy*. (1)

(Total 5 marks)

12. The emission spectrum of potassium includes a number of lines corresponding to the transitions involving the valence electron falling from excited states back to the 4s orbital. The graph shows the wavelength λ_n of a number of these lines in the spectrum plotted against the difference in wavelength between consecutive lines ($\Delta\lambda = \lambda_n - \lambda_{n+1}$).



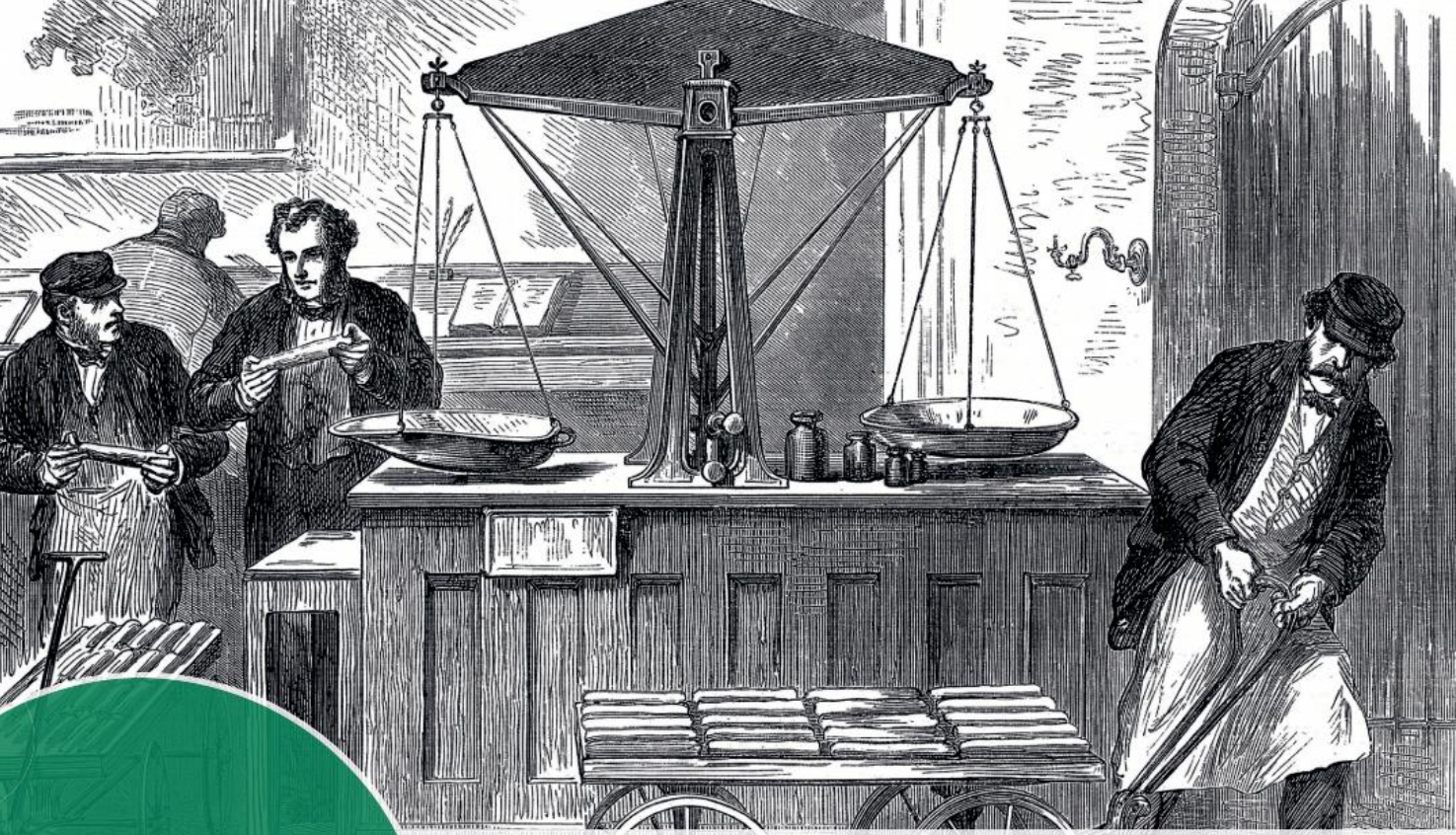
Determine the wavelength that corresponds to ionization of potassium and calculate the ionization energy in kJ mol^{-1}. (2)

(Total 2 marks)

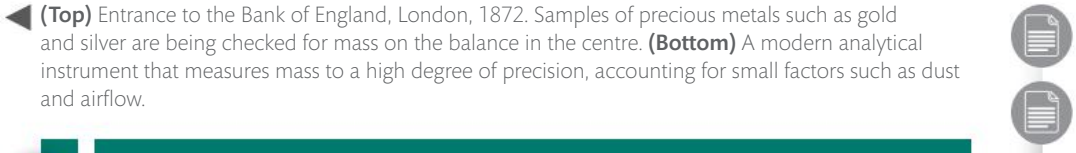
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STRUCTURE

1.4 Counting particles by mass: The mole







(Top) Entrance to the Bank of England, London, 1872. Samples of precious metals such as gold and silver are being checked for mass on the balance in the centre. **(Bottom)** A modern analytical instrument that measures mass to a high degree of precision, accounting for small factors such as dust and airflow.

Nature of Science

Advances in technology have led to increasingly precise ways of measuring mass, as well as units derived from it, such as concentration. This means that values which were previously too low to be detected can now be reported accurately. This makes possible changes in regulations and laws, such as levels of pollutants in fluids and of illegal drugs in the bloodstream. Authorities and governments often depend on measurements such as these in making judgements and enforcing the law. It is therefore essential that the data collected are reliable and include clearly stated uncertainties.

Guiding Question

How do we quantify matter on the atomic scale?

Chemical change involves interactions between atoms that have fixed mass. Yet the mass of an individual atom is so small that it is not practical to measure it directly in a laboratory. The upper limit of precision of very high quality analytical balances is generally about 1×10^{-8} kg, whereas, for example, a single atom of carbon weighs 1.99×10^{-26} kg.

Clearly, we need a way to close the gap between what can be measured and what is happening on the atomic scale. In this chapter we will learn how solving this problem led to the development of the chemical unit of amount, the mole. The mole is a fundamental unit in the SI system and is one of the most widely used tools in chemistry. It allows a form of book-keeping at the atomic level, making that important link between the measurable mass and the number of reacting particles.

Structure 1.4.1 – The mole as the unit of amount

Structure 1.4.1 – The mole (mol) is the SI unit of amount of substance. One mole contains exactly the number of elementary entities given by the Avogadro constant. Convert the amount of substance, *n*, to the number of specified elementary entities.	
An elementary entity may be an atom, a molecule, an ion, an electron, any other particle or a specified group of particles. Avogadro's constant (N_A) is given in the data booklet. It has the units mol^{-1}.	

The Avogadro constant defines the mole as the unit of amount in chemistry

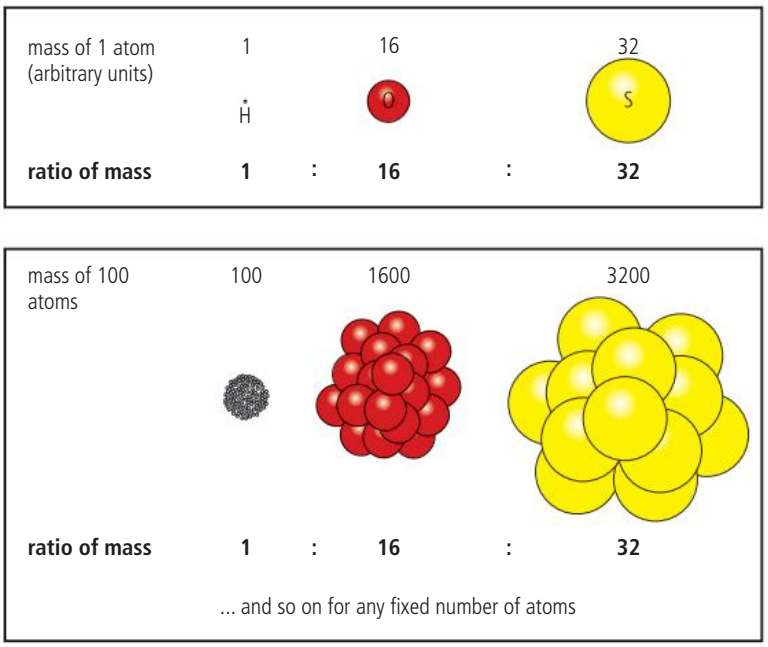
The mole. Full details of how to carry out this activity with a worksheet are available in the eBook.

SKILLS

We know that even with the very best experimental apparatus available, we are unable to measure the mass of individual atoms in the laboratory directly. They are simply too small. This is not really a problem because all we need to do is to weigh an appropriately large number of atoms to give a mass that will be a useful quantity in grams. As atoms do not react individually but in very large numbers, this approach makes sense. So how many atoms shall we lump together in our 'appropriately large number'?

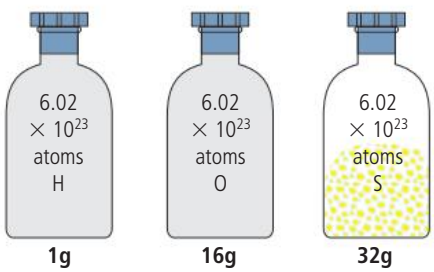
Let us first consider that atoms of different elements have different masses because they contain different numbers of particles, mostly **nucleons** in their nucleus, as discussed in Structure 1.2. This means we can compare their masses with each other in relative terms. For example, an atom of oxygen has a mass approximately 16 times greater than an atom of hydrogen, and an atom of sulfur has a mass about twice that of an atom of oxygen. The good news is that these ratios will stay the same when we increase the number of atoms, *so long as we ensure we have the same number of each type of atom.*

100 atoms of H, O and S have the same mass ratio as one atom of each element, 1 : 16 : 32.



If we could take 6×10^{23} atoms of hydrogen, it would have a mass of 1 g. It follows from the ratios above that *the same number of atoms* of oxygen would have a mass of 16 g, while *the same number of atoms* of sulfur would have a mass of 32 g. We now have a quantity of atoms that we can measure in grams (Figure 1).

S1.4 Figure 1 6.02×10^{23} atoms of H, O and S have the same mass ratio as one atom of each element. This number of atoms gives an amount that we can see and measure in grams.



This number, accurately stated as $6.02214129 \times 10^{23}$, is known as the Avogadro number and it is the basis of the unit of **amount** used in chemistry known as the **mole**. In other words, one mole of a substance contains the Avogadro number of particles. Mole, the unit of amount, is one of the base units in the SI system and has the unit symbol **mol.**

The example in Figure 1 is illustrative only, as in reality hydrogen and oxygen do not occur stably as single atoms, but as diatomic molecules, H_2 and O_2, as explained in Structure 2.2. Other substances exist as particles of different types, so the term **elementary entity** is used to cover the broad range of possible particles. An elementary entity may be an atom, a molecule, an ion, an electron, any other particle or a specified group of particles.

In 2019, the International Union of Pure and Applied Chemistry (IUPAC) published a change to the definition of the mole. The new definition emphasizes that the quantity 'amount of substance' is concerned with counting entities, rather than measuring the mass of a sample.

The SI refers to the metric system of measurement based on seven base units. These are metre (m) for length, kilogram (kg) for mass, second (s) for time, ampere (A) for electric current, kelvin (K) for temperature, candela (cd) for luminous intensity and mole (mol) for amount. All other units are derived from these. The SI system is the world's most widely used system of measurement.

The International Bureau of Weights and Measures (BIPM according to its French initials) is an international standards organization, which aims to ensure uniformity in the application of SI units around the world. The BIPM officially introduced updated definitions to these base units, including the mole, in 2019.

So 'mole' is simply a word that represents a number, just as 'couple' is a word for 2 and 'dozen' is a word for 12. A mole is a very large number, bigger than we can easily imagine or ever count, but it is nonetheless a fixed number. So a mole of any substance contains the Avogadro number, 6.02×10^{23}, of entities. It can refer to atoms, molecules, ions, electrons and so on – it can be applied to any entity because it is just a number. And from this, we can easily calculate the number of particles in any fraction or multiple of a mole of a substance.



Each sample contains one mole, 6.02×10^{23} particles, of a specific element. Each has a characteristic mass, known as its molar mass. Clockwise from upper left the elements are: carbon (C), sulfur (S), iron (Fe), copper (Cu) and magnesium (Mg).

Amedeo Avogadro (1776–1856) was an Italian scientist who made several experimental discoveries. He clarified the distinction between atoms and molecules, and used this to propose the relationship between gas volume and number of molecules. His ideas were not accepted in his time, largely due to a lack of consistent experimental evidence. After his death, when his theory was confirmed by fellow Italian Cannizzaro, his name was given in tribute to the famous constant that he helped to establish.

The mole is the SI unit of amount of substance. One mole contains exactly 6.022×10^{23} elementary entities. This number is the fixed numerical value of the Avogadro constant, N_A.

The Avogadro number, 6.02×10^{23}, is the fixed numerical value of the Avogadro constant, *NA*, which has the units mol^{-1}.

The Avogadro constant is so large a number that we cannot comprehend its scale. For example:

- a population of 6.02×10^{23} people would need 75 trillion Earths each with the current population of nearly 8 billion
- 6.02×10^{23} pencil erasers would cover the Earth to a depth of about 500 m
- 6.02×10^{23} drops of water would fill all the oceans of the Earth many times over.

SKILLS

Experimental estimation of the Avogadro constant. Full details of how to carry out this experiment with a worksheet are available in the eBook.

Number of particles = number of moles (n) × Avogadro constant (N_A).

TOK

The magnitude of the Avogadro constant is beyond the scale of our everyday experience. What is the difference between 'data', 'information' and 'knowledge'?

Worked example

A tablespoon holds 0.500 moles of water. How many molecules of water are present?

Solution

1.00 mole of water has 6.02×10^{23} molecules of water

So 0.500 moles of water has $0.500 \text{ mol} \times 6.02 \times 10^{23}$ molecules

$0.500 \text{ mol} = 3.01 \times 10^{23}$ molecules of water

Worked example

A solution of ammonia and water contains 2.10×10^{23} molecules of H_2O and 8.00×10^{21} molecules of NH_3. How many moles of hydrogen atoms are present?

Solution

First total the number of hydrogen atoms.

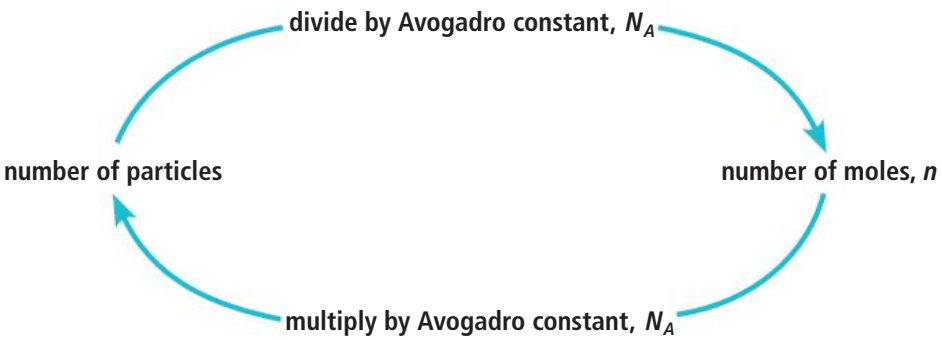
from water, H_2O: number of H atoms $= 2 \times (2.10 \times 10^{23}) = 4.20 \times 10^{23}$

from ammonia, NH_3: number of H atoms $= 3 \times (8.00 \times 10^{21}) = 0.240 \times 10^{23}$

so total H atoms $= (4.20 \times 10^{23}) + (0.240 \times 10^{23}) = 4.44 \times 10^{23}$

To convert atoms to moles, divide by the Avogadro constant:

$$\frac{4.44}{6.02} \times \frac{10^{23}}{10^{23}} = 0.738 \text{ mol H atoms}$$



Using the Avogadro constant to calculate the number of particles in a sample has its uses, but it still leaves us with numbers that are beyond our comprehension. What is much more useful, as you have probably realized, is the link between the Avogadro constant and the mass of one mole of a substance, which is based on the relative atomic mass.

Nature of Science

Accurate determinations of the Avogadro constant require the measurement of a single quantity using the same unit on both the atomic and macroscopic scales. This was first done following Millikan's work measuring the charge on a single electron. The charge on a mole of electrons, known as the Faraday constant, was already known through electrolysis experiments. Dividing the charge on a mole of electrons 96 485.3383 C by the charge on a single electron, $1.60217653 \times 10^{-19}$ C e^{-1}, gives a value for the Avogadro constant of $6.02214154 \times 10^{23}$ mol^{-1}. Later work used X-ray crystallography of very pure crystals to measure the spacing between particles and so the volume of one mole. The validity of data in science is often enhanced when different experimental approaches lead to consistent results.

Exercise

Q1. Calculate how many hydrogen atoms are present in:

(a) 0.020 moles of C_2H_5OH

(b) 2.50 moles of H_2O

(c) 0.10 moles of $Ca(HCO_3)_2$

Q2. Propane has the formula C_3H_8. If a sample of propane contains 0.20 moles of C, how many moles of H are present?

Q3. Calculate the amount of sulfuric acid, H_2SO_4, which contains 6.02×10^{23} atoms of oxygen.

SKILLS

When doing multiplication or division, the answer should be given to the same number of significant figures as the data value with the least number of significant figures. When doing addition or subtraction, the answer should be given to the same number of decimal places as the data value with the least number of decimal places.

Structure 1.4.2 – Relative atomic mass and relative formula mass

Structure 1.4.2 – Masses of atoms are compared on a scale relative to ^{12}C and are expressed as relative atomic mass (A_r) and relative formula mass (M_r). Determine relative formula masses (M_r) from relative atomic masses (A_r).	
Relative atomic mass and relative formula mass have no units. The values of relative atomic masses given to two decimal places in the data booklet should be used in calculations.	Structure 3.1 – Atoms increase in mass as their position descends in the periodic table. What properties might be related to this trend?

The isotope carbon–12 is used as the reference point for comparing masses of atoms

Relative atomic mass

On page 90 the whole numbers used to compare the masses of the elements H, O and S are approximate. This is mostly because of the existence of isotopes, atoms of the same element that differ in their mass, as is explained in Structure 1.2. A sample of an

element containing billions of atoms will include a mix of these isotopes according to their relative abundance. The mass of an individual atom in the sample is therefore taken as a **weighted average** of these different masses.

The relative scale for comparing the mass of atoms needs a reference point. The international convention for this is to take the specific form of carbon known as the **isotope carbon-12** as the standard, and assign this a value of 12 units. In other words, one twelfth of an atom of carbon-12 has a value of exactly 1.

Relative atomic mass, A_r, is the weighted average mass of one atom of an element relative to $\frac{1}{12}$ the mass of an atom of carbon-12.

Putting this together, we can define the **relative atomic mass** as follows:

$$\text{relative atomic mass, } A_r = \frac{\text{weighted average mass of one atom of the element}}{\frac{1}{12}\text{ mass of one atom of carbon-12}}$$

Values for A_r do not have units as it is a relative term, which simply compares the mass of atoms against the same standard. As they are average values, they are not whole numbers. Section 7 of the data booklet gives A_r values to two decimal places. Some examples are given below.

A_r values are often rounded to whole numbers for quick calculations, but when using values for more accurate calculations, it is usually best to use the exact value given in Section 7 of the data booklet.

Element	Relative atomic mass (A_r)
carbon C	12.01
oxygen O	16.00
hydrogen H	1.01
lithium Li	6.94
sodium Na	22.99
potassium K	39.10

You will notice that the A_r of carbon is slightly greater than the mass of the isotope carbon-12 used as the standard, suggesting that carbon has isotopes with mass number greater than 12. In Structure 3.2 we discuss how relative atomic mass is calculated from isotope abundances, using data from mass spectrometry.

Structure 3.1 – Atoms increase in mass as their position descends in the periodic table. What properties might be related to this trend?

The table shows the increase in relative atomic mass of group 1 elements H, Li, Na and K as we descend the group. Successive elements in the group also have an additional energy level of electrons, which increases the atomic radius and therefore the distance of the outermost electrons from the nucleus. The larger atoms tend to lose electrons more easily, increasing their reactivity as metals. This is discussed in greater detail in Structure 3.1.

Challenge yourself

1. Periodic tables usually, but not always, position hydrogen at the top of group 1. What are the arguments for and against different positions for the placement of hydrogen in the periodic table?

Note that the term *relative molecular mass* was previously used, but can accurately be applied only to substances that exist as molecules. The term *relative formula mass* is preferred as it is more inclusive. It can be applied to both ionic and covalently bonded entities.

Relative formula mass

We can extend the concept of relative atomic mass to compounds (and to elements occurring as molecules) to obtain the **relative formula mass**, M_r. This simply involves adding the relative atomic masses of all the atoms or ions present in its formula. Note that M_r, like A_r, is a relative term and so has no units.



One mole of different compounds, each showing the molar mass. The chemical formulas of these ionic compounds are, clockwise from lower left: NaCl, $FeCl_3$, $CuSO_4$, KI, $Co(NO_3)_2$ and $KMnO_4$.

Challenge yourself

2. Three of the compounds in the photograph above are hydrated, containing water of crystallization as described on page 101. Use the formulas given in the caption and the masses marked on the photograph to deduce which compounds are hydrated, and the full formula of each.

Worked example

Use the values for A_r in Section 7 of the data booklet to calculate the M_r of the following:

(a) chlorine Cl_2

(b) ammonium nitrate NH_4NO_3

(c) aluminium sulfate $Al_2(SO_4)_3$

Solution

(a) $M_r = 35.45 \times 2 = 70.90$

(b) $M_r = 14.01 + (1.01 \times 4) + 14.01 + (16.00 \times 3) = 80.06$

(c) $M_r = (26.98 \times 2) + [32.07 + (16.00 \times 4)] \times 3 = 342.17$

Relative formula mass, M_r, is the sum of the weighted average of the atoms of an element in a formula unit relative to $\frac{1}{12}$ of an atom of carbon-12.

Exercise

Q4. The two most common isotopes of chlorine are ^{35}Cl and ^{37}Cl. The A_r of chlorine is 35.45. What can you conclude about the relative abundance of these two isotopes? (no calculation required)

Q5. Calculate the M_r of the following compounds:

(a) magnesium phosphate $Mg_3(PO_4)_2$

(b) ascorbic acid (vitamin C) $C_6H_8O_6$

(c) calcium nitrate $Ca(NO_3)_2$

(d) hydrated sodium thiosulfate $Na_2S_2O_3.5H_2O$

Structure 1.4.3 – Molar mass

Structure 1.4.3 – Molar mass (M) has the units g mol^{-1}. Solve problems involving the relationships between the number of particles, the amount of substance in moles and the mass in grams.	
The relationship $n = \frac{m}{M}$ is given in the data booklet.	Reactivity 2.1 – How can molar masses be used with chemical equations to determine the masses of the products of a reaction?

Molar mass is the mass of one mole of a substance

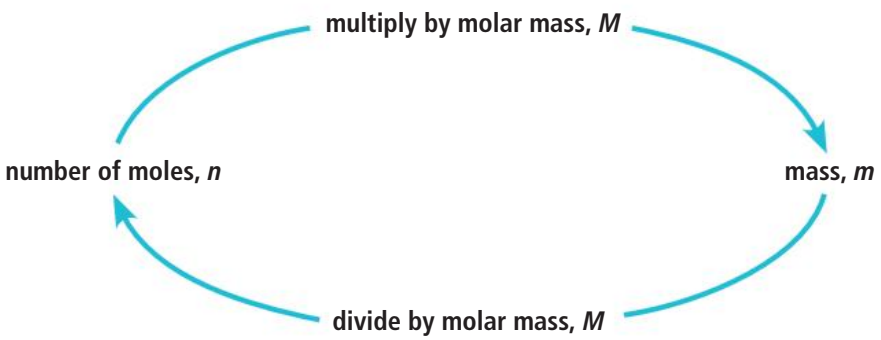
The molar mass of a substance is its relative atomic mass, A_r, or its relative formula mass, M_r, expressed in grams. It has the units g mol^{-1}.

The Avogadro constant is defined so that the mass of one mole of a substance is exactly equal to the substance's relative atomic mass or relative formula mass expressed in grams. This is known as the **molar mass** and is given the symbol ***M*** with the unit g mol^{-1}, which is a derived SI unit. Using examples discussed already in this chapter, we can now deduce the following.

Element or compound	Molar mass (M)
hydrogen H	1.01 g mol^{-1}
oxygen O	16.00 g mol^{-1}
chlorine Cl_2	70.90 g mol^{-1}
ammonium nitrate NH_4NO_3	80.06 g mol^{-1}
aluminium sulfate $Al_2(SO_4)_3$	342.17 g mol^{-1}

Now we are able to use the concept of the mole to make that all-important link between the number of particles and their mass in grams. The key to this is conversions of grams to moles and moles to grams. The following notations are used for these calculations:

- n = number of moles (mol)
- m = mass in grams (g)
- M = molar mass (g mol^{-1})



Worked example

What is the mass of the following?

(a) 6.50 moles of NaCl **(b)** 0.10 moles of OH^- ions

Solution

In all these questions, we must first calculate the molar mass, M, to know the mass of 1 mole in g mol^{-1}. Multiplying M by the specified number of moles, n, will then give the mass, m, in grams.

(a) $M(NaCl) = 22.99 + 35.45 = 58.44\,g\,mol^{-1}$

$n(NaCl) = 6.50\,mol$

$\therefore m(NaCl) = 58.44\,g\,mol^{-1} \times 6.50\,mol = 380\,g$

(b) OH^- ions carry a charge because electrons have been transferred, but change to the mass is negligible so can be ignored in calculating M.

$M(OH^-) = 16.00 + 1.01 = 17.01\,g\,mol^{-1}$

$n(OH^-) = 0.10\,mol$

$\therefore m(OH^-) = 17.01\,g\,mol^{-1} \times 0.10\,mol = 1.7\,g$

Worked example

What is the amount in moles of the following?

(a) 32.50 g $(NH_4)_2SO_4$ **(b)** 273.45 g N_2O_5

Solution

Again we calculate the molar mass, M, to know the mass of one mole. Dividing the given mass, m, by the mass of one mole will then give the number of moles, n.

(a) $M((NH_4)_2SO_4) = [14.01 + (1.01 \times 4)] \times 2 + 32.07 + (16.00 \times 4) = 132.17\,g\,mol^{-1}$

$m\,((NH_4)_2SO_4) = 32.50\,g$

$$\therefore n((NH_4)_2SO_4) = \frac{32.50\,g}{132.17\,g\,mol^{-1}} = 0.2459\,mol$$

(b) $M(N_2O_5) = (14.01 \times 2) + (16.00 \times 5) = 108.02\,g\,mol^{-1}$

$m\,(N_2O_5) = 273.45\,g$

$$\therefore n(N_2O_5) = \frac{273.45\,g}{108.02\,g\,mol^{-1}} = 2.532\,mol$$

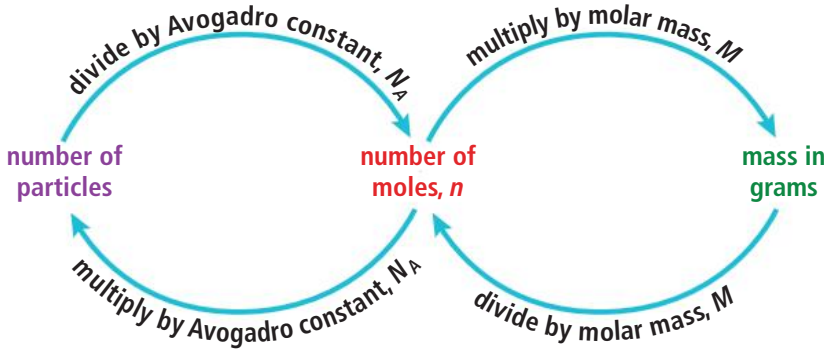
These simple conversions show that:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} \qquad n(\text{mol}) = \frac{m\,(g)}{M\,(g\,mol^{-1})}$$

This is a very useful relationship and it is better for you to understand how it is derived, rather than just memorizing it.

Dimensional analysis, or the factor-label method, is a widely used technique to determine conversion factors on the basis of cancelling the units. This method is not specifically used in the examples here, but the units *are* shown through the calculations. This can be helpful to check that the units on both sides of the equation are balanced, and are appropriate for the answer, which is often a useful check on the steps taken. The units on both sides of the equation cancel to be balanced. As in all cases, there is no one correct way to set out calculations, so long as the steps are clear.

The diagram below summarizes the central role of the number of moles, *n*, in converting between the number of particles and the mass in grams.



Calculations involving mass in chemistry always involve converting *grams to moles* and *moles to grams*. Think of these conversions as fundamental tools for chemists, and so make sure you are fully comfortable with carrying them out effectively.

$$\text{amount} = \frac{\text{mass}}{\text{molar mass}}$$

$$n(\text{mol}) = \frac{m(\text{g})}{M(\text{g mol}^{-1})}$$

Chemical equations show the simplest ratio of chemical entities reacting together. As molar masses represent a fixed number of entities, these *M* values can be used directly in chemical equations to calculate the relative masses that react. For example, in the equation for the combustion of hydrogen, we can deduce the following:

	$2H_2(g)$	+	$O_2(g)$	→	$2H_2O(l)$
reacting ratio	2 molecules		1 molecule		2 molecules
moles	2 moles		1 mole		2 moles
grams	$2 \times (1.01 \times 2)$		16.00×2		$2 \times [(1.01 \times 2) + 16.00]$
	= 4.04 g		= 32.00 g		= 36.04 g

Reactivity 2.1 – How can molar masses be used with chemical equations to determine the masses of the products of a reaction?

This simple example shows that 36.04 g of water can be produced from the combustion of 4.04 g of hydrogen. This type of calculation is the basis of all work on measuring the yield of industrial processes, considerations of atom economy and other aspects of Green Chemistry. These applications are discussed in more detail in Reactivity 2.1.

Exercise

Q6. Calcium arsenate $Ca_3(AsO_4)_2$ is a poison which was widely used as an insecticide. What is the mass of 0.475 mol of calcium arsenate?

Q7. How many moles of carbon dioxide are there in 66 g of carbon dioxide, CO_2?

Q8. How many moles of chloride ions, Cl^-, are there in 0.50 g of copper(II) chloride, $CuCl_2$?

Q9. How many carbon atoms are there in 36.55 g of diamond (which is pure carbon)?

Q10. What is the mass in grams of a 0.500 mol sample of sucrose, $C_{12}H_{22}O_{11}$?

Q11. Which contains the greater number of particles, 10.0 g of water, H_2O, or 10.0 g of mercury, Hg?

Q12. Put the following in descending order of mass.

I. 1.0 mol N_2H_4 II. 2.0 mol N_2

III. 3.0 mol NH_3 IV. 25.0 mol H_2

Structure 1.4.4 – Empirical and molecular formulas

Structure 1.4.4 – The empirical formula of a compound gives the simplest ratio of atoms of each element present in that compound. The molecular formula gives the actual number of atoms of each element present in a molecule.

Interconvert the percentage composition by mass and the empirical formula.
Determine the molecular formula of a compound from its empirical formula and molar mass.

	Tool 1 – How can experimental data on mass changes in combustion reactions be used to derive empirical formulas? Nature of Science, Tool 3, Structure 3.2 – What is the importance of approximation in the determination of an empirical formula?

The empirical formula of a compound gives the simplest ratio of its atoms

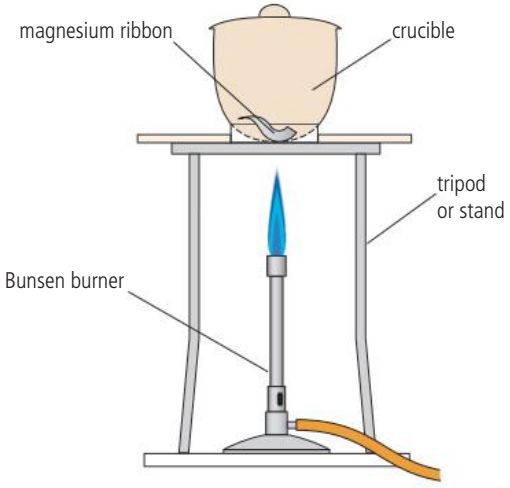
Magnesium burns brightly in air to form a white solid product. If we want to know how many atoms of magnesium combine with how many atoms of oxygen in this reaction, we can use the central role of the mole to relate the number of reacting particles to the measured mass.

The steps in the process are:

- calculate the moles of Mg from the measured mass of Mg used
- calculate the moles of oxygen that reacted from the increase in mass on heating
- express the ratio of moles Mg : moles O in its simplest form
- the ratio of moles is the ratio of atoms, so we can deduce the simplest formula of magnesium oxide.



Magnesium burns with a bright white flame, combining with oxygen from the air to form the white solid magnesium oxide.



Apparatus used to measure mass changes on burning magnesium.

Determining the empirical formula of a compound. Full details of how to carry out this experiment with a worksheet are available in the eBook.

An experiment for determining the empirical formula of magnesium oxide can be found on this page of your eBook (see Skills box on the left). Sample processed data for this experiment are given below:

	Magnesium, Mg	Oxygen, O
Mass /g ±0.002	0.043	0.029
M / g mol^{-1}	24.31	16.00
Moles / mol	0.00177	0.00181

ratio moles Mg : moles O = 1 : 1.02

So the ratio atoms Mg : atoms O approximates to 1 : 1.

Tool 1 – How can experimental data on mass changes in combustion reactions be used to derive empirical formulas?

From the result of this experiment, we conclude that the formula of magnesium oxide is MgO. This is known as an **empirical formula**, which gives the simplest whole-number ratio of the atoms of each element in a compound.

Nature of Science, Tool 3, Structure 3.2 – What is the importance of approximation in the determination of an empirical formula?

Empirical formulas are often derived from combustion data such as these. As the result must be a whole number ratio, some rounding of the numbers is often required, as we saw above. Sometimes this may involve a further mathematical step.

For example, data from combustion analysis gave:

ratio of atoms Fe : atoms O = 1 : 1.5

multiplying by 2 gives ratio of atoms Fe : atoms O = 2 : 3

so the empirical formula is **Fe_2O_3**.

Judging when approximation is a valid process in a calculation is an important tool in science. The need for approximation can sometimes indicate experimental errors. Where systematic errors can be identified, modifications to the experiment can lead to increasing the accuracy of the result.

Nature of Science

Scientific investigations based on quantitative measurements are subject to errors, both random and systematic. Analysis of the impact of these errors is inherent in the practice of science. It is good practice in all experimental work to record the sources of errors, consider their effect on the results, and suggest modifications that aim to reduce their impact. Scientists have the responsibility to communicate their results as realistically and honestly as possible, and this must include uncertainties and errors.

The empirical formula is the simplest whole-number ratio of the elements in a compound.

Worked example

Which of the following are empirical formulas?

I. C_6H_6 benzene

II. C_3H_8 propane

III. N_2O_4 dinitrogen tetroxide

IV. $Pb(NO_3)_2$ lead nitrate

Solution

Only II and IV are empirical formulas, as their elements are in the simplest whole-number ratio.

I has the empirical formula CH; III has the empirical formula NO_2.

The formulas of all ionic compounds, made of a metal and a non-metal such as magnesium oxide, are empirical formulas. This is explained in Structure 2.1. But as we see in I and III in the worked example above, the formulas of some covalent compounds are not empirical formulas. We will learn about molecular formulas in the next section.

Worked example

A sample of urea contains 1.210 g N, 0.161 g H, 0.480 g C and 0.640 g O.
What is the empirical formula of urea?

Solution

- Convert the mass of each element to moles by dividing by its molar mass, M.
- Divide by the smallest number to give the ratio.
- Approximate to the nearest whole number.

Element	Nitrogen, N	Hydrogen, H	Carbon, C	Oxygen, O
mass / g	1.120	0.161	0.480	0.640
M / g mol^{-1}	14.01	1.01	12.01	16.00
number of moles / mol	0.0799	0.159	0.0400	0.0400
divide by smallest	2.00	3.98	1.00	1.00
nearest whole number ratio	**2**	**4**	**1**	**1**

So the empirical formula of urea is N_2H_4CO, usually written as $CO(NH_2)_2$.



Hydrated copper sulfate, $CuSO_4.5H_2O$, is blue due to the presence of water of crystallization within the molecular structure of the crystals. The anhydrous form is white, as shown in the lower part of the tube. Heating removes the water molecules, leading to the colour being lost. The process is reversible, and the addition of water to the anhydrous crystals restores their blue colour.

A modification of this type of question is to analyse the composition of a **hydrated salt.** These are compounds that contain a fixed ratio of water molecules, known as **water of crystallization**, within the crystalline structure of the compound. The water of crystallization can be driven off by heating, and the change in mass used to calculate the ratio of water molecules to the **anhydrous salt**. The formula of the hydrated salt is shown with a dot before the number of molecules of water, for example $CaCl_2.4H_2O$.

Empirical formulas and percentage composition by mass can be interconverted

Data on the composition of a compound are often given as percentage by mass. Percentage data effectively give us the mass present in a 100 g sample of the compound.

Converting percentage by mass to empirical formulas

We can use percentage by mass data in the same way as in the examples above to determine the ratio of moles of each element in a compound.

- Divide the percentage mass of each element by its molar mass, *M*, to convert it to moles.
- Divide the moles of each element by the smallest number to give the ratio of moles.
- Approximate to the nearest whole number.

Worked example

The mineral celestine consists mostly of a compound of strontium, sulfur and oxygen. It is found by combustion analysis to have the composition 47.70% by mass Sr, 17.46% sulfur and the remainder is oxygen. What is its empirical formula?

When working with percentage figures, always check that they add up to 100. Sometimes an element is omitted from the data and you are expected to deduce its identity and percentage from the information given.

Solution

First we must calculate the percentage of oxygen by subtraction of the total given masses from 100.

% O = 100 – (47.70 + 17.46) = 34.84

Element	Strontium, Sr	Sulfur, S	Oxygen, O
% by mass	47.70	17.46	34.84
M / g mol^{-1}	87.62	32.07	16.00
moles	0.5443	0.5444	2.178
divide by the smallest	1.000	1.000	4.001

So the empirical formula of the mineral is $SrSO_4$

GENERAL PURPOSE 20-10-20
(For continuous liquid feed programs)

Guaranteed analysis	F1143
Total nitrogen (N)	20%
7.77% ammoniacal nitrogen	
12.23% nitrate nitrogen	
Available phosphate (P_2O_5)	10%
Soluble potash (K_2O)	20%
Magnesium (Mg)(Total)	0.05%
0.05% Water soluble magnesium (Mg)	
Boron (B)	0.0068%
Copper (Cu)	0.0036%
0.0036% Chelated copper (Cu)	
Iron (Fe)	0.05%
0.05% Chelated iron (Fe)	
Manganese (Mn)	0.025%
0.025% Chelated manganese (Mn)	
Molybdenum (Mo)	0.0009%
Zinc (Zn)	0.0025%
0.0025% Chelated zinc (Zn)	

Derived from: ammonium nitrate, potassium phosphate, potassium nitrate, magnesium sulfate, boric acid, copper EDTA, manganese EDTA, iron EDTA, zinc EDTA, sodium molybdate. Potential acidity: 487 lbs. calcium carbonate equivalent per ton.

The label on a fertilizer bag shows the percentage by mass of macro- and micronutrients that it contains.

Fertilizers contain nutrients that are added to the soil, usually to replace those used by cultivated plants. The elements needed in the largest quantities, so-called **macronutrients**, include nitrogen, phosphorus and potassium. Fertilizers are often labeled with an N-P-K rating, such as 30–15–30, to show the quantities of each of these three elements. The numbers indicate respectively the percentage by mass, N, percentage by mass diphosphorus pentoxide, P_2O_5, and percentage by mass potassium oxide, K_2O. The percentage data for P_2O_5 and K_2O represent the most oxidized forms of elemental phosphorus and potassium present in the fertilizer. Ammonium salts are the most common source of nitrogen used in fertilizers.

Challenge yourself

3. A fertilizer has an N-P-K rating of 18-51-20. Use the information in the box above to determine the percentage by mass of nitrogen, phosphorus and potassium present.

An understanding of percentage by mass data helps to evaluate information that is commonly given on products such as foods, drinks, pharmaceuticals, household cleaners as well as fertilizers. For example, a common plant fertilizer is labeled as pure sodium tetraborate pentahydrate, $Na_2B_4O_7.5H_2O$, and claims to be 15.2% boron. How accurate is this claim?

Converting empirical formulas to percentage by mass

We can see in the example above that, even though the mineral celestine has only one atom of strontium for every four atoms of oxygen, strontium nonetheless accounts for 47.70% of its mass. This, of course, is because an atom of strontium has significantly greater mass than an atom of oxygen, and the percentage by mass of an element in a compound depends on the *total* contribution of its atoms. We can calculate this as follows.

Worked example

What is the percentage by mass of N, H and O in the compound ammonium nitrate, NH_4NO_3?

Solution

First calculate the molar mass M:

$M\ (NH_4NO_3) = 14.01 + (1.01 \times 4) + 14.01 + (16.00 \times 3) = 80.06\,g\,mol^{-1}$

Then for each element, total the mass of its atoms, divide by M and multiply by 100:

$$\%\ N = \frac{14.01 \times 2}{80.06} \times 100 = 35.00\ \%\ \text{by mass}$$

$$\%\ H = \frac{1.01 \times 4}{80.06} \times 100 = 5.05\ \%\ \text{by mass}$$

$$\%\ O = \frac{16.00 \times 3}{80.06} \times 100 = 59.96\ \%\ \text{by mass}$$

(or this last term can be calculated by subtraction from 100)

Finally check that the numbers add up to 100%. Note that rounding here means that the total is 100.01%

The molecular formula of a compound gives the actual number of atoms in a molecule

It is possible for different compounds to have the same empirical formula but different molecular formulas. This is particularly the case in organic chemistry.

The empirical formula gives us the simplest ratio of atoms present in a compound, but this may not be the full information about the actual *number* of atoms in a molecule. For example, CH_2 is an empirical formula but there is no molecule that exists with just one atom of carbon and two atoms of hydrogen. There are many molecules with multiples of this ratio, such as C_2H_4, C_3H_6 and so on. Formulas that show all the atoms present in a molecule are called **molecular formulas**.

The molecular formula can be deduced from the empirical formula if the molar mass is known.

$$(\text{mass of empirical formula})_x = M \text{ where } x \text{ is an integer}$$

Worked example

Calomel is a compound once used in the treatment of syphilis. It has the empirical formula HgCl and a molar mass of 472.08 g mol^{-1}. What is its molecular formula?

Solution

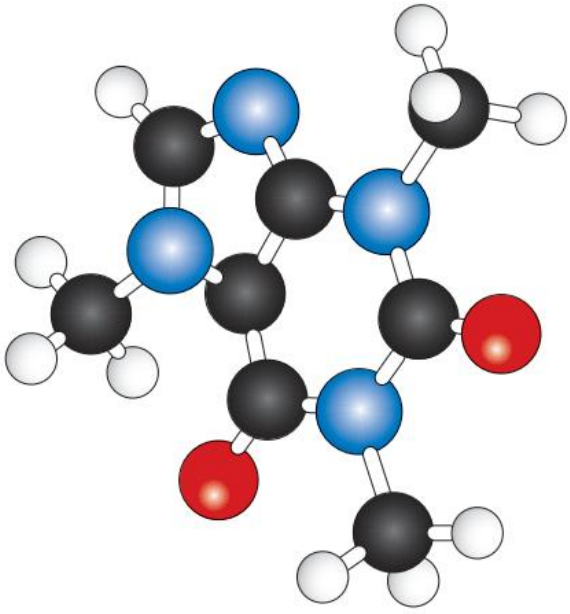
First calculate the mass of the empirical formula:

mass(HgCl) = 200.59 + 35.45 = 236.04 g mol^{-1}

$(236.04)_x = M = 472.08$

$\therefore x = 2$

molecular formula = Hg_2Cl_2



A molecular model of the stimulant caffeine. The atoms are colour coded as follows: black = carbon, grey = hydrogen, red = oxygen, blue = nitrogen. Can you deduce the molecular formula, the empirical formula and the molar mass of caffeine?

The molecular formula shows all the atoms present in a molecule. It is a multiple of the empirical formula.

Combustion analysis usually gives data on the mass of compounds formed

The data presented so far may suggest that combustion analysis directly gives information on the relative masses of individual elements in a compound. In fact this is rarely the case, but instead elements are converted into new compounds, typically their oxides, by reaction with oxygen. So the primary data obtained are the masses of carbon dioxide, water, sulfur dioxide and so on, which are measured by infrared absorption as described in Structure 3.2. Processing these data simply involves an extra step.

Worked example

A 0.5438 g sample of a compound known to contain only carbon, hydrogen and oxygen was burned completely in oxygen. The products were 1.0390 g CO_2 and 0.6369 g H_2O. The compound has a molar mass of 46.08 g mol^{-1}. Determine the empirical formula and the molecular formula of the compound.

Solution

First we must convert the mass of each product to moles in the usual way. From the number of moles of CO_2 and H_2O we can deduce the number of moles of C atoms and H atoms.

$$n(CO_2) = \frac{1.0390}{12.01 + (16.00 \times 2)} = 0.02361 \text{ mol } CO_2 \Rightarrow 0.02361 \text{ mol C atoms}$$

$$n(H_2O) = \frac{0.6369}{(1.01 \times 2) + 16.00} = 0.03534 \text{ mol } H_2O \Rightarrow 0.03534 \times 2$$

$$= 0.07068 \text{ mol H atoms}$$

In order to know the mass of O in the original sample, we must convert the number of moles of C and H atoms to mass by multiplying by their molar mass, M.

$$\text{mass C} = 0.02361 \text{ mol} \times 12.01 \text{ g mol}^{-1} = 0.2836 \text{ g}$$

$$\text{mass H} = 0.07068 \text{ mol} \times 1.01 \text{ g mol}^{-1} = 0.07139 \text{ g}$$

$$\therefore \text{ mass O} = 0.5438 - (0.2836 + 0.07139) = 0.1888 \text{ g}$$

$$\text{mol O atoms} = \frac{0.1888 \text{ g}}{16.00 \text{ g mol}^{-1}} = 0.01180 \text{ mol}$$

Now we can proceed as with the previous examples, converting mass of O to moles and then comparing the mole ratios.

Element	Carbon, C	Hydrogen, H	Oxygen, O
mass / g			0.1888
moles	0.02361	0.07068	0.0118
divide by smallest	2.00	5.98	1.00
nearest whole number ratio	2	6	1

So the empirical formula is C_2H_6O.

Mass of empirical formula = $(12.01 \times 2) + (1.01 \times 6) + 16.00 = 46.08\,g\,mol^{-1}$

$(\text{mass of empirical formula})_x = M$

$(46.08)_x = 46.08\,g\,mol^{-1} \therefore x = 1$

molecular formula = C_2H_6O.

Exercise

Q13. Give the empirical formulas of the following compounds:

(a) ethyne C_2H_2

(b) glucose $C_6H_{12}O_6$

(c) sucrose $C_{12}H_{22}O_{11}$

(d) octane C_8H_{18}

(e) oct–1-yne C_8H_{14}

(f) ethanoic acid CH_3COOH

Q14. A sample of a compound contains only the elements sodium, sulfur and oxygen. It is found by analysis to contain 0.979 g Na, 1.365 g S and 1.021 g O. Determine its empirical formula.

Q15. A sample of a hydrated compound was analysed and found to contain 2.10 g Co, 1.14 g S, 2.28 g O and 4.50 g H_2O. Determine its empirical formula.

Q16. A street drug has the following composition: 83.89% C, 10.35% H, 5.76% N. Determine its empirical formula.

Q17. The following compounds are used in the production of fertilizers. Determine which has the highest percentage by mass of nitrogen: NH_3, $CO(NH)_2$, $(NH_4)_2SO_4$.

Q18. A compound has the formula M_3N where M is a metal and N is nitrogen. It contains 0.673 g of N per gram of the metal M. Determine the relative atomic mass of M and so its identity.

Q19. Compounds of cadmium are used in the construction of photocells. Show which of the following has the highest percentage by mass of cadmium: CdS, CdSe, CdTe.

Q20. Benzene is a hydrocarbon, a compound of carbon and hydrogen only. It is found to contain 7.74% H by mass. Its molar mass is $78.10\,g\,mol^{-1}$. Determine its empirical and molecular formulas.

Q21. A weak acid has a molar mass of $162\,g\,mol^{-1}$. Analysis of a 0.8821 g sample showed the composition by mass is 0.0220 g H, 0.3374 g P and the remainder oxygen. Determine its empirical and molecular formulas.

Q22. ATP is an important molecule in living cells. A sample with a mass of 0.8138 g was analysed and found to contain 0.1927 g C, 0.02590 g H, 0.1124 g N, and 0.1491 g P. The remainder was oxygen. Determine the empirical formula of ATP. Its formula mass was found to be $507\,g\,mol^{-1}$. Determine its molecular formula.

Q23. A 0.30 g sample of a compound that contains only carbon, hydrogen and oxygen was burned in excess oxygen. The products were 0.66 g of carbon dioxide and 0.36 g of water. Determine the empirical formula of the compound.

Q24. You are asked to write your name on a suitable surface, using a piece of chalk that is pure calcium carbonate, $CaCO_3$. How could you calculate the number of carbon atoms in your signature?

Structure 1.4.5 – Molar concentration

Structure 1.4.5 – The molar concentration is determined by the amount of solute and the volume of solution. Solve problems involving the molar concentration, amount of solute and volume of solution.	
The use of square brackets to represent molar concentration is required. Units of concentration should include g dm^{-3} and mol dm^{-3} and conversion between these.	Tool 1 – What are the considerations in the choice of glassware used in preparing a standard solution and a serial dilution? Tool 1, Inquiry 2 – How can a calibration curve be used to determine the concentration of a solution?

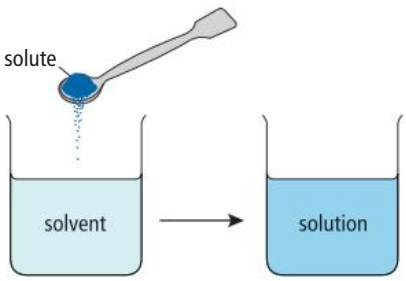
The molar concentration of a solution is based on moles of solute and volume of solution

When we are working with liquids, we often focus on measuring their volume. Some liquids in common use are pure substances, such as water (H_2O), bromine (Br_2) and hexane (C_6H_{14}), but more commonly liquids are **solutions** containing two or more components.

A solution is a homogeneous mixture of two or more substances, which may be solids, liquids or gases, or a combination of these. The **solvent** is the component present in the greatest quantity, in which the **solute** is dissolved. Some examples of solutions include:

- solid / solid: metal alloy such as brass (copper and zinc)
- solid/ liquid: sea water (salt and water), aqueous copper sulfate (copper sulfate and water)
- liquid / liquid: wine (ethanol and water)
- gas / liquid: fizzy drinks (carbon dioxide and water)

In this section we will be considering solutions made by dissolving a solid solute in a liquid solvent.



A solution is made by dissolving a solute in a solvent.

For solutions, we express the amount as its **concentration**. The molar concentration of a solution (c) is determined by the amount of solute (n) and the volume of solution (V).

$$\text{molar concentration of solution (mol dm}^{-3}) = \frac{\text{amount of solute (mol)}}{\text{volume of solution (dm}^3)} \text{ or } c = \frac{n}{V}$$

$\therefore$ amount of solute (mol) = conc (mol dm^{-3}) × volume (dm^3) or $\boldsymbol{n = cV}$

The molar concentration of a solution refers to the amount of solute per volume of solution. It has the units mol dm^{-3} and is often shown using square brackets.

A useful convention in chemistry is to use square brackets to represent 'the molar concentration of' a solution. For example, [HCl] = 1.0 mol dm^{-3}.

Worked example

A student is supplied with a solution of NaCl(aq) of concentration 0.400 mol dm^{-3}. He needs 0.250 mol of NaCl. What volume of solution, in cm^3, should he use?

Solution

Substituting the values given into the equation: $n = cV$

$0.250\text{ mol} = 0.400\text{ mol dm}^{-3} \times V$

$$\therefore V = \frac{0.250\text{ mol}}{0.400\text{ mol dm}^{-3}} = 0.625\text{ dm}^3$$

$1\text{ dm}^3 = 1000\text{ cm}^3 \Rightarrow 0.625\text{ dm}^3 = 625\text{ cm}^3$

moles of solute (mol) = concentration of solute (mol dm^{-3}) × volume of solution (dm^3) $n = cV$

Concentration can also be expressed as mass of solute (g) per volume of solution (dm^3).

$$\text{Concentration of solution (g dm}^{-3}) = \frac{\text{mass of solute (g)}}{\text{volume of solution (dm}^3)}$$

We can use molar mass to convert grams to moles in order to obtain the molar concentration.

Worked example

What is the molar concentration of a solution of sodium carbonate, Na_2CO_3, which has a concentration of 4.24 g dm^{-3}?

Solution

$M(Na_2CO_3) = (22.99 \times 2) + 12.01 + (16.00 \times 3) = 105.99\text{ g mol}^{-1}$

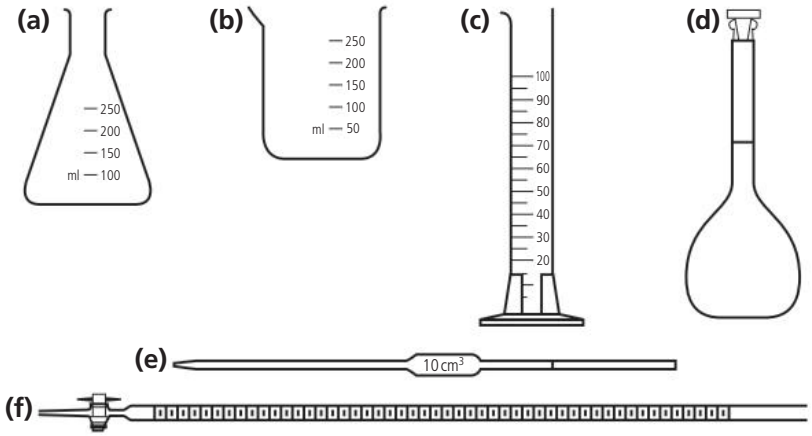
Substituting the values given in the equation: $m = nM$

$4.24\text{ g} = n\text{ (mol)} \times 105.99\text{ g mol}^{-1}$

$$\therefore n = \frac{4.24\text{ g}}{105.99\text{ g mol}^{-1}} = 0.0400\text{ mol}$$

$\therefore [Na_2CO_3] = 0.0400\text{ mol dm}^{-3}$

Note that concentration is specified per volume of final *solution*, not per volume of *solvent* added. This is because volume changes occur on dissolving the solute.



S1.4 Figure 2 Glassware commonly used in the laboratory. (a) conical or Erlenmeyer flask, its shape makes it easy to mix liquids as the flask can be easily swirled; (b) beaker; (c) measuring or graduated cylinder; (d) volumetric flask; (e) pipette; (f) burette.

Challenge yourself

4. When sodium hydroxide, NaOH, pellets dissolve in water, there is a *decrease* in the total volume of the solution. Explain what might cause this.



Different types of laboratory glassware, some of which which are identified in Figure 2.

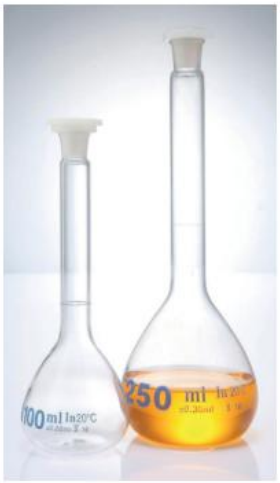
In quantitative work, it is essential to select glassware that measures volume to an appropriate level of precision. Most glassware is marked with a given uncertainty at a specified temperature – the smaller the uncertainty, the more precise the measurement. Beakers and conical flasks have very large uncertainties and are not used for precise volume measurements. Different manufacturers calibrate glassware to different levels of precision, but some typical values for laboratory apparatus are shown below.

Glassware	Volume / cm^3	± Uncertainty / cm^3	Uncertainty / %
beaker	50	5	10
measuring cylinder	50.0	0.5	1
burette	50.00	0.05	0.1

The accuracy of a measurement is increased by using glassware with the smallest adequate volume. For example, if we need 40 cm^3 of liquid, we choose a measuring cylinder of 50 cm^3 rather than one of 100 cm^3. It is also important to read the volume at the bottom of the meniscus when the glassware is supported on a horizontal surface.

The term *molarity*, *M*, has been widely used to express amount concentration, but it is falling out of common usage. It will not be used in IB examination questions, so make sure you are fully familiar with the terms mol dm^{-3} and g dm^{-3}. (Note that *M* is used specifically to refer to molar mass.)

Tool 1 – What are the considerations in the choice of glassware in preparing a standard solution and a serial dilution?



Volumetric flasks of 100 cm^3 ± 0.20 cm^3 and 250 cm^3 ± 0.30 cm^3 at 20 °C. (Note millilitre 'ml' as marked is the same as cm^3, which is the correct SI unit). Which flask has the greater percentage uncertainty?

Chemists routinely prepare solutions of known concentration, referred to as **standard solutions**. The mass of solute required is accurately measured and then transferred carefully to a volumetric flask, which is precisely calibrated for a specific volume. The solvent is added steadily with swirling to help the solute to dissolve, until the final level reaches the mark on the flask. Note that distilled water, not tap water, must be used as the solvent in the preparation of all aqueous solutions.

Worked example

Explain how you would prepare 100 cm^3 of a 0.10 mol dm^{-3} solution of NaCl.

Solution

Ensure that cm^3 are converted to dm^3 by dividing by 1000.

$n = c\,V$

$$n = 0.10\,\text{mol dm}^{-3} \times \frac{100}{1000}\,\text{dm}^3 = 0.0100\,\text{mol}$$

$M(NaCl) = 22.99 + 35.45 = 58.44\,\text{g mol}^{-1}$

$\therefore$ mass required $= 0.0100\,\text{mol} \times 58.44\,\text{g mol}^{-1} = 0.584\,\text{g}$

Add 0.584 g NaCl(s) to a 100 cm^3 volumetric flask, and make up to the mark with distilled water.

A standard solution is one of accurately known concentration.

The increased popularity, in many countries, of bottled water over tap water for drinking has raised several concerns, including the environmental costs of transport and packaging, and the source of the water and its solute (dissolved mineral) content. Significant differences exist in the regulation of the bottled water industry in different countries. In the USA, the Food and Drug Administration (FDA) requires that mineral water should contain between 500 and 1500 mg dm^{-3} of total dissolved solids. In Europe, mineral water is defined by its origin rather than by content, and the European Union prohibits the treatment of any water bottled from a source. The global cost of bottled water exceeds billions of dollars annually. As the United Nations General Assembly has explicitly recognized that access to safe, clean and affordable drinking water is a human right, there is an urgent need for money and technology to be diverted to improving tap water supplies globally to help make this a reality for all.

A different unit of concentration is known as **ppm**, parts per million. It denotes one part per 10^6 parts of the whole solution, and is useful in describing very low concentrations. This unit is widely used in reporting levels of pollutants in air, water, soil and food. For example, in the USA the FDA has set a maximum permissible level of 1 part of methylmercury in a million parts of seafood (1 ppm).



Label on water bottle listing the mineral content in milligrams per dm^3.

Dilutions of solutions reduce the concentration



A series of dilutions of cobalt(II) chloride solutions. In coloured solutions such as these, the effect of lowering the concentration of the solution can be observed.

As a solution is diluted, the number of moles of solute remains the same, but because the volume of solution increases, the concentration decreases. In other words, the number of moles n = a constant, and as $n = cV \Rightarrow cV$ must be constant through dilution.

$\therefore c_1V_1 = c_2V_2$ where c_1V_1 refer to the initial concentration and volume, respectively and c_2V_2 refer to the diluted concentration and volume, respectively.

This equation provides an easy way to calculate concentration changes on dilution.

Worked example

Determine the final concentration of a 75 cm^3 solution of HCl of concentration 0.40 mol dm^{-3}, which is diluted to a volume of 300 cm^3.

Solution

$c_1V_1 = c_2V_2$

$c_1 = 0.40\ mol\ dm^{-3}$, $V_1 = 75\ cm^3$, $V_2 = 300\ cm^3$

$\therefore (0.40\ mol\ dm^{-3}) \times (75\ cm^3) = c_2 \times (300\ cm^3)$

c_2 diluted concentration = $0.10\ mol\ dm^{-3}$

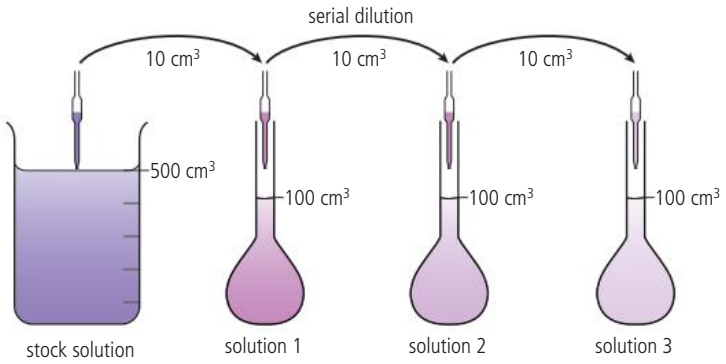
A quick check shows that the volume has increased four times, so the concentration must have decreased four times.

SKILLS

A common practice in laboratory work is to make a **dilution** from a more concentrated starting solution called the **stock solution,** by adding solvent. For all aqueous solutions, distilled water, rather than tap water, must be used.

Note that in the equation $c_1V_1 = c_2V_2$, volume terms appear on both sides of the equation and so their units will cancel. This means that *any* units of volume can be used directly (there is no need to convert them to dm^3), *so long as* they are consistent on both sides of the equation.

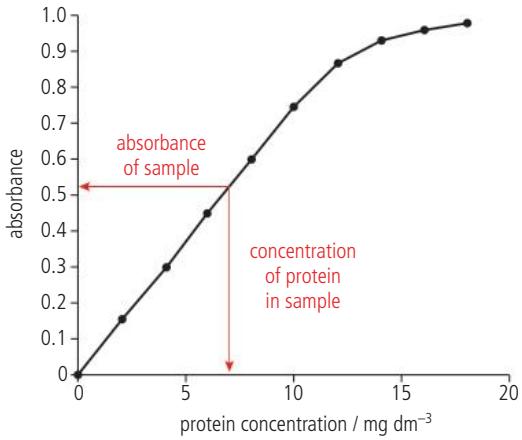
A **serial dilution** is a series of dilutions of a standard solution, where the concentration is reduced by a fixed amount at each step. It generates a series of solutions of known concentration, e. g. 1.00 mol dm^{-3}, 0.100 mol dm^{-3}, 0.0100 mol dm^{-3}, 0.00100 mol dm^{-3}. Dilution is carried out into volumetric flasks so that the final volume of the solution is measured, taking account of volume changes that may occur on dilution.



A serial dilution is prepared by using a pipette to transfer 10 cm^3 from the stock solution into a 100 cm^3 volumetric flask. The solution is then made up to the mark with distilled water. Repeating this process generates a series of solutions, each 10 times less concentrated than the previous one.

This series of solutions of known concentration can be used to form a standard in a technique known as **ultraviolet-visible spectroscopy,** which uses the direct relationship between the concentration of a solution and its absorbance. The absorbance of each solution is measured and the results plotted as a **calibration curve**. This curve is then used to determine the unknown concentration of a sample containing the same solute.

Preparing a calibration curve for spectrophotometric determinations. Full details of how to carry out this experiment with a worksheet are available in the eBook.



S1.4 Figure 3 A calibration curve can be used to find the protein concentration of a sample.

Tool 1, Inquiry 2 – How can a calibration curve be used to determine the concentration of a solution?

Challenge yourself

5. From the shape of the calibration curve in Figure 3, what can you conclude about the relationship between concentration and absorbance at higher concentration? How might this affect the calculation of the unknown concentration?

Titration is an important technique in volumetric analysis. It is used to determine the concentration of a solution when it reacts exactly with another solution of known concentration. Titrations typically involve reactions between acids and bases, or between oxidizing and reducing agents. Precise glassware including burettes and pipettes is used to obtain the precision required in measurement. These techniques are discussed in Reactivity 3.1 and Reactivity 3.2.

Exercise

Q25. Calculate the mass of potassium hydroxide, KOH, required to prepare 250 cm^3 of a 0.200 mol dm^{-3} solution.

Q26. Calculate the mass of magnesium sulfate heptahydrate, $MgSO_4.7H_2O$, required to prepare 0.100 dm^3 of a 0.200 mol dm^{-3} solution.

Q27. Calculate the number of moles of chloride ions in 0.250 dm^3 of 0.0200 mol dm^{-3} of zinc chloride, $ZnCl_2$, solution.

Q28. 250 cm^3 of a solution contains 5.85 g of sodium chloride. Calculate the concentration of sodium chloride in mol dm^{-3}.

Q29. Concentrated nitric acid, HNO_3, is 16.0 mol dm^{-3}. What volume of concentrated acid would you need to prepare 100 cm^3 of 0.50 mol dm^{-3} HNO_3?

Q30. Sodium sulfate, Na_2SO_4, reacts in aqueous solution with lead nitrate, $Pb(NO_3)_2$, as follows:

$$Na_2SO_4(aq) + Pb(NO_3)_2(aq) \rightarrow PbSO_4(s) + 2NaNO_3(aq)$$

In an experiment, 35.30 cm^3 of a solution of sodium sulfate reacted exactly with 32.50 cm^3 of a solution of lead nitrate. The precipitated lead sulfate was dried and found to have a mass of 1.13 g. Determine the concentrations of the original solutions of lead nitrate and sodium sulfate. State what assumptions are made.

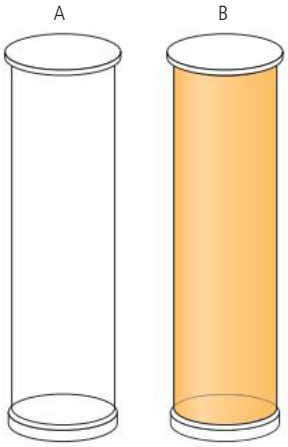
Structure 1.4.6 – Avogadro's law

Structure 1.4.6 – Avogadro's law states that equal volumes of all gases measured under the same conditions of temperature and pressure contain equal numbers of molecules.	
Solve problems involving the mole ratio of reactants and/or products and the volume of gases.	
	Structure 1.5 – Avogadro's law applies to ideal gases. Under what conditions might the behaviour of a real gas deviate most from an ideal gas?

Avogadro's law directly relates gas volumes to moles

Gases, like liquids, are fluids and it is therefore often convenient to focus on their volume as a measure for quantitative work. This means we need to know the relationship between gas volume and the number of moles.

Consider the following demonstration (Figure 4) where two gas jars are each filled with different gases – hydrogen (H_2) in flask A and bromine (Br_2) in flask B. The flasks are at the same temperature and pressure and have equal volumes.



S1.4 Figure 4 Flask A contains hydrogen molecules, flask B contains bromine molecules. The two flasks are under the same conditions of temperature and pressure.

Scientists know, from many experimental measurements on gas volumes, that the number of particles in the two flasks in Figure 4 is the same. At first this might seem surprising – after all, bromine molecules are much larger and heavier than hydrogen molecules. But we need to consider the nature of the gaseous state. We learn on page 15 that the particles in a gas are widely spaced out with negligible forces between them. In simple terms, most of a gas volume is empty space. For this reason, the chemical nature of the gas is irrelevant to its volume. Gas volume is determined only by the number of particles, and by the temperature and pressure.

Avogadro's law states that equal volumes of all gases at the same conditions of temperature and pressure contain equal numbers of particles $V \propto n$.

This understanding is known as Avogadro's law, which states that:

Equal volumes of all gases, when measured at the same temperature and pressure, contain an equal number of particles.

Alternatively, it can be stated that equal numbers of particles of all gases, when measured at the same temperature and pressure, occupy equal volumes.

Using V for volume and n for number of moles, $\boldsymbol{V \propto n}$

This relationship enables us to relate gas volumes of any gas to the number of moles, and so to reacting ratios in equations.

Airbags have become a standard safety fitting in most vehicles. They are designed to act as a cushion or shock absorber by inflating rapidly on sudden impact of the vehicle during a collision. Airbags work on the principle of a chemical reaction triggered by the impact producing a gaseous product that causes a sudden volume change. The key reaction used is the conversion of sodium azide, NaN_3, to nitrogen gas, N_2. To avoid the production of dangerously reactive sodium metal, potassium nitrate, KNO_3 and silicon dioxide, SiO_2, are also included so that harmless silicates are produced instead.

Challenge yourself

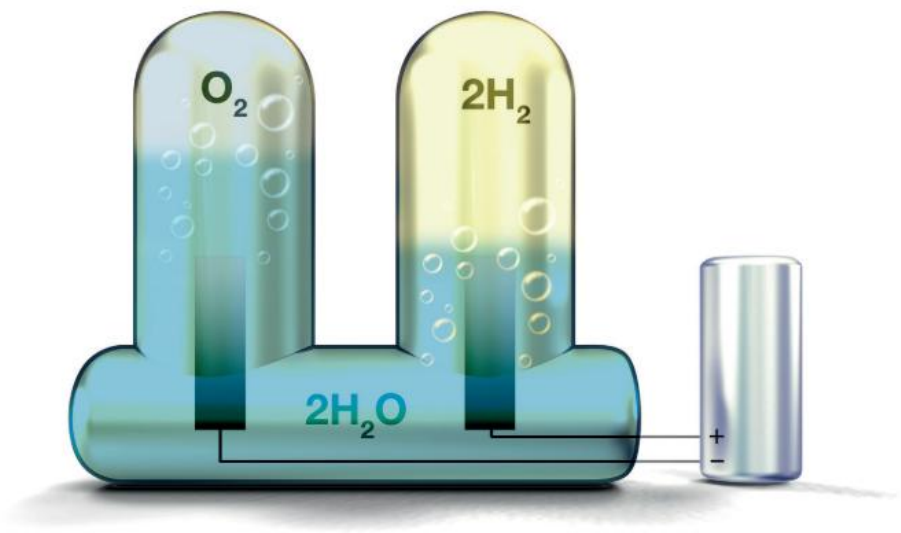
6. Use the explanation above to deduce the chemical equations for the reactions taking place in a deployed airbag.



▲ Illustration of an airbag and seat belt in action during a car accident. On impact, the airbag inflates and the seat belt slows the forward force of the body, protecting the driver's head and chest.

Structure 1.5 – Avogadro's law applies to ideal gases. Under what conditions might the behaviour of a real gas deviate most from an ideal gas?

Avogadro's law is based on the assumptions outlined above that the particles in a gas occupy negligible volume and have no forces of attraction between them. These are postulates of the **ideal gas model** which is discussed in more detail in Structure 1.5. Real gases will deviate most from this model when conditions bring the gas closer to forming a liquid, that is, lower temperature and higher pressure.



▲ The apparatus shows the use of electrolysis to split water into hydrogen and oxygen in the following reaction: $H_2O(l) \rightarrow 2\ H_2(g) + O_2(g)$. How can you explain the observed difference in volumes of the two gases produced?

Worked example

40 cm^3 of carbon monoxide reacts with excess oxygen in the reaction:

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

What volume of oxygen will be used and what volume of carbon dioxide is produced? (Assume all volumes are measured at the same temperature and pressure.)

Solution

Data given in the question are shown in black, deduced data are shown in blue.

First identify the mole ratios in the equation

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$
$$2\text{ moles} \quad 1\text{ mole} \quad 2\text{ moles}$$

The mole ratio is equal to the ratio of reacting gas volumes, so:

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$
$$40\,cm^3 \quad 20\,cm^3 \quad 40\,cm^3$$

Therefore 20 cm^3 of oxygen will be used and 40 cm^3 of carbon dioxide produced.

Worked example

When 10 cm^3 of a gaseous hydrocarbon (a compound containing only carbon and hydrogen) is burned in excess oxygen, the products consist of 30 cm^3 of carbon dioxide and 30 cm^3 of water vapour, measured under the same conditions of temperature and pressure. Determine the molecular formula of the hydrocarbon.

Solution

'Excess' oxygen indicates that the combustion reaction is complete.

	C_xH_y + excess O_2	→	CO_2 +	H_2O
Given volumes:	10 cm^3		30 cm^3	30 cm^3
ratio of volumes / mole ratio:	1		3	3

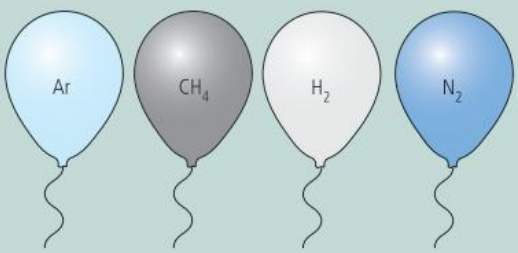
$\therefore$ 1 molecule hydrocarbon → 3 molecules CO_2 + 3 molecules H_2O

3 C atoms 6 H atoms

The molecular formula is C_3H_6.

Exercise

Q31. These four balloons are each filled with 1 dm^3 of gas. At 25 °C and 100 kPa, they each contain 0.044 mol or 2.65×10^{22} atoms or molecules. Which balloon is the heaviest?



Q32. A balloon contains a certain mass of argon gas. The pressure and temperature are kept constant, and the same mass of neon gas is added to the balloon. What happens?

A The volume of the balloon expands by two times.

B The volume of the balloon expands by more than two times.

C The volume of the balloon expands by less than two times.

D None of the above.

Q33. The following reaction takes place in the industrial production of ammonia, NH_3:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

What volume of hydrogen would be required to produce 30 dm^3 of ammonia?

Q34. At a certain temperature and pressure, one mole of hydrogen gas, H_2, occupies a volume of 10 dm^3. What would be the volume of one mole of H atoms under the same conditions?

Guiding Question revisited

How do we quantify matter on the atomic scale?

In this chapter we have introduced the mole as the unit of amount in chemistry.

- One mole of any substance contains the Avogadro number of elementary entities.
- Elementary entities can be any form of particle, including atoms, molecules, ions, electrons, or a specified group of particles.
- The Avogadro constant enables us to interconvert the number of moles and the number of entities.
- The molar mass, M, of a substance is its relative atomic mass, A_r, or relative formula mass, M_r, expressed in grams. A_r and M_r are expressed relative to carbon-12, and are a weighted average taking into account the abundance of isotopes.
- The molar mass enables us to interconvert the number of moles and the mass of the substance.
- The empirical formula of a compound can be determined from its percentage composition by mass. It gives the simplest ratio of atoms of elements in the compound.
- The molecular formula can be determined from the empirical formula and the molar mass. It gives the actual number of atoms of each element present in a molecule.
- The molar concentration of a solution is expressed as the moles of solute per volume of solution.
- Equal volumes of all gases at the same temperature and pressure contain the same number of moles.



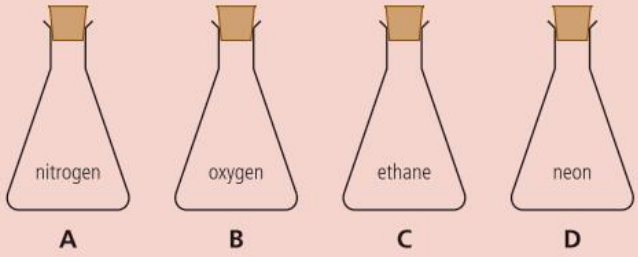
How many atoms of calcium are in Avogadro's name written in chalk?

Practice questions

1. How many oxygen **atoms** are in 0.100 mol of $CuSO_4.5H_2O$?

   A 5.42×10^{22} **B** 6.02×10^{22} **C** 2.41×10^{23} **D** 5.42×10^{23}

2. Four identical containers under the same conditions are filled with gases as shown below. Which container and contents will have the highest mass?



3. What is the amount, in moles, of sulfate ions in 100 cm^3 of 0.020 mol dm^{-3} $FeSO_4(aq)$?

A 2.0×10^{-3} **B** 2.0×10^{-2} **C** 2.0×10^{-1} **D** 2.0

4. 1.7 g of $NaNO_3$ ($M_r = 85$) is dissolved in water to prepare 0.20 dm^3 of solution. What is the concentration of the resulting solution in mol dm^{-3}?

A 0.01 **B** 0.1

C 0.2 **D** 1.0

5. The relative formula mass of a gas is 56 and its empirical formula is CH_2. What is the molecular formula of the gas?

A CH_2 **B** C_2H_4

C C_3H_6 **D** C_4H_8

6. What is the total number of hydrogen atoms in 1.0 mol of benzamide, $C_6H_5CONH_2$?

A 7 **B** 6.0×10^{23}

C 3.0×10^{24} **D** 4.2×10^{24}

7. What is the concentration of NaCl, in mol dm^{-3}, when 10.0 cm^3 of 0.200 mol dm^{-3} NaCl solution is added to 30.0 cm^3 of 0.600 mol dm^{-3} NaCl solution?

A 0.450 **B** 0.300

C 0.500 **D** 0.800

8. On analysis, a compound with molar mass 60 g mol^{-1} was found to contain 12 g of carbon, 2 g of hydrogen and 16 g of oxygen. What is the molecular formula of the compound?

A CH_2O **B** CH_4O

C C_2H_4O **D** $C_2H_4O_2$

9. 300 cm^3 of water is added to a solution of 200 cm^3 of 0.5 mol dm^{-3} sodium chloride. What is the concentration of sodium chloride in the new solution?

A 0.05 mol dm^{-3} **B** 0.1 mol dm^{-3}

C 0.2 mol dm^{-3} **D** 0.3 mol dm^{-3}

10. What is the approximate molar mass, in g mol^{-1}, of $MgSO_4.7H_2O$?

A 120 **B** 130

C 138 **D** 246

11. Which is both an empirical and a molecular formula?

A C_5H_{12} **B** C_5H_{10}

C C_4H_8 **D** C_4H_{10}

12. A hydrate of potassium carbonate has the formula $K_2CO_3.xH_2O$. A 10.00 g sample of the hydrated salt is heated and forms 7.93 g of anhydrous salt.

(a) Calculate the number of moles of water in the hydrated sample. (1)

(b) Calculate the number of moles of anhydrous salt that form. (1)

(c) Determine the formula of the hydrate. (1)

(d) How could you determine when all the hydrated salt has been converted into anhydrous form? (1)

(Total 4 marks)

13. An organic compound contains carbon, hydrogen and oxygen. The percentage by mass of carbon is 62.02%, and hydrogen is 10.43%.

Determine the empirical formula of the compound, showing your working. (3)

(Total 3 marks)

14. Phosphorus formed an oxide by reaction with air which contained 43.6% by mass phosphorus.

(a) Determine the empirical formula of the oxide, showing the steps in your calculation. (3)

(b) The molar mass of the oxide is approximately 285 g mol^{-1}. Determine the molecular formula of the oxide. (1)

(Total 4 marks)

15. (a) A student needs to prepare 250.00 cm^3 of a solution of sodium hydrogencarbonate with a concentration of 0.500 mol dm^{-3}. Explain the steps in the process starting with the solid salt, and stating the apparatus and glassware used. (5)

(b) Explain how, starting with the solution prepared in **(a)**, 100 cm^3 of solutions with concentrations of 0.0500 mol dm^{-3} and 0.00500 mol dm^{-3} could be prepared. (4)

(Total 9 marks)



STRUCTURE

1.5 Ideal gases

◀ Computer artwork of the Earth with half of its atmosphere removed. The atmosphere is a layer of gases surrounding the planet. It reaches approximately 100 kilometres above the Earth's surface.

Guiding Question

How does the model of ideal gas behaviour help us to predict the behaviour of real gases?

Gases surround us in the atmosphere and the first experiments on gases concerned the physical properties of air. Robert Boyle first experimented on the 'springiness of the air' in the 17th century and further investigations on other properties followed in the 18th century when people began to fly in hot air balloons. Simple empirical laws relating pressure, volume, temperature and amount of gases were identified, with the suggestion that all gases behaved in the same way.

The gaseous state is the easiest state to describe and model. In Structure 1.1, we describe a gas as a collection of widely separated particles in chaotic, random motion and it is this randomness that makes the model so simple. A model of an ideal gas, based on kinetic theory, can be defined in terms of a small number of axioms. The volume of the gas particles and the attractive forces between the particles are considered to be negligible and the pressure of a gas is due to particles colliding with the walls of the container. The model, and the application of some simple physics, gives accurate quantitative predictions of how gas pressure changes with temperature and volume and shows that temperature is a measure of the average kinetic energy of the particles.

The initial empirical laws were, however, only approximations and more precise experiments showed that real gases deviate from this ideal behaviour at high pressure and low temperature. These deviations highlight some limitations of the initial assumptions of the ideal gas model. The volume of the gas particles and the intermolecular forces cannot be ignored under all conditions.



▲ Joseph Louis Gay-Lussac (1778–1850), French chemist and physicist, in a daring 1804 balloon ascent to investigate the composition of air at high altitude. He, along with another chemical balloonist, Jacques Charles, and Robert Boyle investigated the properties of the gases.

Structure 1.5.1 – The ideal gas model

Structure 1.5.1 – An ideal gas consists of moving particles with negligible volume and no intermolecular forces. All collisions between particles are considered elastic.

Recognize the key assumptions in the ideal gas model.

An ideal gas consists of moving particles with negligible volume and no intermolecular forces

You will be familiar with some behaviour of gases through everyday experiences such as blowing up balloons or bicycle tyres. Perhaps you have noticed how inflated balloons shrink in colder temperatures and expand when it is warmer. Experiments show that all gases respond in the same way to changes in volume, pressure and temperature when the mass of gas is fixed. The chemical nature of the gas makes no difference. The gaseous state is the easiest state to describe using kinetic theory.

The theoretical model of an **ideal gas** is assumed to obey the following axioms:

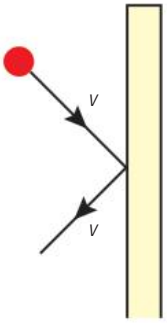
1. The particles in a gas have negligible volume compared with the volume the gas occupies.
2. There are no intermolecular forces between the particles except when the molecules collide.
3. Gas particles have a range of speeds and move randomly. The average kinetic energy of the particles is proportional to the temperature.
4. The collisions of the particles with the walls of the container and with each other are **elastic:** kinetic energy is conserved.

If a gas particle was the size of a tennis ball, it would typically travel the length of a tennis court between collisions.

Although no real gas fits this description exactly, the application of Newton's Second Law (force = mass × acceleration) can be used to make accurate quantitative predictions for the physical properties of most gases under typical conditions of temperature and pressure.

The pressure of a gas is due to gas particles colliding with the walls of the container

When a gas particle collides with the wall of a container, it bounces back with the same speed (Figure 1). The collision is elastic, according to the fourth axiom above. The pressure of a gas is a result of a large number of such collisions and is the same on all walls. This is because the particles move randomly with no preferred direction, according to the third axiom.



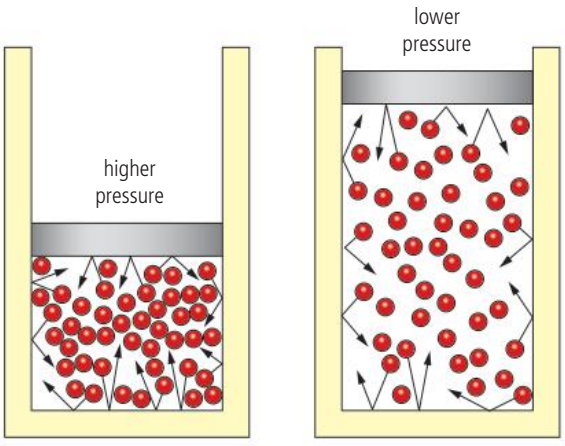
S1.5 Figure 1 The pressure of a gas is due to the particles colliding with the wall.



The so-called Mentos-soda fountain reaction. Dissolved carbon dioxide in the soda changes quickly into gas in the presence of the mint Mentos. The sudden pressure change causes the soda to be ejected in a fountain of foam.

This simple model allows us to explain the pressure changes that occur when the temperature and volume of a gas changes. The volume of a gas is the total volume of its container as the particles spread out to fill all available space.

- When the volume of a gas increases, the gas particles collide less frequently with the walls as they must travel greater distances between collisions. This decreases the pressure. The model correctly predicts that increasing the volume decreases the pressure (Figure 2).



S1.5 Figure 2 As the volume of a gas increases, the gas particles collide less frequently with the walls of the container.

- When the temperature of a gas increases, the gas particles have increased kinetic energy according to the third axiom. The collisions with the walls are more energetic and more frequent as the particles are moving faster. Both these factors increase the pressure.

Challenge yourself

1. What would happen to the pressure of a gas if molecular collisions were not perfectly elastic?

Exercise

Q1. The volume of an ideal gas in a container is increased at constant temperature. What happens as a result of this change?

A The frequency of collisions of the molecules with the container wall decreases.

B The intermolecular force between the molecules decreases.

C The speed of the particles increases.

D The volume of a gas particle increases.

Q2. Identify an assumption of the ideal gas model.

A Molecules have zero mass.

B The forces between the molecules of the gas and the container are always zero.

C Collisions between molecules and the walls of the container are elastic.

D The kinetic energy of a given molecule of the gas is constant.

Q3. The temperature of a closed gas container is increased. What happens to the pressure and average speed of the particles?

	Pressure	Average speed
A	increases	faster
B	decreases	faster
C	increases	no change in speed
D	decreases	no change in speed

Q4. Which of the following are assumptions of the kinetic model of ideal gases?

I. Particles are perfectly elastic spheres.

II. The interactions between the particles are negligible when not colliding.

III. The particles are in continuous random motion.

A I and II **B** I and III **C** II and III **D** I, II and III

Q5. Why does the pressure of an ideal gas change when the temperature is increased?

A The particles collide with each other more frequently.

B The time of contact between the molecules and the wall is reduced.

C The force of attraction between the molecules is reduced.

D The particles collide with the walls of the container more frequently.

Q6. Identify which of the four assumptions listed on page 122 applies to a monatomic gas.

Structure 1.5.2 – Real gases

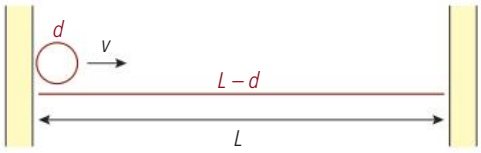
Structure 1.5.2 – Real gases deviate from the ideal gas model, particularly at low temperature and high pressure.	
Explain the limitations of the ideal gas model.	
No mathematical coverage is required.	Structure 2.2 – Under comparable conditions, why do some gases deviate more from ideal behaviour than others?

Real gases deviate from the ideal gas model

There is no such thing as an ideal gas. All gases, known as **real gases**, deviate to some extent from ideal behaviour as the assumptions 1 and 2 made on page 122 do not apply to real gases under all conditions.

1. *The volume of the gas particles is not negligible*

If the volume of the particles is not negligible, they travel less distance between collisions with the wall (Figure 3). The collisions are more frequent than predicted by the ideal gas model and the pressure is greater.

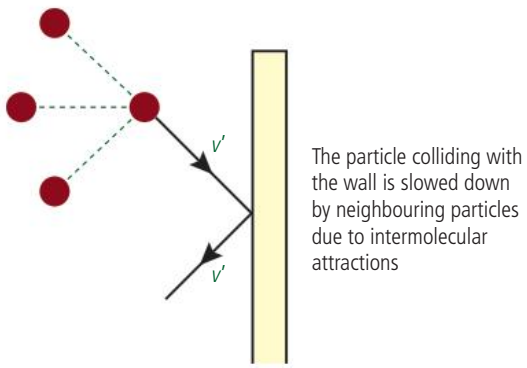


S1.5 Figure 3 An ideal gas particle travels distance 2*L* between collisions with the same wall. A real gas particle, of diameter *d*, travels 2(*L* – *d*). Real gas particles travel shorter distances and collide more frequently. The difference is most significant when *L* is small, which occurs at high pressures and low temperatures.

This effect is most noticeable at very high pressures and low temperatures, when the particles are confined in a small volume and the distance between the particles significantly reduced.

2. *There are attractive forces between the particles*

When a particle is approaching the wall of a container, attractive forces from other particles pull in the opposite direction (Figure 4). This reduces the speed of the colliding particle and leads to a less energetic collision with the wall. The pressure is lower than for an ideal gas.



S1.5 Figure 4 Intermolecular forces reduce the speed of particles approaching the wall. They reduce the kinetic energy of the collision and the pressure.

This reduction in speed is most significant when the average speed is relatively low at low temperatures.

Structure 2.2 – Under comparable conditions, why do some gases deviate more from ideal behaviour than others?

Exercise

Q7. Gases deviate from ideal gas behaviour because their particles:

A have negligible volume **B** have forces of attraction between them

C are polyatomic **D** are not attracted to one another

Q8. **(a)** List the main features of the kinetic theory for ideal gases.

(b) Explain the reason for the difference in behaviour between real and ideal gases at low temperature.

Q9. Under what conditions of temperature and pressure are real gases likely to behave like ideal gases?

Structure 1.5.3 and 1.5.4 – The ideal gas laws

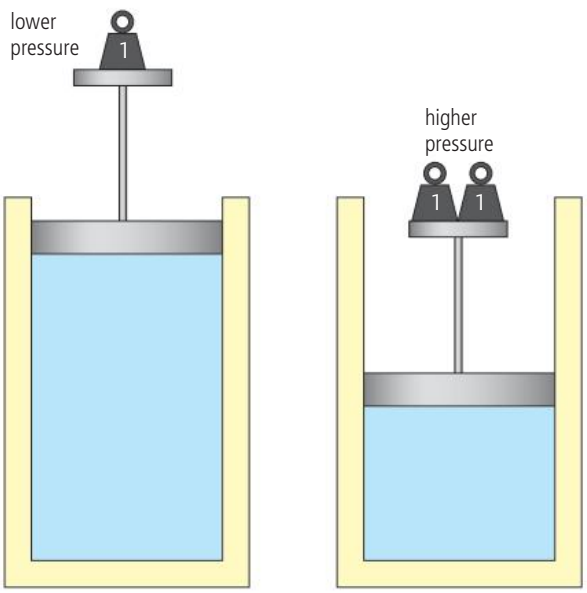
Structure 1.5.3 – The molar volume of an ideal gas is constant at a specific temperature and pressure. Investigate the relationship between temperature, pressure and volume for a fixed mass of an ideal gas and analyse graphs relating these variables.	
The names of specific gas laws will not be assessed. The value for the molar volume of an ideal gas under standard temperature and pressure (STP) is given in the data booklet.	Nature of Science, Tools 2 and 3, Reactivity 2.2 – Graphs can be presented as sketches or as accurately-plotted data points. What are the advantages and limitations of each representation?

Structure 1.5.4 – The relationship between the pressure, volume, temperature and amount of an ideal gas is shown in the ideal gas equation $PV = nRT$ and the combined gas law $$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$ Solve problems relating to the ideal gas equation.	
Units of volume and pressure should be SI only. The value of the gas constant R, the ideal gas equation, and the combined gas law are given in the data booklet.	Tool 1, Inquiry 2 – How can the ideal gas law be used to calculate the molar mass of a gas from experimental data?

Investigating gases

The state of a fixed mass of gas is described by its pressure, volume and temperature. To discover relationships between these variables, a number of simple experiments can be performed.

The relationship between the pressure and volume



S1.5 Figure 5 As the pressure on a gas is increased, its volume decreases proportionately.

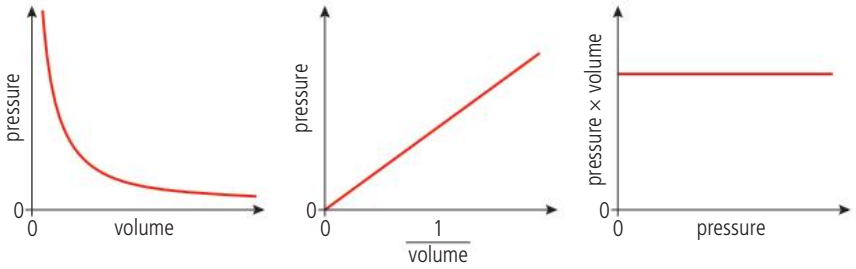
If the temperature of a gas is held constant, it is found that increasing the pressure of a fixed mass of gas decreases its volume (Figure 5). More precisely, the pressure of a gas is inversely proportional to its volume, and the product of pressure and volume is a constant (Figure 6).

$$P \propto \frac{1}{V}$$

PV = a constant

SKILLS

Investigating Boyle's law. Full details of how to carry out this experiment with a worksheet are available in the eBook.

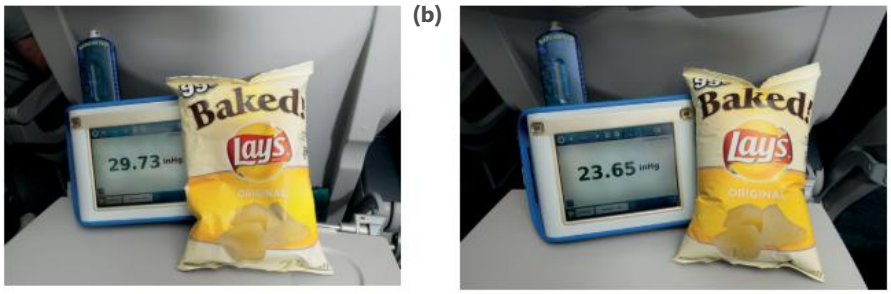


S1.5 Figure 6 Gas pressure is inversely proportional to its volume.

As we discussed at the beginning of the chapter, this relationship can be explained in terms of the decreased frequency of particle collisions with the walls of the container as the gas expands.

Nature of Science

Although many scientific discoveries, such as the gas laws, are named after the key scientists involved, the theories and laws of science stand apart from the individual discoverers.



Chip bag on airplane **(a)** at sea level and **(b)** with increased volume because of lower atmospheric pressure at high altitude. Boyle's law has application in transport and storage.

A note about units of pressure

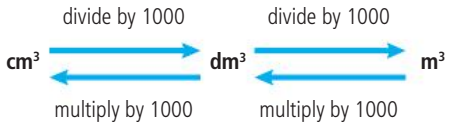
The SI unit of pressure is the pascal (Pa) which is equivalent to 1 $N\,m^{-2}$. Other commonly used non-SI units are the atmosphere, atm, which is equal to 1.013×10^5 Pa and the bar (10^5 Pa) which it is conveniently close to 1 atm.

A note about units of volume

The SI unit of volume is m^3 but other units such as the dm^3 or cm^3 are commonly used. It is important to be able to interconvert these.

$1\,dm^3 = 10^{-3}\,m^3$ $\qquad$ $1000\,dm^3 = 1\,m^3$

$1\,cm^3 = 10^{-3}\,dm^3$ $\qquad$ $1000\,cm^3 = 1\,dm^3$



$1\,m^3 = 1000\,dm^3 = 1\,000\,000\,cm^3$. In the laboratory, volumes are usually measured in cm^3 or dm^3 and often these measurements need to be converted to m^3 in calculations.

TOK

This relationship is often known as Boyle's law, as it was established by Robert Boyle in 1662. It was discovered independently by Edme Mariotte in 1679 and is also known, particularly in France, as Mariotte's law. To what extent do the names and labels we use help or hinder the acquisition of knowledge in different areas?

$P \propto \frac{1}{V}$

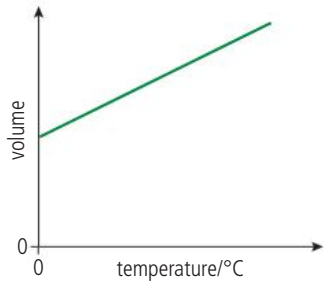
PV = a constant

Different countries continue to use a variety of units for pressure, including millimetres of mercury (mm Hg), torr, and pounds per square inch (psi).

The litre (l or L) is widely used in place of dm^3, and millilitre (ml or mL) used in place of cm^3. You will not be penalized for using these terms in an examination, but they will not be used in questions. It is however essential that you can interconvert m^3, dm^3 and cm^3.

Relationship between volume and temperature

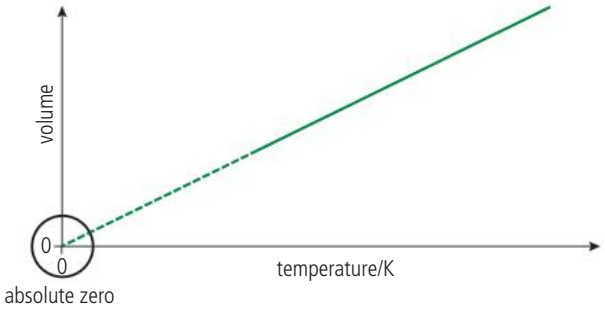
If the pressure is held constant, it is found that increasing the temperature of a fixed mass of gas increases its volume. If the temperature is measured in degrees Celsius, it is a **linear** relationship (Figure 7).



S1.5 Figure 7 The volume of a gas increases linearly with the temperature in degrees Celsius.

Determining the value of absolute zero. Full details of how to carry out this experiment with a worksheet are available in the eBook.

When the straight line is extended backwards it always crosses the temperature axis, with the volume = 0, at −273 °C. This suggests that there exists a minimum possible temperature, namely −273 °C which is absolute zero or 0 K. If the temperature is measured in kelvin, the relationship can be stated more precisely: the volume of a gas is directly proportional to its absolute temperature measured in kelvin (Figure 8).



S1.5 Figure 8 Charles' law. Gas volume is proportional to the absolute temperature. Note the dotted line represents an extrapolation, as data at temperatures down to 0 K are not obtainable.

$$V \propto T(\text{K})$$

$$\frac{V}{T(\text{K})} = \text{a constant}$$



Balloons dipped in a mixture of dry ice (solid CO_2) and water rapidly deflate as the air inside contracts at low temperature.

This relationship, often known as Charles' law, was first established by French scientist Jacques Charles in the late 18th century. A demonstration of the relationship is found by immersing dented table tennis balls in warm water. As the air inside the ball reaches the temperature of the water, it expands, pushing the dents out on the surface. As we discussed at the beginning of the chapter, it is explained in terms of the increases in kinetic energy of the gas particles as the temperature increases. As each particle collides with more kinetic energy, the pressure will only remain constant if the frequency of the collisions decreases. This can only happen if the volume of the container increases.

$V \propto T(\text{K})$

$\frac{V}{T(\text{K})}$ = a constant

A note about units of temperature

In all calculations involving gases, it is essential to use values for temperature in kelvin (K), not in Celsius (°C). Temperature in kelvin is known as the absolute temperature, and is based on a scale where absolute zero, 0 K, is the point when the gas particles have no kinetic energy. The conversion between the Kelvin and Celsius scale is discussed in Structure 1.1.

Absolute zero, the lowest conceivable temperature, is impossible to reach in practice as it would require an infinite amount of energy to reach it. Even if you could reach it, the uncertainty principle discussed in Structure 1.3 dictates that there would still be some uncertainty about the momentum of the atoms and molecules. The particles would have some energy – the so-called zero-point energy. The closer a substance approaches absolute zero, the stranger its properties become. Liquid helium, for example, turns into a superfluid, a liquid that flows without the resistance of friction. Other materials become superconductors below a critical temperature: they offer no resistance to electric currents.

TOK

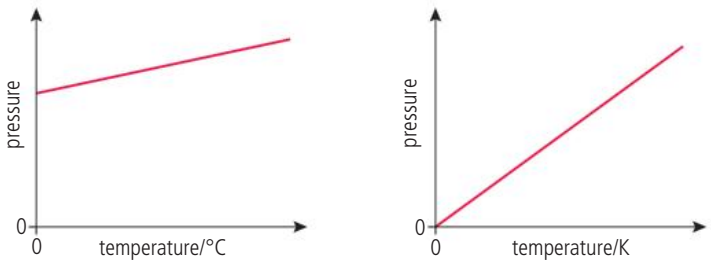
Without Charles, Boyle and Mariotte the relationships between pressure, volume, and temperature of a gas would still exist. This is very different from the arts. Without Shakespeare, there would have been no *Hamlet*, without Picasso, no *Guernica*. In what ways have influential individuals contributed to the development of the natural sciences as an area of knowledge?

Relationship between pressure and temperature

If the volume is held constant, increasing the temperature of a fixed mass of gas increases the pressure. If the temperature is measured in kelvin, it is a proportional relationship and the pressure divided by the absolute temperature is a constant (Figure 9).

$$P \propto T(\text{K})$$

$$\frac{P}{T(\text{K})} = \text{a constant}$$



S1.5 Figure 9 Gas pressure is proportional to the absolute temperature.

Graphical techniques have widespread applications across the syllabus, and in experimental work. You should be able to recognize the different sketch graphs that illustrate the gas laws and analyse graphs of gas behaviour to determine more detailed information from gradients and intercepts.

Again, this relationship can be explained by the ideal gas model. An increase in temperature increases the average kinetic energy of the particles. The particles move faster and collide with the walls of the container with more energy and greater frequency, resulting in an increase in pressure.

Nature of Science, Tools 2 and 3, Reactivity 2.2 – Graphs can be presented as sketches or as accurately-plotted data points. What are the advantages and limitations of each representation?

The label on the aerosol can warns of the dangers of exposing the pressurized contents to high temperature.



$P \propto T(\text{K})$

$\frac{P}{T(\text{K})}$ = a constant

You need to use temperature in kelvin when applying these relationships.

Pressurized cans, such as soda or beer, often carry a warning to be stored in a cool place. The pressure inside the can rises at higher temperatures and could cause it to explode.

Exercise

Q10. Which two values of temperature are equivalent (to the nearest degree) when measured on the Kelvin and Celsius scales?

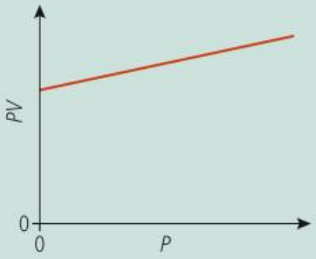
	Kelvin scale	Celsius scale
A	25	298
B	50	323
C	283	110
D	323	50

Q11. An ideal gas in a container of fixed volume at a temperature of 27 °C and a pressure of 4.0 atm is heated. Determine the new pressure when the temperature is increased by 300 °C.

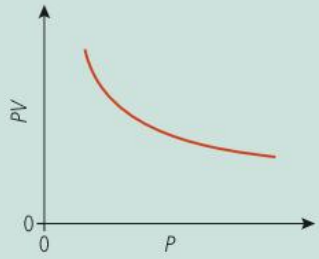
A 0.44 atm **B** 2.0 atm **C** 8.0 atm **D** 44 atm

Q12. The volume V for a fixed mass of an ideal gas was measured at constant temperature and different pressures P. Identify the graph that shows the correct relationship.

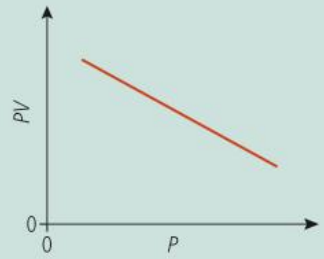
A



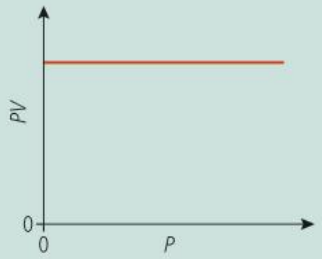
B



C



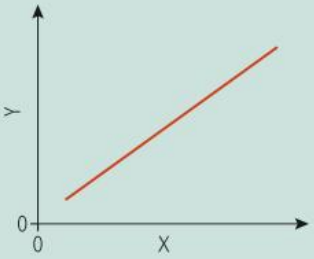
D



Q13. A 200 cm^3 container contains a gas at 15 °C and 1.0 $\times 10^5$ Pa. The gas is then heated to 160 °C. Deduce the new pressure of the gas.

A 1.1 $\times 10^5$ Pa **B** 1.5 $\times 10^5$ Pa **C** 1.1 $\times 10^4$ Pa **D** 1.5 $\times 10^4$ Pa

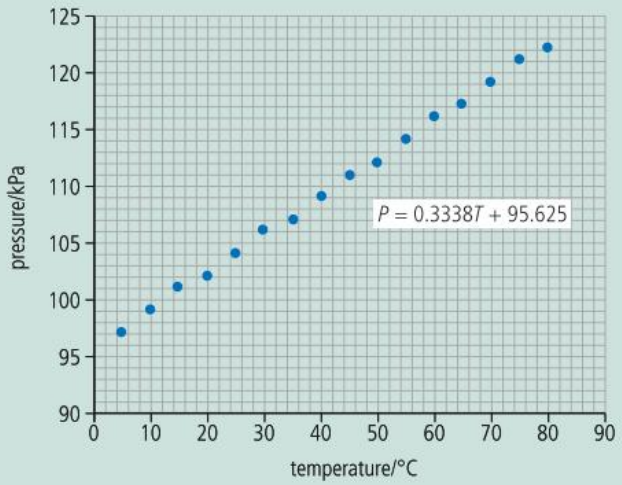
Q14. The graph shows the experimental relationship between two properties of a constant amount of a gas.



Identify X and Y and the control variable.

	X	Y	Control variable
A	pressure (atm)	volume (dm^3)	temperature
B	temperature (°C)	pressure (Pa)	volume
C	temperature (°C)	volume (m^3)	pressure
D	1/pressure (Pa^{-1})	volume (cm^3)	temperature

Q15. A student investigated the relationship between temperature and pressure of a gas and produced a graph of their results.



(a) Describe the relationship between T measured in °C and pressure.

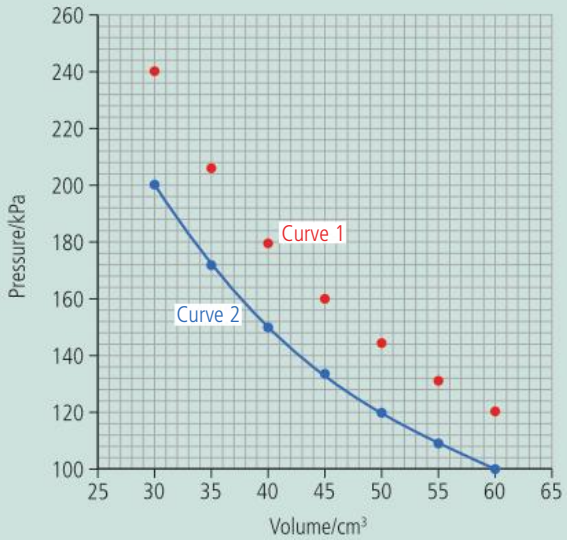
(b) Use the graph to predict the temperature in °C when the pressure is zero.

(c) Comment on the accuracy of the student's results.

(d) Describe the expected relationship between pressure and temperature when measured in K.

(e) Explain the relationship between pressure and temperature using the ideal gas model. Does the model agree completely with the experimental results?

Q16. A student investigates the pressure and volume of a fixed mass of gas at two temperatures.



State and explain which curve corresponds to the higher temperature.

Q17. A helium cylinder that inflates a balloon has a volume of 0.0400 m^3 and a pressure of 2.02×10^6 N m^{-2}.

(a) Calculate the volume of the balloon assuming there is no change of temperature as the balloon is filled and the pressure is atmospheric pressure (1.01×10^5 N m^{-2}).

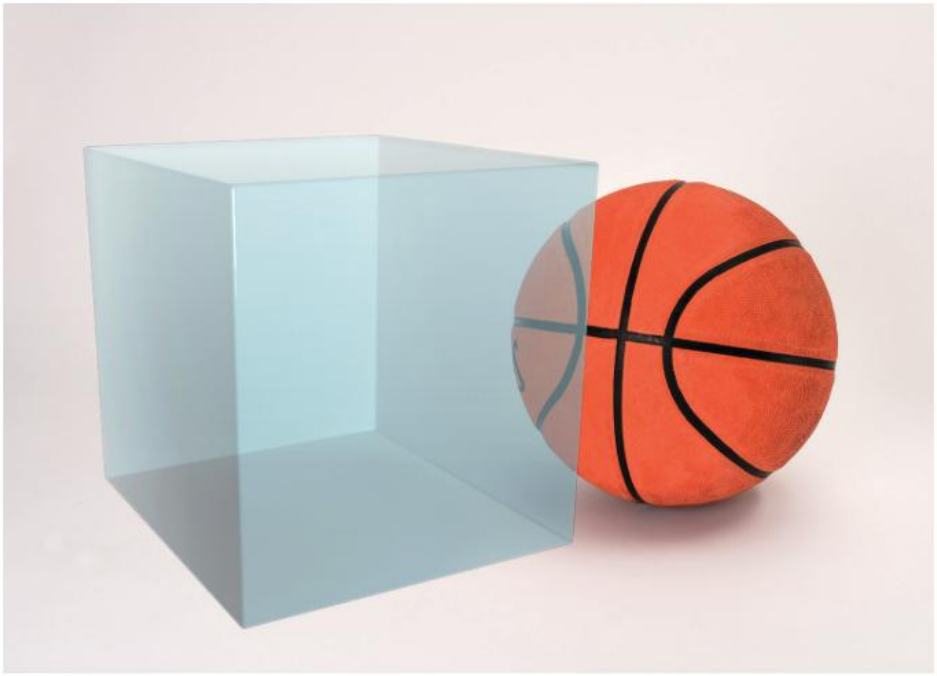
(b) The temperature of the air decreases with altitude. State the effect of this temperature change on the helium atoms as the balloon rises.

The molar volume of an ideal gas is a constant at a specific temperature and pressure

The first axiom in the ideal gas model stated that the particles in a gas have negligible volume compared with the volume the gas occupies. This suggests that changing the identity of the gas particles would have a negligible effect on the volume of the gas. This prediction is consistent with Avogadro's law, discussed in Structure 1.4. Equal volumes of all gases measured under the same conditions of temperature and pressure contain equal numbers of molecules.

One consequence of Avogadro's law is that the volume occupied by one mole of any gas must be the same for *all* gases when measured under the same conditions of temperature and pressure. This is known as the **molar volume.**

For reference purposes, the molar volume of a gas given in Section 2 of the data booklet is given under standard conditions of temperature and pressure (**STP**). This shows that when the temperature is 0 °C (273 K) and the pressure is 100 kPa, one mole of a gas has a volume of $2.27 \times 10^{-2}\,m^3\,mol^{-1}$ ($= 22.7\,dm^3\,mol^{-1}$).



The box contains 1 mole of gas. The molar volume of an ideal gas is 22.7 dm^3 at STP. A basketball fits loosely into a box having this volume.

STP refers to a temperature of 273 K and a pressure of 100 kPa.

Note that the conditions of STP (standard temperature and pressure) are not the same as those used to define the 'standard state', used in thermodynamic data and explained in Reactivity 1.1.

Structure 1.4 shows how the molar volume can be used to calculate the amount of gas in a similar way to the use of molar mass. Here though, the calculations are simpler, as all gases have the same molar volume.

$$\text{number of moles of gas } (n) = \frac{\text{volume } (V)}{\text{molar volume}}$$

number of moles of gas (n) = $\frac{\text{volume } (V)}{\text{molar volume}}$

Worked example

Calculate the volume occupied by 0.020 g of helium at standard temperature and pressure.

Solution

First convert the mass of helium to moles.

$$n = \frac{m}{M} = \frac{0.020}{4.00} = 0.0050\ \text{mol}$$

Volume = $0.0050\,\text{mol} \times 22.7\,dm^3\,mol^{-1} = 0.114\,dm^3$

The ideal gas equation and the combined gas law

The combined gas law

The three gas laws for a fixed mass of gas:

$$P \propto \frac{1}{V} \text{ at constant temperature}$$

$$V \propto T \text{ at constant pressure}$$

$$P \propto T \text{ at constant volume}$$

can be combined to give one equation:

$$\frac{PV}{T} = \text{a constant}$$

$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$ where 1 and 2 refer to initial and final conditions respectively.

Application of this **combined gas law** enables gas volume, pressure and temperature to be calculated as conditions change for a fixed mass.

Worked example

What happens to the volume of a fixed mass of gas when its pressure and its absolute temperature are both doubled?

Solution

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$P_2 = 2 \times P_1$ and $T_2 = 2 \times T_1$, so these can be substituted into the equation:

$$\frac{P_1V_1}{T_1} = \frac{2P_1V_2}{2T_1}$$

We can cancel P_1 and T_1 from both sides, and 2s on the right side, leaving

$V_1 = V_2$

The volume does not change.

Worked example

The molar volume of a gas at STP is 22.7 $dm^3 mol^{-1}$. Calculate the molar volume at 25.0 °C at the same pressure.

Solution

As the pressure is not changing, we do not need to insert P_1 and P_2 into the combined gas equation. Temperature must be converted from °C to K.

$T_1 = 273\,K, T_2 = 25.0 + 273 = 298\,K$

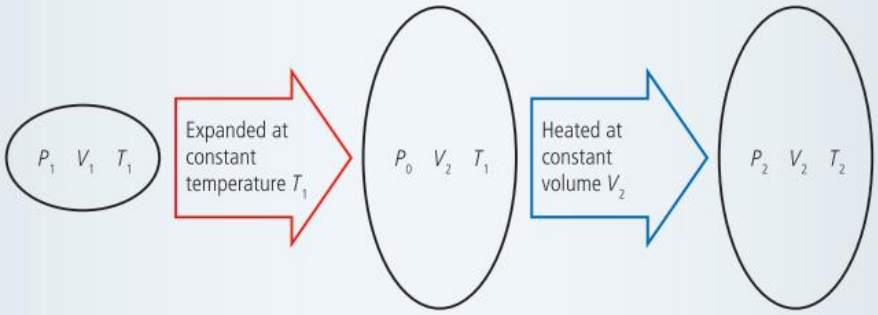
$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{22.7\,dm^3}{273\,K} = \frac{V_2}{298\,K}$$

$$V_2 = \frac{298 \times 22.7\,dm^3}{273} = 24.8\,dm^3$$

Challenge yourself

2. Consider a sample of gas at pressure P_1, volume V_1, and temperature T_1 (K) which is expanded to a new volume V_2 at constant temperature T_1 with a new pressure P_0 (Figure 10).



S1.5 Figure 10 A gas undergoes two changes. The volume is increased at constant temperature and then the gas is heated at constant volume.

(a) State the relationship between P_1, V_1, P_0 and V_2 for expansion at constant temperature T_1.

(b) The gas is then heated at constant volume V_2 to new conditions P_2, V_2 and T_2. State the relationship between P_0, T_1, P_2 and T_2 when the gas is heated at constant volume V_2.

(c) Deduce a relationship between the initial conditions P_1, V_1 and T_1 and the final conditions P_2, V_2 and T_2.

Note that temperature must be in kelvin in these calculations. However, the units of volume and pressure are not important, so long as they are consistent on both sides of the equation.

The ideal gas equation is derived from the combined gas equation and Avogadro's law

The gas equation and Avogadro's law can be combined to give:

$$\frac{PV}{T} \propto n$$

This can be made into an equation by introducing a constant, **R.** This is known as the **universal gas constant** as it does not depend on the identity of the gas.

$\therefore \quad \frac{PV}{T} = nR$ which is usually written as $\boldsymbol{PV = nRT}$

This equation, known as the **ideal gas equation,** is given in Section 1 of the data booklet. The value of R can be calculated by substituting known values into the equation, such as those for the molar volume of a gas at STP.

Worked example

Determine the gas constant from the molar volume of a gas at STP.

Solution

$P = 10^5\,\text{Pa}\,(\text{N m}^{-2})$, $V = 2.27 \times 10^{-2}\,\text{m}^3$, $T = 273\,\text{K}$, $n = 1$

$$R = \frac{PV}{nT} = \frac{10^5\,\text{N m}^{-2} \times 2.27 \times 10^{-2}\,\text{m}^3}{(1\,\text{mol} \times 273\,\text{K})}$$

$R = 8.31\,\text{N m K}^{-1}\,\text{mol}^{-1}$ or $8.31\,\text{J K}^{-1}\,\text{mol}^{-1}$

The ideal gas equation is *PV* = *nRT*

This value for *R*, the gas constant, is given in Section 2 in the data booklet and should be used for all calculations involving the ideal gas equation.

Use of the ideal gas equation enables us to calculate how systems respond to changes in pressure, volume and temperature, and to calculate molar mass. Gas density can also be determined by applying the relationship:

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

These calculations usually involve simply substituting values into the equation, but the use of units needs special attention. The guidelines below, based on the use of SI units only, should help you avoid some of the common mistakes that arise.

- *Pressure, P*: must be in Pa ($N\,m^{-2}$); if kPa are used, multiply by 10^3.
- *Volume, V*: must be in m^3; if dm^3 are given, divide by 10^3, if cm^3 are given, divide by 10^6.
- *Number of moles, n*: this is often derived by application of $n = \frac{m}{M}$.
- *Temperature, T*: must be in kelvin; if °C is given, add 273.15.

Many sources give data for ideal gas law questions in non-SI units such as atmospheres, which require a mathematical conversion. You will not be expected to be familiar with these conversions in IB examinations.

The ideal gas equation can be deduced directly from the assumptions listed on page 122 with the application of simple physics. What is the role of reason, perception, intuition, and imagination in the development of scientific models?

Nature of Science

Changes in gas pressure were predicted from the axioms of the kinetic theory of the ideal gas model by considering particle collisions. These collisions are not directly observable and the predictions are of limited value without the evidence provided by the experimental gas laws. The laws are descriptive statements derived from regular patterns in the evidence. The laws supported the theory, and the theory explained the laws. This is typical of how science progresses.

Worked example

A helium party balloon has a volume of 18.0 dm^3. At 25 °C the internal pressure is 108 kPa. Calculate the mass of helium in the balloon.

Solution

First ensure that all data are in SI units:

$P = 108\,\text{kPa} = 108 \times 10^3\,\text{Pa}$

$V = 18.0\,\text{dm}^3 = 18.0 \times 10^{-3}\,\text{m}^3$

$T = 25\,^\circ\text{C} = 298\,\text{K}$

$$PV = nRT$$

$$108 \times 10^3\,\text{Pa} \times 18.0 \times 10^{-3}\,\text{m}^3 = n \times 8.31\,\text{J K}^{-1}\,\text{mol}^{-1} \times 298\,\text{K}$$

$\therefore\ n(\text{He}) = 0.785\,\text{mol}$

$\therefore\ \text{mass (He)} = nM = 0.785\,\text{mol} \times 4.00\,\text{g mol}^{-1} = 3.14\,\text{g}$

As this example shows, if pressure is given in kPa and volume is given in dm^3, the same answer is obtained if these values are used directly in the ideal gas equation.

Worked example

A sample of gas has a volume of 445 cm^3 and a mass of 1.50 g at a pressure of 95.0 kPa and a temperature of 28.0 °C. Calculate its molar mass.

Solution

Substitute $n = \frac{m}{M}$ into the ideal gas equation, and rearrange to solve for M.

$$M = \frac{mRT}{PV}$$

Ensure all data are in SI units:

$P = 95.0\,kPa = 95.0 \times 10^3\,Pa$

$V = 445\,cm^3 = 445 \times 10^{-6}\,m^3$

$T = 28.0\,°C = 301\,K$

$$\therefore M = \frac{1.500\,g \times 8.31\,J\,K^{-1}\,mol^{-1} \times 301\,K}{95 \times 10^3\,Pa \times 445 \times 10^{-6}\,m^3}$$

$= 88.8\,g\,mol^{-1}$ (to 3 significant figures)

Worked example

A gas has a density of 1.65 g dm^{-3} at 27 °C and 92.0 kPa. Determine its molar mass.

Solution

From the density data we know 1.65 g occupies 1.00 dm^3

As before $M = \frac{mRT}{PV}$

$$\therefore M = \frac{1.65\,g \times 8.31\,J\,K^{-1}\,mol^{-1} \times 300\,K}{92 \times 10^3\,Pa \times 1.00 \times 10^{-3}\,m^3} = 44.71\,g\,mol^{-1}$$

Challenge yourself

3. Blowing up a balloon increases its volume as the number of particles increases. What do you think would happen to this inflated balloon on the top of a very high mountain?



Blowing up a balloon increases its volume as the number of particles increases.

SKILLS

The molar mass of carbon dioxide can be experimentally determined by applying the ideal gas equation. Full details with a worksheet are available in the eBook.

Exercise

Q18. The ideal gas equation is $pV = nRT$.

Identify the units of R when the pressure is measured in Pa, and volume is measured in m^3.

A JK^{-1} **B** $Pa\,m^3\,K^{-1}\,mol^{-1}$ **C** $J\,mol^{-1}$ **D** $J\,mol\,K^{-1}$

Q19. The volume of a gas was measured with a gas syringe. 0.0673 g of the gas was found to occupy 41.0 cm^3, measured at standard temperature and pressure (25 °C and 1.0×10^5 Pa).

What is the relative molecular mass of the gas?

A 28 **B** 32 **C** 40 **D** 44

Q20. A 2.50 dm^3 container of helium at a pressure of 85 kPa was heated from 25 °C to 75 °C. The volume of the container expanded to 2.75 dm^3. What was the final pressure of the helium?

Q21. After a sample of nitrogen with a volume of 675 cm^3 and a pressure of 1.00×10^5 Pa was compressed to a volume of 350 cm^3 and a pressure of 2×10^5 Pa, its temperature was 27.0 °C. Determine its initial temperature.

Q22. The absolute temperature of 4.0 dm^3 of hydrogen gas is increased by a factor of three and the pressure is increased by a factor of four. Deduce the final volume of the gas.

Q23. To find the volume of a flask, it was first evacuated so that it contained no gas at all. When 4.40 g of carbon dioxide was introduced, it exerted a pressure of 90.0 kPa at 27 °C. Determine the volume of the flask.

Q24. An unknown noble gas has a density of 5.84 g dm^{-3} at STP. Calculate its molar mass, and so identify the gas.

Q25. A 12.1 mg sample of a gas has a volume of 255 cm^3 at a temperature of 25.0 °C and a pressure of 1300 Pa. Determine its molar mass.

Q26. Which has the greater density at STP, hydrogen or helium?

Q27. A cyclist pumps his tyres up very hard before a trip over a mountain pass at high altitude. Near the summit one of his tyres explodes. Suggest why this may have occurred.

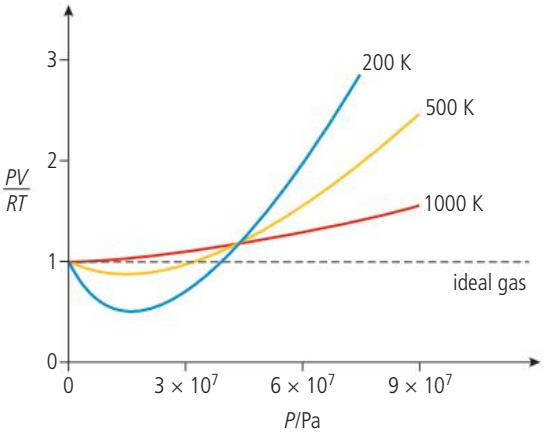
Nature of Science

The ideal gas model explains the observable properties of gases in terms of particles which cannot be directly observed. It provides a useful conceptual image of gas behaviour, and its predictions are approximately consistent with the results. It has some limitations as we will see on the next page. This does not mean that the model should be discarded – it can still be useful but we should be aware that it is an over-simplification, which does not apply accurately under all conditions.

Real gases do not obey the ideal gas law $PV = nRT$ under all conditions

An ideal gas is defined as one that obeys the ideal gas law $PV = nRT$ under all conditions. This means that for one mole of gas, the relationship $\frac{PV}{RT}$ should be equal to 1, and so a graph of $\frac{PV}{RT}$ against P for an ideal gas is a horizontal line of intercept 1 (Figure 11).

But, as we noted earlier, there is no such thing as an ideal gas so for real gases $PV \neq nRT$ at all conditions, and the value of $\frac{PV}{RT}$ for one mole will vary. An example of the extent of this variation from 1 at different conditions is shown in Figure 12.



We can draw the following conclusions from the graph:

- the gas behaves most like an ideal gas at low pressure and shows the greatest deviation at high pressure
- the gas behaves most like an ideal gas at high temperature and shows the greatest deviation at low temperature.

As discussed earlier, this is because assumptions 1 and 2 made on page 122 in defining an ideal gas do not apply under all conditions.

1. *If the volume of the gas particles is not negligible,* $\frac{PV}{nRT} > 1$

The collisions with the walls of the container are more frequent than predicted by the ideal gas model and the pressure is greater, $\frac{PV}{nRT} > 1$

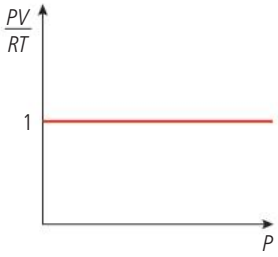
2. *There are attractive forces between the particles,* $\frac{PV}{nRT} < 1$

Attractive forces from other particles reduce the speed of the colliding particle and lead to a less energetic collision with the wall. The pressure is lower than for an ideal gas and $\frac{PV}{nRT} < 1$.

Challenge yourself

4. (a) Calculate the volume of 18.0 g of steam at a temperature of 500 K and a pressure of 1.00×10^5 Pa and show that the volume occupied by the particles is negligible.

(b) Show that the volume occupied by the particles is not negligible when the pressure is increased to 5.00×10^7 Pa and the temperature is reduced to 400 K.



S1.5 Figure 11 For one mole of an ideal gas, the relationship $\frac{PV}{RT}$ is a constant at all pressures.

S1.5 Figure 12 The deviation from ideal behaviour of nitrogen at different temperatures and pressures. Curves go above 1 when the volume of the particles is not negligible and below 1 when the intermolecular forces cannot be ignored.

Overall, we can conclude that real gases deviate from ideal behaviour when either or both of the assumptions on the previous page are not valid. This occurs at high pressure and low temperature. It makes sense intuitively that a gas behaves in a less perfect way under these conditions, as they are closest to it changing into a liquid.

Attempts to modify the ideal gas equation to take these factors into account and make it apply accurately to real gases led to the **van der Waals' equation**, which makes corrections for both the volume of the particles and the intermolecular attractions. Happily, for a wide range of conditions under which gases are studied, the ideal gas equation is a sufficiently accurate expression, and has the big advantage that it is a single equation for all gases.

One form of the van der Waals' equation is: $\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$ where a is a measure of the attraction between the particles, and b is the volume excluded by 1 mol of particles. The constants a and b are specific to different gases. van der Waals was awarded the 1910 Nobel Physics Prize for his work.

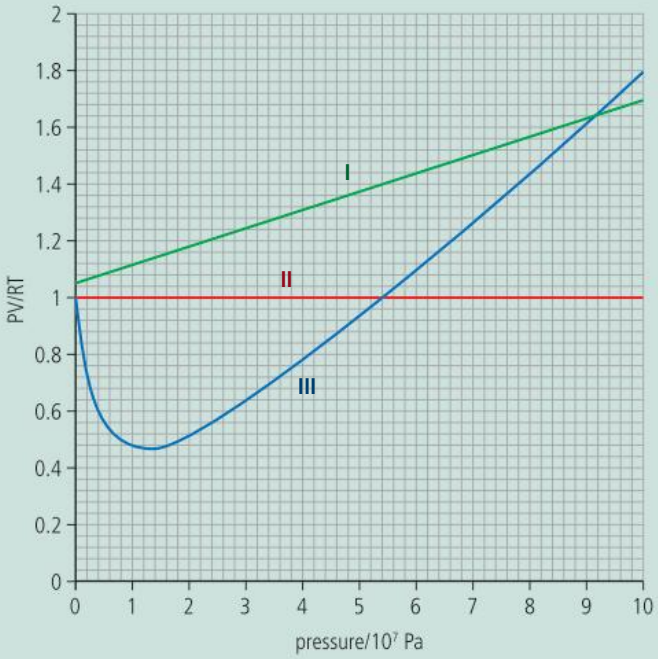
Challenge yourself

5. Show that the van der Waals' equation correctly predicts values of $\frac{PV}{RT} > 1$ for 1 mol of gas at very high pressures.
6. Show that the van der Waals' equation correctly predicts values of $\frac{PV}{RT} < 1$ for 1 mol of gas at very low pressures.

Exercise

Q28. Ammonia, NH_3, forms a relatively strong type of intermolecular attraction known as a hydrogen bond, whereas methane, CH_4, does not. Explain the relative deviation from ideal behaviour that each gas is likely to show.

Q29. The behaviour of three gases was investigated over a range of pressures.



(a) Identify the gas with the strongest intermolecular forces and justify your answer.

(b) Identify the gas with the largest molecular volume and justify your answer.

Guiding Question revisited

How does the model of ideal gas behaviour help us to predict the behaviour of real gases?

We introduced the chapter with the kinetic model of an ideal gas, which can be used to explain the experimental gas laws that relate the pressure, volume and temperature of a real gas under typical conditions. The limitations of the model were also identified with real gases deviating from ideal behaviour at high pressure and low temperatures.

- The kinetic theory of gases defines an ideal gas as one in which the particles have negligible volume and move in random chaotic motion with no intermolecular forces.
- The absolute temperature of the gas is proportional to the average kinetic energy of the particles.
- Gases exert pressure due to the impact of their collisions on the walls of the container.
- The gas laws describe the relationship between the pressure, volume and temperature of gases. They are a very good approximation of real gases under most conditions but strictly apply to ideal gases only.
- The gas laws can be summarized by the combined gas law $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$
- The incorporation of Avogadro's hypotheses leads to the ideal gas law: $PV = nRT$
- The ideal gas law can be applied to predict the changes that occur when the conditions of temperature, pressure or volume are changed. The molar mass of a gas can be obtained by measuring the density of a gas:

$$M = (m/PV)RT$$

- Real gases behave differently from ideal gases especially at high pressure and low temperature. These differences are due to the presence of intermolecular forces which reduce the pressure compared with an ideal gas under the same conditions or the non-negligible volume of the particles which increase the pressure.

Practice questions

1. The volume of a sample of gas is increased and the temperature is kept constant.

What is the effect of this change on the particles?

	Collisions between particles	Movement of particles
A	occur less often	slower
B	occur with more energy	slower
C	occur less often	no change in speed
D	occur with more energy	no change in speed

2. 1.0 dm^3 of an ideal gas at 100 kPa and 25 °C is heated to 50 °C at constant pressure. What is the new volume in dm^3?

A 0.50 **B** 0.90 **C** 1.1 **D** 2.0

3. What is the volume of gas when the pressure on 80 cm^3 of gas is changed from 300 kPa to 150 kPa at constant temperature?

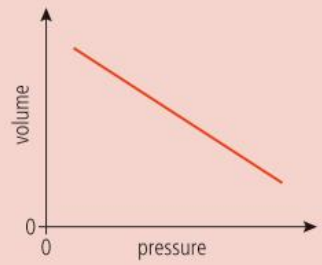
A 40.0 cm^3 **B** 80 cm^3 **C** 120 cm^3 **D** 160 cm^3

4. The volume of a sample of gas measured at 27 °C is 5.0 dm^3. What is the temperature when the volume is reduced, at the same pressure, to 4.0 dm^3?

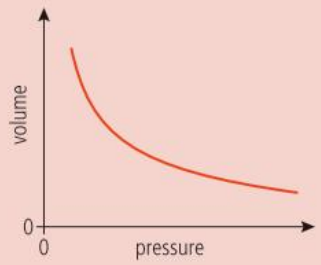
A −33.0 °C **B** −3.0 °C **C** 21.6 °C **D** 24.3 °C

5. Identify the graph that shows the relationship between the volume and pressure of a fixed amount of an ideal gas.

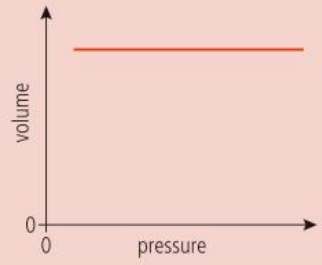
A



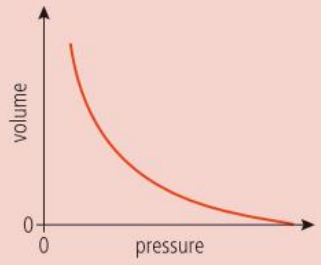
B



C



D



6. Why does nitrogen deviate from the ideal gas law at high pressures?

A Intermolecular forces increase the volume compared to that for an ideal gas.

B Increasing the pressure decreases the volume of the molecules.

C Nitrogen molecules have finite volume.

D Collisions between molecules occur more frequently at high pressure.

7. Identify the phenomenon that is best explained by the molecular kinetic model.

A The difference between the Celsius and Kelvin temperature scales

B The value of the universal gas constant

C The ideal gases equation

D The existence of noble gases

8. Identify the conditions when carbon dioxide is best described by the ideal gas model.

A Low density and low pressure **B** Low density and high pressure
C High density and low pressure **D** High density and high pressure

9. 4 mol of an ideal gas, X, at 25 °C is in a container of fixed volume.

Which of the following changes would lead to the greatest increase in pressure inside the flask?

A Increasing the temperature from 25 °C to 300 °C
B Adding another 2 mol of gas X into the flask at fixed temperature
C Adding 1 mol of argon gas and increasing the temperature from 25 °C to 200 °C
D Removing 1 mol of gas X and increasing the temperature from 25 °C to 350 °C

10. Which gas closely approaches ideal behaviour at room temperature and pressure?

A carbon dioxide **B** chlorine **C** hydrogen fluoride **D** neon

11. **(a)** Explain why helium behaves as an ideal gas over a wide range of pressures, volumes and temperatures. (2)

(b) The volume of a helium gas cylinder is $3.00 \times 10^{-2}\,m^3$. Determine the number of moles of helium in the cylinder if the pressure is 2.00×10^6 Pa and the temperature is 27.0 °C. (2)

(c) Calculate the number of helium atoms in the cylinder and estimate the average volume occupied by one gas atom in the cylinder. (2)

(d) Calculate the distance between neighbouring helium atoms. (1)

(Total 7 marks)

12. Airbags are an important safety feature in vehicles. Sodium azide, potassium nitrate, and silicon dioxide have been used in one design of airbag.

Two students looked at data in a simulated computer-based experiment to determine the volume of nitrogen generated in an airbag.

Sodium azide, a toxic compound, undergoes the following decomposition reaction under certain conditions.

$$2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$$

Using the simulation program, the students entered the following data into the computer.

Temperature (T) / °C	Mass of $NaN_3(s)$ (m) / kg	Pressure (p) / atm
25.00	0.0650	1.08

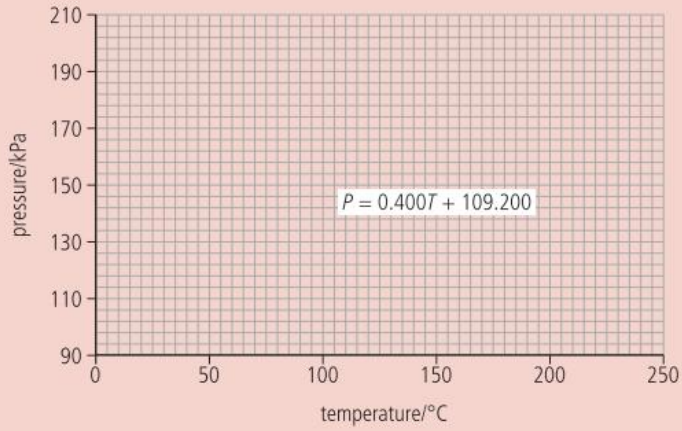
(a) State the number of significant figures for the temperature, mass, and pressure data. (1)

(b) Calculate the amount, in mol, of sodium azide present. (1)

(c) Determine the volume of nitrogen gas, in dm^3, produced under these conditions based on this reaction. (4)

(Total 6 marks)

13. The graph shows the variation in pressure P with temperature T for a sample of 0.193 g of a gas in a container with a fixed volume of $1.0 \times 10^{-3}\,m^3$.



(a) Does the gas behave ideally under these conditions? Justify your answer. (2)

(b) Deduce the identity of the gas in the container. (2)

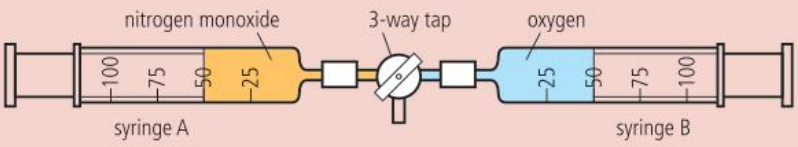
(Total 4 marks)

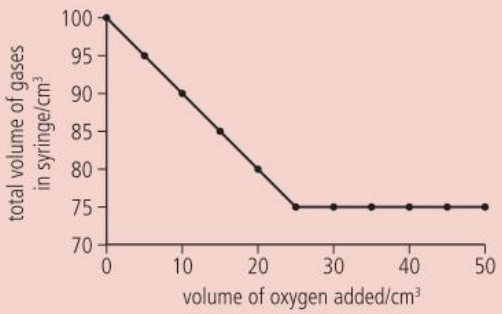
14. An alkane gas has a density of $1.94\,g\,dm^{-1}$ at STP. Determine the molecular mass of the gas and identify the alkane. (2)

(Total 2 marks)

15. Nitrogen monoxide, NO(g), reacts with oxygen, $O_2(g)$, to form one gaseous product X.

Syringe A contains 50 cm^3 of nitrogen monoxide. Syringe B contains 50 cm^3 of oxygen gas. In the experiment, 5.0 cm^3 portions of oxygen were pushed from syringe B into syringe A. After each addition, the tap was closed. After the gases had returned to their original temperature, the total volume of gases remaining was measured. The results are shown graphically below.





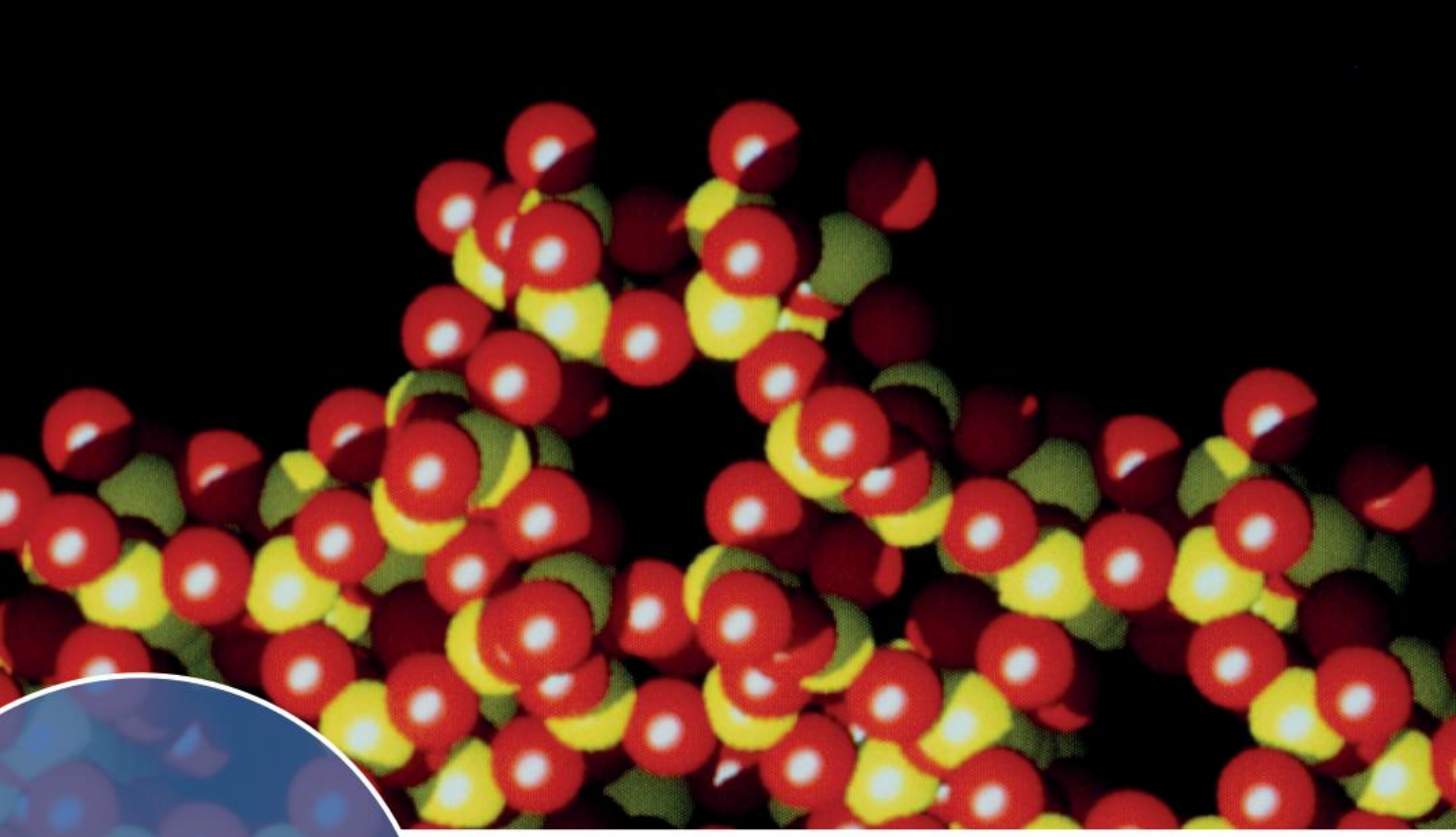
(a) State the total volume of oxygen remaining when the reaction is complete. (1)

(b) Calculate the amount of nitrogen dioxide and oxygen that react. (2)

(c) State the total amount of X produced. (2)

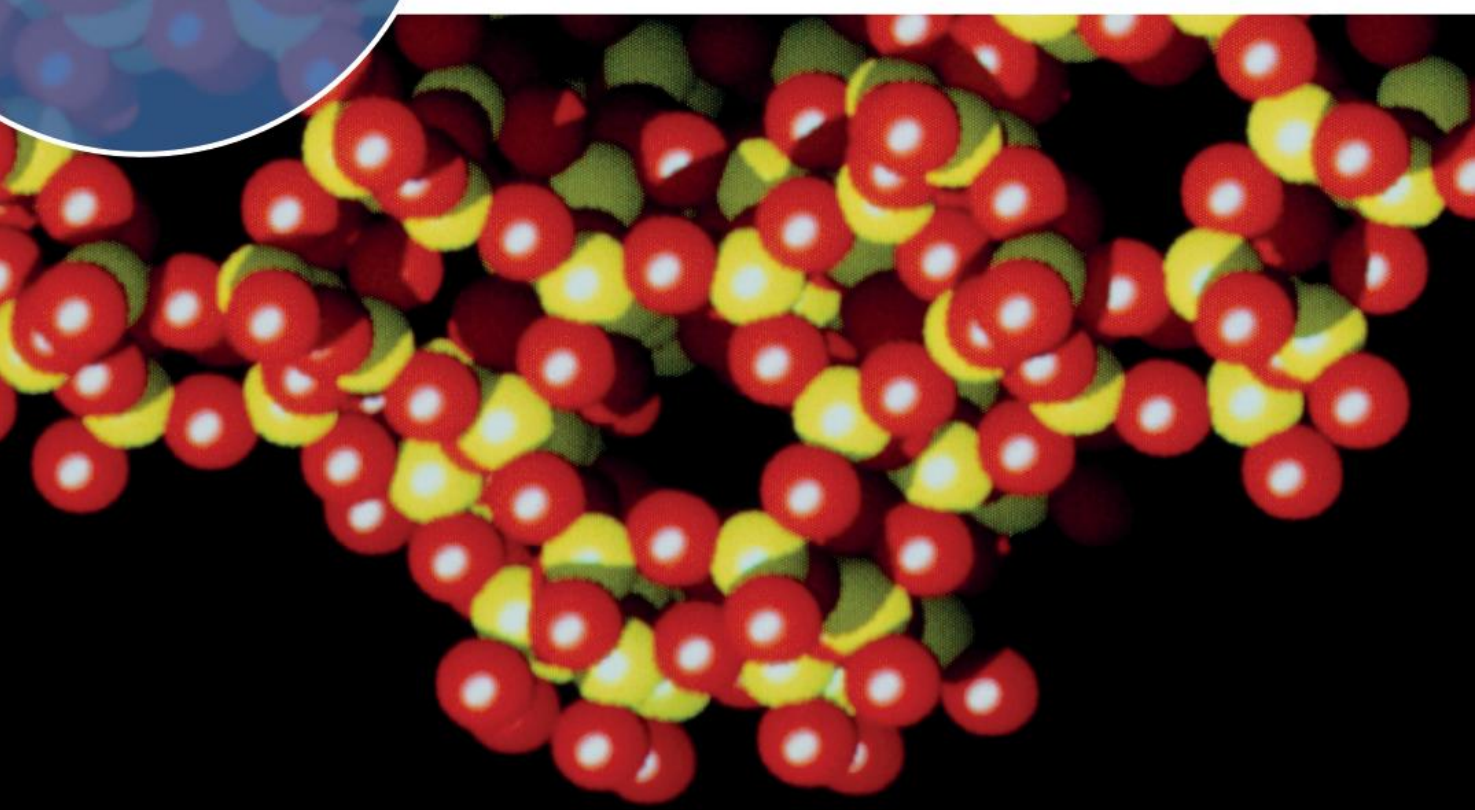
(d) Deduce a balanced equation for the reaction. (2)

(Total 7 marks)



STRUCTURE 2

Models of bonding and structure





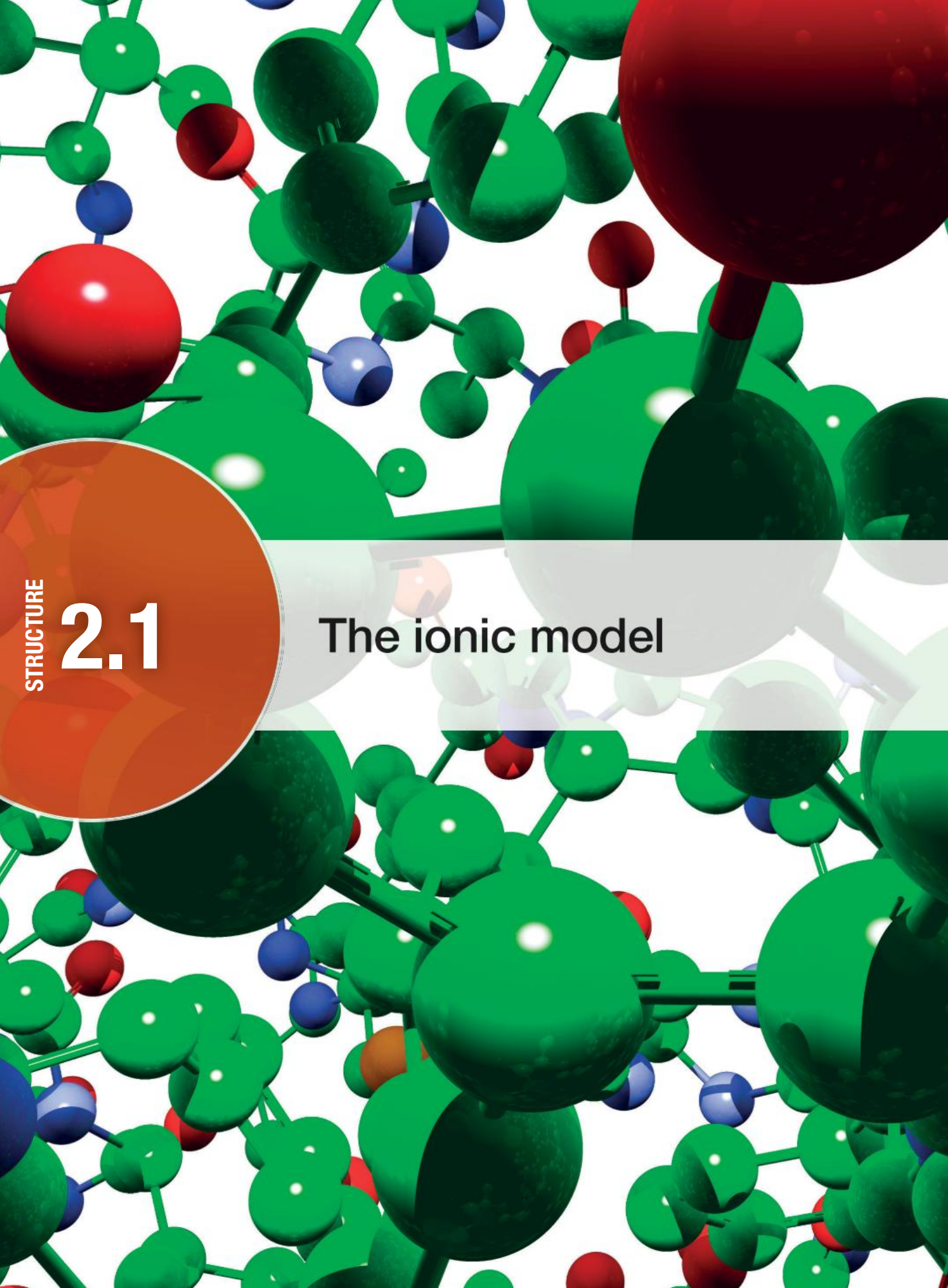
Computer graphic representation of the structure of zeolite-Y. Silicon and aluminium atoms are shown in yellow and oxygen atoms in red.
The open caged structure of zeolites gives them excellent catalytic properties.

Structure 1.2 shows that all elements are made of atoms but that there are only just over 100 chemically different types of atom. We know that we live in a world made up of millions of different substances: which somehow must all be formed from combinations of these 100 atomic building blocks. The extraordinary variety of the material world arises from the myriad of different ways these atoms can bond together to form different structures. Atoms come together in small numbers or large, with similar atoms or very different atoms, but a stable association known as a chemical bond is always the result. Atoms linked together by bonds therefore have very different properties from their parent atoms.

All chemical bonds occur as a result of changes in the distribution of electrons, but this can happen in different ways. In this chapter, we will study the ionic bond, where electrons are transferred from one atom to another, the covalent bond where electrons are shared between bonded atoms, and the metallic bond where electrons are delocalized or shared throughout a structure of many atoms. We will also consider intermolecular forces that help to hold covalent substances together.

Our study of the covalent bond at this level will use some of the concepts from the quantum theory developed in Structure 1.2 to explain the shapes and properties of molecules in more detail. As electrons are the key to the formation of all these bonds, a solid understanding of electron configurations will help you.

Chemical reactions take place when some bonds break and others re-form. The ability to predict and understand the nature of the bonds within a substance is therefore central to explaining its chemical reactivity.



STRUCTURE

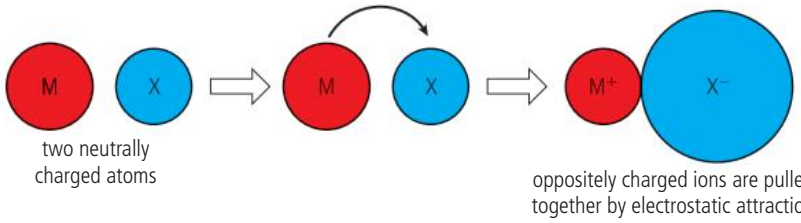
2.1 The ionic model

A molecule of insulin, the hormone essential for the regulation of glucose in the body. The ball-and-stick model shows all the atoms and bonds within the protein molecule. Insulin was the first protein to have its entire structure determined.

Guiding Question

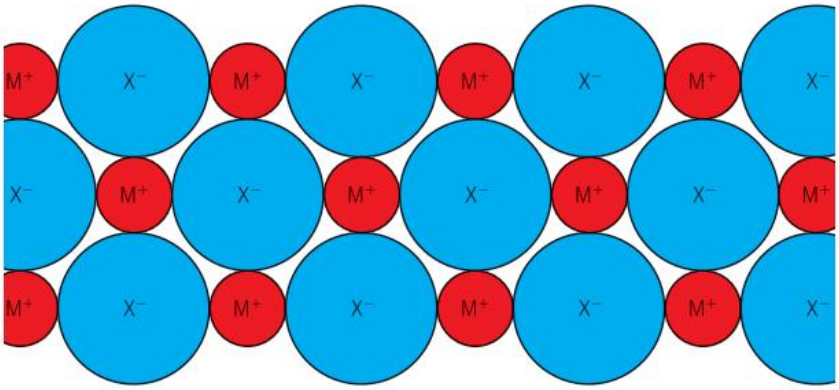
What determines the ionic nature and properties of a compound?

We see in Structure 1.2 that all atoms are electrically neutral as the number of protons is equal to the number of electrons. The transfer of an electron from one atom M to another atom X is a possible mechanism to facilitate the increased interaction between the atoms of M and X. The resulting ions have opposite charges and so are electrostatically attracted to each other (Figure 1).



S2.1 Figure 1 The transfer of an electron between atoms produces ions of opposite charge which are attracted to each other. As we will discover, M is generally a metal and X is a non-metal. Note that the ions have a different size than the atoms from which they are formed. This is discussed in Structure 3.1.

The strength of the ionic bond and the reason it exists is that many ions can arrange themselves in a lattice structure of low energy with oppositely charged ions placed next to each other (Figure 2).



S2.1 Figure 2 Positive and negative ions form a regular structure with oppositely charged ions arranged next to each other.

The resulting regular structure accounts for the crystalline structure of ionic compounds and their physical properties.

The elements M and X play opposite roles in this liaison and it is energetically most feasible when they come from opposite regions of the periodic table. The ionic character of the bond can be related to the distance between the elements' positions in the periodic table.



Crystals of calcium fluoride (CaF_2). Ionic compounds have crystalline structures due to the regular arrangement of the ions in a lattice structure.

Structure 2.1.1 and 2.1.2 – The ionic bond

Structure 2.1.1 – When metal atoms lose electrons, they form positive ions called cations.

When non-metal atoms gain electrons, they form negative ions called anions.

Predict the charge of an ion from the electron configuration of the atom.

The formation of ions with different charges from a transition element should be included.	Structure 3.1 – How does the position of an element in the periodic table relate to the charge of its ion(s)? HL Structure 1.3 – How does the trend in successive ionization energies of transition elements explain their variable oxidation states?

Structure 2.1.2 – The ionic bond is formed by electrostatic attractions between oppositely charged ions.

Deduce the formula and name of an ionic compound from its component ions, including polyatomic ions.

Binary ionic compounds are named with the cation first, followed by the anion. The anion adopts the suffix 'ide'.

Interconvert names and formulas of binary ionic compounds.

The following polyatomic ions should be known by name and formula: ammonium NH_4^+, hydroxide OH^-, nitrate NO_3^-, hydrogencarbonate HCO_3^-, carbonate CO_3^{2-}, sulfate SO_4^{2-}, phosphate PO_4^{3-}.	Reactivity 3.2 – Why is the formation of an ionic compound from its elements a redox reaction? HL Structure 2.2 – How is formal charge used to predict the preferred structure of sulfate? HL Reactivity 3.1 – Polyatomic anions are conjugate bases of common acids. What is the relationship between their stability and the conjugate acid's dissociation constant, K_a?

Metal atoms lose electrons to form positive ions and non-metal atoms gain electrons to form negative ions

The atomic number of an element is defined in terms of the number of protons. The number of protons and the identity of the element do not change during a chemical reaction. It is the outer electrons, known as the valence electrons, that are involved in chemical reactions. They are furthest from the electrostatic attraction of the nucleus and so more open to external influences. When an atom loses electrons it forms a positive ion or **cation**, as the number of protons is now greater than the number of electrons. Negative ions or **anions** are formed when atoms gain an additional negatively charged electron.

The outer electrons of metal atoms experience a smaller effective nuclear charge than the outer electrons of non-metals

Electron transfers occur if they are energetically feasible. The concept of effective nuclear charge is helpful in explaining when this is likely to be the case. As discussed in Structure 1.2, the **nuclear charge** of the atom is given by the atomic number and so increases by one between successive elements in the periodic table, as a proton is added to the nucleus. The outer electrons which determine the chemical properties of the atom do not, however, experience the full attraction of this charge as they are **shielded** from the nucleus and repelled by the inner electrons.



(a) Hydrogen atom **(b)** Multi-electron atom

(a) An electron in the hydrogen atom experiences the full attraction of the nuclear charge.
(b) In a multi-electron atom, the attraction for the nucleus is reduced as the outer electron is shielded from the nucleus and repelled by inner electrons.

The presence of the inner electrons reduces the attraction of the nucleus for the outer electrons in (b) above and the **effective charge** experienced by the outer electrons is less than the full nuclear charge.

Consider, for example, a sodium atom with a nuclear charge of +11. The outer electron in the 3s orbital is shielded from this charge by the 10 electrons in the first and second energy levels ($1s^2 2s^2 2p^6$ = [Ne]). If we assume that the 10 electrons of the neon core are completely shielding, they reduce the effective nuclear charge to +1. Similar results for other elements in period 3 are shown.

Element	Na	Mg	Al	Si	P	S	Cl
Nuclear charge	11	12	13	14	15	16	17
Electron configuration	[Ne] $3s^1$	[Ne] $3s^2$	[Ne] $3s^2 3p^1$	[Ne] $3s^2 3p^2$	[Ne] $3s^2 3p^3$	[Ne] $3s^2 3p^4$	[Ne] $3s^2 3p^5$
Effective nuclear charge experienced by valence electrons	≈ 11 – 10 ≈ +1	≈ 12 – 10 ≈ +2	≈ 13 – 10 ≈ +3	≈ 14 – 10 ≈ +4	≈ 15 – 10 ≈ +5	≈ 16 – 10 ≈ +6	≈ 17 – 10 ≈ +7

As the period is crossed from left to right, one proton is added to the nucleus and one electron is added to the valence electron energy level. The effective charge increases with the nuclear charge as there is no change in the number of inner electrons. The atoms all have a noble gas core of 10 electrons ([Ne] = $1s^2 2s^2 2p^6$).

We can illustrate the changes in effective nuclear charge down a group by considering the elements in group 1.

Element	Nuclear charge	Electron configuration	Effective nuclear charge experienced by valence electrons
Li	3	$1s^2 2s^1$	≈ 3 – 2 ≈ +1
Na	11	$1s^2 2s^2 p^6 3s^1$	≈ 11 – 10 ≈ +1
K	19	$1s^2 2s^2 p^6 3s^2 3p^6 4s^1$	≈ 19 – 10 ≈ +1

As we descend the group, the increase in the nuclear charge is largely offset by the increase in the number of inner electrons; both increase by eight between successive elements in the group. The effective nuclear charge experienced by the outer electrons remains approximately +1 down the group.

The effective nuclear charge experienced by an atom's outer electrons increases with the group number of the element. It increases across a period but remains approximately the same down a group.

Metal atoms form positive ions as they have low ionization energies

First ionization energies are discussed in Structure 1.3 where we see that they increase across a period. This can be accounted for by the increase in effective nuclear charge. The increased attraction between the outer electrons and the nucleus makes the valence electrons more difficult to remove. An element M is more likely to lose an electron and form a positive ion if it is a metal on the left of the periodic table where elements have the lowest ionization energies. As ionization energies decrease down a group, metals on the bottom left of the periodic table will have the greatest tendency to lose electrons and form ionic compounds.

Challenge yourself

1. As shown in Structure 1.3, although there is a general increase in ionization energies across a period, there are some regular discontinuities in this trend. The first ionization energy of aluminium, for example, is lower than the first ionization of magnesium. How can the calculation of effective nuclear charge be refined to explain these discontinuities?

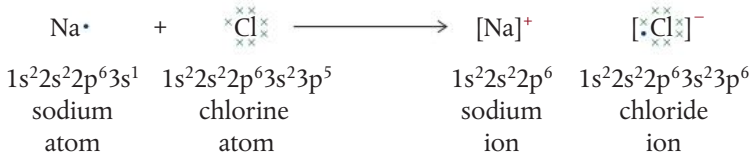
An ion is a charged particle. Ions form from atoms or from groups of atoms by loss or gain of one or more electrons.

Non-metal atoms form negative ions as they have high effective nuclear charges

Electron transfer will also be more likely to occur if the non-metal element X attracts the transferred electrons more strongly. This is the case if X is a non-metal on the top right of the periodic table. Such elements have the highest effective nuclear charges and the smallest atomic radii.

Sodium chloride is formed when one electron is transferred from sodium to chlorine

Sodium reacts with chlorine to form the ionic compound sodium chloride. The outer 3s electron from a sodium atom moves to the chlorine atom and acts like a harpoon. Once the transfer is complete, the resulting electrostatic attraction between the oppositely charged Na^+ and Cl^- ions pulls the ions together (Figure 3).



S2.1 Figure 3 An electron is transferred from sodium to chlorine. This is an example of a redox reaction (discussed more fully in Reactivity 3.2). Note that both ion products, Na^+ and Cl^-, have the electron configuration of a noble gas.

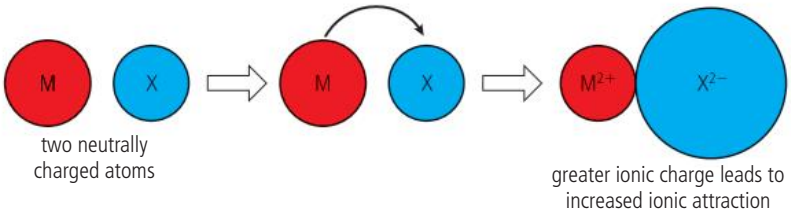
Similar reactions occur between other group 1 metals and other group 17 elements. The most vigorous reaction occurs between the elements that are furthest apart in the periodic table. The most reactive alkali metal, caesium, near the bottom of group 1, has the lowest ionization energy and loses electrons most readily. Fluorine is the most reactive halogen, at the top of group 17, as it has the smallest atomic radius and attracts the transferred electron the most strongly.



Coloured scanning electron micrograph of crystals of table salt, sodium chloride, NaCl. The very reactive elements sodium and chlorine have combined to form this stable compound containing Na^+ and Cl^- ions.

The attraction between ions increases with ionic charge but removing multiple electrons has an energy cost

Singly charged ions are formed with the transfer of one electron. More generally, ions of greater charge can be formed if more than one electron is transferred. For example, magnesium oxide is formed when the two valence electrons from a magnesium atom are transferred to an oxygen atom. The resulting ions have a greater charge and there is an increased force of attraction between them.



The transfer of two electrons produces doubly charged ions which are attracted to each other more strongly.

The formation of a multiply charged ion does not however come without an energy cost.

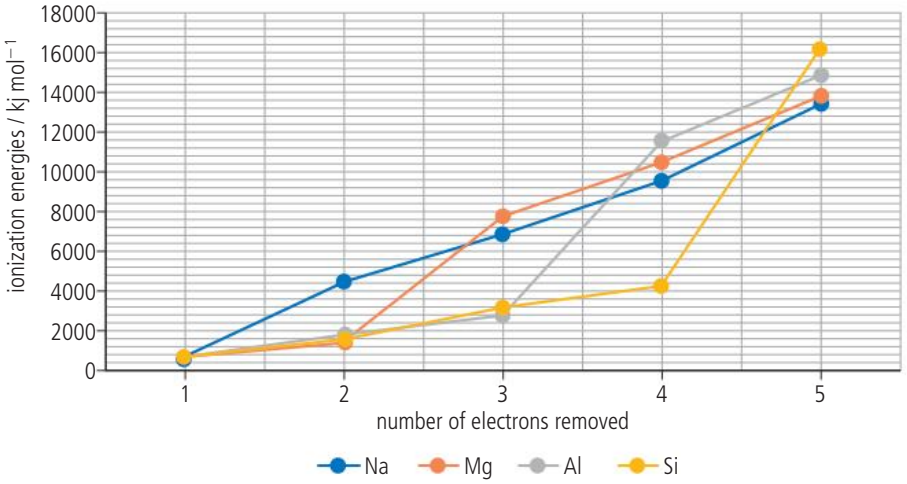
Reactivity 3.2 – Why is the formation of an ionic compound from its elements a redox reaction?

TOK

The electron involved in the bonding of sodium is described as a harpoon. How useful are similes and metaphors in the sciences? Does the language we use have a descriptive or interpretive function?

HL

The ionization energies of sodium, magnesium, aluminium and silicon are shown in Figure 4.



S2.1 Figure 4 Increases in successive ionization energies as an electron is removed from an inner energy level make the formation of Na^{2+}, Mg^{3+}, Al^{4+} and Si^{4+} ions energetically unfeasible.

Successive ionization energies of an element increase and, as we see in Structure 1.3, there is a large jump in ionization energies when electrons are removed from an inner energy level. Sodium, for example, forms the Na^+ ion readily but not Na^{2+} because the second ionization energy prohibits further electron loss. For the same reason, aluminium forms the Al^{3+} ion but not Al^{4+}. The first ionization energy of silicon is too high to make electron loss feasible.

Silicon does not form the Si^{4+} ion in chemical reactions.

HL end

Negative ions are more attractive with increased charge

The group 17 elements have one vacancy in their outer energy level and a high effective nuclear charge so they can accept one electron readily into their outer energy level and form the halide X^- ion. Group 16 elements, such as oxygen, have two vacancies but the outer electrons only experience an effective nuclear charge of +6. They can form X^{2-} ions but do not attract electrons as strongly as the halogens. Phosphorus has three vacancies and so can accommodate three additional electrons and form the P^{3-} ion. The outer electrons in phosphorus only experience an effective nuclear charge of +5 so it forms ionic compounds less readily than chlorine or sulfur. The addition of electrons becomes more difficult with increasing negative charge of the ion due to increased electron–electron repulsion. The formation of the silicon Si^{4-} is not feasible for this reason.

The high ionization energies of the noble gases and their complete energy levels make them unreactive

We see in Structure 1.3 that the noble gases have very high first ionization energies. The nucleus of a noble gas holds on tightly to its outer electrons making them unavailable for any chemical activity. The noble gases also have complete outer shells with no vacancies to accommodate extra electrons so any added electron would have to occupy an empty outer energy level where they would experience an effective nuclear charge of zero. These factors explain the non-reactivity of the group. The full outer energy level of the noble gases can be thought of as the 'ultimate goal' for all atoms. The noble gases do not react as they have already achieved this goal. Metal atoms lose electrons to achieve the stable electron configuration of the preceding noble gas and non-metals gain electrons to achieve the stable electron configuration of the succeeding noble gas. As we saw earlier, when sodium reacts it loses an electron to achieve the electron configuration of neon and the chloride ion has the electron configuration of argon.



Sparks fly as an argon welder joins two metals together. The unreactive argon gas provides an inert environment which prevents the hot metals from reacting with the air.

The charge on the ion can be predicted from an element's position in the periodic table

Metals that have a small number of electrons in their outer shells (groups 1, 2, and 13) will lose these electrons and form cations. Non-metals that have higher numbers of electrons in their outer shells (groups 15, 16, and 17) will gain electrons and form anions.

Metals form cations by losing valence electrons. Non-metals form anions by gaining electrons.

We are now able to summarize how the position of an element in the periodic table enables us to predict the ion it forms. The table shows the ions formed by the elements in period 3.

It may help you to remember: CATion is PAWsitive and aNion is Negative.

Group number	Element	Electron configuration of atom	Number of valence electrons	Number of electrons transferred	Charge on ion formed	Electron configuration of ion	Type of element
1	Na	$[Ne]3s^1$	1	1 lost	1+	[Ne]	metal
2	Mg	$[Ne]3s^2$	2	2 lost	2+	[Ne]	metal
13	Al	$[Ne]3s^23p^1$	3	3 lost	3+	[Ne]	metal
14	Si	$[Ne]3s^23p^2$	4	–	–	–	metalloid
15	P	$[Ne]3s^23p^3$	5	3 gained	3–	$[Ne]3s^23p^6 = [Ar]$	non-metal
16	S	$[Ne]3s^23p^4$	6	2 gained	2–	$[Ne]3s^23p^6 = [Ar]$	non-metal
17	Cl	$[Ne]3s^23p^5$	7	1 gained	1–	$[Ne]3s^23p^6 = [Ar]$	non-metal

Silicon and other elements in group 14, with four electrons in their outer shell, do not form ions readily. These elements react to form different, covalent, bonds as discussed in Structure 2.2.

Hydrogen is difficult to place in the periodic table and this is reflected in the ions it forms. It generally loses its 1s electron like the group 1 metals and forms the H^+ ion but can also form the less common H^- (hydride) ion by completing its outer energy level like the halogens.

When writing the symbols for ions, note the charge is written as a superscript with the number first and the charge next, e.g., N^{3-}. When an ion X carries a charge of 1+ or 1– it is written just as X^+ or X^-.

Challenge yourself

2. What evidence based on simple observations supports the existence of ions?

Do you *know* that sodium chloride is made up of Na^+ and Cl^- ions or do you simply *believe* this to be the case? What is needed to change a belief into knowledge?

TOK

Structure 3.1 – How does the position of an element in the periodic table relate to the charge of its ion(s)?

Worked example

Refer to the periodic table to deduce the charge on the ion formed when the following elements react:

(a) lithium **(b)** oxygen **(c)** carbon

Solution

(a) lithium is in group 1 so forms Li^+

(b) oxygen is in group 16 so forms O^{2-}

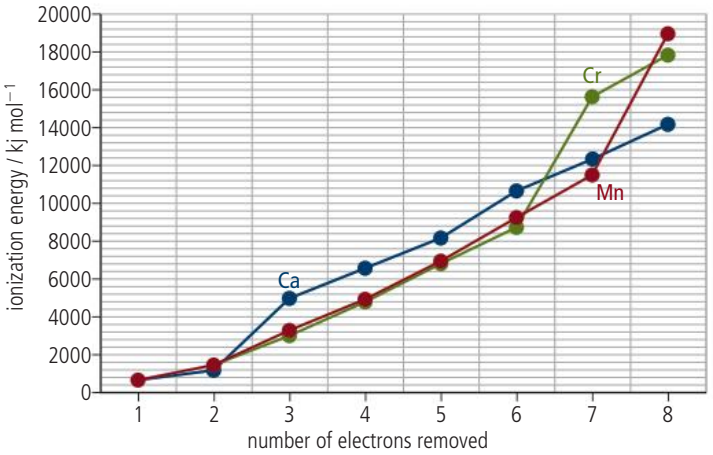
(c) carbon is in group 14 so does not form ions

Transition metals form ions of different charges and show a range of oxidation states

HL

In Structure 1.3 we see that the wide range of oxidation states that the transition metals display in their compounds are related to patterns in successive ionization energies (see S1.3 Figure 16). The first two ionization energies of titanium, manganese and chromium (see Figure 5 below) are very similar so we would expect all three elements to form M^{2+} ions.

The formation of the Ca^{3+} ion is energetically unfavourable as there is a large jump between the second and third ionization energies, but manganese and chromium can both form M^{3+} ions as the ionization energies continue to increase linearly in small steps as more electrons are removed. Ions with a charge greater than +3 generally show covalent character as they have such a large charge density that they polarize negative ions and increase the covalent character of the compound (Figure 6).

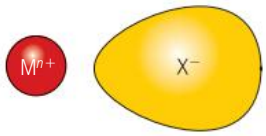


S2.1 Figure 5 Successive ionization energies for Ca, Cr and Mn.



The blue solution on the right contains $Cr^{3+}(aq)$ ions. The yellow solution on the left contains $CrO_4^{2-}(aq)$ ions with chromium in the +6 oxidation state.

It is more correct to refer to oxidation states rather than ionic charge for such species. The maximum oxidation state is reached when this linear pattern ends. Chromium has a maximum oxidation state at +6 as there is a big jump in the ionization energies when the seventh electron is removed. Manganese has a maximum at +7 as there is a large jump in ionization energy with the removal of the eighth electron.



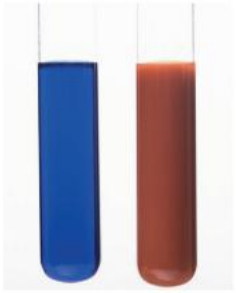
S2.1 Figure 6 The high charge density of the transition metal ions M^{n+} pulls the weakly held outer electrons of the X^- ion. This polarization of negative ions increases the covalent character of the transition metal compounds with oxidation states greater than +3.

HL end

Other notable examples include iron which can form Fe^{2+} and Fe^{3+} ions and copper which forms Cu^{2+} and Cu^+ ions. The iron and copper ions of different charge form compounds with different properties including colour.



The beaker on the left contains $Fe^{2+}(aq)$ and the beaker on the right contains $Fe^{3+}(aq)$. When iron rusts, it reacts with oxygen to form these different ions.



The tube on the left contains the blue Cu^{2+} ion, the tube on the right contains the red Cu^+ ion. These two ions are observed when Fehling's reagent is warmed with glucose or other 'reducing sugars'. The blue Cu^{2+} is reduced to the red Cu^+.

HL

The oxidation states of the first-row d block elements are summarized below. The more common states are highlighted in blue.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
								+1	
+2	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3	+3	
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5	+5	+5			
			+6	+6	+6				
				+7					

HL end

There are other notable examples of elements forming ions that are not obvious from their position in the periodic table:

- lead (Pb) and tin (Sn) form stable M^{4+} and M^{2+} ions despite being in group 14
- silver, Ag, forms the ion Ag^+.

Oxidation states are discussed more fully in Reactivity 3.2.

HL Structure 1.3 – How does the trend in successive ionization energies of transition elements explain their variable oxidation states?

Oxidation state is shown with a '+' or '–' sign and an Arabic numeral, e.g. +2. Oxidation number is shown by inserting a Roman numeral in brackets after the name or symbol of the element.

Systematic names of compounds use oxidation numbers

The Fe^{2+} ion forms an oxide with the formula FeO and Fe^{3+} ions form Fe_2O_3. These compounds were traditionally distinguished as ferrous oxide and ferric oxide, but IUPAC introduced a nomenclature using **oxidation numbers** to make the names more systematic. A Roman numeral corresponding to the oxidation state is inserted in brackets after the name of the element. So FeO is iron(II) oxide and Fe_2O_3 is iron(III) oxide.

The terms 'oxidation number' and 'oxidation state' are often used interchangeably, and either term is acceptable.

The table shows some common examples of the names of compounds with different oxidation states.

Formula of compound	Oxidation state	Name using oxidation number
FeO	Fe +2	iron(II) oxide
Fe_2O_3	Fe +3	iron(III) oxide
Cu_2O	Cu +1	copper(I) oxide
CuO	Cu +2	copper(II) oxide
MnO_2	Mn +4	manganese(IV) oxide

HL Worked example

Deduce the name of the following compounds using oxidation numbers.

(a) V_2O_5 **(b)** $NiCl_2$ **(c)** TiO_2

Solution

1. Work out the oxidation number of the metal.
   (a) V is +5 **(b)** Ni is +2 **(c)** Ti is +4
2. Insert the corresponding Roman numeral after the name of the element. There is no space between the name and the number, and the number is placed in brackets.
   (a) vanadium(V) oxide **(b)** nickel(II) chloride **(c)** titanium(IV) oxide

Although this nomenclature can be used in the naming of all compounds, it is only necessary when an element has more than one common oxidation state. For example, Na_2O could be called sodium(I) oxide, but as Na only shows this oxidation state +1 in compounds, it is simply sodium oxide.

The formula of an ionic compound can be deduced from its component ions

When an ionic compound is formed, there is no net loss or gain of electrons. The ionic compound, like the atoms that formed it, is electrically neutral. Writing the formula for the ionic compound involves *balancing the total number of positive and negative charges*, by taking into account the different charges on each ion.

For example, magnesium oxide is made up of magnesium ions Mg^{2+} and oxide ions O^{2-}. Each magnesium atom has transferred *two* electrons to each oxygen atom and so the compound contains equal numbers of each ion. Its formula, $Mg^{2+}O^{2-}$, is usually written as MgO. When magnesium reacts with fluorine, however, Mg again loses *two* electrons, but *two* F atoms are needed as each F atom can only gain *one* electron. The ionic compound produced has the ratio Mg:F = 1:2 and is written as $Mg^{2+}F^-_2$ or MgF_2.

Worked example

Deduce the formula for the compound that forms between aluminium and oxygen.

Solution

1. Check the periodic table for the ions that each element will form.
   aluminium in group 13 forms Al^{3+}
   oxygen in group 16 forms O^{2-}
2. Balance the charges by finding a common multiple. In this case you need six of each charge:
   $2 \times Al^{3+} = 6+$ and $3 \times O^{2-} = 6-$
3. State the final formula using subscripts to show the number of ions: Al_2O_3

It is common practice to leave the charges out when showing the final formula.

Important polyatomic ions that should be known

Polyatomic ions are made up of more than one atom which together have lost or gained an electron. Many of these polyatomic ions are found in salts formed from common acids. As we will discuss in Reactivity 3.1, the ions are said to be conjugate bases of these acids as they formed when an H^+ ion is removed from the acid. The stronger the acid the more stable the ion.

It will help you to become familiar with the examples in the table below, as you will often use them when writing formulas and equations. (Note that this information is not supplied in the data booklet.)

Polyatomic ion name	Formula	Corresponding acid	Example of compound containing this ion	Example of chemical formula
nitrate	NO_3^-	$HNO_3(aq)$	lead(II) nitrate	$Pb(NO_3)_2(s)$
sulfate	SO_4^{2-}	$H_2SO_4(aq)$	copper sulfate	$CuSO_4(s)$
phosphate	PO_4^{3-}	$H_3PO_4(aq)$	calcium phosphate	$Ca_3(PO_4)_2(s)$
hydroxide	OH^-	$H_2O(l)^{\Delta}$	barium hydroxide	$Ba(OH)_2(s)$
hydrogencarbonate	HCO_3^-	$H_2CO_3(aq)$*	potassium hydrogencarbonate	$K(HCO_3)_2(s)$
carbonate	CO_3^{2-}	$H_2CO_3(aq)$*	magnesium carbonate	$MgCO_3(s)$
ammonium	NH_4^+	$NH_4Cl(aq)$*	ammonium nitrate	$NH_4NO_3(ag)$

* These are weak acids, as discussed in Reactivity 3.1.
$^{\Delta}$ Water can act as an acid or a base, as discussed in Reactivity 3.1.
NH_4^+ is unusual in that it is a positive ion formed from non-metal elements.

In many non-metal elements, the ending of the name changes to '-ide' when ionization occurs. For example, *chlorine* (the element) becomes *chloride* (the ion), *oxygen* becomes *oxide*, *nitrogen* becomes *nitride* etc.

Note the convention in naming ionic compounds is that the positive ion is written first and the negative ion second.

Note that the formula of the compound shows the *simplest ratio* of the ions it contains. So, for example, magnesium oxide is not Mg_2O_2 but MgO.

HL Reactivity 3.1 – Polyatomic anions are conjugate bases of common acids. What is the relationship between their stability and the conjugate acid's dissociation constant, K_a?

The charge of a polyatomic ion can be deduced from the number of Hs in the formula of the corresponding acid.

HL Structure 2.2 – How is formal charge used to predict the preferred structure of sulfate?

The names of compounds give a clue to their composition. The ending '-ate' refers to ions that contain oxygen bonded to another element.

Naming ionic bonds. Full details of how to carry out this activity with a worksheet are available in the eBook.

It should be noted that the bonding within the polyatomic ion is covalent. So in potassium sulfate, for example, the K^+ and SO_4^{2-} ions are attracted together by ionic bonds, but the sulfur and oxygen atoms are held together within the sulfate ion by covalent bonds.

HL The nature of the bonding in the sulfate ion is best understood with the concept of formal charge, which is explained in Structure 2.2.

When writing the formula of a compound with more than one polyatomic ion, parentheses are used around the ion before the subscript.

Worked example

Deduce the formula for ammonium phosphate.

Solution

1. The compound contains two polyatomic ions in the table above and these need to be known: NH_4^+ and PO_4^{3-}
2. Balance the charges by using a common multiple: in this case 3 for each charge:

$$3 \times NH_4^+ = 3+ \text{ and } 1 \times PO_4^{3-} = 3-$$

3. State the formula using subscripts and brackets to show the number of ions:

$$(NH_4)_3PO_4$$

Exercise

Q1. Which is the best description of ionic bonding?

A The electrostatic attraction between positive ions and non-bonding electrons

B The electrostatic attraction between positive ions and bonding electrons

C The electrostatic attraction between positively charged nuclei and an electron pair

D The electrostatic attraction between oppositely charged ions

Q2. What is the formula for the compound formed by aluminium and sulfur?

A AlS **B** AlS_2 **C** AlS_3 **D** Al_2S_3

Q3. What happens when lithium reacts with bromine?

A	lithium atoms gain one electron	bromine atoms gain one electron
B	lithium atoms gain one electron	bromine atoms lose one electron
C	lithium atoms lose one electron	bromine atoms gain one electron
D	lithium atoms lose one electron	bromine atoms lose one electron

Q4. Which of the following are ionic compounds?

I. NH_4Cl II. NH_4NO_3 III. HCl

A I and II only **B** I and III only **C** II and III only **D** I, II and III

Q5. Write the formula for each of the following compounds:

(a) potassium bromide **(b)** zinc oxide **(c)** sodium sulfate
(d) copper(II) bromide **(e)** chromium(III) sulfate **(f)** aluminium hydride

Q6. Name the following compounds:

(a) $Sn_3(PO_4)_2$ **(b)** $Ti(SO_4)_2$ **(c)** $Mn(HCO_3)_2$ **(d)** $BaSO_4$
(e) Hg_2S **(f)** V_2O_3 **(g)** Cr_2O_3 **(h)** PbO_2

Q7. What is the formula of the compound that forms from element X in group 2 and element Y in group 15?

Q8. Explain what happens to the electron configurations of the elements Mg and Br when they react to form the compound magnesium bromide.

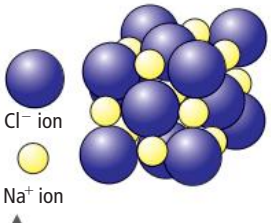
Structure 2.1.3 – Ionic structures and properties

Structure 2.1.3 – Ionic compounds exist as three-dimensional lattice structures, represented by empirical formulas. Explain the physical properties of ionic compounds to include volatility, electrical conductivity and solubility.	
Include lattice enthalpy as a measure of the strength of the ionic bond in different compounds, influenced by ion radius and charge.	Tool 1, Inquiry 2 – What experimental data demonstrates the physical properties of ionic compounds? Structure 3.1 – How can lattice enthalpies and the bonding continuum explain the trend in melting points of metal chlorides across period 3?

Ionic compounds have a lattice structure

Once the ions are formed by electron transfer, they are pulled together by the electrostatic attraction that is the **ionic bond**. An ion pair is rarely formed in isolation, however, and many cations and anions arrange themselves in a three-dimensional lattice structure held together by ionic bonds between oppositely charged ions. The details of the lattice's geometry vary in different compounds, depending mainly on the relative sizes of the ions, but it always involves a fixed arrangement of ions based on a repeating unit or **unit cell**.

A lattice consists of a very large number of ions and can grow indefinitely. Ionic compounds do not have a fixed number of ions, so their formulas are *ratios* of ions present. They are empirical formulas and are known as the **formula unit**, as discussed in Structure 1.4.



S2.1 Figure 7 A unit cell of the NaCl lattice is built up from oppositely charged sodium and chloride ions.

HL

The term coordination number is used to express the number of ions that surround a given ion in the lattice. For example, in the sodium chloride lattice, each Na^+ ion is surrounded by six Cl^- ions and each Cl– ion is surrounded by six Na^+ ions (Figure 7). The coordination number of both ions is the same as the ions are present in equal numbers. This confirms the formula NaCl.

Make sure that you avoid the term 'molecule' when describing ionic compounds, but instead use the term formula unit.

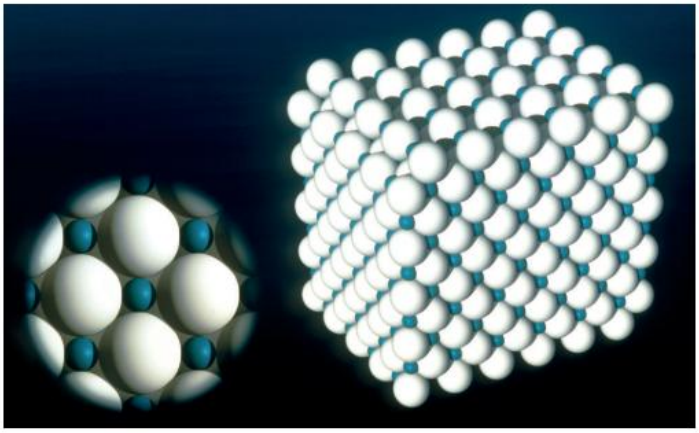
Challenge yourself

3. Consider Figure 7 on the previous page, which shows one unit cell of the sodium chloride structure.

- Each chloride ion on the corner of the cube is a member of eight other unit cells so contributes $\frac{1}{8}$ of an ion to each of the eight unit cells.
- Each chloride ion on the centre of one face is shared by two unit cells and contributes $\frac{1}{2}$ of an ion to both of these unit cells.
- Each sodium ion at the centre of an edge is shared by four unit cells and so contributes $\frac{1}{4}$ of an ion to four unit cells.
- There is a sodium ion at the centre of the cube which belongs exclusively to one unit cell and so contributes one ion.

Deduce the formula of one unit cell and confirm the formula unit to be NaCl.

HL end



Computer graphic of crystallized common salt, NaCl. Small spheres represent Na^+ ions and larger spheres represent Cl^-. The lattice is arranged so each Na^+ ion has six oppositely charged nearest neighbours and vice versa.

Preparing crystals and observing the lattice strcuture. Full details of how to carry out this experiment with a worksheet are available in the eBook.

SKILLS

The physical properties of ionic compounds reflect their lattice structures

Physical properties are those that can be examined without chemically altering the substance. Our knowledge of ionic bonds and lattice structure helps us explain some of these properties of ionic compounds.

Lattice enthalpy as a measure of the strength of the ionic bond

Tool 1, Inquiry 2 - What experimental data demonstrates the physical properties of ionic compounds?

Energy is needed to separate particles that are attracted to each other, and energy is released when the particles come together. For example, when one mole of sodium ions forms a lattice with one mole of chloride ions, 790 kJ of energy is given out. As the energy content of the chemical species decreases, this is expressed as a negative enthalpy change (ΔH) as discussed in Reactivity 1.2.

$$Na^+(g) + Cl^-(g) \rightarrow NaCl(s) \qquad (\Delta H = -790\,kJ\,mol^{-1})$$

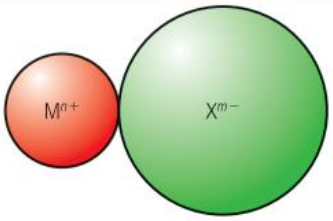
This energy output offsets the energy needed to form the ions and makes the formation of the compound energetically feasible.

The **lattice enthalpy** is defined as the enthalpy change for the reverse process. Energy is needed to separate the ions and the enthalpy change is positive.

$$NaCl(s) \rightarrow Na^+(g) + Cl^-(g) \qquad (\Delta H^\ominus_{lat} = +790 \text{ kJ mol})$$

This enthalpy change can be calculated from the **ionic model**, which assumes the crystal is made up of spherical ions which only interact by electrostatic forces.

HL



An ion pair of cation and anion. Note that both ions are spherical. This is one of the assumptions of the ionic model.

The energy needed to separate two ions is proportional to the product of the ionic charges and inversely proportional to the sum of the ionic radii. The calculation of the lattice enthalpy for one mole of ion pairs is complex, as many ion interactions need to be included, but has the following equation:

$$\Delta H^\ominus_{lat} = \frac{Knm}{(R^{M+} + R^{X-})}$$

- K is a constant for a structure that takes account of the many ion interactions and depends on the geometry of the lattice
- n and m are the magnitude of charges on the ions
- R^{M+} *and* R^{X-} are the ionic radii

HL end

The equation has the following consequences:

- An increase in the ionic charge increases the ionic attraction between the ions and increases the lattice enthalpy.
- An increase in the ionic radius of one of the ions decreases the attraction between the ions and decreases the lattice enthalpy.
- The lattice enthalpy is greater for ions with a larger charge density as they have a small radius and are highly charged.

Ionic compounds have high melting and boiling points and low volatility

The lattice structure results in ionic compounds being crystalline solids at room temperature. They have high melting and boiling points as a large amount of energy is needed to separate the ions in the lattice. This is illustrated in the table below which shows the melting points of four ionic compounds.

Ionic compound	Charge on metal ion	Charge on non-metal ion	Melting point / K
NaF	1+	1−	1266
Na_2O	1+	2−	1548*
MgF_2	2+	1−	1534
MgO	2+	2−	3125

* Na_2O sublimes and turns from a solid directly to a gas.

The melting points are generally higher when the ionic charge is greater due to the increased strength of the ionic bond. The melting points of magnesium fluoride and sodium oxide are both greater than sodium fluoride because doubling one of the ionic charges increases the attraction between the ions. Magnesium oxide has an even higher melting point because the ionic charge on both ions is double that of the ions in sodium fluoride.

The decrease in melting points of the sodium halides below is explained by the increase in the ionic radius of the halide ion down the group. The attraction between the ions decreases with increased ionic radii.

Ionic compound	Melting point / K
NaF	1266
NaCl	1074
NaBr	1020
NaI	934

Challenge yourself

4. We explained that the higher melting point of magnesium fluoride compared to sodium fluoride is due to the increased ionic charge of the Mg^{2+} ion. Explain why this explanation is incomplete.

5. The melting points of aluminium fluoride and oxide are shown in the table. Compare the melting points with the corresponding magnesium compounds and explain any differences.

Ionic compound	Charge on metal ion	Charge on non-metal ion	Melting point / K
AlF_3	3+	1−	1564
Al_2O_3	3+	2−	2345

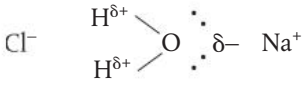
Ionic compounds have low volatility.

Volatility is a term used to describe the tendency of a substance to vaporize. Ionic compounds also generally have high boiling points and are non-volatile with low volatility.

Ionic liquids are efficient solvents with low volatility and are used increasingly as solvents in Green Chemistry for energy applications and industrial processes. They are usually made of organic cations and anions.

Ions compounds are generally soluble in water but not in non-polar liquids

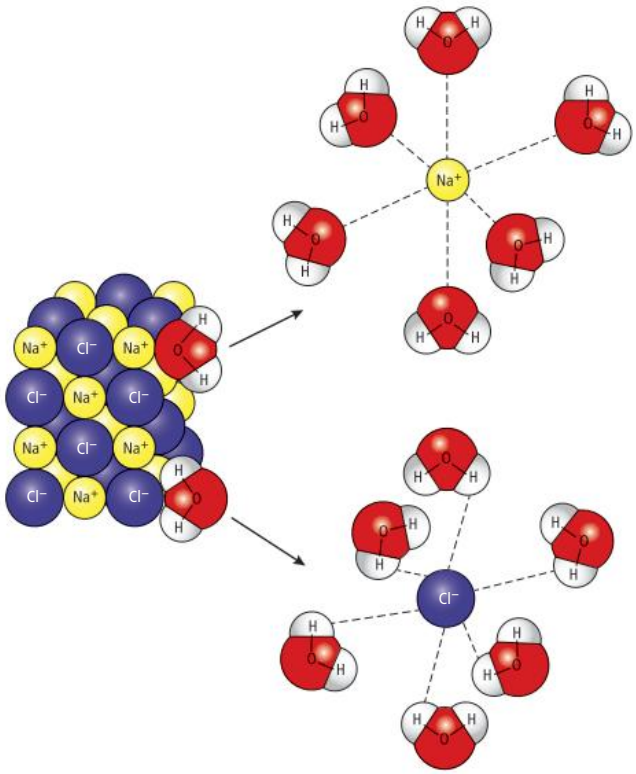
Solubility refers to the maximum amount of solute that can dissolve in a given volume of a solvent to form a solution. Sodium chloride, for example, has a high solubility as a relatively large amount readily dissolves in a given volume of water. As discussed in Structure 2.2, water is a polar molecule. There are small partial positive charges on the hydrogen atoms which attract chloride ions and small negative charges on the oxygen atoms which attract the sodium ions (Figure 8).



S2.1 Figure 8 The polar water molecule can attract cations and anions.

At the contact surface of a crystal, the attraction of the ions to the partial charges in the water molecules pulls the ions away from their lattice positions. As these ions separate from the lattice, they become surrounded by water molecules and are said to be **hydrated** and the solid dissolves (Figure 9). This change is represented with the use of state symbols as follows:

$$NaCl(s) \rightarrow NaCl(aq) \text{ or } NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$$



S2.1 Figure 9 Dissolving of NaCl in water involves the attraction of the polar water molecules to the ions in the NaCl lattice. This results in the hydration of the separated ions.

More generally, for solvents other than water, the solute ions are said to be **solvated** and an appropriate state symbol is used to identify the solvent used.

If the liquid is non-polar like oil or hexane, C_6H_{14}, there is no attraction between the liquid molecules and the ions. The ions remain in the lattice and the solid is insoluble. This leads to the general result that ionic compounds are soluble in polar liquids but insoluble in non-polar liquids. The pattern can be summarized as '*like dissolves like*'. As with many generalizations, you need to be aware of many important exceptions. Calcium carbonate, for example, is an ionic compound that is not soluble in water.

Ionic compounds are generally soluble in ionic or polar solvents but not soluble in non-polar solvents.



The White Cliffs of Dover, UK, are made of calcium carbonate: an ionic compound which is insoluble in water. The surrounding seawater contains many dissolved ionic compounds such as sodium chloride.

Conductivity of an ionic compound and its aqueous solution. Full details of how to carry out this experiment with a worksheet are available in the eBook.

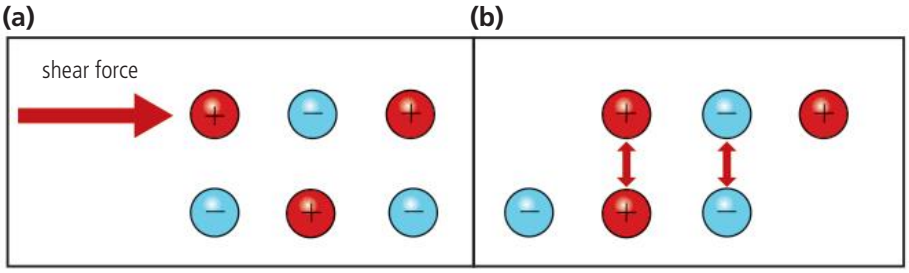
Ionic compounds have high electrical conductivity in the liquid and aqueous states

The ability of an ionic compound to conduct electricity depends on whether the ions are able to move. Ionic compounds are not able to conduct electricity in the solid state because the ions are fixed within the lattice but they can conduct electricity in the liquid or aqueous states where the ions are mobile.

'Water, water, every where, Nor any drop to drink.' (From the *'The Rime of the Ancient Mariner'* by S.T. Coleridge). Nearly 98% of water on Earth is seawater, which contains dissolved ions and so is unfit for drinking and many industrial processes. The solubility of ionic compounds in water has global consequences.

Ionic compounds are generally brittle

Ionic compounds are usually brittle, as the crystal tends to shatter when a shear force is applied. The force displaces some ions within the lattice, which results in ions of the same charge being positioned alongside each other. The repulsive forces between the ions then cause the lattice to split.



Ionic compounds are brittle. (a) A strong shear force is applied to a layer of ions. (b) Ions of the same charge are forced to be together and the top layer repels the bottom layer and the structure falls apart.

Ionic compounds do not conduct electricity in the solid state but do conduct when molten or in aqueous solution.

Nature of Science

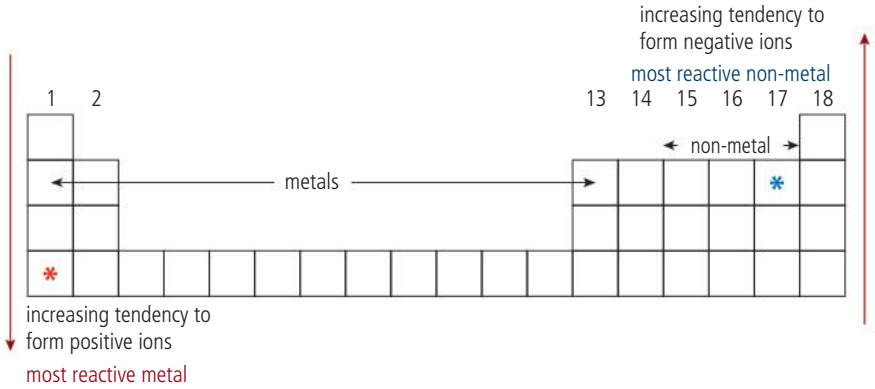
The ionic model leads to some predictions about the physical properties of ionic compounds, which can be tested by observation and experiment. This is central to the scientific process. The general patterns discussed here on volatility, solubility, and conductivity support the lattice model. There are however some exceptions, which need to be explained. The melting point of aluminium oxide, for example, is not as high as predicted from the ionic model and calcium carbonate is insoluble in water. The model is limited and incomplete. Other types of bonding need to be included to account for these unexpected properties.

The high melting point of ionic compounds is an economic consideration in many industrial processes, such as the electrolysis of molten aluminium oxide used to extract aluminium as discussed in Reactivity 3.2. It is very expensive to maintain the high temperatures needed.

Some ionic compounds deviate significantly from the ionic model

When two elements react to form an ionic compound, they show *very different tendencies to lose or gain electrons.* As discussed, this is related to the position of the elements in the periodic table. Metals on the bottom left of the table lose electrons most easily, while non-metals on the top right gain electrons most easily. Caesium and fluorine react together to form the compound with the most ionic character and group 1 halides generally show typical ionic properties. The ionic character of the other halides, however, decreases across a period.

Caesium fluoride is used instead of francium fluoride as it has been estimated that at any one time there are only 17 francium atoms on the Earth.



The pairs of elements that react most readily to form ionic compounds are metals on the bottom left of the periodic table and non-metals on the top right, indicated here by asterisks.

Period 3 chlorides are less ionic across the period

The melting points and electrical conductivity of the period 3 chlorides are summarized in the table below.

Formula of chloride	NaCl(s)	$MgCl_2$(s)	$AlCl_3$(s)/ Al_2Cl_6(g)	$SiCl_4$(l)	PCl_5(s)	SCl_2(l)	Cl_2(g)
Melting point / K	1074	987	463	203	435	195	170
Electrical conductivity in molten state	high	high	poor	none	none	none	none

The transition from ionic to covalent character can be seen in the data. Sodium chloride is a typical ionic compound whereas aluminium chloride is generally considered to be covalent, as illustrated by its low conductivity in the liquid state. The move from ionic to covalent is also seen in the decrease in melting points. Aluminium chloride has a layer structure in the solid state but exists as a molecular dimer, Al_2Cl_6, in the liquid and gaseous states. The chlorides of the later elements are molecular covalent and have very low melting points, as discussed more fully in Structure 3.1.

The difference between theoretical lattice enthalpies based on the ionic model and experimental values can also be used to measure the covalent character of chlorides.

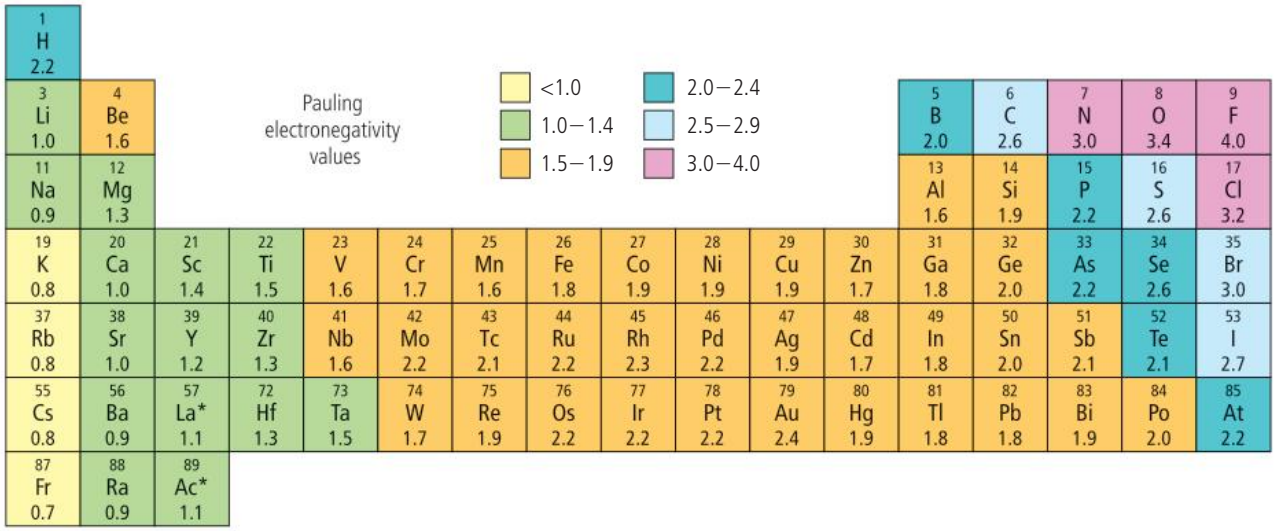
TOK

The periodic table is a diagrammatical representation of general patterns in chemistry. Does it provide an explanation or a description of the ionic character of different compounds? Is the relationship between description and explanations the same in all areas of knowledge?

Structure 3.1 – How can lattice enthalpies and the bonding continuum explain the trend in melting points of metal chlorides across period 3?

Ionic character and electronegativity

The tendency of two elements to form an ionic bond can also be approached from the opposite perspective. How does the bonding deviate from the covalent model? How are the bonding pair of electrons shared between the two bonding elements? If they are shared equally, it is a covalent bond, if not, it is a polar covalent bond. An ionic bond between M and X can be considered as an extreme polar bond. The bonding electrons are not shared but both are located on the same X atom. As explained in Structure 2.2, electronegativity is a measure of the ability of an atom to attract electrons. This can be quantified using the Pauling scale of values given in Section 9 of the data booklet and summarized here.



Periodic trends in electronegativity values show an increase along a period and up a group.

CsF is generally considered to be 100% ionic with an electronegativity difference ($\Delta\chi_P$) of 3.2. The % ionic character can be approximated by the formula:

$$\%\ \text{ionic character} \approx \frac{\Delta\chi_P}{3.2}$$

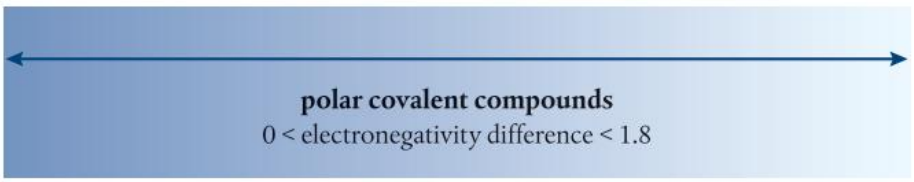
$\Delta\chi_P$ = difference in electronegativity

A difference of electronegativity of 1.6 corresponds to 50% ionic character. A difference of 1.8 is often taken as corresponding to predominantly ionic.

Clearly the ionic model gives an incomplete picture of the bonding in many substances, and we will consider other types of bonding in the next chapters. We will see that the distinction between ionic and covalent bonding is not black and white but is best described as a **bonding continuum** with all intermediate types possible (Figure 10).

ionic compounds
reactive metal + reactive non-metal
electronegativity difference > 1.8

covalent compounds
two non-metals
electronegativity difference << 1.8



S2.1 Figure 10 The bonding continuum.

A more complete method of determining the bonding character of a compound is to use both the difference and average values of the electronegativities. As discussed in Structure 2.4, the nature of the bonding can be identified from the Triangular bonding diagram in Section 17 of the data booklet.

Worked example

Which pair of elements is most likely to form an ionic bond?

A B and F **B** Si and O **C** N and Cl **D** K and Cl

Solution

Consider the difference in electronegativity of each pair:

A 2.0 and 4.0 $\Delta\chi_P = 2.0$ **B** 1.9 and 3.4 $\Delta\chi_P = 1.5$ **C** 3.0 and 3.2 $\Delta\chi_P = 0.2$ **D** 0.8 and 3.2 $\Delta\chi_P = 2.4$

D has the greatest difference, so the compound KCl is the most ionic.

Exercise

Q9. Describe the bonding in ammonium nitrate.

Q10. Which fluoride is the most ionic?

A NaF **B** CsF **C** MgF_2 **D** BaF_2

Q11. You are given two white solids and told that only one of them is an ionic compound. Describe three tests you could carry out to determine which is the ionic compound.

Q12. Element **E** is in group 1 of the periodic table and element **G** is in group 16. E and G are not the symbols for the elements.

(a) Deduce the formula of the compound formed between E and G.

A EG **B** EG_6 **C** EG_2 **D** E_2G

(b) Identify the nature of the bonding in the compound formed between E and G.

A ionic **B** covalent **C** dative covalent **D** metallic.

(c) Describe the electrical conductivity of the compound formed between E and G.

A conducts when solid and liquid
B conducts when solid but not when liquid
C conducts when liquid but not when solid
D does not conduct when solid or liquid

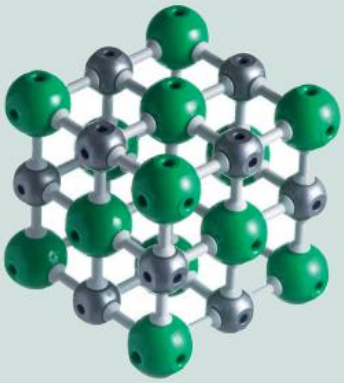
Q13. HL Which one of the following compounds would be expected to have the highest lattice enthalpy?

A Na_2O **B** MgO **C** CaO **D** KCl

The extent of ionic character is determined by the difference in electronegativity between the bonded elements.

Nature of Science

Models are simplifications of complex systems and can be physical representations. All models have limitations that need to be considered in their application. A model of the lattice structure of NaCl, with sodium ions shown in green and chloride ions shown in grey.



Challenge yourself

6. Discuss the usefulness of the model above in describing the real structure of sodium chloride. Compare it with the models pictured earlier in the chapter and consider which you think may be the best model.

Guiding Question revisited

What determines the ionic nature and properties of a compound?

In this chapter we have developed an ionic model to explain the structure and properties of many compounds formed between metals and non-metals. This model is particularly effective in describing the properties of compounds formed between elements at different sides of the periodic table: the group 1 halides. The model does however have some limitations and other compounds show ionic properties to varying degrees as the bonding shows covalent character.

- An ion is a charged particle formed when atoms lose or gain electrons.
- Metals lose electrons to form positive ions (cations); non-metals gain electrons to form negative ions (anions).
- The number of charges on an ion is equal to the number of electrons lost (positive ion) or gained (negative ion) by an atom.
- The charge on an ion can usually be predicted from the group of the element in the periodic table; transition metal elements can form ions with different charges.
- The formula of common molecular ions can be related to the molecular formula of common acids.
- Ionic lattices consist of ions held together by ionic bonds which are electrostatic forces of attraction.

- Ionic compounds are electrically neutral as the total number of positive charges is balanced by the total number of negative charges.
- The formula of the compound is expressed as its simplest ratio, e.g. the ions X^{m+} and Y^{n-} will form the compound X_nY_m. The unit formula of an ionic compound is also the empirical formula.
- HL In the ionic lattice, each ion is surrounded by a fixed number of ions of the opposite charge, known as the coordination number.
- Ionic compounds usually have high melting and boiling points, and are more soluble in **polar** solvents such as water than in **non-polar** solvents.
- Positive ions are attracted to the O atom in a water molecule, which has a partial negative charge. Negative ions are attracted to the H atoms, which have a partial positive charge.
- Ions are not free to move in the solid state, so ionic compounds do not conduct electricity in the solid state. They can, however, conduct electricity when molten or in aqueous solution as the ions are free to move.
- The difference in electronegativities of two atoms gives an indication of the ionic character of the compound.
- Most ionic compounds are formed between metals on the bottom left of the periodic table and non-metals on the top right, excluding the noble gases.
- Ionic and covalent bonding are two extremes as many substances show intermediate character. The nature of the bonding can be related to bond polarity and the difference in electronegativity values ($\Delta\chi_P$) of the bonded atoms.

Practice questions

1. Which element does not generally form ions during chemical reactions?

A aluminium **B** calcium **C** carbon **D** iodine

2. Which statement is true for most ionic compounds?

I. They contain metal and non-metal elements.

II. They conduct electricity in the solid state.

III. They have high melting and boiling points.

A I and II only **B** I and III only **C** II and III only **D** I, II and III

3. Which electron transfer describes the reaction between aluminium and oxygen?

$$2Al(s) + 3O_2(g) \rightarrow Al_2O_3(s)$$

A Each Al atom loses two electrons. **B** Each Al atom loses three electrons.

C Each O atom loses two electrons. **D** Each O atom loses three electrons.

4. Three substances, **X**, **Y** and **Z** have the physical properties shown.

Substance	**X**	**Y**	**Z**
Melting point / °C	747	1610	2614
Boiling point / °C	1390	2230	2850
Electrical conductivity of liquid state	high	poor	high

Identify X, Y and Z.

	X	Y	Z
A	CaO	NaBr	SiO_2
B	CaO	SiO_2	NaBr
C	NaBr	CaO	SiO_2
D	NaBr	SiO_2	CaO

5. What is the formula of barium phosphate?

A Ba_3P_2 **B** $Ba_3(PO_4)_2$ **C** Ba_2P_3 **D** $Ba_2(PO_4)_3$

6. Which substance shows the most ionic character?

	Electrical conductivity in aqueous solution	Solubility in heptane	Volatility
A	low	low	high
B	low	high	low
C	high	low	low
D	high	low	high

7. What are the IUPAC names for CuBr and CuO?

A copper bromide and copper oxide

B copper(I) bromide and copper(I) oxide

C copper(II) bromide and copper(I) oxide

D copper(I) bromide and copper(II) oxide

8. Which of the following substances show predominantly ionic character?

I. magnesium chloride II. iron(II) chloride III. silicon tetrachloride

A I and II only **B** I and III only **C** II and III only **D** I, II and III

9. Explain why the melting point of magnesium oxide is higher than barium sulfide? (3)

(Total 3 marks)

10. Iron forms many compounds with oxygen.

(a) Describe the bonding in Fe_2O_3. (2)

(b) State the full electron configuration of the bonding species. (2)

(c) The compound Fe_2O_3 was previously known as ferric oxide. State the IUPAC name for the compound. (1)

(d) Explain why iron(III) oxide can demonstrate brittleness. (2)

(e) Magnetite, Fe_3O_4, contains an additional ion of iron. Identify the ion. (1)

(Total 8 marks)

11. **(a)** Describe the structure and bonding in potassium sulfide at room temperature. (2)

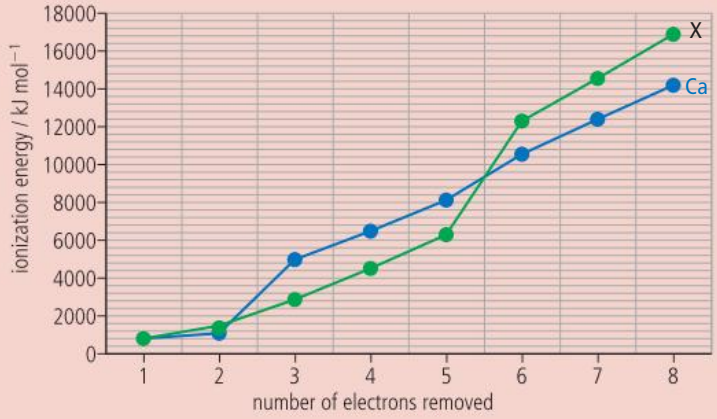
(b) State the full electron configuration of the bonding species. (2)

(c) Compare the size of the bonding species. (2)

(d) Describe and explain the electrical conductivity of solid and molten potassium sulfide. (2)

(Total 8 marks)

12. Successive ionization energies of calcium and a transition element **X** are shown.



(a) Deduce the maximum oxidation state shown by X and explain your answer. (2)

(b) Deduce the formula of the oxide of X in this oxidation state and explain why it is unlikely to be ionic. (2)

(c) Identify the ions X forms in its ionic compounds. (1)

(Total 5 marks)

13. HL Describe the bonding in sodium nitrate. (2)

(Total 2 marks)



STRUCTURE

2.2 The covalent model



Stephanie Louise Kwolek (1923–2014), US chemist, holding a molecular model. Kwolek spent 40 years working as a research chemist at the DuPont Company. In 1965, she developed the first in a family of liquid crystal polymers that provided the basis for the Kevlar™ brand fibre. Kwolek was inducted into the National Inventors Hall of Fame in 1995, and was awarded the DuPont Company's Lavoisier Medal (1995) and the National Medal of Technology (1996).

Guiding Question

What determines the covalent nature and properties of a substance?

The term 'covalence' relates to the idea that atoms can combine by sharing pairs of valence electrons. This concept dates back to the early 20th century and the work of US chemist Gilbert Lewis, who first proposed the idea of the **covalent bond**. The notation he used to represent the sharing of electrons in a chemical structure is called a **Lewis formula**, in which pairs of electrons are arranged so that each atom gains a full valence shell. The tendency of atoms to gain a full valence shell is known as the **octet rule** because in most instances, eight electrons are required.

Building upon these fundamental understandings, this chapter will explore how Lewis formulas can be used to predict the shapes of molecules by considering the repulsion between regions of electron density, known as **electron domains**, around a central atom. By considering the strength of attraction between individual atoms and shared pairs of electrons, we can also identify when there will be unequal charge distribution, known as a **bond dipole**, in a covalent bond. This, combined with our knowledge of **molecular geometries**, can explain the relative polarity of molecules, which plays a large part in determining the strength of **intermolecular forces** and the resultant physical and chemical properties. For some covalent substances, such as diamond and graphene, we will see distinct sets of properties which can be explained by their **network structure**.

HL In cases where experimental data do not match predictions in terms of bond length, bond strength and chemical reactivity, we will explore concepts including **resonance** and **hybridization** to better explain our findings. Benzene, C_6H_6, is an interesting historical example where these concepts provided grounds to rethink August Kekulé's proposed model.

In the context of models of bonding and structure, we should recognize the position of the covalent model on a continuum with other models of bonding to best explain their observed properties. As in all areas of science, it will also be important to understand the limitations of, and exceptions to, the various rules, models and theories that we will apply.

Structure 2.2.1 – Covalent bonding, the octet rule and Lewis formulas

Structure 2.2.1 – A covalent bond is formed by the electrostatic attraction between a shared pair of electrons and the positively charged nuclei.

The octet rule refers to the tendency of atoms to gain a valence shell with a total of eight electrons.

Deduce the Lewis formula of molecules and ions for up to four electron pairs on each atom.

Lewis formulas (also known as electron dot or Lewis structures) show all the valence electrons (bonding and non-bonding pairs) in a covalently bonded species.

Electron pairs in a Lewis formula can be shown as dots, crosses and/or dashes.

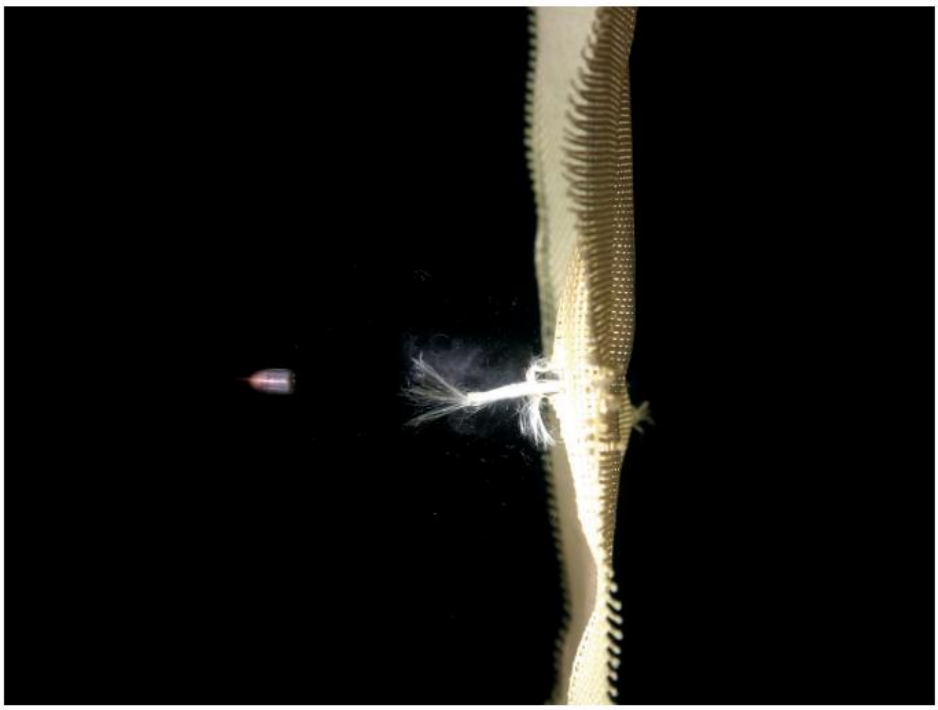
Molecules with atoms having fewer than an octet of electrons should be covered.

Organic and inorganic examples should be used.

Nature of Science – What are some of the limitations of the octet rule?

Structure 1.3 – Why do noble gases form covalent bonds less readily than other elements?

Structure 2.1 – Why do ionic bonds only form between different elements while covalent bonds can form between atoms of the same element?



A .22 calibre bullet hitting Kevlar™. The bullet is travelling at 220 metres per second (660 feet per second). This image shows the collision of the bullet and Kevlar™ at 1/1 000 000th of a second. Kevlar™, a synthetic fibre comprised of large covalent molecules, has a high tensile strength-to-weight ratio, five times stronger than steel, leading to applications in fields such as ballistic resistant materials, industrial conveyor belts and automotive components.

A covalent bond is the electrostatic attraction between a shared pair of electrons and the positively charged nuclei. A group of atoms held together by covalent bonds forms a molecule.

A covalent bond forms by atoms sharing electrons

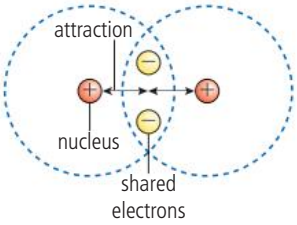
When atoms of two non-metals react together, each is seeking to gain valence electrons in order to achieve the stable electron structure of a noble gas. By sharing an electron pair, they are effectively each able to achieve this. The shared pair of electrons is concentrated in the region between the two nuclei and is attracted to them both. The electrostatic attraction between the shared pair of electrons and the positively charged nuclei holds the atoms together and is known as a covalent bond (Figure 1).

For example, two hydrogen atoms form a covalent bond as follows.

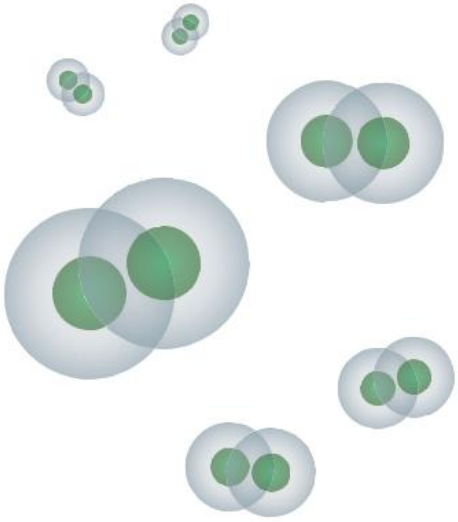
$$H^{\times} + {}^{\bullet}H \longrightarrow H^{\times}{}_{\bullet}H$$

two hydrogen atoms (2H) → a molecule of hydrogen (H_2)

Note that in the molecule H_2, each hydrogen atom has a share of two electrons so it has gained the stability of the electron arrangement of the noble gas helium, He.

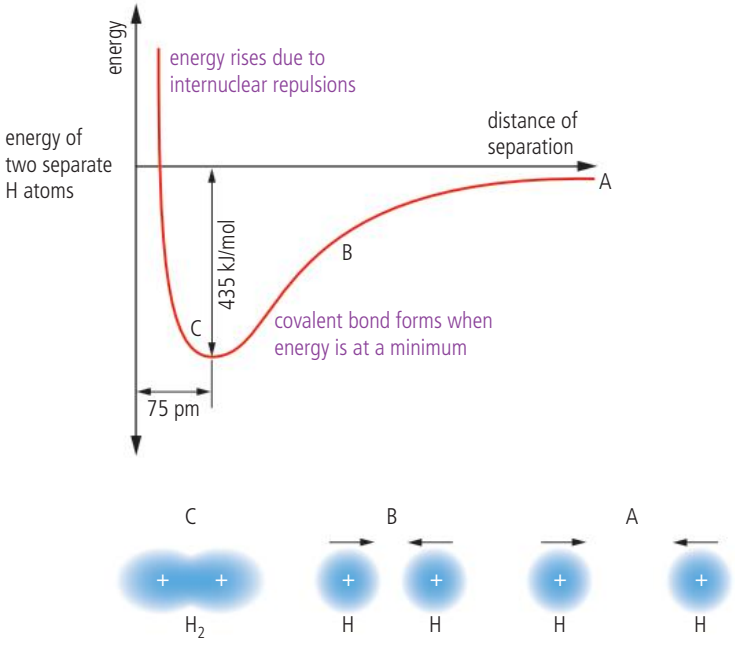


S2.2 Figure 1 In a covalent bond, the nuclei of both atoms are attracted to the shared pair of electrons.



Hydrogen molecules. Each molecule consists of two hydrogen atoms bonded covalently.

The system containing these two hydrogen atoms will be stabilized when the forces of attraction between the nuclei and shared electrons are balanced by the forces of repulsion between the two nuclei. This holds the atoms at a fixed distance apart. Figure 2 shows how the covalent bond forms at this point of lowest energy as two hydrogen atoms approach each other and their electron density shifts.

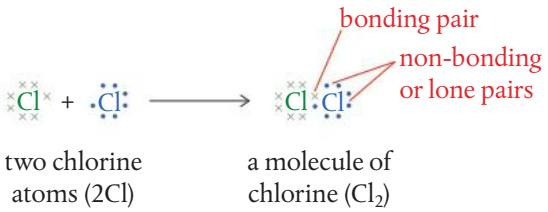


S2.2 Figure 2 When two hydrogen atoms form a covalent bond, the distance between them corresponds to the lowest energy. The letters A, B and C show the correspondence between shifts in electron density and the distance apart of the atoms.

The octet rule can be used to predict stable arrangements of atoms in covalent bonding

Similarly, two chlorine atoms react together to form a chlorine molecule in which both atoms have gained a share of eight electrons in their outer shells (the electron arrangement of argon, Ar). This tendency of atoms to gain a valence shell with a total of eight electrons is referred to as the octet rule. The diagram below only shows the outer electrons, not the inner full shells, as the outer electrons are the only electrons that take part in bonding.

The octet rule refers to the tendency of atoms to gain a valence shell with a total of 8 electrons.



Note that the octet rule should be considered as a guideline only, as there are exceptions – notably hydrogen, the transition elements, radicals, and atoms that form an incomplete or expanded octet.

It is sometimes useful to use different symbols or colours to distinguish between the electrons of different atoms, as you see here. However, in reality all electrons are the same so it is not always necessary to do this. What is crucial is to have the correct number of valence electrons in the atoms.

Note that in the chlorine molecule, each atom has three pairs of electrons that are not involved in forming the bond. These are known as **non-bonding pairs**, or **lone pairs**, and they play an important role in determining the shape of more complex molecules, as we will see later.

Structure 2.1 – Why do ionic bonds only form between different elements while covalent bonds can form between atoms of the same element?

The ability of two identical atoms to form a covalent bond is due to the similar strength with which they attract valence electrons. In contrast, ionic bonds can only form between elements with significant differences in their attraction to valence electrons. This is why we see the formation of ions in a reaction between metal and non-metal atoms instead of the sharing of electrons.

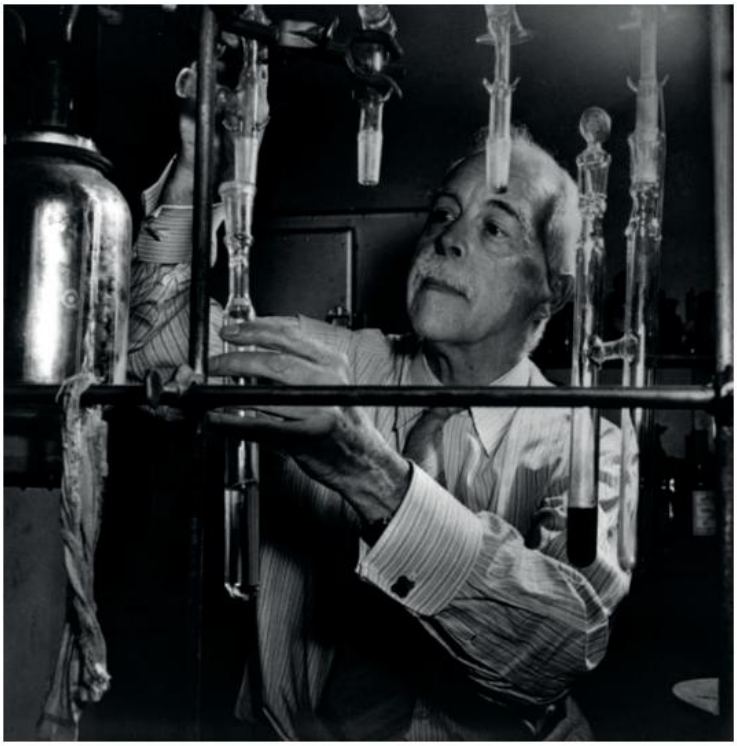
Hydrogen and chlorine also react together to form a molecule of hydrogen chloride, HCl, which has the structure shown below. Note that the formation of the covalent bond enables both H and Cl to gain a stable outer shell.



Structure 1.3 – Why do noble gases form covalent bonds less readily than other elements?

The octet rule can provide a useful insight into the chemical properties of the noble gases. With the exception of helium, the atoms of all elements in group 18 have a complete octet without the need to share electrons. This is why they display low levels of chemical reactivity and do not tend to form covalent bonds with other elements.

Lewis formulas show all of the valence electrons in a covalently bonded species



American chemist Gilbert Lewis (1875–1946).

Gilbert Lewis (1875–1946), responsible for the electron-pair theory of the covalent bond, was nominated 41 times for the Nobel Prize in Chemistry without winning. In 1946, he was found dead in his laboratory where he had been working with the toxic compound hydrogen cyanide.

When describing the structure of covalent molecules, the most convenient method is known as a Lewis formula. This uses a simple notation of dots, crosses or a dash to represent each pair of electrons in the outer energy level, or valence shell, of all the atoms in the molecule. It can be derived as follows.

1. Calculate the total number of valence electrons in the molecule by multiplying the number of valence electrons of each element by the number of atoms of the element in the formula and totalling these.
2. Identify the skeletal structure of the molecule by drawing a pair of crosses, a pair of dots, or a single dash to show one electron pair between the central atom and each of the outer atoms.
3. Beginning with the outer atoms and then the central atom, add electron pairs until each has completed the octet rule with 8 valence electrons (except hydrogen, which must have 2 valence electrons, and the other exceptions noted later in the chapter).
4. Check that the total number of electrons in your finished Lewis formula is equal to your calculation in the first step.

Note that the terms 'valence electrons' and 'outer shell electrons' are used interchangeably. They both refer to the electrons that take part in bonding.

Note: If there are not enough electrons to complete the octet on each atom, we can use non-bonding pairs of electrons to form double and triple covalent bonds as described in the next section.

We can represent electron pairs using dots, crosses, a combination of dots and crosses, or a dash. Use whichever notation you prefer, but be prepared to recognize all versions. The important thing is to be clear and consistent, and to avoid vague and scattered dots.

Worked example

Draw the Lewis formula for the molecule CCl_4.

Solution

Note that in Lewis formulas, as in the examples on page 178, only the valence electrons are shown, as these are the only ones that take part in bonding.

1. Total number of valence electrons
$= (4 \times 1) + (7 \times 4)$
$= 32$

2. Skeletal structure



3. Completed Lewis formula


(32 electrons)

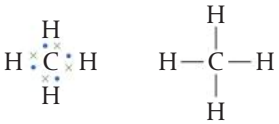
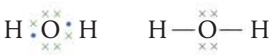
4. Check the total number of electrons.

The 32 electrons in the Lewis formula correctly match the calculated number in step 1.

There are several different ways of drawing Lewis formulas, and some alternative acceptable forms are shown below.



This table shows some examples of molecules with their Lewis formulas.

Molecule	Total number of valence electrons	Lewis formula
CH_4	$4 + (1 \times 4) = 8$	
NH_3	$5 + (1 \times 3) = 8$	
H_2O	$(1 \times 2) + 6 = 8$	

When drawing the Lewis formula of ions, note that you must:

- calculate valence electrons as above and then add one electron for each negative charge and subtract one electron for each positive charge;
- put the Lewis formula in a square bracket with the charge shown outside.

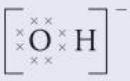
Worked example

Draw the Lewis formulas for:

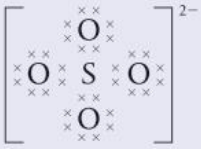
(i) OH^- (ii) SO_4^{2-}

Solution

(i) valence electrons = 6 + 1 + 1 = 8



(ii) valence electrons = (6 × 1) + (6 × 4) + 2 = 32



When drawing the Lewis formula of an ion, make sure you remember to put a square bracket around the structure with the charge shown clearly outside the bracket.

The octet rule is not always followed

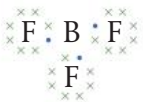
There are a few molecules that are exceptions to the octet rule. Small atoms such as beryllium (Be) and boron (B) form stable molecules in which the central atom has fewer than eight electrons in its valence shell. This is known as an **incomplete octet**. For example, the structures of $BeCl_2$ and BF_3 are shown below.

Common examples of elements that can form an incomplete octet are hydrogen, beryllium, boron and aluminium.

$BeCl_2$ valence electrons = 2 + (7 × 2) = 16



BF_3 valence electrons = 3 + (7 × 3) = 24



These examples demonstrate a limitation of the octet rule when dealing with small central atoms with a limited number of valence electrons. The small size of beryllium and boron, for example, limits the number of atoms that can get close enough to share the required number of electrons for a complete octet.

HL We will also see examples where a central atom can have more than 8 valence electrons, known as an 'expanded' octet, by using unoccupied d-orbitals to form additional covalent bonds. Formal charge, seen later in this chapter, will provide greater insight into many of the exceptions to the octet rule.

Nature of Science – What are some of the limitations of the octet rule?

Nature of Science

Scientific *rules* and *principles* are descriptive statements that are generally accurate in predicting the behaviour of matter but will likely have exceptions. For this reason, it is often as important to understand the exceptions as it is to know the rules or principles themselves.

Exercise

Q1. Which is the best definition of a covalent bond?

A the attraction between positively charged ions and a shared pair of electrons

B the attraction between pairs of shared electrons

C the attraction between positively charged nuclei and a shared pair of electrons

D the attraction between a pair of positively charged nuclei

Q2. Which best describes the octet rule?

A the tendency of atoms to gain a valence shell with a total of 8 electrons

B the tendency of atoms to lose 8 electrons

C the tendency of atoms to gain 8 electrons

D the tendency of atoms to form bonds with 8 other atoms

Q3. Draw the Lewis formulas of the following molecules:

(a) HF **(b)** CF_3Cl **(c)** PCl_3 **(d)** OF_2

(e) $SeCl_2$ **(f)** C_2H_6 **(g)** N_2H_4

Q4. How many valence electrons are in the following molecules?

(a) $BeCl_2$ **(b)** BCl_3 **(c)** CCl_4

(d) PH_3 **(e)** SCl_2 **(f)** NCl_3

Q5. Draw Lewis formulas of the following ions:

(a) NH_4^+ **(b)** H_3O^+ **(c)** HS^-

Structure 2.2.2 – Single, double and triple covalent bonds

Structure 2.2.2 – Single, double and triple bonds involve one, two and three shared pairs of electrons respectively. Explain the relationship between the number of bonds, bond length and bond strength.	
	Reactivity 2.2 – How does the presence of double and triple bonds in molecules influence their reactivity?

Atoms can share more than one pair of electrons to form multiple bonds

Sometimes it seems there are not enough electrons to achieve octets on all the atoms in a molecule. In these cases, the atoms will have to share more than one electron pair, in other words, form a multiple bond. A **double bond** forms when two electron pairs, a total of four electrons, are shared; a **triple bond** forms when three electron pairs, a total of six electrons, are shared.

Worked example

Draw the Lewis formula for the molecule O_2.

Solution

Following the flow chart steps on page 179:

1. Total number of valence electrons
   $= (6 \times 2) = 12$
2. Skeletal structure



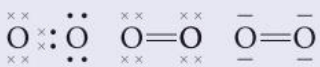
3. Add electron pairs until each atom has completed the octet rule



   At this point, you will notice that in order to complete the octet on both atoms, we need to use a non-bonding pair of electrons from the oxygen on the left to form a second shared pair between the atoms. This is a double bond.
4. Check the total number of electrons.

   The 12 electrons in the Lewis formula correctly match the calculated number in step 1.

   There are several different ways of drawing Lewis formulas, and some alternative acceptable forms are shown below.



Similar to oxygen, the most abundant gas in air, nitrogen, exists as diatomic molecules but requires a triple covalent bond in order to complete the octet of both atoms:

 or  triple bond

The triple bond in nitrogen (N_2) is difficult to break, making the molecule very stable. This is why, although nitrogen makes up about 78% of the atmosphere, it does not readily take part in chemical reactions. For example, although the element is essential for all life forms, N_2 from the atmosphere is only rarely used directly by organisms as their source of nitrogen for synthesis reactions.

Reactivity 2.2 – How does the presence of double and triple bonds in molecules influence their reactivity?

This table shows some examples of Lewis formulas of molecules with multiple bonds.

Molecule	Total number of valence electrons	Lewis formula
CO_2	$4 + (6 \times 2) = 16$	
HCN	$1 + 4 + 5 = 10$	

As shown above, it is often convenient to use a line to represent a shared pair of electrons, two lines to represent a double bond, and three lines to represent a triple bond.

HL Despite this notation, we learn in Structure 2.2.15 that multiple bonds contain unequal bonds. Double bonds contain one sigma bond and one pi bond, while triple bonds contain one sigma bond and two pi bonds.

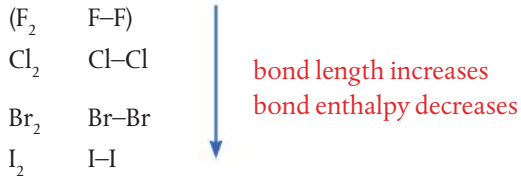
Short bonds are strong bonds

Every covalent bond is characterized by two values.

Data on both these values are given in Sections 10 and 11 of the data booklet.

- **Bond length**: a measure of the distance between the two bonded nuclei;
- **Bond strength**: usually described in terms of bond enthalpy, which is discussed in Reactivity 1.2, and is effectively a measure of the energy required to break the bond.

Since atomic radius increases as we go down a group, we would expect the atoms to form molecules with longer bonds.

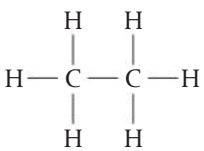
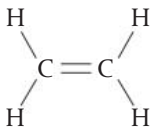


As a result, the shared electron pair is further from the pull of the nuclei in the larger molecules, and so the bond would be expected to be weaker. Data on group 17 elements, which exist as diatomic molecules, mostly confirm these trends.

Challenge yourself

1. Fluorine, F_2, is shown in brackets because a close look at its bond enthalpy data shows that it is an outlier in the trends described here. What explanation might account for this?

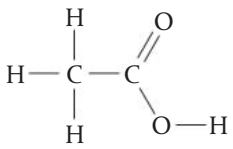
Multiple bonds have a greater number of shared electrons and so have a stronger force of electrostatic attraction to the bonded nuclei. This means there is a greater pulling power between the atoms, bringing them closer together, resulting in bonds that are shorter and stronger than single bonds. We can see this by comparing different bonds between the same atoms, such as in the hydrocarbons.

Hydrocarbon	C_2H_6	C_2H_4	C_2H_2
Structural formula			
Bond between carbon atoms	single	double	triple
Bond length / pm	154	134	120
Bond enthalpy / kJ mol^{-1}	346	614	839

The data confirm that triple bonds are shorter and stronger than double bonds, which are shorter and stronger than single bonds.

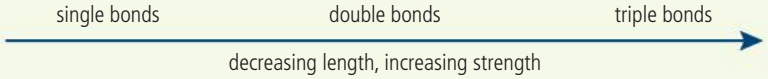
HL Note though that the double bond is not twice as strong as the single bond, due to the fact that it is made up of two different bonds – one sigma bond and one pi bond that is weaker. These bonds are described more fully on pages 237 and 238.

Also, we can compare two different carbon–oxygen bonds within the molecule of ethanoic acid, CH_3COOH.



	C–O	C=O
Bond length / pm	143	122
Bond enthalpy / kJ mol^{-1}	358	804





Exercise

Q6. Draw the Lewis formulas of the following molecules:

(a) C_2H_6 **(b)** C_2H_4 **(c)** C_2H_2

Q7. Suggest which of the following molecules would have the shortest carbon–carbon bond length.

A C_2H_6 **B** C_2H_4 **C** C_2H_2

Q8. Draw Lewis formulas of the following ions:

(a) NO_3^- **(b)** NO^+ **(c)** NO_2^-

Q9. Which of the following molecules contains the shortest bond between carbon and oxygen?

A CO_2 **B** H_3COCH_3 **C** CO **D** CH_3COOH

Q10. Which of the following best describes the general trend in bond length and bond strength?

	Bond strength	Bond length
A	triple > double > single	single > double > triple
B	triple > double > single	triple > double > single
C	single > double > triple	triple > double > single
D	single > double > triple	triple > double > single

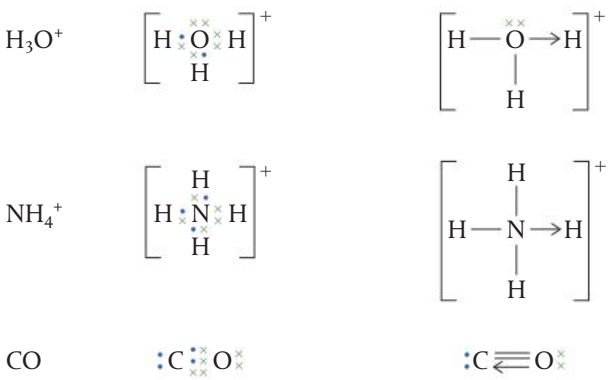
Structure 2.2.3 – Coordination bonds

Structure 2.2.3 – A coordination bond is a covalent bond in which both the electrons of the shared pair originate from the same atom. Identify coordination bonds in compounds.	
HL Include coverage of transition element complexes.	HL Reactivity 3.4 – Why do Lewis acid–base reactions lead to the formation of coordination bonds?

A coordination bond is a covalent bond in which both shared electrons originate from the same atom

The examples so far involve covalent bonds where each bonded atom contributes one electron to the shared pair. However, sometimes the bond forms by *both* the electrons in the pair originating from the same atom. This means that the other atom accepts and gains a share in a donated electron pair. Such bonds are called **coordination bonds**. An arrow on the head of the bond is sometimes used to show a coordination bond, with the direction indicating the origin of the electrons.

For example:



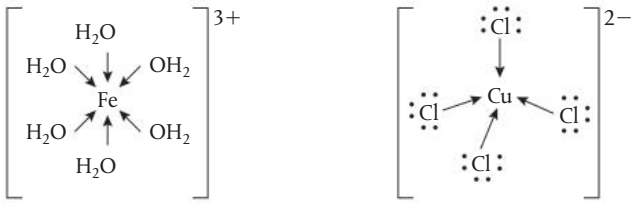
A coordination bond is a covalent bond in which both the electrons of the shared pair originate from the same atom.

Note that in CO, the triple bond consists of two bonds that involve sharing an electron from each atom, and the third bond is a coordination bond where both electrons come from the oxygen. The three bonds are nonetheless identical to each other. This illustrates an important point about coordination bonds: once they are formed, they are no different from other covalent bonds.

HL

As shown in Reactivity 3.4, species that can accept or donate a pair of electrons in a chemical reaction are known as **Lewis acids** and **Lewis bases** respectively. A reaction between these two species results in a coordination bond. A good example of a Lewis acid–base reaction is the formation of a **transition element complex** in which an aqueous transition element ion (the Lewis acid) accepts electron pairs from another reactant in a solution (the Lewis base). Bases include water molecules, H_2O, or aqueous ions, such as the chloride ion, Cl^-, that are able to donate a non-bonding pair of electrons to form a coordination bond. When they are bonded in the complex, they are known as **ligands**.

HL Reactivity 3.4 – Why do Lewis acid–base reactions lead to the formation of coordination bonds?



Structure of $[Fe(H_2O)_6]^{3+}$ and $[CuCl_4]^{2-}$ complex ions. In both structures, the Lewis bases, known as ligands, donate a pair of electrons to form coordination bonds, shown as arrows, with a transition metal ion.

Note that transition element ions are able to behave as Lewis acids by using orbitals in an unoccupied energy level. The Fe^{3+} ion, for example, can use empty 4s and 4p orbitals to accept pairs of electrons from Lewis bases.

HL end



Tetrachlorocopper(II) ion solution, $[CuCl_4]^{2-}$ (aq). The Lewis acid–base reaction between transition metal ions and ligands often results in the formation of coloured solutions.

SKILLS

Qualitative observation of coordination bond formations.

Exercise

Q11. Which best describes a coordination bond?

A A covalent bond containing a shared pair of electrons.

B A covalent bond in which each atom shares one electron.

C A covalent bond involving a transition metal.

D A covalent bond in which both the electrons of the shared pair originate from the same atom.

Q12. Which of the following are features of a coordination bond?

I. Contains a shared pair of electrons.

II. Both shared electrons originate from the same atom.

III. Shorter in length than a normal covalent bond.

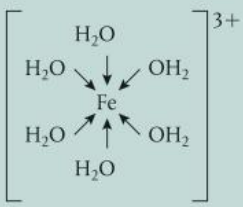
A I and II **B** I and III **C** II and III **D** I, II and III

Q13. Which of the following species contain a coordination bond?

I. H_3O^+ II. NH_3 III. CO

A I and II **B** I and III **C** II and III **D** I, II and III

Q14. HL Which of the following statements are true about the transition element complex below?



I. The iron ion accepts pairs of electrons.

II. Six coordination bonds are formed.

III. Water molecules donate pairs of electrons.

A I and II **B** I and III **C** II and III **D** I, II and III

Q15. Ammonia, NH_3, can react with boron trifluoride, BF_3, to form ammonia boron trifluoride, NH_3BF_3. Draw a Lewis formula of ammonia boron trifluoride and show the coordination bond using an arrow.

Structure 2.2.4 – The Valence Shell Electron Pair Repulsion (VSEPR) model

Structure 2.2.4 – The Valence Shell Electron Pair Repulsion (VSEPR) model enables the shapes of molecules to be predicted from the repulsion of electron domains around a central atom.	
Predict the electron domain geometry and the molecular geometry for species with up to four electron domains.	
Include predicting how non-bonding pairs and multiple bonds affect bond angles.	Nature of Science – How useful is the VSEPR model at predicting molecular geometry?

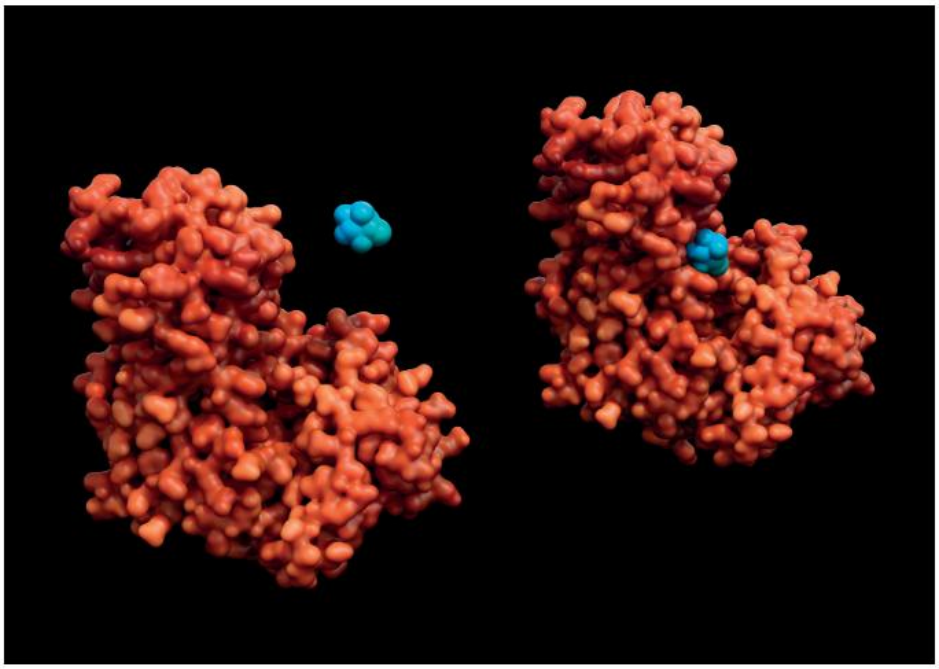
SKILLS

Modelling VSEPR. Full details of how to carry out this experiment with a worksheet are available in the eBook.

The shape of a molecule is determined by repulsion between electron domains around a central atom

Once we know the Lewis formula of a molecule, we can predict how the bonds will be orientated with respect to each other in space – in other words, the three-dimensional shape of the molecule. This is often a crucial feature of a substance in determining its reactivity.

Biochemical reactions depend on a precise 'fit' between the enzyme, which controls the rate of the reaction, and the reacting molecule, known as the substrate. Anything that changes the shape of either of these may therefore alter the reaction dramatically. Many drugs work in this way.



A computer simulation of the hexokinase enzyme (large, orange) binding to glucose (small, blue) to form an enzyme–substrate complex. The function and activity of biochemicals are often dependent on their shape.

TOK

People often find this topic easier to understand when they can build and study models of the molecules in three dimensions. Does this suggest different qualities to the knowledge we acquire in different ways?

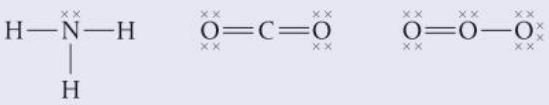
Predictions of molecular shape are based on the **Valence Shell Electron Pair Repulsion (VSEPR) model**. As its name suggests, this theory is based on the simple notion that *because electron pairs in the same valence shell carry the same charge, they repel each other and so spread themselves as far apart as possible.*

Before using this model, it is useful to clarify some of the language involved because the term VS**EP**R, evidently referring to **E**lectron **P**airs, is actually an over-simplification. As we have seen, molecules frequently contain multiple pairs of shared electrons, and these behave as a single unit in terms of repulsion because they are orientated together. So a better, more inclusive, term than electron pair is **electron domain**. This includes all electron locations in the valence shell, whether they are occupied by non-bonding pairs, single, double, or triple bonded pairs. What matters in determining shape is the *total number of electron domains*, and this can be determined from the Lewis formula.

Worked example

How many electron domains exist in the central atom of the following molecules whose Lewis formulas are shown?

(i) (ii) (iii)



Solution

(i) (ii) (iii)



(i) 4 electron domains: 3 bonding and 1 non-bonding

(ii) 2 electron domains: 2 bonding and 0 non-bonding

(iii) 3 electron domains: 2 bonding and 1 non-bonding

Technically then, the VSEPR model should be called Valence Shell Electron Domain Repulsion. It can be summarized as follows:

- The repulsion applies to electron domains, which can be single, double, or triple bonding electron pairs, or non-bonding pairs of electrons.
- The total number of electron domains around the central atom determines the geometrical arrangement of the electron domains.
- The shape of the molecule is determined by the angles between the bonded atoms.
- Non-bonding pairs (lone pairs) and multiple bonds cause slightly more repulsion than a bonding pair for the following reasons:
  - Non-bonding pairs have a higher concentration of charge than bonding pairs because they are not shared between two atoms.
  - Multiple bonds have a higher concentration of charge because they contain two or three pairs of electrons.

We expect the repulsive force to decrease in the following order:

non-bonding pair > multiple bond > single bond

As a result, molecules with lone pairs or multiple bonds on the central atom have some distortions in their structure that reduce the angle between the bonded atoms.

Note that in the diagrams in this section, non-bonding electrons on the surrounding atoms have been omitted for clarity – these are therefore *not* Lewis formulas.

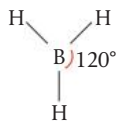
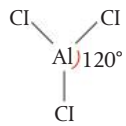
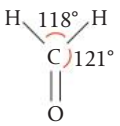
Species with two electron domains

Molecules with two electron domains will position them at **180°** to each other, giving a **linear** shape to the molecule.

$BeCl_2$	Cl—Be—Cl	**linear 180°**
CO_2	O=C=O	
C_2H_2	H—C≡C—H	

Species with three electron domains

Molecules with three electron domains will position them at approximately **120°** to each other, giving a **triangular planar** shape to the **electron domain geometry**. If all three electron domains are bonding, the **molecular geometry** will also be triangular planar.

	BH_3	$AlCl_3$	HCOH
Molecular geometry	Triangular planar 	Triangular planar 	Triangular planar 
Bond angles	H–B–H is 120°	Cl–Al–Cl is 120°	O=C–H is slightly more than 120° H–C–H is slightly less than 120°

You do not need to memorize specific distortions in bond angles but you do need to identify when they might be slightly more or less than the angle predicted by the VSEPR model.

Note that although each of the three molecules has a triangular planar shape, the bond angles in HCOH are slightly distorted due to the increased repulsion from the double bond. The VSEPR model is very useful for predicting molecular geometries but requires additional understanding to explain small differences in bond angles in similar shapes.

Nature of Science – How useful is the VSEPR model at predicting molecular geometry?

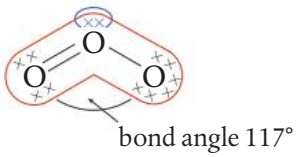
HL An understanding of resonance structures, seen later in this chapter, will also be helpful to explain discrepancies in predictions.

The electron domain geometry is determined by the positions of *all* the electron domains, but the molecular geometry depends only on the positions of the *bonded* atoms.

However, if one of the electron domains is a lone pair, this will not be 'seen' in the overall shape of the molecule, as it is part of the central atom. The molecular shape is determined by the positions of the atoms fixed by the bonding pairs only. A further consideration is that, as described above, lone pairs and multiple bonds cause slightly more repulsion than bonding pairs, so in their presence, the angles are slightly altered.

In the example on the next page, the Lewis formula of ozone, O_3, has three electron domains around the central oxygen atom. Therefore the electron domain geometry of the molecule is still triangular planar. But, as only two of the three electron domains contain bonding electrons, the molecular geometry will not be triangular planar. The red outline shows the positions of the bonding electrons that determine the shape.

The molecule is described as **bent** or **V-shaped**. The extra repulsion due to the lone pair of electrons and double bond distorts the shape slightly, so the angle is slightly less than 120°; it is approximately 117°.

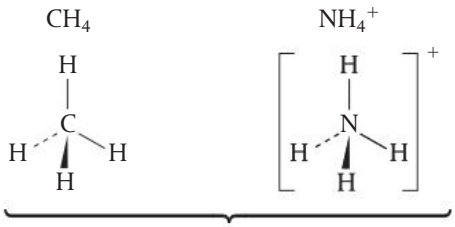


bent or V-shaped

If there are lone pairs on the central atom, the electron domain geometry and the molecular geometry will not be the same as each other.

Species with four electron domains

Molecules with four electron domains will position them at approximately **109.5°** to each other, giving a **tetrahedral** electron domain geometry. If all four electron domains are bonding, the molecular geometry will also be tetrahedral.

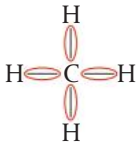
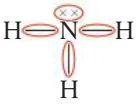
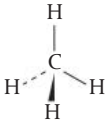
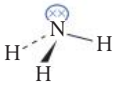


tetrahedral: 109.5°

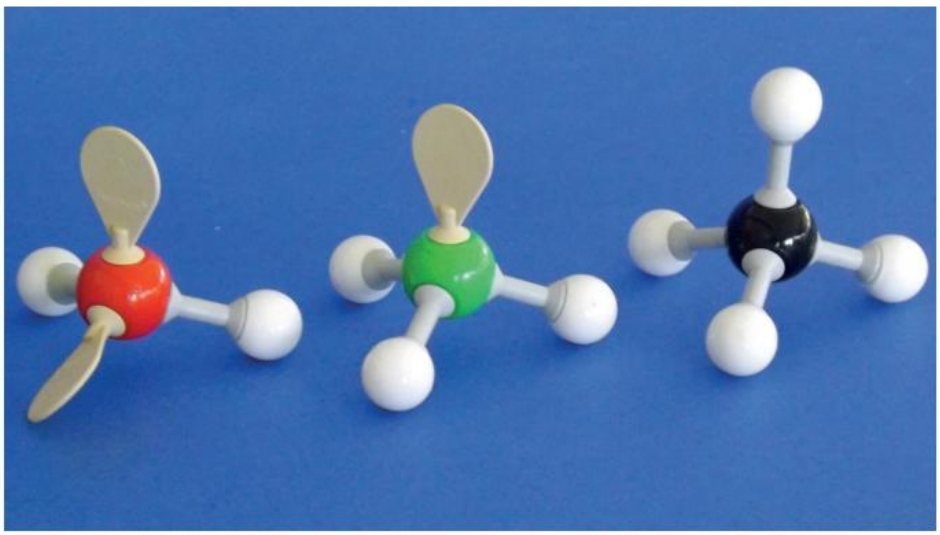
SKILLS

Calculating structural properties using computer modelling. Full details of how to carry out this activity with a worksheet are available in the eBook.

However, if one or more of the electron domains is a lone pair, we must again focus on the number of bonded pairs to determine the shape of the molecule. The table below compares molecules with 0, 1, and 2 lone pairs respectively.

	CH_4	NH_3	H_2O
Lewis formula			
Number of electron domains	4	4	4
Electron domain geometry	tetrahedral	tetrahedral	tetrahedral
Number of lone pairs	0	1	2
Number of bonded electron domains	4	3	2
Molecular geometry	tetrahedral 	trigonal pyramidal 	bent or V-shaped 
Bond angles	109.5°	approximately 107°	approximately 104.5°

Note that the presence of two lone pairs in H_2O causes more repulsion than the single lone pair in NH_3. This is why the bond angle is reduced further in H_2O from the 109.5° of the symmetrical tetrahedron.



Models of H_2O, NH_3 and CH_4 showing the different molecular geometries due to the different numbers of non-bonding pairs on the central atom.

Here is a summary of the steps used in determining the shape of a molecule.

Always draw the Lewis formula before attempting to predict the shape of a molecule, as you have to know the total number of bonding pairs and lone pairs around the central atom.

1. Draw the Lewis formula, following the steps on page 179.
2. Count the total number of electron domains on the central atom.
3. Determine the electron domain geometry as follows:
   2 electron domains → linear
   3 electron domains → triangular planar
   4 electron domains → tetrahedral
4. Determine the molecular geometry from the number of bonding electron domains.
5. Consider the extra repulsion caused by the lone pairs and adjust the bond angles accordingly.

The geometries of molecules for two, three and four electron domains are summarized in the table on page 231.

Exercise

Q16. Predict the geometry and bond angles of the following molecules:

(a) H_2S **(b)** CF_4 **(c)** HCN **(d)** NF_3

(e) BCl_3 **(f)** NH_2Cl **(g)** OF_2

Q17. Predict the geometry and bond angles of the following ions:

(a) NO_2^+ **(b)** NO_2^- **(c)** ClF_2^+ **(d)** $SnCl_3^-$

Q18. How many electron domains are there around the central atom in molecules that have the following shapes?

(a) tetrahedral **(b)** bent **(c)** linear

(d) trigonal pyramidal **(e)** triangular planar



VSEPR model in nature. Different numbers of snowberries growing together spontaneously adopt the geometry of maximum repulsion. Clockwise from the top: four berries form a tetrahedral shape (bond angle 109.5°), three berries form a triangular planar shape (bond angle 120°), and two berries are linear (bond angle 180°). What other examples of VSEPR shapes can you find in nature?

Structure 2.2.5 – Bond polarity

Structure 2.2.5 – Bond polarity results from the difference in electronegativities of the bonded atoms.	
Deduce the polar nature of a covalent bond from electronegativity values.	
Bond dipoles can be shown either with partial charges or vectors. Electronegativity values are given in the data booklet.	Structure 2.1 – What properties of ionic compounds might be expected in compounds with polar covalent bonding?

Polar bonds result from unequal sharing of electrons

Not all sharing is equal. If electron pairs spend more time with one atom than the other, they are not equally shared. This occurs when there is a difference in the **electronegativities** of the bonded atoms (Figure 3). Electronegativity is a measure of the ability of an atom to attract electrons in a covalent bond, and is described using the Pauling scale of values. These values can be found in the data booklet and the trends are explored in Structure 3.1.3.

Electronegativity is a measure of the ability of an atom to attract electrons in a covalent bond. It is described using the Pauling scale from 0-4.

1 H 2.2																	
3 Li 1.0	4 Be 1.6											5 B 2.0	6 C 2.6	7 N 3.0	8 O 3.4	9 F 4.0	
11 Na 0.9	12 Mg 1.3											13 Al 1.6	14 Si 1.9	15 P 2.2	16 S 2.6	17 Cl 3.2	
19 K 0.8	20 Ca 1.0	21 Sc 1.4	22 Ti 1.5	23 V 1.6	24 Cr 1.7	25 Mn 1.6	26 Fe 1.8	27 Co 1.9	28 Ni 1.9	29 Cu 1.9	30 Zn 1.7	31 Ga 1.8	32 Ge 2.0	33 As 2.2	34 Se 2.6	35 Br 3.0	
37 Rb 0.8	38 Sr 1.0	39 Y 1.2	40 Zr 1.3	41 Nb 1.6	42 Mo 2.2	43 Tc 2.1	44 Ru 2.2	45 Rh 2.3	46 Pd 2.2	47 Ag 1.9	48 Cd 1.7	49 In 1.8	50 Sn 2.0	51 Sb 2.1	52 Te 2.1	53 I 2.7	
55 Cs 0.8	56 Ba 0.9	57 La* 1.1	72 Hf 1.3	73 Ta 1.5	74 W 1.7	75 Re 1.9	76 Os 2.2	77 Ir 2.2	78 Pt 2.2	79 Au 2.4	80 Hg 1.9	81 Tl 1.8	82 Pb 1.8	83 Bi 1.9	84 Po 2.0	85 At 2.2	
87 Fr 0.7	88 Ra 0.9	89 Ac* 1.1															

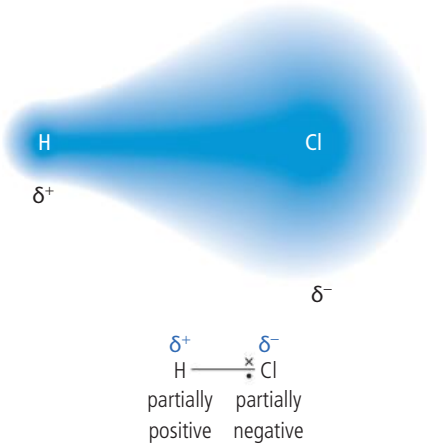
Pauling electronegativity values

<1.0
1.0–1.4
1.5–1.9
2.0–2.4
2.5–2.9
3.0–4.0

S2.2 Figure 3 Periodic trends in electronegativity values show an increase along a period and up a group.

Challenge yourself

2. Given the definition of 'electronegativity', why are the group 18 elements often not assigned a Pauling value?



S2.2 Figure 4 The distribution of electrons in the H–Cl bond is unsymmetrical, with a greater electron density over the Cl atom.

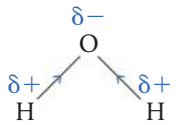
As the more electronegative atom exerts a greater pulling power on the shared electrons, it gains more 'possession' of the electron pair. The bond is now unsymmetrical with respect to electron distribution and is said to be **polar**.

The term **bond dipole** is often used to indicate the fact that this type of bond has two partially separated opposite electric charges. The more electronegative atom with the greater share of the electrons has become partially negative or $\delta-$, and the less electronegative atom has become partially positive or $\delta+$.

For example, in HCl the shared electron pair is pulled more strongly by the Cl atom than by the H atom, resulting in a polar molecule (Figure 4).

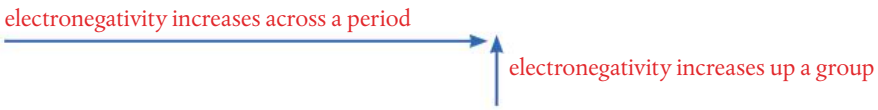
Note that the symbol δ (Greek letter, pronounced 'delta') is used to represent a partial charge. This has no fixed value but is always less than the unit charge associated with an ion such as X^+ or X^-.

In water, the electronegativity difference results in polar O–H bonds with the electron density greater on the oxygen. Note that the structure has been drawn to represent the V-shaped geometry of the molecule.



There are several ways to denote the polar nature of a bond in a structure. One is to write the partial charges δ+ and δ– over the less electronegative and more electronegative atom respectively. Another is to represent the direction of electron pull as a vector with an arrow on the bond indicating the pull on the electrons by the more electronegative atoms.

The extent of polarity in a covalent bond varies, depending on how big a difference exists in the electronegativity values of the two bonded atoms. We can estimate this from knowledge of the periodic trends in electronegativity, discussed in Structure 3.1 and summarized here.



General trends in electronegativity.

As fluorine is the most electronegative atom, we can predict it will have a greater electron density whenever it is covalently bonded to another element. Fluorine has a value of 4.0 on the Pauling scale of electronegativity given on page 193. This scale can be used to assess the relative polarity of a bond. For example, the table on the next page compares the polarities of the hydrogen halides.

	Electronegativity values of atoms		Difference in electronegativity
H–F	2.2	4.0	1.8
H–Cl	2.2	3.2	1.0
H–Br	2.2	3.0	0.8
H–I	2.2	2.7	0.5



increasing bond polarity

Challenge yourself

3. Oxygen is a very electronegative element with a value of 3.4 on the Pauling scale. Can you determine the formula of a compound in which oxygen would have a partial positive charge?

Worked example

Use the electronegativity values on page 193 to put the following bonds in order of decreasing polarity.

N–O in NO_2 N–F in NF_3 H–O in H_2O N–H in NH_3

Solution

bond polarity: H–O > N–F > N–H > N–O

difference in electronegativity values: 1.2, 1.0, 0.8, 0.4

The only bonds that are truly non-polar are bonds between the same atoms such the bonds in F_2, H_2, and O_2, because clearly here the *difference* in electronegativity is zero. These bonds are sometimes referred to as **pure covalent** to express this. All other bonds have some degree of polarity, although it may be very slight. The C–H bond, universal in organic chemistry, is often considered to be largely non-polar, although in fact carbon is slightly more electronegative than hydrogen. As we see in Structure 3.2, the low polarity of the C–H bond is an important factor in determining the properties of organic compounds.

The presence of polar bonds in a molecule has a significant effect on its properties. Effectively, the partial separation of charges introduces some ionic nature into covalent bonds, so the more polar the bond, the more like an ionic compound the molecule behaves. Polar bonds are therefore considered to be intermediates in relation to pure covalent bonds and pure ionic bonds, part of the bonding *continuum* that is discussed in Structure 2.4. This explains why we begin to see overlap in the properties of ionic and covalent substances. Hydrogen chloride, HCl, for example, dissolves in water to form H^+ and Cl^- ions and will therefore be able to conduct electricity in this aqueous state. We now see why the boundaries between ionic and covalent bonds are somewhat 'fuzzy', and why it is often appropriate to describe substances using terms such as 'predominantly' covalent or ionic, or being 'strongly' polar.

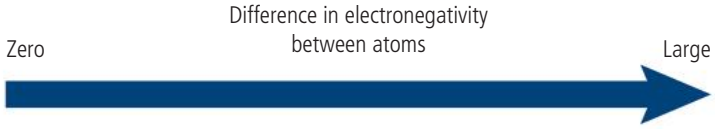
The idea of the bonding continuum is summarized on the next page.

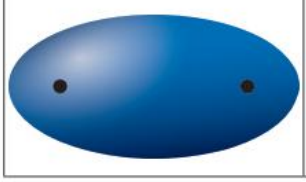
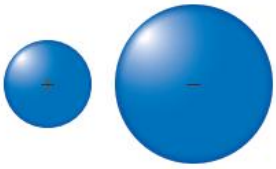


In a covalent bond, the greater the difference in the electronegativity values of the atoms, the more polar the bond.



Structure 2.1 – What properties of ionic compounds might be expected in compounds with polar covalent bonding?



Pure covalent	Polar covalent	Ionic
equal sharing of electrons	partial transfer of electrons unequal sharing of electrons	complete transfer of electrons
Cl_2	HF, HCl, HBr, HI	NaCl, LiF, K_2O
discrete molecules	→	lattice of oppositely charged ions
		

Nature of Science

Scientists observe the natural world where variations in structure or properties are often continuous rather than discontinuous. In other words, a spectrum of intermediates exists and this can make classification difficult. At the same time, the properties of such intermediates can strengthen our understanding. For example, we have seen here that the existence of polar covalent molecules in the bonding continuum adds to our interpretation of electron behaviour in bond formation.

Exercise

Q19. Which substance contains only ionic bonds?

A $NaNO_3$ **B** H_3PO_4 **C** NH_4Cl **D** $CaCl_2$

Q20. For each of these molecules, identify any polar bonds and label them using δ+ and δ– appropriately.

(a) HBr **(b)** CO_2 **(c)** ClF **(d)** O_2 **(e)** NH_3

Q21. Use the electronegativity values in Section 9 of the data booklet to predict which bond in each of the following pairs is more polar.

(a) C–H or C–Cl **(b)** Si–Li or Si–Cl **(c)** N–Cl or N–Mg

Structure 2.2.6 – Molecular polarity

Structure 2.2.6 – Molecular polarity depends on both bond polarity and molecular geometry.	
Deduce the net dipole of a molecule or ion by considering bond polarity and geometry.	
Examples should include species in which bond dipoles do and do not cancel each other.	HL Structure 3.2 – What features of a molecule make it 'infrared (IR) active'?

Molecular polarity depends on both bond polarity and molecular geometry

We have learned that **bond polarity** depends on the charge separation between its two bonded atoms, which is a result of differences in their electronegativities. The polarity of a *molecule* (**molecular polarity**), however, depends on:

- the polar bonds that it contains;
- the way in which such polar bonds are orientated with respect to each other, in other words, the **molecular geometry**.

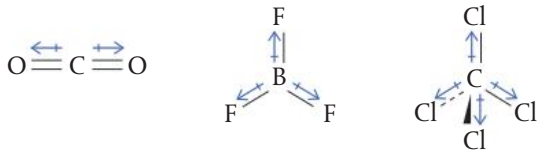
If the bonds are of equal polarity (i.e. involving the same elements) *and* are arranged symmetrically with respect to each other, their charge separations will oppose each other and so will effectively cancel each other out. In these cases, the molecule will be non-polar, despite the fact that it contains polar bonds. It is a bit like a game of tug-of-war between players who are equally strong and symmetrically arranged (Figure 5).



S2.2 Figure 5 Equal and opposite pulls cancel each other out.

Molecules with up to four electron domains

The molecules below are all non-polar because the dipoles cancel out. The arrow, shown here in blue, is the notation for a dipole that results from the pull of electrons in the bond towards the more electronegative atom.



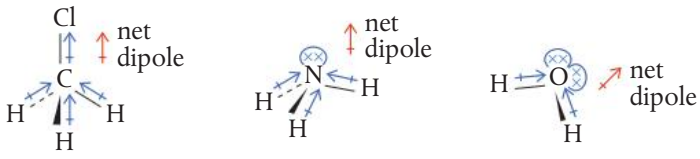
CO_2 BF_3 CCl_4

However, if *either* the molecule contains bonds of different polarity, *or* its bonds are not symmetrically arranged, then the dipoles will not cancel out, and the molecule will be polar. Another way of describing this is to say that it has a **net dipole**, which refers to its turning force in an electric field. This is what would happen in a game of tug-of-war if the players were not equally strong or were not pulling in exactly opposite directions (Figure 6).



S2.2 Figure 6 When the pulls are not equal and opposite there is a net pull.

The molecules below are all polar because the dipoles do not cancel out.



CH_3Cl NH_3 H_2O

HL Molecules can absorb electromagnetic infrared (IR) radiation to become *excited*, meaning that they vibrate at a higher frequency. However, a molecule will only be **IR active** if it contains an overall dipole moment related to the position and vibration of its bonds. For diatomic molecules, which have only one mode of vibration (stretching), the bond must be polar for it to interact with IR radiation. Polyatomic molecules, on the other hand, have multiple modes of vibration including

Bond dipoles can be thought of as vectors, so the polarity of a molecule is the resultant force. This approach may help you to predict the overall polarity from the sum of the bond dipoles.

HL Structure 3.2 – What features of a molecule make it 'infrared (IR) active'?

A microwave oven generates microwaves that have lower frequencies and longer wavelengths than visible light. Microwaves are used for cooking because certain wavelengths are absorbed by polar molecules, notably water, and also by sugar and fat. The absorption causes the water to heat up and cook the food, leaving the oven surface and containers of glass, plastic, or ceramic unaffected.

the stretching and bending of bonds so can achieve an overall dipole moment even if they do not contain polar bonds. Methane, CH_4, is an example of an IR active molecule that does not contain polar bonds. This is discussed in more detail in Structure 3.2.

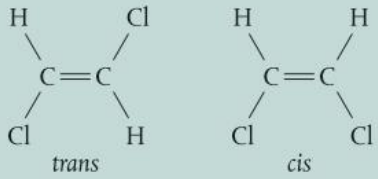
Exercise

Q22. Predict whether the following will be polar or non-polar molecules.

(a) PH_3 **(b)** CF_4 **(c)** HCN **(d)** $BeCl_2$

(e) C_2H_4 **(f)** ClF **(g)** F_2 **(h)** BF_3

Q23. The molecule $C_2H_2Cl_2$ can exist as two forms known as *cis–trans* isomers, which are shown below.



Determine whether either of these has a net dipole moment.

Structure 2.2.7 – Covalent network structures

Structure 2.2.7 – Carbon and silicon form covalent network structures. Describe the structures and explanation of the properties of silicon, silicon dioxide and carbon's allotropes: diamond, graphite, fullerenes and graphene.	
Allotropes of the same element have different bonding and structural patterns in the same physical state, and so have different chemical and physical properties.	Structure 3.1 – Why are silicon–silicon bonds generally weaker than carbon–carbon bonds?

Some covalent substances form covalent network structures

Covalent network structures are also commonly known as 'giant molecular' or 'macromolecular' structures.

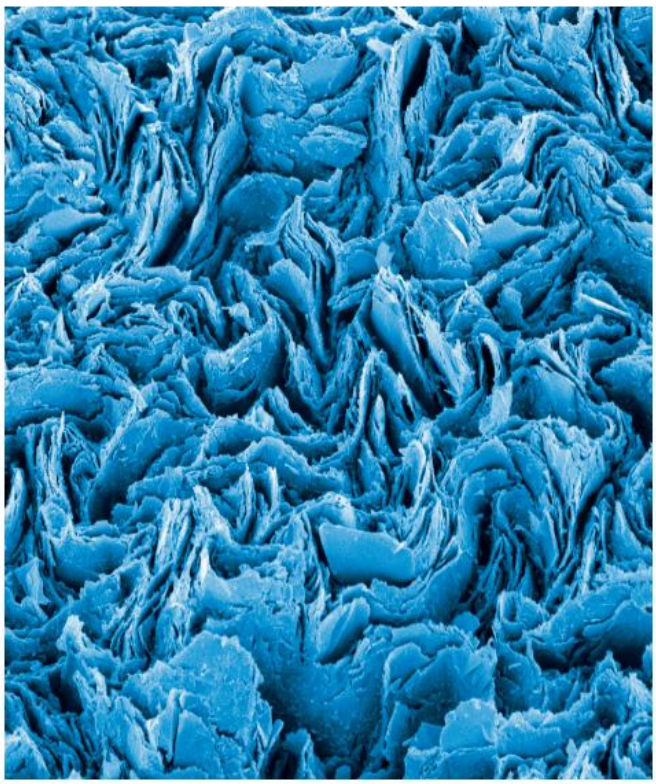
Most covalent substances exist as discrete molecules with a finite number of atoms. However, there are some substances that have a very different structure, a crystalline lattice in which the atoms are linked together by covalent bonds. Effectively, the crystal is a single molecule with a regular repeating pattern of covalent bonds, so has no finite size. It is referred to as a **covalent network structure**. As we might expect, such crystalline structures have very different properties from other smaller covalent molecules. A few examples are considered here.

Allotropes of carbon

Allotropes have different bonding and structural patterns of the same element in the same physical state, and so have different chemical and physical properties. Molecular oxygen (O_2) and ozone (O_3), which both exist as gases, are examples of allotropes of oxygen.

Carbon has several allotropes and these are described and compared in the table on page 200.

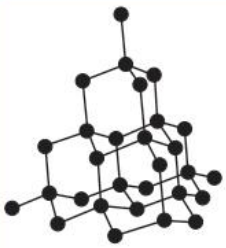
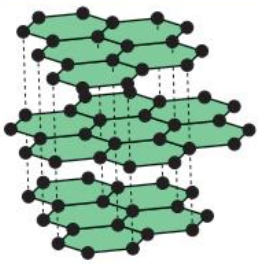
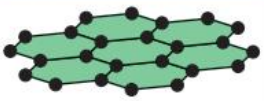
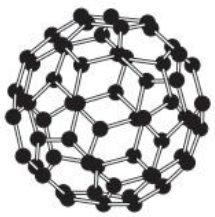
HL References to hybridization are explained in the last section of this chapter.



Coloured scanning electron micrograph of layers making up the core of a graphite pencil. Because graphite is a soft form of carbon, the tip of the pencil disintegrates under pressure to leave marks on the paper.

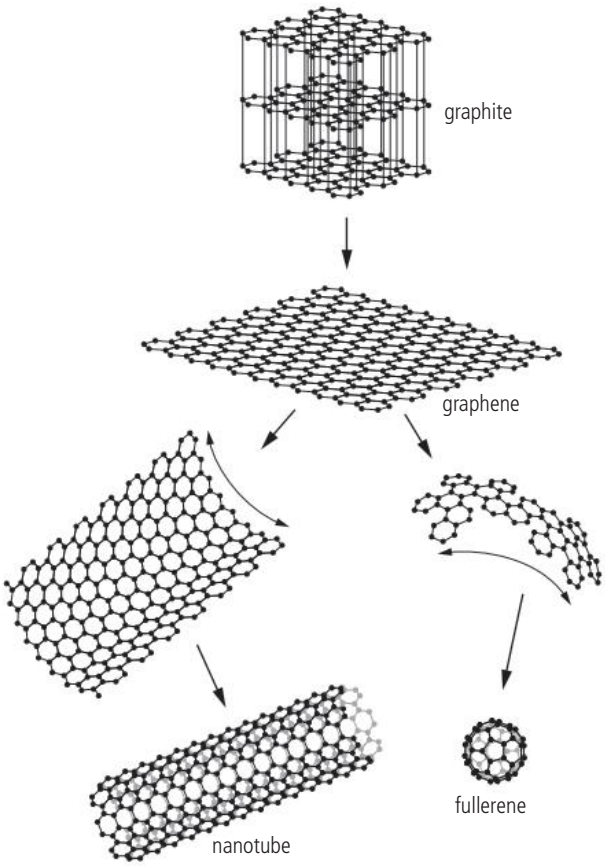


Cut and polished diamond. Diamond is a naturally occurring form of carbon that has crystallized under great pressure. It is the hardest known mineral. Beautiful crystals are found in South Africa, Russia, Brazil, and Sierra Leone.

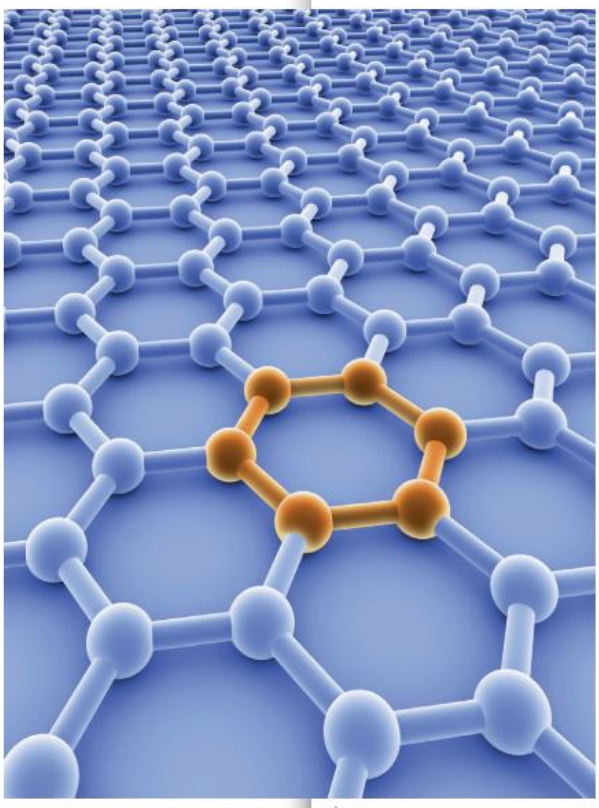
	Diamond	Graphite	Graphene	C_{60} Fullerene
Structure	 Each C atom is sp^3 hybridized and covalently bonded to 4 others, tetrahedrally arranged in a regular repetitive pattern with bond angles of 109.5°.	 Each C atom is sp^2 hybridized and covalently bonded to 3 others, forming hexagons (shown in green) in parallel layers with bond angles of 120°. The remaining valence electron on each carbon is delocalized so it can move freely across the layer. The layers are held only by weak London dispersion forces so they can slide over each other.	 Each C atom is sp^2 hybridized and covalently bonded to 3 others, as in graphite, forming hexagons with bond angles of 120°. But it is a single layer, so it exists as a two-dimensional material only. It is often described as a honeycomb or chicken wire structure. As with graphite, the remaining valence electron on each carbon is delocalized.	  Each C atom is sp^2 hybridized and bonded in a sphere of 60 carbon atoms, consisting of 12 pentagons and 20 hexagons. The structure is a closed spherical cage in which each carbon is bonded to 3 others. (Note it is not a giant molecule as it has a fixed formula.)
Electrical conductivity	Non-conductor of electricity; all electrons are bonded and so non-mobile.	Good electrical conductor; contains one non-bonded, delocalized electron per atom that gives electron mobility.	Very good electrical conductor; one delocalized electron per atom gives electron mobility across the layers.	C_{60} fullerenes are poor conductors of electricity; although individual molecules have delocalized electrons, there is little electron movement between molecules.
Thermal conductivity	Very efficient thermal conductor, better than metals.	Not a good conductor, unless the heat can be forced to conduct in a direction parallel to the crystal layers.	Best thermal conductivity known, even better than diamond.	Very low thermal conductivity.
Appearance	Highly transparent, lustrous crystal.	Non-lustrous, grey crystalline solid.	Almost completely transparent.	Black powder.
Physical and chemical properties	The hardest known natural substance; it cannot be scratched by other materials; brittle; very high melting point.	Soft and slippery due to slippage of layers over each other; brittle; very high melting point; the most stable allotrope of carbon.	The thickness of just one atom so the thinnest material ever to exist; but also the strongest – 100 times stronger than steel; very flexible; very high melting point.	Very light and strong; reacts with K to make superconducting crystalline material; low melting point.
Uses	Polished for jewellery and ornamentation; tools and machinery for grinding and cutting glass.	A dry lubricant; in pencils; electrode rods in electrolysis.	TEM (transmission electron microscopy) grids, photo-voltaic cells, touch screens, high-performance electronic devices; many applications are still being developed.	Lubricants, medical, and industrial devices for binding specific target molecules; related forms are used to make nanotubes and nanobuds used as capacitors in the electronics industry, and catalysts.

Challenge yourself

4. For the most part, good electrical conductors are also good thermal conductors, but this is not the case with diamond. Can you think why this might be, and whether there are other substances that are not electrical conductors but good thermal conductors?



Graphite occurs naturally, and a single separated layer is graphene. A rolled up layer of graphene is a nanotube, and a closed cage is a fullerene.

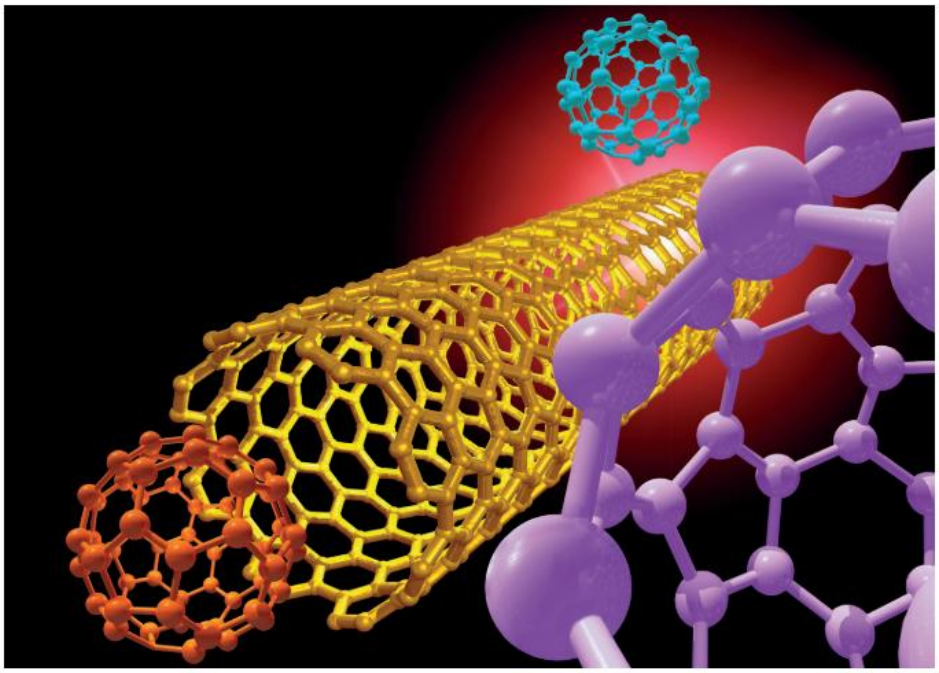


Graphene is a planar sheet of carbon atoms arranged in a hexagonal pattern.

Graphene is a relatively new form of carbon, isolated for the first time in 2004. Given its hardness, strength, lightness, flexibility, conductivity, and chemical inertness, it has enormous potential applications. Currently though, many of these are only in the development stage as they are dependent on the production of large sheets of pure graphene, which is difficult to achieve economically. But this is an intense field of research and breakthroughs are common.

TOK

Whether graphene will realize its potential and lead to innovative materials and applications remains an open question. What is the role of imagination in helping to direct the research focus of scientists?



Computer artwork of spherical and cylindrical fullerenes – buckyballs and carbon nanotubes. These substances are being investigated for a wide range of technical and medical uses. Here the carbon nanotubes have been engineered to have a diameter just large enough to allow buckyballs to pass through them.

The name 'fullerene' was given to the newly discovered spheres C_{60} in honour of the American architect R. Buckminster Fuller. He had designed the World Exhibition building in Montreal, Canada, on the same concept of hexagons and a small number of pentagons to create a curved surface known as a geodesic dome. The dome of the Epcot Centre in Disney World, Florida, is similarly designed. Perhaps more familiarly it is also the structure of a European soccer ball. The term 'buckyballs' has slipped into common usage, derived from the full name of the structure 'buckminsterfullerene'.



The structure of fullerene has the same arrangement of hexagons and pentagons as a soccer ball.

Nature of Science

The discoveries of the allotropes of carbon – buckminsterfullerene and graphene – illustrate the importance of collaboration between scientists.

The discovery of fullerenes in 1985 was the result of teamwork between scientists with different experience and research objectives. Harold Kroto working at the University of Sussex, UK was interested in red giant stars and how carbon might polymerize near them. Robert Curl and Richard Smalley working in Texas, USA, had developed a technique using a laser beam for evaporating and analyzing different substances. When they worked together and applied this technique to graphite, clusters of stable C_{60} and C_{70} spheres were formed. The three scientists shared the Nobel Prize in Chemistry for 1996.

The isolation of graphene was announced by Kostya Novoselov and Andre Geim in 2004, both working at the University of Manchester, UK. It led to their shared award of the Nobel Prize in Physics in 2010. Novoselov and Geim were research collaborators over many years in different countries, originally as research student and supervisor respectively. Their work involved the use of adhesive tape to rip successively thinner flakes off graphite and analyze the flakes by attachment to a layer of silicon oxide. Many scientists over many years had attempted to isolate graphene, and through their successes and failures indirectly contributed to the later discovery.

The development of structures such as nanotubes, nanobuds, and graphene is part of the growing science of **nanotechnology**, which deals with the atomic scale manipulation of matter. An interesting development is a new material called graphene-hBN, which is made by adding a hexagonal layer of boron and nitrogen atoms onto graphene. The combination of boron nitride, an excellent electrical insulator, and the conductive properties of graphene has some interesting potential for applications in LEDs and quantum computing.

Challenge yourself

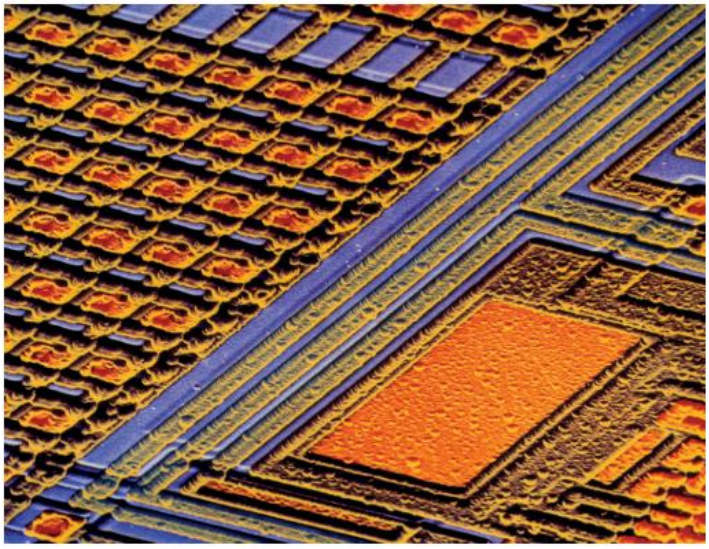
5. Graphite is thermodynamically more stable than diamond. The reaction

$$C(\text{diamond}) \rightarrow C(\text{graphite})$$

is accompanied by a loss of energy, $\Delta H = -2\ \text{kJ mol}^{-1}$.

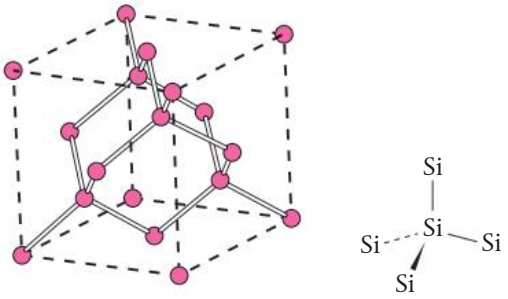
But we commonly hear that 'diamonds are forever'. Are they?

Silicon and silicon dioxide



Coloured scanning electron micrograph of the surface of a microprocessor computer chip. Silicon chips are tiny pieces of silicon as small as 1 mm^2 made to carry minute electrical circuits used in computers and transistors. Silicon is the most widely used semiconductor.

Like carbon, silicon is a group 14 element and so its atoms have four valence shell electrons. In the elemental state, each silicon atom is covalently bonded to four others in a tetrahedral arrangement. This results in a giant lattice structure much like diamond.



The silicon crystal structure and the arrangement of bonds around a central silicon atom.

Silicon dioxide, SiO_2, commonly known as silica or quartz, also forms a giant covalent structure based on a tetrahedral arrangement (Figure 7). But here the bonds are between silicon and oxygen atoms, where each Si atom is covalently bonded to four O atoms, and each O to two Si atoms. You can think of the oxygen atoms as forming bridges between the tetrahedrally bonded silicon atoms.

Silicon is the most abundant element in the Earth's crust after oxygen, occurring as silica (SiO_2) in sand and in silicate minerals. Since silicon is just below carbon in group 14, the possibility of silicon-based life has been proposed. But unlike carbon, silicon is not able to form long chains, multiple bonds, or rings, so cannot compete with the diversity possible in organic chemistry, based on carbon. However, there is some evidence that the first forms of life were forms of clay minerals that were probably based on the silicon atom.

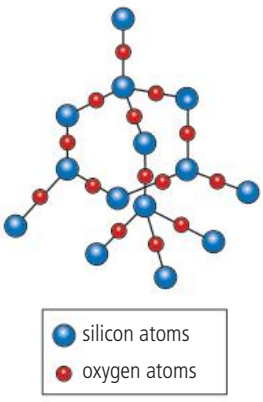


Quartz crystals shown in a coloured scanning electron micrograph. Quartz is a form of silica (SiO_2) and the most abundant mineral in the Earth's crust. Quartz is used in optical and scientific instruments and in electronics such as mobile phones and laptops.

Note that here the formula SiO_2 refers to the *ratio* of atoms within the giant molecule – it is an empirical formula and the actual number of atoms present will be a very large multiple of this. As the atoms are strongly held in tetrahedral positions that involve all four silicon valence electrons, the structure has the following properties:

- strong;
- insoluble in water;
- high melting point;
- non-conductor of electricity.

These are all properties we associate with glass and sand – different forms of silica.



S2.2 Figure 7 The structure of quartz, SiO_2.

A notable difference between the network structures of carbon and silicon is the tendency for carbon to form covalent bonds with other carbon atoms (known as catenation) whereas silicon is more commonly found bonded with oxygen. This is due to the greater strength of a C–C bond, approximately 346 kJ mol^{-1}, compared to a Si–Si bond which has a bond enthalpy of 226 kJ mol^{-1}. This can be explained by the smaller atomic radius of carbon resulting in a greater electrostatic attraction between nuclei and shared pairs of electrons. In contrast, the Si–O bond found in silica has a bond enthalpy of 466 kJ mol^{-1}.

Structure 3.1 – Why are silicon–silicon bonds generally weaker than carbon-carbon bonds?

Pure silicon is a poor conductor of electricity at low temperatures. However, as its temperature is increased, the thermal energy provides the necessary energy to free some electrons from the covalent bonds, causing the electrical conductivity to increase dramatically. Each freed electron leaves behind a positively charged hole allowing other electrons to move through the lattice to occupy these holes. This process repeats to allow silicon to conduct electricity. Silicon can also be 'doped' with group 13 and 15 elements such as arsenic and boron in very small concentrations to increase its electrical conductivity. The 'Silicon Valley' region in North California owes its name to the wide range of applications of silicon in the electronics that make these industries possible.



Silicon Valley in Northern California is home to many large high-tech corporations.

Exercise

Q24. Outline the similarities and differences in the structures of diamond and graphite.

Q25. Describe the similarities and differences you would expect in the properties of silicon and diamond.

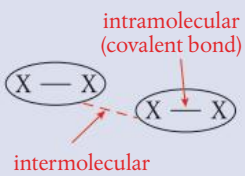
Q26. Explain why graphite and graphene are good conductors of electricity whereas diamond is not.

Structure 2.2.8 and 2.2.9 – Intermolecular forces

Structure 2.2.8 – The nature of the force that exists between molecules is determined by the size and polarity of the molecules. Intermolecular forces include London (dispersion), dipole-induced dipole, dipole–dipole and hydrogen bonding. Deduce the types of intermolecular force present from the structural features of covalent molecules.	
The term 'van der Waals forces' should be used as an inclusive term to include dipole–dipole, dipole-induced dipole, and London (dispersion) forces. Hydrogen bonds occur when hydrogen, being covalently bonded to an electronegative atom, has an attractive interaction with a neighbouring electronegative atom.	Structure 1.5 – To what extent can intermolecular forces explain the deviation of real gases from ideal behaviour? Nature of Science, Structure 1.1, 2.1, 2.3 – How do the terms 'bonds' and 'forces' compare? Nature of Science – How can advances in technology lead to changes in scientific definitions, e.g. the updated International Union of Pure and Applied Chemistry (IUPAC) definition of the hydrogen bond?

Structure 2.2.9 – Given comparable molar mass, the relative strengths of intermolecular forces are generally: London (dispersion) forces < dipole–dipole forces < hydrogen bonding. Explain the physical properties of covalent substances to include volatility, electrical conductivity and solubility in terms of their structure.	
	Tool 1, Inquiry 2 – What experimental data demonstrates the physical properties of covalent substances? Structure 3.2 – To what extent does a functional group determine the nature of the intermolecular forces?

Note that the prefix *intra-* refers to *within*, whereas the prefix *inter-* refers to *between*. For example, the internet is worldwide while an intranet is a computer network within an organization.



Structure 1.5 – To what extent can intermolecular forces explain the deviation of real gases from ideal behaviour?

Forces of attraction between molecules are called intermolecular forces

Covalent bonds hold atoms together *within* molecules, but of course molecules do not exist in isolation. A gas jar full of chlorine, Cl_2, for example, will contain millions of molecules of chlorine. So what are the attractive forces that exist *between* these molecules, the so-called intermolecular forces? The answer depends on the polarity and size of the molecules involved, and so the intermolecular forces will vary for different molecules. We will consider four types of intermolecular force here, and see how they differ from each other in origin and in strength.

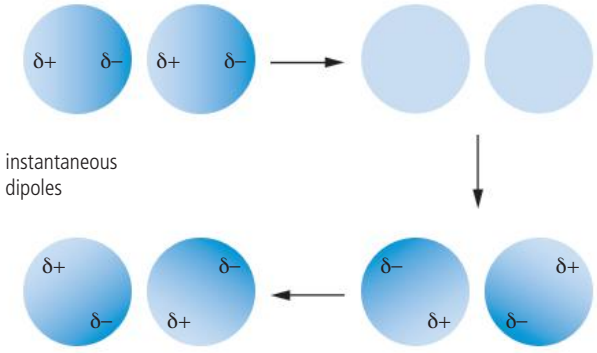
The strength of intermolecular forces determines the physical properties of a substance. Volatility, solubility and conductivity can all be predicted and explained from knowledge of the nature of the forces between molecules.

An understanding of intermolecular forces can also be used to explain one aspect of why the behaviour of *real* gases deviates from that described by the *ideal* gas model. The attractive forces between gaseous atoms and/or molecules become more significant at low temperature and high pressure so limit the predictive accuracy of the ideal gas equation and the combined gas law.

London dispersion forces

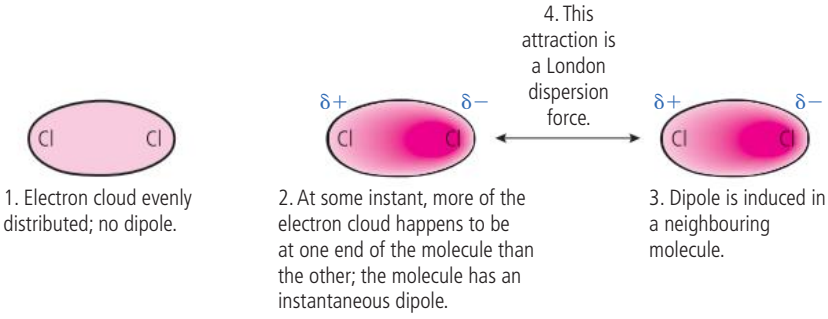
Non-polar molecules such as chlorine, Cl_2, have no permanent separation of charge within their bonds because the shared electrons are pulled equally by the two chlorine atoms. In other words, they do not have a permanent dipole.

However, because electrons behave somewhat like mobile clouds of negative charge, the density of this cloud may at any one moment be greater over one atom than the other. When this occurs, the bond will have some separation of charge – a weak dipole known as a 'temporary' or 'instantaneous' dipole (Figure 8). This will not last for more than an instant as the electron density is constantly changing, but it may influence the electron distribution in the bond of a neighbouring molecule, causing an **induced dipole**.



S2.2 Figure 8 A series of instantaneous views of electron density in two molecules (each represented as a sphere). Each image is like a snap-shot of a possible electron distribution at a moment in time. A temporary dipole in one molecule can induce a temporary dipole in another. Note that in the top right pair of molecules, there was no temporary dipole in either at that moment in time.

As a result, weak forces of attraction, known as **London dispersion forces**, will occur between opposite ends of these two temporary dipoles in the molecules (Figure 9). These are the weakest form of intermolecular force. Their strength increases with increasing molecular size. This is because a greater number of electrons within a molecule increases the probability and magnitude of temporary dipoles developing.



S2.2 Figure 9 Instantaneous dipole–induced dipole London dispersion forces between molecules of Cl_2.

London dispersion forces are the *only* forces that exist between non-polar molecules. Such molecules generally have low melting and boiling points, because relatively little energy is required to overcome the weak London dispersion forces and separate the molecules from each other. This is why many non-polar elements and compounds are gases at room temperature, for example, O_2, Cl_2, and CH_4. Boiling point data also indicates how the strength of London dispersion forces increases with increasing

Fritz London (1900–1954) was a German physicist who pioneered the interpretation of covalent bond formation and intermolecular forces in the emerging field of quantum mechanics. As he was of Jewish descent, he had to leave his university post in Germany during the Nazi regime before the Second World War, and completed most of his research in Duke University, USA.

molecular size. This is shown in the tables below that compare the boiling points of the halogens (group 17 elements) and of the family of hydrocarbons known as the alkanes.

Element	M_r	Boiling point / °C	State at room temperature
F_2	38	−188	gas
Cl_2	71	−34	gas
Br_2	160	59	liquid
I_2	254	185	solid

boiling point increases with increasing number of electrons

Alkane	M_r	Boiling point / °C
CH_4	16	−164
C_2H_6	30	−89
C_3H_8	44	−42
C_4H_{10}	58	−0.5

boiling point increases with increasing number of electrons

When asked to name forces between molecules, London dispersion forces should be given in all cases, regardless of what additional forces may be present.

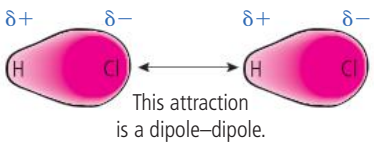
Although London dispersion forces are weak, they are responsible for the fact that non-polar substances can be condensed to form liquids and sometimes solids at low temperatures. For example, nitrogen gas, N_2, liquefies below −196 °C, and even helium gas has been liquefied at the extremely low temperature of −269 °C.

London dispersion forces are also components of the forces between polar molecules, but often get somewhat overlooked because of the presence of stronger forces.

Dipole–dipole attraction

Polar molecules such as hydrogen chloride, HCl, have a permanent separation of charge within their bonds as a result of the difference in electronegativity between the bonded atoms. One end of the molecule is electron deficient with a partial positive charge ($\delta+$), while the other end is electron-rich with a partial negative charge ($\delta-$). This is known as a **permanent dipole**. It results in opposite charges on neighbouring molecules attracting each other, generating a force known as a **dipole–dipole attraction**.

Permanent dipoles cause forces of dipole–dipole attraction between molecules of HCl.



The strength of this intermolecular force will vary depending on the distance and relative orientation of the dipoles. But dipole–dipole forces are always stronger than London dispersion forces, as we might expect from their basis in permanent rather than instantaneous dipoles. These forces cause the melting and boiling points of polar compounds to be higher than those of non-polar substances of comparable molecular mass.

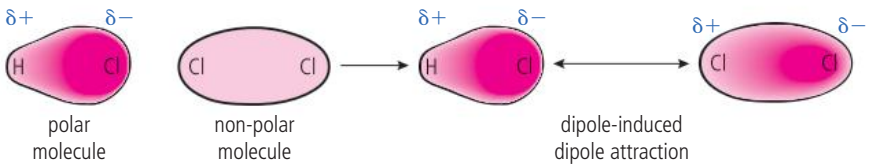
	C_3H_8	CH_3OCH_3
Molar mass / g mol^{-1}	44	46
Intermolecular attraction	London dispersion forces	London dispersion forces and dipole–dipole attraction
Boiling point / K	229	249

When examining the boiling points of different substances to see the effect of different intermolecular forces, it is important to compare substances with a similar molecular mass. Otherwise the difference could be attributed solely to stronger London dispersion forces in the molecules with more mass (therefore more electrons).

Note that dipole–dipole attractions can occur between any combination of polar molecules, such as between PCl_3 and $CHCl_3$, and generally lead to the solubility of polar solutes in polar solvents.

Dipole–induced dipole attraction

When a mixture contains both polar and non-polar molecules, the permanent dipole of a polar molecule can cause a temporary separation of charge on a non-polar molecule. The resulting force is known as a **dipole-induced dipole attraction** (Figure 10).



S2.2 Figure 10 Dipole-induced dipole forces between molecules of HCl and Cl_2.

This intermolecular force would act in addition to London dispersion forces between non-polar molecules and dipole–dipole forces between polar molecules.

The term **van der Waals' force** is used to include London dispersion forces, dipole-induced dipole and dipole–dipole attractions. In other words, van der Waals' forces refer to all forces between molecules that do not involve electrostatic attractions between ions or bond formation. We can summarize this as follows:

London dispersion force	Cl_2----Cl_2	van der Waals' forces
dipole–dipole attraction	HCl----HCl	
dipole–induced dipole	HCl----Cl_2	

In some cases, van der Waals' forces may occur within a molecule (intramolecularly) if the different groups can position themselves appropriately. This is an important feature in explaining the structure and behaviour of proteins.

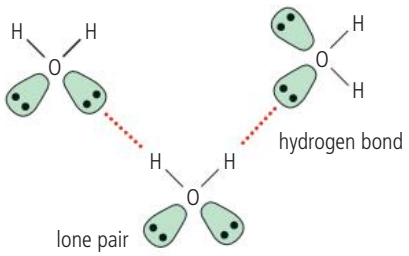
Hydrogen bonding

When a molecule contains hydrogen covalently bonded to a very electronegative atom (fluorine, nitrogen, or oxygen), these molecules are attracted to each other by a particularly strong type of intermolecular force called a **hydrogen bond**. The hydrogen bond is in essence a particular case of dipole–dipole attraction. The large electronegativity difference between hydrogen and the bonded fluorine, oxygen, or nitrogen results in the electron pair being pulled away from the hydrogen. Given its small size and the fact that it has no other electrons to shield the nucleus, the hydrogen now exerts a strong attractive force on a lone pair in the electronegative atom of a neighbouring molecule (Figure 11). This is the hydrogen bond.

For two substances of similar molecular mass, the more polar substance will have the higher boiling point.

Johannes van der Waals (1837–1923) from the Netherlands established himself as an eminent physicist in his first publication, his PhD thesis. His study of the continuity of the gas and liquid state from which he put forward his 'equation of state' led James Clerk Maxwell to comment, 'there can be no doubt that the name of van der Waals will soon be among the foremost in molecular science'. van der Waals did indeed fulfil this early promise, being awarded the Nobel Prize in Physics in 1910.

Hydrogen bonding only occurs between molecules in which hydrogen is bonded directly to fluorine, nitrogen, or oxygen.

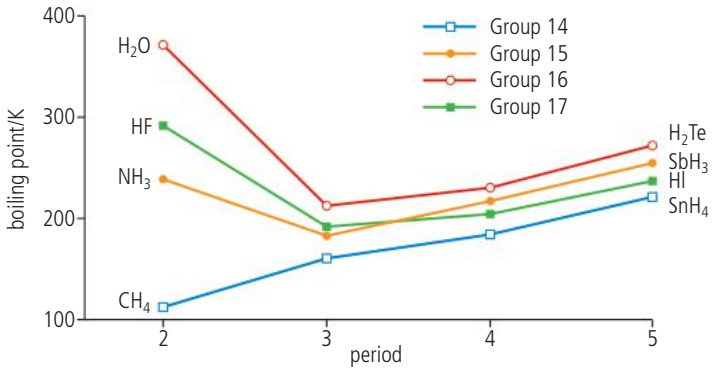


S2.2 Figure 11 Hydrogen bonding between water molecules.

Nature of Science – How can advances in technology lead to changes in scientific definitions, e.g. the updated IUPAC definition of the hydrogen bond?

There is ongoing debate about the nature of the hydrogen bond and IUPAC defines six criteria that should be used as evidence for its occurrence. Several of these criteria are dependent on technological advancements, such as the use of infrared and nuclear magnetic resonance spectrometers to analyse the interactions occurring in a substance.

Hydrogen bonds are the strongest form of intermolecular attraction. Consequently, they cause the boiling points of substances that contain them to be significantly higher than would be predicted from their molar mass. We can see this in Figure 12, in which boiling points of the hydrides from groups 14 to 17 are compared down the periodic table.



S2.2 Figure 12 Periodic trends in the boiling points of the hydrides of groups 14–17.

In all four groups there is an observable trend that boiling point increases down the group as molar mass increases. The anomalies are NH_3, HF, and H_2O, which all have significantly higher boiling points than would be expected from their molar mass. This can only be explained by the presence of hydrogen bonding in these molecules. If it was not for the fact that it is hydrogen bonded, H_2O would be a gas not a liquid at room temperature.

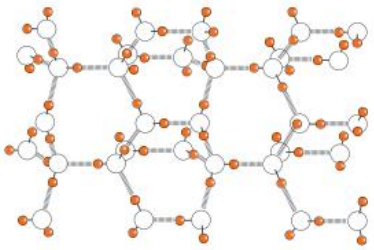
Likewise, when we compare the boiling points of some organic molecules that have similar or equal values of molar mass, we find a higher value where hydrogen bonding occurs between the molecules. For example, the following table compares two different forms of C_2H_6O, known as isomers, both with a molar mass of 46.

$CH_3–O–CH_3$	$CH_3CH_2–O–H$
methoxymethane	ethanol
$M = 46\ g\ mol^{-1}$	$M = 46\ g\ mol^{-1}$
does not form hydrogen bonds	forms hydrogen bonds
boiling point = –23 °C	boiling point = +79 °C

Water makes a particularly interesting case for the study of hydrogen bonding. Here, because of the two hydrogen atoms in each molecule and the two lone pairs on the oxygen atom, each H_2O can form up to *four* hydrogen bonds with neighbouring molecules. Liquid water contains fewer than this number, but in the solid form, ice, each H_2O is maximally hydrogen bonded in this way. The result is a tetrahedral arrangement that holds the molecules a fixed distance apart, forming a fairly open structure, which is actually *less* dense than the liquid (Figure 13). This is a remarkable fact – in nearly all other substances the solid form with closer packed particles is *more* dense than its liquid. The fact that ice floats on water is evidence of the power of hydrogen bonds in holding the molecules together in ice. This density change means that water expands on freezing, which can lead to all kinds of problems in cold climates such as burst pipes and cracked machinery. The same force of expansion is at work in the Earth's crust, fragmenting and splitting rocks, ultimately forming sand and soil particles. The humble hydrogen bond is responsible for massive geological changes!



Icebergs float on water. Hydrogen bonds in water create a very open structure in ice, which is less dense than liquid water.



S2.2 Figure 13 The arrangement of water molecules in ice. Each molecule is held by hydrogen bonds to four other molecules in a tetrahedral arrangement.

In these examples, we have looked at hydrogen bonds as an intermolecular force, that is, *between* molecules, but like van der Waals' forces, they can occur *within* large molecules where they play a key role in determining properties. Another fascinating example is DNA (deoxyribonucleic acid) which, as the chemical responsible for storing the genetic information in cells, is able to replicate itself exactly, a feat only possible because of its use of hydrogen bonding.



Computer artwork of a DNA molecule replicating. DNA is composed of two strands, held together by hydrogen bonds and twisted into a double helix. Before replication, the strands separate from each other by breaking the hydrogen bonds and each strand then acts as a template for the synthesis of a new molecule of DNA.

We can now summarize the intermolecular forces we have discussed in this section.

		Non-polar molecules	Polar molecules	Molecules which contain H–O, H–N, or H–F
London dispersion forces	van der Waals' forces	✓	✓	✓
Dipole-induced dipole		requires a mixture of polar and non-polar molecules		
Dipole–dipole attractions			✓	✓
Hydrogen bonding				✓

increasing strength of inter-molecular force

Nature of Science, Structure 1.1, 2.1, 2.3 – How do the terms 'bonds' and 'forces' compare?

It is important to note that although hydrogen bonds are strong in relation to other types of intermolecular force, they are significantly weaker (about 15–20 times) than covalent bonds and ionic bonds. So although intermolecular forces and intramolecular forces are both categories of electrostatic attraction, there is a significant difference in their relative strengths.

The physical properties of covalent compounds are largely a result of their intermolecular forces

Tool 1, Inquiry 2 – What experimental data demonstrate the physical properties of covalent substances?

If we know the type of intermolecular force in a substance, we are in a good position to predict its physical properties. Experimental data on melting and boiling points, solubility in polar and non-polar solvents, and electrical conductivity can be used to verify our predictions.

Melting and boiling points

Make sure you realize that when a covalent substance melts or boils, it is the attractive forces *between* the molecules that are overcome, not the bonds *within* the molecules. When you boil a kettle of water, you do not fill the kitchen with separated oxygen and hydrogen atoms.

Changing state by melting or boiling both involve separating particles by overcoming the forces between them. So the stronger the interparticle forces, the more energy will be required to do this, and the higher the substance's melting and boiling points will be.

Covalent substances generally have lower melting and boiling points than ionic compounds. The forces to be overcome to separate the molecules are the relatively weak intermolecular forces, which are significantly easier to break than the electrostatic attractions in the ionic lattice. This is why many covalent substances are liquids or gases at room temperature.

As discussed on page 207, the strength of the intermolecular forces increases with increasing molecular size and with an increase in the extent of polarity within the molecule, and so these features help us to predict relative melting and boiling points.

Worked example

Put the following molecules in order of increasing boiling point and explain your choice:

CH_3CHO CH_3CH_2OH $CH_3CH_2CH_3$

Solution

1. First check the value of *M* for each molecule:

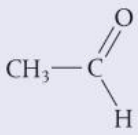
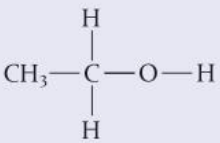
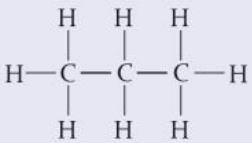
   $CH_3CHO = 44$

   $CH_3CH_2OH = 46$

   $CH_3CH_2CH_3 = 44$

   These molar masses are nearly identical so we would expect very similar strength London dispersion forces.

2. Now consider the structure of each molecule and predict additional intermolecular forces:

CH_3CHO	CH_3CH_2OH	$CH_3CH_2CH_3$
		
polar molecule ⇒ dipole–dipole forces	O–H bond ⇒ hydrogen bonding	non-polar molecule ⇒ London dispersion forces only

So the order, starting with the lowest boiling point, will be:

$CH_3CH_2CH_3 < CH_3CHO < CH_3CH_2OH$

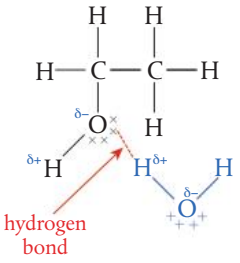
An understanding of functional groups in organic molecules is extremely helpful to identify the types of intermolecular forces present in these substances. The hydroxyl functional group (R–OH), for example, will lead to the formation of hydrogen bonding in all alcohols. We should recognize, however, that other factors such as the size and orientation of the molecules can also influence the nature of these attractions.

Structure 3.2 – To what extent does a functional group determine the nature of the intermolecular forces?

By contrast, macromolecular or giant covalent structures have high melting and boiling points, often at least as high as those of ionic compounds. This is because covalent bonds must be broken in these compounds for the change of state to occur. Diamond, for example, remains solid until about 4000 °C.

Volatility

Volatility is a term used to describe the tendency of a substance to vaporize. As we have seen in the explanation for boiling points, a substance with stronger intermolecular forces will have a lower tendency to vaporize and vice versa. Propan-1-ol, C_3H_7OH, for example, will be considerably less volatile than butane, C_4H_{10}, given the additional hydrogen bonding.



S2.2 Figure 14 Water and ethanol form hydrogen bonds and mix readily.

Solubility

Non-polar substances are generally able to dissolve in non-polar solvents by the formation of London dispersion forces between solute and solvent. For example, the halogens, all of which are non-polar molecules (e.g. Br_2), are readily soluble in the non-polar solvent, paraffin oil. It is another example of *like dissolves like*, which is a useful guiding principle here.

Likewise, polar covalent compounds are generally soluble in water, a highly polar solvent. Here the solute and solvent interact through dipole interactions and hydrogen bonding. Common examples include the aqueous solubility of HCl, glucose ($C_6H_{12}O_6$), and ethanol (C_2H_5OH) (see Figure 14). Biological systems are mostly based on polar covalent molecules in aqueous solution.

The solubility of polar compounds is, however, reduced in larger molecules where the polar bond is only a small part of the total structure. The non-polar parts of the molecule, unable to associate with water, reduce its solubility. For example, while ethanol (C_2H_5OH) is readily soluble in water, the larger alcohol heptanol ($C_7H_{15}OH$) is not. The difference is the size of the non-polar hydrocarbon group.



The moss plant *Philonotis fontana* has a waxy substance on its surface which repels water. The wax is a large non-polar covalent molecule that is unable to form hydrogen bonds with water.

Predictably, this inability of non-polar groups to associate with water means that non-polar covalent substances do not dissolve well in water. Nitrogen, N_2, for example, has very low solubility in water at normal pressure, as do hydrocarbons such as candle wax and large covalent molecules such as chlorophyll. If you think about the substances that mark clothes and are not easily removed with water – grease, red wine, grass stains, and gravy are good examples – they are all relatively large insoluble non-polar molecules.

Dry cleaning is a process where clothes are washed without water. Instead, a less polar organic liquid is used which may be a better solvent for stains caused by large non-polar molecules such as grass and grease.

Likewise, polar substances have low solubility in non-polar solvents as they will remain held to each other by their dipole–dipole attractions and cannot interact well with the solvent. You can observe this by putting some sugar into cooking oil, and noticing that it does not dissolve.

Non-polar covalent substances dissolve best in non-polar solvents, and polar substances dissolve best in polar solvents.

Giant molecular substances are generally insoluble in all solvents, as too much energy would be required to break the strong covalent bonds in their structure. Beaches made primarily of sand, SiO_2, do not dissolve when the tide comes in and a diamond ring can safely be immersed in water.

Electrical conductivity

Covalent compounds do not contain ions, and so are not able to conduct electricity in the solid or liquid state. Some polar covalent molecules, however, in conditions where they can ionize, will conduct electricity. For example, HCl dissolved in water (hydrochloric acid) is an electrical conductor.

As discussed on page 200, the giant covalent molecules graphite and graphene are electrical conductors. In addition, fullerene and silicon have semi-conductivity properties. Diamond is a non-conductor of electricity.

Summary of physical properties

We can now summarize the physical properties of ionic and covalent compounds, though it should be recognized that the table below gives only general trends and does not apply universally.

	Ionic compounds	Polar covalent compounds	Non-polar covalent compounds	Giant covalent
Volatility	low	higher	highest	low
Solubility in polar solvent, e.g. water	soluble	solubility increases as polarity increases	non-soluble	non-soluble
Solubility in non-polar solvent, e.g. hexane	non-soluble	solubility increases as polarity decreases	soluble	non-soluble
Electrical conductivity	conduct when molten (l) or dissolved in water (aq)	non-conductors	non-conductors	non-conductors except graphite, graphene and semiconductivity of Si and fullerene

Challenge yourself

6. If you were given two solutions and told one contained a polar substance and the other a non-polar substance, suggest experiments that might enable you to identify which is which.

Exercise

Q27. The physical properties of five solids labelled A, B, C, D and E are summarized below. The substances are: an ionic compound, a non-polar molecular solid, a metal, a polar molecular solid, and a covalent network substance. Classify each correctly.

Sample	Solubility in water	Conductivity of solution	Conductivity of solid	Relative melting point
A	insoluble	–	yes	third to melt
B	insoluble	–	no	highest
C	soluble	no	no	second to melt
D	insoluble	–	no	lowest
E	soluble	yes	no	fourth to melt

Q28. Which substance is the most soluble in water?

A CH_3OH **B** CH_4 **C** C_2H_6 **D** C_2H_5OH

Q29. State the intermolecular forces that exist between molecules of each of the following.

(a) dry ice, $CO_2(s)$ **(b)** $NH_3(l)$ **(c)** $N_2(l)$

(d) $CH_3OCH_3(g)$ **(e)** a mixture of $CH_3OCH_3(l)$ and $C_6H_{14}(l)$

Q30. Which of each pair has the lower boiling point?

(a) C_2H_6 and C_3H_8 **(b)** H_2O and H_2S

(c) Cl_2 and Br_2 **(d)** HF and HCl

Structure 2.2.10 – Intermolecular forces and chromatography

Structure 2.2.10 – Chromatography is a technique used to separate the components of a mixture based on their relative attractions involving intermolecular forces to mobile and stationary phases. Explain, calculate and interpret the retardation factor values, R_f.	
The use of locating agents is not required. The operational details of a gas chromatograph or high-performance liquid chromatograph will not be assessed.	Tool 1 – How can a mixture be separated using paper chromatography or thin layer chromatography (TLC)?

Chromatography is a technique used to separate the components of a mixture

Chromatography is a useful technique for separating and identifying the components of a mixture. The basic principle is that the components have different affinities for two phases, a **stationary phase** and a **mobile phase**, and so are separated as the mobile phase moves through the stationary phase. The levels of solubility of each component in each of the phases is dependent on the intermolecular forces present.

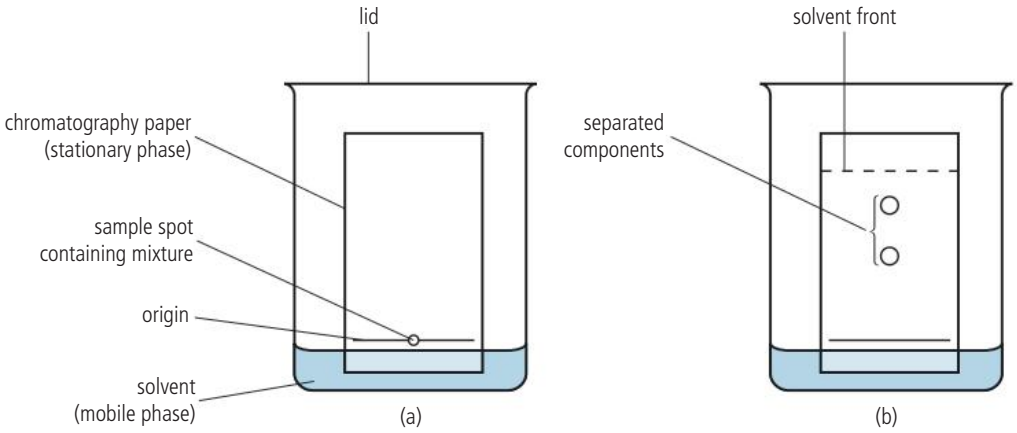
Paper chromatography

Racing compounds on TLC. Full details of how to carry out this experiment with a worksheet are available in the eBook.

SKILLS

Paper chromatography involves the use of a piece of chromatographic paper and a solvent to separate a mixture. It is used mainly for qualitative analysis. The paper, which contains about 10% water, is the stationary phase. Water is adsorbed by forming hydrogen bonds with the –OH groups in the cellulose of the paper. The solvent is the mobile phase as it rises up the paper by capillary action. As it does so it dissolves the components of the mixture to different extents, so carrying them at different rates. We often have to trial a number of different solvents until we identify one which will separate components of the mixture to a suitable extent.

As shown in Figure 15, the procedure is simple to run. A small sample of the mixture is spotted near the bottom of the chromatographic paper. This position, known as the **origin**, needs to be clearly marked (in pencil so as not to dissolve in the solvent and interfere with the experiment). The paper is then suspended in a chromatographic tank containing a small volume of solvent, ensuring that the spot is above the level of the solvent.



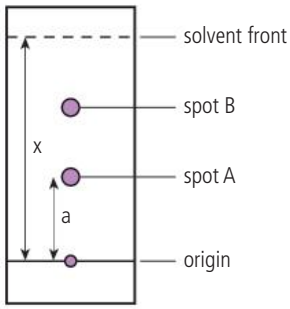
S2.2 Figure 15 Showing (a) the apparatus used to separate a mixture by paper chromatography and (b) the resulting separation of components in the mixture after the solvent rises up the chromatography paper.

As the solvent rises up the paper, it will pass over the sample spot. The components in the spot will distribute themselves between the two phases and so move up the paper at different speeds. As a result, they become spread out according to their different solubilities in the mobile and stationary phases. When the solvent reaches almost to the top of the paper, its final position is marked and is known as the *solvent front*. Each component can be distinguished as a separate isolated spot up the length of the paper. The final result is known as a *chromatogram*.

The position of each component on the chromatogram can be represented as an R_f value (retardation factor), which is calculated as shown in Figure 16.

$$R_f = \frac{\text{distance moved by component}}{\text{distance moved by solvent}}$$

So, for component A, $R_f = \frac{a}{x}$



S2.2 Figure 16 Calculation of R_f values in chromatography.

Specific substances have characteristic R_f values when measured under the same conditions, so can be identified by comparing the values obtained with data tables.

In chromatography, the R_f value can be used to identify the components of a mixture.

$$R_f = \frac{\text{distance moved by component}}{\text{distance moved by solvent}}$$

When measuring the distances to calculate R_f values, be careful to measure from the origin and not from the bottom of the paper. Similarly, the solvent moves as far as the solvent front, not to the top of the paper.

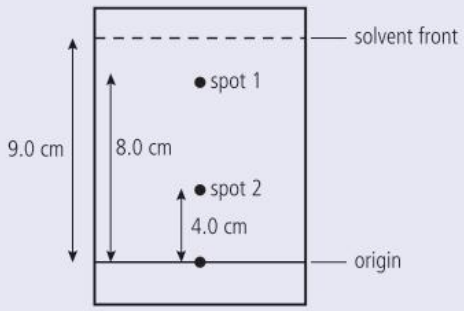
Thin layer chromatography

Another common chromatographic technique is **thin layer chromatography**. It works on the same principles as paper chromatography but the stationary phase is a uniform layer of silica (silicon dioxide) or alumina (aluminium oxide) coated onto a piece of glass, metal or plastic. The surfaces of both silica and alumina contain hydroxyl groups so are considered polar and able to form hydrogen bonding with components in a sample mixture.

Tool 1 - How can a mixture be separated using paper chromatography or thin layer chromatography (TLC)?

Worked example

A sample is known to contain two different substances. After carrying out paper chromatography using a solvent of butan-1-ol, propanone and water, the following chromatogram was obtained.



Calculate the R_f values for both spots.

Solution

Use this formula for both spots: $R_f = \dfrac{\text{distance moved by component}}{\text{distance moved by solvent}}$

Spot 1 $R_f = \dfrac{8.0}{9.0} = 0.89$

Spot 2 $R_f = \dfrac{4.0}{9.0} = 0.44$

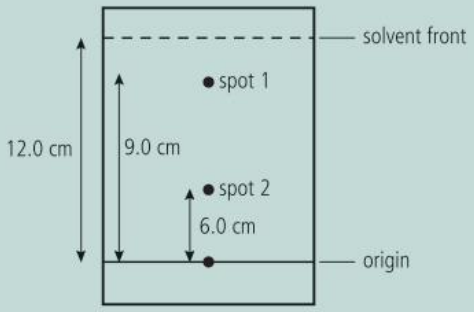
Chromatography is routinely used for the identification of amino acids found in proteins. As amino acids are colourless in solution they are usually treated with a locating reagent such as ninhydrin at the end of the process. Most amino acids will now appear purple and can be distinguished as separate isolated spots up the length of the paper. The R_f of these spots can be compared with known values calculated using the same solvent.

Exercise

Q31. Which two measurements are required to calculate the retardation factor value for a component spot in chromatography?

	Measurement 1	Measurement 2
A	height of origin	height of spot
B	height of solvent front	height of chromatography paper
C	height of solvent front	height of spot
D	height of origin	height of solvent front

Q32. Calculate the R_f values for the two spots on the following chromatogram.



Q33. A mixture of two organic compounds was separated by TLC using a non-polar solvent.

Compound	Distance travelled / mm
X	24
Y	72
Solvent	80

(a) Calculate the R_f values of X and Y.

(b) Outline why compound Y has travelled the greater distance.

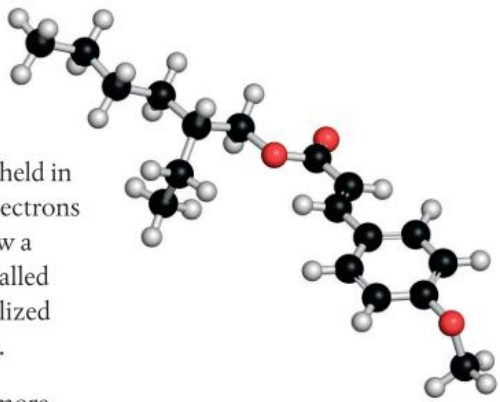
HL

Structure 2.2.11 – Resonance structures

Structure 2.2.11 – Resonance structures occur when there is more than one possible position for a double bond in a molecule.	
Deduce resonance structures of molecules and ions.	
Include the term 'delocalization'.	Structure 1.3 – Why are oxygen and ozone dissociated by different wavelengths of light?

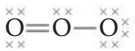
Resonance structures occur when there is more than one possible position for a double bond in a molecule

Our account of covalent bonding so far describes a bond as a pair of electrons held in a specific position within a molecule. However, in some molecules, bonding electrons are less restricted than this. Instead of being confined to one location they show a tendency to be shared between more than one bonding position in a process called **delocalization**. Free from the constraints of a single bonding position, delocalized electrons spread themselves out, giving greater stability to the molecule or ion.

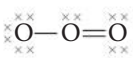


▲ Molecular model of $C_{18}H_{26}O_3$, found in sunscreen. Carbon atoms are shown in black, hydrogen atoms in white, and oxygen atoms in red. Note the benzene ring and carbon–carbon double bonds in the molecule. Sunscreens help to protect the skin from sun damage by absorbing UV radiation and releasing it as heat. They are able to do this due to the many double bonds and delocalized electrons in their structure.

Delocalization is a characteristic of electrons in multiple bonds when there is more than one possible position for a double bond within a molecule. For example, let us look again at the Lewis formula of ozone, O_3, from page 191,



We can see that a different Lewis structure would be equally valid:



These structures suggest that the molecule should contain one oxygen–oxygen double bond and one oxygen–oxygen single bond, which we would expect to be different in bond length and bond strength. However, experimental data reveal that ozone actually contains two *equal* oxygen–oxygen bonds, intermediate in length and strength between single and double bonds.

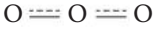
Resonance occurs when more than one valid Lewis formula can be drawn for a particular molecule. The true structure is an average of these, known as a resonance hybrid.

	O–O single bond	O=O double bond	oxygen–oxygen bonds in O_3
Bond length / pm	148	121	127
Bond enthalpy / kJ mol^{-1}	144	498	364

The intermediate bond length and strength found in ozone can be explained by the concept of **resonance**, where we find that the true structure of the molecule is a combination of the two Lewis formulas depicted below.



Lewis formulas with more than one possible position for a double bond are known as **resonance structures**. The electrons from the double bond delocalize and spread themselves equally between both possible bonding positions. Therefore, the true structure of ozone is a blend or *hybrid* of these Lewis formulas. We can represent this structure using dashed lines to indicate where electrons from the double bond are shared between bonding positions. This is known as a **resonance hybrid**.



It is as if you were trying to explain to someone what a zorse (a cross between a zebra and a horse) looks like: you might draw a zebra and a horse and a double-headed arrow between them implying the zorse is an intermediate. You would not mean that the animal is a zebra one minute and a horse the next! Likewise, resonance structures do not represent forms that flip from one to the other. Resonance structures can be drawn for any molecule in which there is more than one possible position for a double bond; the number of structures will equal the number of different possible positions.



A zorse is a hybrid of a zebra and a horse.

The concept of resonance can be used to explain why O_2 molecules, containing an oxygen–oxygen double bond, require shorter wavelength (higher energy) light to dissociate (< 242 nm) compared to molecules of O_3 (< 330 nm).

Structure 1.3 – Why are oxygen and ozone dissociated by different wavelengths of light?

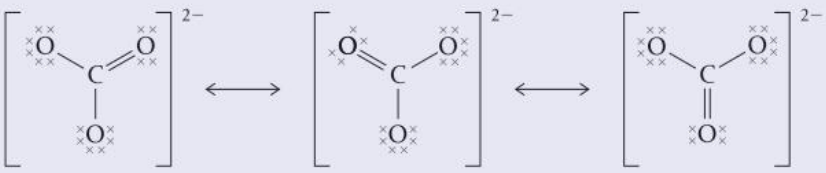
Worked example

Draw the resonance structures for the carbonate ion CO_3^{2-}.

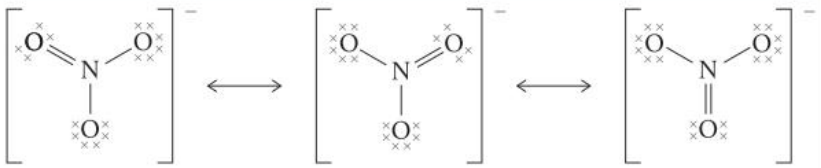
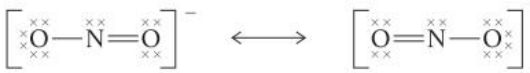
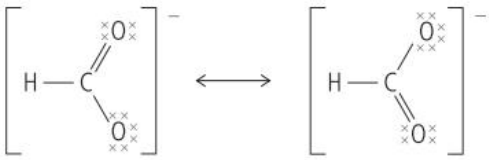
Solution

Count the number of valence electrons: 4 + (6 × 3) + 2 = 24

Draw the Lewis formula, noting that there are three possible positions for the double bond. This means there will be three resonance structures, as follows:



Some other ions and molecules that have delocalized electrons, and so can be represented by resonance structures, are shown in the table on the next page.

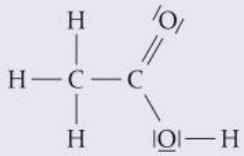
Species name and formula	Number of valence electrons	Resonance structures
nitrate, NO_3^-	24	
nitrite, NO_2^-	18	
methanoate, $HCOO^-$	18	

Worked example

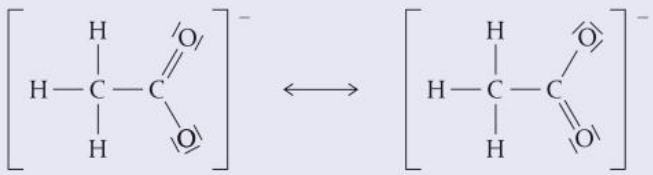
Compare the structures of CH_3COOH and CH_3COO^- with reference to their possible resonance structures.

Solution

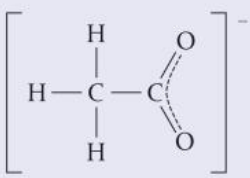
Draw the Lewis formula of each structure, and note if there is more than one possible position for a double bond to be placed.

CH_3COOH 

There is only one possible Lewis formula, so the molecule has one carbon–oxygen double bond and one carbon–oxygen single bond.

CH_3COO^- 

Two resonance structures exist, so the ion exists as a hybrid with two equal carbon–oxygen bonds, intermediate in length and strength between the two carbon–oxygen bonds in CH_3COOH.



You can deduce how many resonance structures exist for a molecule or ion by looking at the number of possible positions for its double bond(s).

We do not draw lone pairs of electrons on the structure of a resonance hybrid as they are involved in the process of delocalization so do not have a fixed position.

Resonance is an important concept that gives special properties to the structures where it occurs. We have seen its influence on bond lengths and strengths, which in turn can influence reactivity. The different strengths of organic acids and bases, for example, can often be explained by resonance.

Exercise

Q34. Draw the two resonance structures of the nitrite ion, NO_2^-.

Q35. Put the following species in order of increasing carbon–oxygen bond length:

CO CO_2 CO_3^{2-} CH_3OH

Q36. By reference to their resonance structures, compare the nitrogen–oxygen bond lengths in the nitrate ion (NO_3^-) and nitric acid (HNO_3).

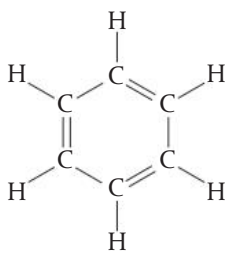
Q37. Draw the resonance hybrid of the methanoate ion, $HCOO^-$, by using a dotted line to represent the delocalized electrons.

Structure 2.2.12 – Benzene

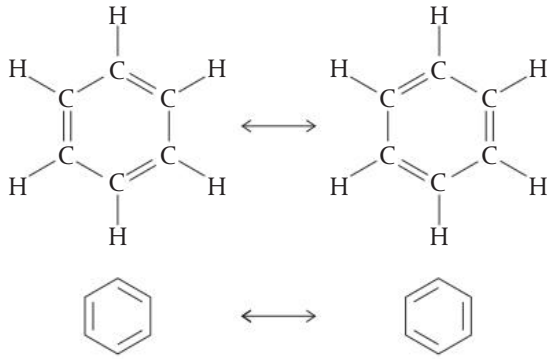
Structure 2.2.12 – Benzene, C_6H_6, is an important example of a molecule that has resonance. Discuss the structure of benzene from physical and chemical evidence.	
	Reactivity 2.1, 2.2 – How does the resonance energy in benzene explain its relative unreactivity? Reactivity 3.4 – What are the structural features of benzene that favour it undergoing electrophilic substitution reactions?

Benzene is an important example of a molecule which has resonance

Benzene, C_6H_6, is a particularly interesting case of a molecule with delocalized electrons. The six carbon atoms are arranged in a hexagonal ring, each also bonded to a hydrogen atom, in a triangular planar arrangement with 120° bond angles. A possible Lewis structure is:



But we can see there are other possible positions for the double bonds, indicating the existence of resonance structures.

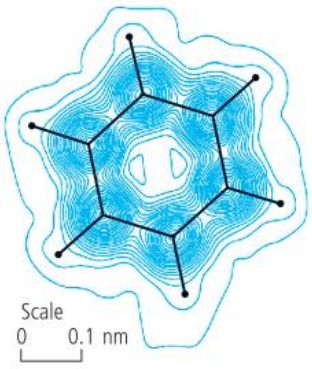


The true form of benzene is the resonance hybrid:

 , which is most commonly represented by: 

The circle inside the hexagon represents delocalized electrons, which are spread equally through the ring, rather than being in confined double bonds. As we would expect, this results in carbon–carbon bonds that are equal in length and strength, and intermediate between those of single and double bonds.

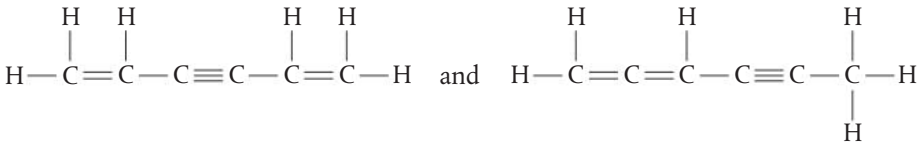
	C–C single bond	C=C double bond	carbon–carbon bonds in benzene
Bond length / pm	154	134	139
Bond enthalpy / kJ mol^{-1}	346	614	507



▲ Electron density map for benzene at −3 °C. The blue lines join parts of the molecule with equal electron density, showing that all bonds between carbon atoms are equal and of length 0.139 nm.

Benzene does not behave like other unsaturated molecules

The 1:1 ratio of carbon to hydrogen in benzene, C_6H_6, indicates a high degree of unsaturation, greater than that of alkenes or alkynes. Yet early observations of benzene indicated that it does not show the characteristic properties of possible structures such as:



Note that organic compounds are often represented with a skeletal formula. Straight lines represent covalent bonds and carbons are found where these lines meet. Hydrogen atoms are ignored unless they are part of a functional group.

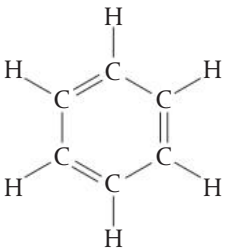
Make sure that when you are drawing the structure of benzene you do not forget to include the ring inside the hexagon. If you do forget, and draw this  instead, it denotes an entirely different structure, cyclohexane C_6H_{12}.

For example, benzene has no isomers, and is reluctant to undergo addition reactions – both features that would be expected from these molecules.

TOK

There is a well-established account that Kekulé visualized the ring structure of benzene after experiencing a dream about snakes biting each other's tails. To what extent can imagination and unconscious processes be important in scientific advancement?

In 1865 Kekulé suggested a cyclic arrangement of the carbon atoms with alternating single and double bonds. This is 1,3,5-cyclohexatriene:



which is usually drawn without the atoms marked as



The symmetry of this model explained some of the known properties of benzene, such as the fact that it has no isomers, but again fell short of explaining benzene's atypical reactivity for such an unsaturated molecule. Clearly, modifications to the Kekulé structure were needed. Advances in technology, such as X-ray diffraction, provided data that helped to develop the current model of benzene structure.



Non-polar liquids such as benzene can be separated from aqueous solutions using a separating funnel because they form a separate layer and the lower liquid can be drained. Here, the lower aqueous layer has been coloured purple to make the separation more visible.

Friedrich August Kekulé von Stradonitz (1829–1896) was a German organic chemist who also spent parts of his working life in France, Switzerland, and England. He was a principal founder of the theory of chemical structure, establishing the tetravalence of carbon and the ability of carbon atoms to link to each other. He provided the first molecular formulas using lines to represent bonds between atoms, and most famously the ring structure of benzene. In addition, he was evidently an influential teacher as three of the first five Nobel Prizes in Chemistry were won by his students: van't Hoff in 1901, Fischer in 1902, and Baeyer in 1905.

The special stability of the benzene ring is the result of delocalized electrons

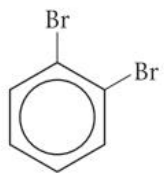
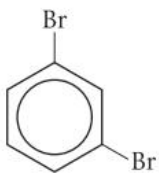
We have already seen that the usual convention for depicting benzene uses a ring inside the hexagon to denote the delocalized electrons.



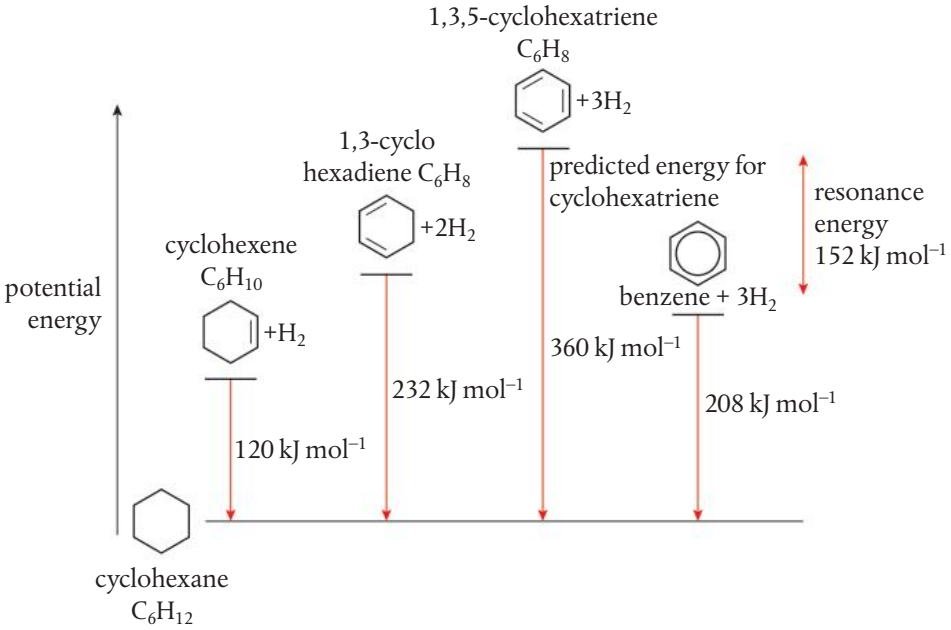
As we will see later in this chapter, the delocalized electron density is concentrated in two donut-shaped rings above and below the plane of the ring. This is a very stable arrangement and lowers the internal energy of the ring.

This model is supported by **physical** and **chemical evidence**, and provides explanations for most observed properties of benzene, as described below.

Reactivity 3.4 – What are the structural features of benzene that favour it undergoing electrophilic substitution reactions?

Property	Observation / evidence	Explanation
1 Bond lengths	All carbon–carbon bond lengths in benzene are equal, and intermediate in length between single and double bonds.	Each bond contains a share of three electrons between the bonded atoms. X-ray bond length data (nm): alkane single bond C–C 0.154 nm alkene double bond C=C 0.134 nm benzene  0.139 nm
2 $\Delta H_{hydrogenation}$ for the reaction $C_6H_6 + 3H_2 \rightarrow C_6H_{12}$	Theoretical value based on adding H_2 across three C=C double bonds = -362 kJ mol^{-1} Experimental value for benzene = -210 kJ mol^{-1} Benzene is more stable than predicted from the Kekulé structure by approx. 152 kJ mol^{-1}.	Delocalization minimizes the repulsion between electrons and so gives benzene a more stable structure, lowering its internal energy by 152 kJ mol^{-1}. This is the amount of energy that would have to be supplied in order to overcome the special stability of the delocalized ring. It is called the *resonance energy* or the *stabilization energy* of benzene.
3 Type of reactivity	Benzene is reluctant to undergo addition reactions and is more likely to undergo substitution reactions.	Addition reactions are energetically not favoured as they would involve disrupting the ring of delocalized electrons. The resonance energy would have to be supplied and the product, without the delocalized ring of electrons, would be *less* stable. Benzene can instead undergo substitution reactions that preserve the stable ring structure.
4 Isomers	Only three isomers of dibromobenzene exist.	As benzene is a symmetrical cyclic molecule with no alternating single and double bonds, two bromine atoms can replace hydrogen atoms in only three possible configurations.  1,2-dibromobenzene  1,3-dibromobenzene  1,4-dibromobenzene This would not be the case for most other possible structures of C_6H_6.

Enthalpy changes for the hydrogenation of benzene and related molecules.



Reactivity 2.1, 2.2 – How does the resonance energy in benzene explain its relative unreactivity?

The resonance energy labelled in this graph shows the difference between the predicted energy change of the reaction compared to the actual value. This illustrates the relative stability of the delocalized system compared to what we would expect from alternating single and double bonds.

Nature of Science

The changing model of the structure of benzene has largely been a result of advances in technology and instrumentation. The Kekulé model seemed to explain many of the known properties of benzene at the time, but had to be reconsidered when new quantitative data was obtained. X-ray diffraction experimentation on bond lengths, and the resistance of benzene to undergo addition reactions, are two examples of counter-evidence to the Kekulé model. The progress of science sometimes demands a refinement or abandonment of a model as new data are obtained, and the acceptance of this is dependent on the objectivity and openness of scientists.

The substitution reactions of benzene are discussed further in Reactivity 3.4.

Benzene is an important industrial solvent and is used in the synthesis of drugs, dyes, and plastics such as polystyrene. Because of its frequent use, benzene has become widespread in the environment of developed countries. In the USA, petroleum contains up to 2% benzene by volume and it may be as high as 5% in other countries. But benzene is a toxic compound and a known carcinogen. Chronic exposure at low levels can lead to aplastic anaemia and leukaemia. Regulating bodies in many countries have set permissible exposure limits for benzene levels in drinking water, foods, and air in the workplace.

Exercise

Q38. Draw the Lewis formulas of the two resonance structures of benzene.

Q39. Explain why the carbon–carbon bond length in benzene is an intermediate value between that of a C–C bond and a C=C bond.

Q40. Describe the bonding in a benzene molecule and use it to explain benzene's energetic stability.

Q41. Which of the following are evidence of delocalization in the structure of benzene?

I. C–C bond enthalpy data
II. reluctance to undergo addition reactions
III. existence of only 3 isomers of dibromobenzene

A I and II **B** I and III **C** II and III **D** I, II and III

Structure 2.2.13 – Molecules with an expanded octet

Structure 2.2.13 – Some atoms can form molecules in which they have an expanded octet of electrons. Represent Lewis formulas for species with five and six electron domains around the central atom. Deduce the electron domain geometry and the molecular geometry for these species using the VSEPR model.	
	Structure 3.1 – How does the ability of some atoms to expand their octet relate to their position in the periodic table?

Some molecules contain a central atom with an expanded octet

Earlier in the chapter, we explored the shapes of molecules having two, three and four electron domains – that is, those with up to eight electrons, an octet, around the central atom. The octet, being associated with a special stability for most atoms, is the most common electron arrangement.

However, when the central atom is an element from period 3 or below, we sometimes find compounds in which there are more than eight electrons around the central atom. This is known as an **expanded octet**. This arrangement is possible because the d orbitals available in the valence shell of these atoms have energy values relatively close to those of the p orbitals. So promotion of electrons, for example, from 3p to empty 3d orbitals, will allow additional electron pairs to form. This is how elements such as phosphorus and sulfur expand their octets, forming species with five or six electron domains. These will have characteristic shapes, as discussed on the next page. In the following diagrams, as before, non-bonding electron pairs on the surrounding atoms are not shown, to aid clarity, so these are *not* Lewis formulas.



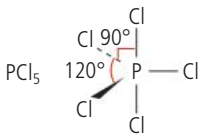
Structure 3.1 – How does the ability of some atoms to expand their octet relate to their position in the periodic table?



Exceptions to the octet rule:
- **Small atoms such as Be and B form stable molecules with fewer than an octet of electrons.**
- **Atoms of elements in period 3 and below may expand their octet by using d orbitals in their valence shell.**

Species with five electron domains

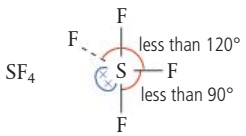
Molecules with five electron domains will position them in a **triangular bipyramidal** shape, which has angles of 90° and 120°. If all five electron domains are bonding electrons, the shape of the molecule is also triangular bipyramidal.



However, as we saw in the examples with three and four electron domains on page 197, if one or more of the electron domains are non-bonding electrons, then the shape of the *molecule* will be different as it is determined by the positions only of the *bonded atoms*.

In determining the position of the non-bonding pairs of electrons, remember that they cause greater repulsion than bonding pairs so will arrange themselves in the position offering the greatest distance from a neighbouring pair. In the triangular bipyramidal structure, this will mean in the equatorial plane, as shown in the examples below.

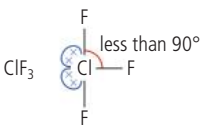
- One non-bonding pair gives an **unsymmetrical tetrahedron** or **see-saw** shape.



There will be some distortion of the shape due to the greater repulsion of the non-bonding pair of electrons, so bond angles will be less than 90° and less than 120°.

Note that to minimize the additional repulsion between non-bonding and bonding electron domains, we find the lone pair of electrons located in an equatorial position (in the horizontal plane around the central atom) instead of an axial position (above or below the horizontal plane).

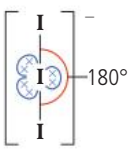
- Two non-bonding pairs give a **T-shaped** structure.



The bond angles are less than 90°.

Again, we find that the lone pairs of electrons are located in an equatorial position to minimize repulsion between them.

- Three non-bonding pairs give a **linear** shape.



The bond angle is 180°.

Compounds containing two different halogen atoms bonded together are called interhalogen compounds. They are interesting because they contain halogen atoms in unusual oxidation states. The more electronegative halogen has its typical negative oxidation number, whereas the less electronegative halogen has a positive oxidation number. For example, in ClF_3 described here, the oxidation number of each F is –1 and the oxidation number of Cl is +3. You can read more about oxidation states in Structure 3.1.

Challenge yourself

7. The position of bonding and non-bonding pairs of electrons in molecules or ions with five electron domains can be predicted by identifying the arrangement with the lowest number of lone pair–lone pair 90° angles followed by the lowest number of 90° angles between lone pairs and bonding pairs.

   Can you use this approach to show why we observe see-saw, T-shaped and linear geometries for SF_4, ClF_3 and I_3^- seen in this section?



Iodine starch test. 'Iodine solution' actually contains $I_2(s)$ dissolved in KI(aq). The I_3^- species present in this solution turns from orange to blue-black when mixed with starch – confirming the presence of starch in the bread.

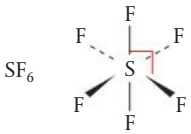
The species I_3^- described here as having a linear structure is the form of iodine used in the widely used starch test. The iodine reagent is made by dissolving iodine in water in the presence of potassium iodide, forming the soluble tri-iodide ion.

$I_2(s) + I^-(aq) \rightarrow I_3^-(aq)$

When this species is added to starch, it slides into coils in the starch structure causing an intense blue-black colour.

Species with six electron domains

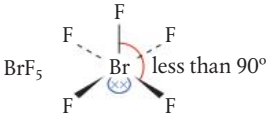
Molecules with six electron domains will position them in an **octahedral** shape with angles of 90°. So a molecule having all six of its electron domains as bonding pairs of electrons will have this symmetrical octahedral shape.



The bond angles are 90°.

The shape of a molecule in which there are one or more non-bonding pairs of electrons is based on considering where the non-bonding pairs will be placed for minimum repulsion.

- One non-bonding pair gives a **square pyramidal** shape. The additional repulsion from the non-bonding pair will cause the bond angles to be slightly less than 90°.

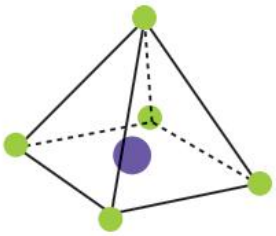


The eight-sided octahedral shape is determined by the six electron domains directed to each corner.



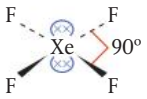
This is a shape commonly found in the complexes of metal ions with ligands, described more fully in Structure 3.1.

Due to their stable electron configuration, group 18 compounds are very unreactive. Compounds exist only between the elements with larger atoms that have lower ionization energies, and the most electronegative elements fluorine and oxygen. Xenon tetrafluoride (XeF_4), described here, is stable at normal temperatures and occurs as colourless crystals. Its square planar structure was determined by NMR spectroscopy and X-ray crystallography in 1963.



Geometric model showing the position of atoms in iodine pentafluoride, IF_5. The fluorine atoms are shown as small green spheres and the iodine atom as a large violet sphere. Like BrF_5 described in the text, this molecule has a square pyramidal shape to maximize the distance between the valence shell electron pairs including the lone pair that is not shown in this model.

- Two non-bonding pairs will maximize their distance apart by arranging those pairs on opposite sides of the central atom. This gives a **square planar** shape with bond angles of 90°.



XeF_4

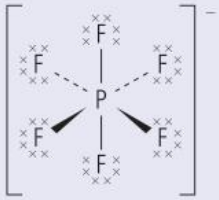
Worked example

Predict the shape and bond angles found in PF_6^-.

Solution

First work out its Lewis structure following the steps on page 179.

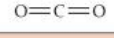
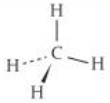
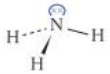
total number of valence electrons = 5 + (7 × 6) + 1 = 48



So there are six bonding electron domains around the central atom P, which will be arranged in an octahedral shape. All bond angles are 90°.

Summary of molecular geometries predicted from the VSEPR model

The geometries of molecules for two, three, four, five, and six electron domains are summarized in the table on the following page. This table is also available as a PDF in the eBook.

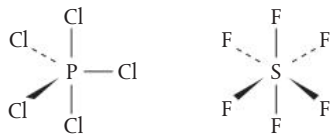
Number of electron domains around central atom	Electron domain geometry	Number of bonding electron domains	Number of non-bonding pairs of electrons	Molecular geometry	Example
2	linear	2	0	linear	CO_2 
3	planar triangular	3	0	planar triangular	BF_3 
3	planar triangular	2	1	V-shaped	SO_2 
4	tetrahedral	4	0	tetrahedral	CH_4 
4	tetrahedral	3	1	pyramidal	NH_3 
4	tetrahedral	2	2	V-shaped	H_2O 
5	triangular bipyramidal	5	0	triangular bipyramidal	
5	triangular bipyramidal	4	1	unsymmetrical tetrahedron/ see-saw	PCl_5 SF_4 
5	triangular bipyramidal	3	2	T-shaped	
5	triangular bipyramidal	2	3	linear	ClF_3 I_3^- 
6	octahedral	6	0	octahedral	SF_6 
6	octahedral	5	1	square pyramidal	BrF_5 
6	octahedral	4	2	square planar	XeF_4 

Only 2, 3 and 4 electron domains are required at Standard Level.

Molecular polarity in molecules with five and six electron domains

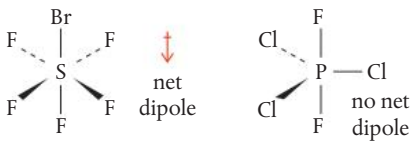
As we have seen on page 197, the net dipole of a molecule can be deduced by considering bond dipoles and molecular geometry. The same principles can be applied to molecules with five and six electron domains. For example, PCl_5 and SF_6 are both non-polar because all bonded atoms are identical and there are no lone pairs on the central atom.

Non-polar molecules:

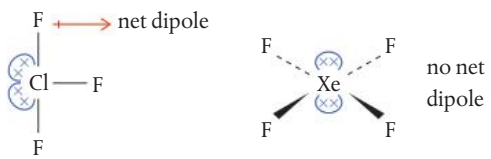


PCl_5 SF_6

If the atoms attached to the central atom are not all the same, there may or may not be a net dipole depending on the symmetry. For example, $SBrF_5$ has a net dipole and is polar; PCl_3F_2 has no net dipole due to cancellation, so it is non-polar.



The presence of lone pairs often, but not always, results in a polar molecule. It again depends on symmetry and whether dipoles cancel. For example, ClF_3 is polar, whereas XeF_4 is not.



Exercise

Q42. Predict the geometries and bond angles of the following molecules and ions:

(a) XeF_2 **(b)** ClO_3^- **(c)** OF_2

(d) XeO_4 **(e)** PCl_6^- **(f)** IF_4^+

Q43. How many electron domains are there around the central atom in molecules that have the following geometry?

(a) square planar **(b)** octahedral **(c)** square pyramidal

(d) trigonal bipyramidal **(e)** linear

Q44. What bond angles do you expect for each of the following?

(a) the F–Kr–F angle in KrF_4

(b) the Cl–P–Cl angle in PCl_3

(c) the F–Xe–F angle in XeF_4

Q45. Predict the shapes and bond angles in the following ions.

(a) IO_4^- **(b)** BrF_4^- **(c)** PCl_4^+ **(d)** FCl_2^+

Q46. Predict the shapes and bond angles of the following molecules and identify which would be expected to be polar.

(a) XeF_2 **(b)** OF_2 **(c)** XeO_4

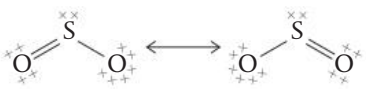
(d) $ClBr_3$ **(e)** TeF_6

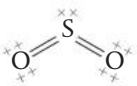
Structure 2.2.14 – Formal charge

Structure 2.2.14 – Formal charge values can be calculated for each atom in a species and used to determine which of several possible Lewis formulas is preferred. Apply formal charge to determine a preferred Lewis formula from different Lewis formulas for a species.	
	Structure 3.1, Reactivity 3.2 – What are the different assumptions made in the calculation of formal charge and of oxidation states for atoms in a species?

Formal charge can be used to predict a preferred Lewis formula

Sometimes, when you follow the rules for drawing Lewis formulas, you can come up with more than one possible structure that seems to be acceptable. This happens especially with molecules that are able to form an expanded octet, where we can broaden our study of resonance structures. A classic example is sulfur dioxide, SO_2,

which in different sources is represented as 

or as a structure with an expanded octet on S 

These three are all resonance structures as they differ only in the distribution of electrons, not in the position of the atoms in the skeletal structure. They all have the same shape with a bond angle of approximately 117°.

Can we determine which of these represents the most stable structure? A useful tool to use for this is the concept of **formal charge**. This treats covalent bonds as if they were purely covalent with equal electron distribution – so for this, forget about electronegativity differences between the atoms. The idea is to count how many electrons 'belong' to (are assigned to) each atom in the Lewis formula, and compare this with the number of valence electrons in the non-bonded atom. The difference between these two is the formal charge. It can be expressed as:

formal charge (FC) = **number of valence electrons in unbonded atom** − **number of electrons assigned to atom in Lewis formula**

- The number of valence electrons is determined from its group in the periodic table.
- The number of electrons assigned to an atom in the Lewis formula is calculated by assuming that:
  (a) each atom has an equal share of a bonding electron pair (one electron per atom), even if it is a coordination bond;
  (b) an atom owns its lone pairs completely.

This means that:

number of electrons assigned = $\frac{1}{2}$ **number of electrons in bonded pairs** ($\frac{1}{2}$B) + **number of electrons in lone pairs (L)**

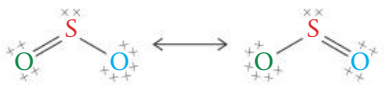
So overall:

$$FC = V - (\tfrac{1}{2}B + L)$$

Formal charge (FC) is determined for each atom in a structure from: $FC = V - (\frac{1}{2}B + L)$ where V = valence electrons, B = number of bonding electrons and L = number of lone pair electrons.

Low formal charges mean that less charge transfer has taken place in forming a structure from its atoms, and in general this represents the most stable or preferred structure.

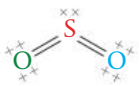
We can now apply this to the different Lewis formulas for SO_2 shown above, and consider the formal charge of each atom in turn in all three structures.

(i) 

S: 3 bonding pairs
1 lone pair
FC = 6 – (3 + 2) = 1

left O: 2 bonding pairs
2 lone pairs
FC = 6 – (2 + 4) = 0

right O: 1 bonding pair
3 lone pairs
FC = 6 – (1 + 6) = –1

(ii) 

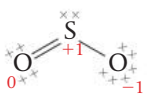
S: 4 bonding pairs
1 lone pair
FC = 6 – (4 + 2) = 0

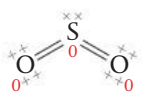
left O: 2 bonding pairs
2 lone pairs
FC = 6 – (2 + 4) = 0

right O: 2 bonding pairs
2 lone pairs
FC = 6 – (2 + 4) = 0

Equivalent Lewis formulas are those that contain the same numbers of single and multiple bonds, such as the resonance structures of ozone. Non-equivalent Lewis formulas contain different numbers of single and multiple bonds, such as the two structures of SO_2 discussed here. Note that the concept of formal charges is used to compare the stabilities of non-equivalent structures, but not for equivalent structures, as they are the same.

The formal charges in each resonance structure can be summarized as follows:

(i) 

(ii) 

We can conclude that structure **(ii)**, where all atoms have a formal charge of zero, is the most stable structure for SO_2.

Challenge yourself

8. Although ozone, O_3, contains three identical atoms, it is a polar molecule. Can you explain why by considering the geometry, resonance structures and formal charge?

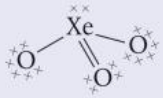
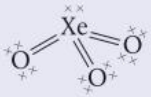
This example shows the use of formal charge in determining which of several possible Lewis formulas is the more stable or preferred structure. In fact, all resonance structures contribute to the electronic structure of the molecule, and the real or observed structure is a combination of them. The more stable structure, the one with the lowest formal charge, contributes more than the less stable structures.

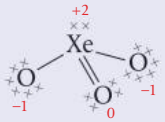
Worked example

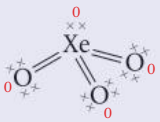
Use the concept of formal charge to determine which of the following Lewis formulas for XeO_3 is preferred.



Solution

		
Xe	FC = 8 – (4 + 2) = +2	FC = 8 – (6 + 2) = 0
left O	FC = 6 – (1 + 6) = –1	FC = 6 – (2 + 4) = 0
central O	FC = 6 – (2 + 4) = 0	FC = 6 – (2 + 4) = 0
right O	FC = 6 – (1 + 6) = –1	FC = 6 – (2 + 4) = 0





The structure on the right with the formal charges closest to zero is preferred.

In general, the Lewis formula with the atoms having values for formal charge closest to zero is preferred.

Note that the sum of the formal charges for a species must be zero for a neutral molecule, or equal to the charge on an ion.

Formal charge is a useful tool but, because it ignores differences in electronegativity values, it does not give the full picture. So, a useful guideline to follow is that the most stable of several Lewis formulas is the structure that has:

- the lowest formal charges *and*
- negative values for formal charge on the more electronegative atoms.

For example, two Lewis formulas with formal charges are shown for N_2O.

(i) (ii)



We can see that both structures have the same difference for formal charge, which suggests equal stability. But **(i)** has the negative charge over the more electronegative atom, O, and so it is preferred.

Structure 3.1, Reactivity 3.2 – What are the different assumptions made in the calculation of formal charge and of oxidation states for atoms in a species?

Formal charge is described here as a tool that helps us to consider the relative stability of molecular structures. In Structure 3.1 we introduce the concept of oxidation number, which similarly considers electron distributions within structures. While formal charge treats covalent bonds as if they were pure covalent bonds with electrons shared equally between atoms, oxidation number treats covalent bonds as if they were ionic, with the transfer of electrons between atoms. So these two models can be viewed as opposite approaches, and in reality neither accurately describes the real charge on atoms. But they both can be useful models, depending on the circumstances.

Nature of Science

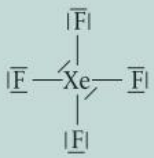
By using formal charge in some situations, and oxidation numbers in another, scientists are applying the principle of Occam's razor. This recognizes that the simplest explanation is often the most appropriate, as it can maximize the explanatory power of a theory.

Challenge yourself

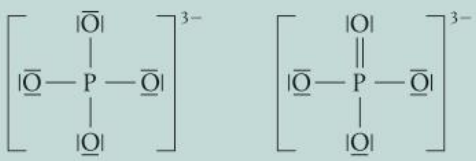
9. There are several covalently bonded molecules and ions that contain transition metals, such as $FeBr_3$ and MnO_4^-. What problems arise in determining the formal charge of species like these?

Exercise

Q47. Identify the formal charge of each atom in xenon tetrafluoride, XeF_4.



Q48. Identify the formal charges on the two possible structures of the phosphate ion (PO_4^{3-}) and determine the preferred structure.



Q49. Use the concept of formal charge to explain why BF_3 is an exception to the octet rule.

Q50. Draw two different Lewis formulas for SO_4^{2-}, one of which obeys the octet rule for all its atoms, the other of which has an octet for S expanded to 12 electrons. Use formal charges to determine which is the preferred structure.

Structure 2.2.15 – Sigma and pi bonds

Structure 2.2.15 – Sigma bonds (σ) form by the head-on combination of atomic orbitals where the electron density is concentrated along the bond axis.
Pi bonds (π) form by the lateral combination of p-orbitals where the electron density is concentrated on opposite sides of the bond axis.
Deduce the presence of sigma bonds and pi bonds in molecules and ions.
Include both organic and inorganic examples.

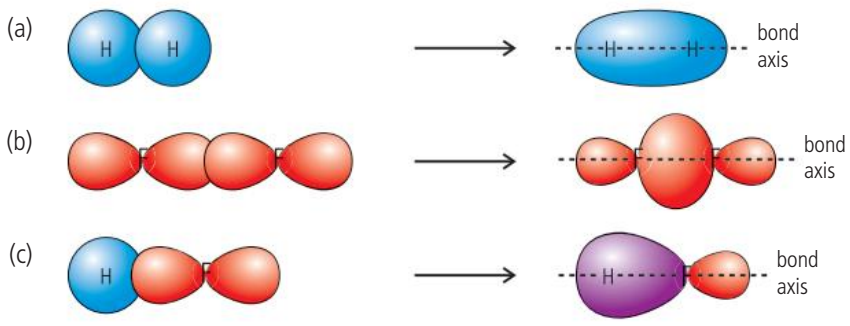
Atomic orbitals overlap to form two types of covalent bond: sigma and pi

The VSEPR model discussed in this chapter gives us a model for predicting the shapes of molecules and ions. But if we stop and think for a moment, it also raises a big question: How can we explain angles such as 109.5°, when the shapes of orbitals described in Structure 2.2 are spherical (s orbitals) or dumb-bell shaped orientated at 90° to each other (p orbitals)? Clearly, these atomic orbitals must undergo some changes during the bonding process to explain the angles that arise.

A full explanation of the interaction between orbitals during bonding, and the resulting electron distributions in covalent bonds, depends on a knowledge of wave mechanics which is not discussed here. But, in simple terms, we can think of a bond as forming when two atomic orbitals, each containing one electron, combine to form a new **molecular orbital** that is at a lower energy level. The shape of this molecular orbital can be predicted from the shapes of the two atomic orbitals, as described below. We will see that there are two main types of molecular orbital, each representing a particular type of covalent bond.

The sigma (σ) bond

When two atomic orbitals combine **head-on** along the **bond axis** – an imaginary line between the two nuclei – the bond is described as a **sigma bond**, denoted using the Greek letter σ. This type of bond forms by the overlap of s orbitals, p orbitals, and hybrid orbitals (described in the next section of this chapter) in different combinations (Figure 17). It is always the bond that forms in a single covalent bond.



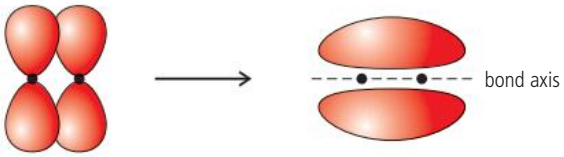
In a sigma bond the electron density is concentrated between the nuclei of the bonded atoms.

All single covalent bonds are sigma bonds. Sigma bonds form by head-on combination of atomic orbitals where the electron density is concentrated along the bond axis.

S2.2 Figure 17 Formation of sigma bond by the overlap of **(a)** s orbitals, e.g. H + H → H_2, **(b)** p orbitals end-on, e.g. F + F → F_2. and **(c)** s and p orbitals, e.g. H + F → HF. The symbol for the element denotes the position of the nucleus. In all cases, the electron density is greatest along the bond axis.

The pi (π) bond

When two p orbitals combine **laterally** (sideways-on) the electron density of the molecular orbital is concentrated in two regions, above and below the plane of the bond axis (Figure 18). This is known as a **pi bond**, denoted using the Greek letter π. This type of bond only forms by the overlap of p orbitals alongside the formation of a sigma bond. In other words, pi bonds only form within a double bond or a triple bond.



S2.2 Figure 18 Formation of pi bond by the lateral combination of p orbitals. The electron density is greatest in two regions above and below the bond axis.

Note that even though the pi bond has two distinct areas of electron density, it is only *one* bond containing a pair of electrons. Both of the electrons can be found anywhere in the two lobes.

The formation of pi bonds within multiple bonds is described more fully in the next section. Pi bonds are weaker than sigma bonds as their electron density is further from the positive charge of the nucleus, and so they break more easily during chemical reactions. We see in Reactivity 3.4.5 how this causes molecules with carbon–carbon double bonds to be more reactive than those with only single bonds.

Double covalent bonds contain one sigma bond and one pi bond.

Triple covalent bonds contain one sigma bond and two pi bonds.

The combinations of atomic orbitals giving rise to each type of bond are summarized in the table below.

Atomic orbitals which combine	Type of bond	Example of bond and molecule
s and s	sigma	H–H in H_2
s and p	sigma	H–Cl in HCl
p and p head-on	sigma	Cl–Cl in Cl_2
hybrid orbitals and s	sigma	C–H in CH_4 N–H in NH_4^+
hybrid orbitals with hybrid orbitals	sigma	C–C in C_2H_6 one of the C=C in C_2H_4 one of the C≡C in C_2H_2
p and p laterally	pi	one of the C=C in C_2H_4 two of the C≡C in C_2H_2 one of the C=O in CO_3^{2-}

Exercise

Q51. Describe the formation of a sigma bond and a pi bond.

Q52. Which of the following would lead to the formation of a sigma bond?

I. hybrid orbital and an s orbital
II. lateral overlap between two p orbitals
III. one s and one p orbital

A I and II **B** I and III **C** II and III **D** I, II and III

Q53. Explain why a carbon–carbon sigma bond is likely to be stronger than a carbon–carbon pi bond.

Q54. Give examples of sigma bonds in molecules that form from overlap of the following orbitals. The first one is completed for you as an example.

(a) s–s: answer H–H in H_2 **(b)** s–p **(c)** p–p end-on
(d) sp^3–s **(e)** sp^2–s **(f)** sp–s **(g)** sp^2–p

Structure 2.2.16 – Hybridization

Structure 2.2.16 – Hybridization is the concept of mixing atomic orbitals to form new hybrid orbitals for bonding.
Analyse the hybridization and bond formation in molecules and ions.
Identify the relationships between Lewis formulas, electron domains, molecular geometry and type of hybridization.
Predict the geometry around an atom from its hybridization, and vice versa.

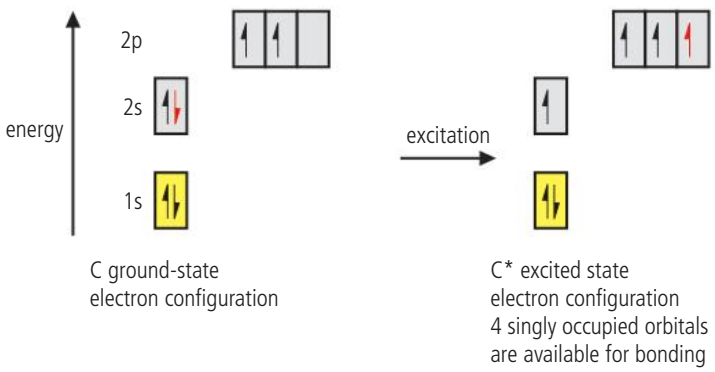
Include both organic and inorganic examples. Only sp, sp^2 and sp^3 hybridization need to be covered.	

The formation of covalent bonds often starts with the excitation of the atoms

Carbon is of great interest in this study as it forms such a vast number of covalently bonded compounds. In all of these compounds, carbon forms *four* covalent bonds. Yet if we consider the electron configuration in the carbon atom, we would not predict this as it has only *two* singly occupied orbitals available for bonding.

C atomic number = 6 electron configuration $1s^2 2s^2 2p_x^1 2p_y^1$

The fact that carbon can – and does – form four covalent bonds indicates that this lowest energy or **ground-state** electron configuration changes during bonding. A process known as **excitation** occurs in which an electron is promoted within the atom from the 2s orbital to the vacant 2p orbital (Figure 19). The atom now has four singly occupied orbitals available for bonding. Hund's rule in Structure 1.3 states that all the electrons in singly occupied orbitals in the same sub-shell have parallel spin.



S2.2 Figure 19 Excitation of carbon showing promotion of the paired s orbital electron (shown in red) to the empty 2p orbital, making four singly occupied orbitals available for bonding.

The amount of energy put in to achieve this is more than compensated by the extra energy released on forming four bonds.

Hybridization involves mixing atomic orbitals to form new hybrid atomic orbitals

Hybridization is the process where atomic orbitals within an atom mix to produce hybrid orbitals of intermediate energy. The atom is able to form stronger covalent bonds using these hybrid orbitals.

The process of excitation explains how carbon is able to form four covalent bonds. But look again at the atomic orbitals now available for bonding – they are not all the same: there is one s orbital, and three p orbitals which are at a slightly higher energy level. So if these different orbitals were used in forming the covalent bonds, we would expect unequal bonds. The fact that methane, CH_4, has four *identical* carbon–hydrogen bonds suggests that these orbitals have been changed and somehow made equal during the bonding process. Again, the details of this are complex and depend on an understanding of quantum mechanics, but in essence unequal atomic orbitals within an atom mix to form new **hybrid atomic orbitals** which are the same as each other, but different from the original orbitals. This mixing of orbitals is known as hybridization. Hybrid orbitals have different energies, shapes, and orientation in space from their parent orbitals and are able to form stronger bonds by allowing for greater overlap.

The explanations given here to explain the formation of covalent bonds, including hybridization, are based primarily on the so-called **valence bond** theory. An alternate theory, known as **molecular orbital** theory, sometimes gives a more accurate picture, especially for describing delocalized pi electrons. Molecular orbital theory, which focuses on the wave nature of electrons, considers them combining either constructively to form a lower energy **bonding molecular orbital**, or destructively to form a higher energy **anti-bonding molecular orbital.** The details are not discussed here but form an important part of more advanced work on covalent bonding.

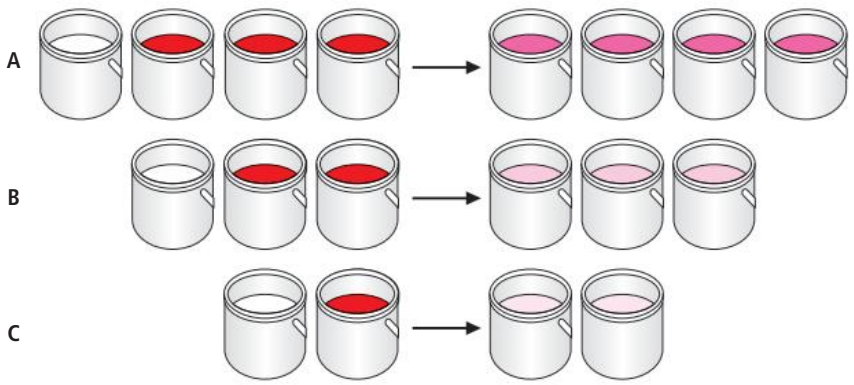
Hybridization can involve different numbers and types of orbital, leading to the formation of distinct hybrid orbitals. We will discuss those involving s and p orbitals here.

A simple analogy may help you to picture this somewhat abstract topic (Figure 20).

A. If you were to mix one bucket of white paint with three buckets of red paint, you would make *four* buckets of equal dark pink paint. Similarly, hybridization of one s orbital with three p orbitals produces *four* so-called **sp^3 hybrid orbitals** that are equal to each other. Their shape and energy have properties of both s and p, but are more like p than s.

B. Mixing one bucket of white paint with two buckets of red paint would produce *three* buckets of equal lighter pink paint; likewise, hybridization of one s orbital with two p orbitals will produce *three* equal **sp^2 hybrid orbitals**.

C. Finally, the hybridization of one s orbital with one p orbital will produce *two* equal **sp hybrid orbitals**.



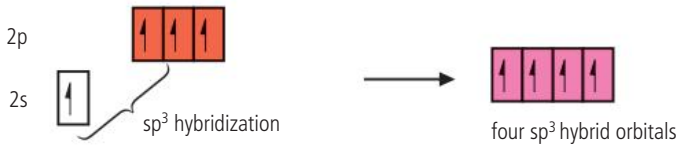
S2.2 Figure 20 Mixing red and white paint makes the hybrid colour pink. The number of buckets and the shade of pink depend on the original number of buckets of red and white.

The overlap of a hybrid orbital with *any* other atomic orbital (s, p, or another hybrid orbital) always forms a sigma bond.

The different types of hybrid orbital have different orientations, defining the shapes of the molecules, as we will see in the examples described using carbon compounds.

sp^3 hybridization

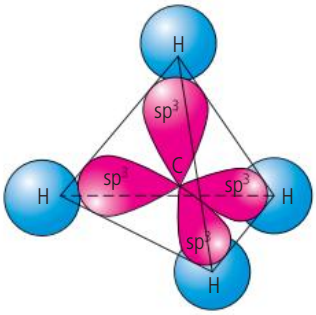
When carbon forms four single bonds, it undergoes sp^3 hybridization, producing four equal hybrid orbitals (Figure 21).



S2.2 Figure 21 sp^3 hybridization

These orbitals orientate themselves at 109.5°, forming a tetrahedron. Each hybrid orbital overlaps with the atomic orbital of another atom forming four sigma bonds.

For example, methane, CH_4 (Figure 22).



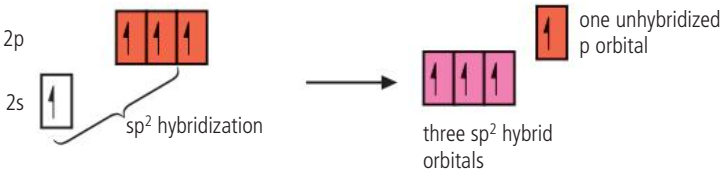


Molecular model of methane, CH_4, clearly showing the tetrahedral shape with angles of 109.5° between the atoms. The carbon atom is sp^3 hybridized, forming four sigma bonds with hydrogen atoms.

S2.2 Figure 22 Tetrahedral structure of methane. The image shows the formation of sigma bonds from the overlap of each of the four sp^3 hybrid orbitals with the s orbital of an H atom.

sp^2 hybridization

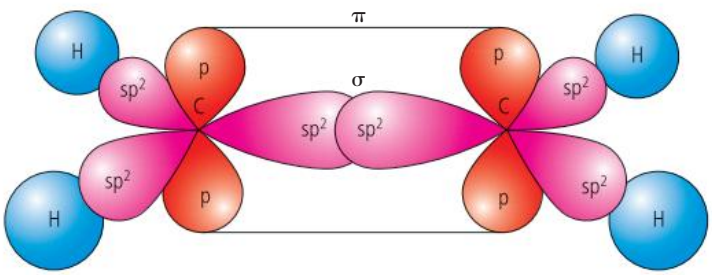
When carbon forms a double bond, it undergoes sp^2 hybridization, producing three equal hybrid orbitals (Figure 23).

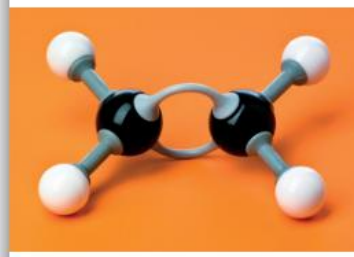


S2.2 Figure 23 sp^2 hybridization

These orientate themselves at 120°, forming a triangular planar shape. Each hybrid orbital overlaps with a neighbouring atomic orbital, forming three sigma bonds.

For example, ethene, C_2H_4 (Figure 24).

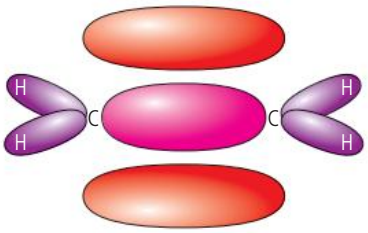




Molecular model of ethene, C_2H_4, showing the triangular planar shape around each carbon. The double bond between the two sp^2 hybridized carbon atoms consists of one sigma bond and one pi bond.

S2.2 Figure 24 Structure of ethene. The three sp^2 hybrid orbitals on each carbon atom form a triangular planar shape, overlapping to form one C–C and two C–H sigma bonds. The unhybridized p orbitals on each carbon atom overlap to form a pi bond.

As the two carbon atoms approach each other, the p orbitals in each atom that did not take part in hybridization and have so retained their dumb-bell shape, overlap sideways. They form a pi bond with its characteristic lobes of electron density above and below the bond axis (Figure 25). So the double bond between the carbon atoms consists of one sigma bond and one pi bond.



S2.2 Figure 25 Molecular orbitals formed in ethene. The five sigma bonds are shown in pink (C–C) and purple (C–H) and the pi bond is shown as red lobes above and below the carbon–carbon bond axis.

sp hybridization

When carbon forms a triple bond, it undergoes sp hybridization, producing two equal hybrid orbitals (Figure 26).



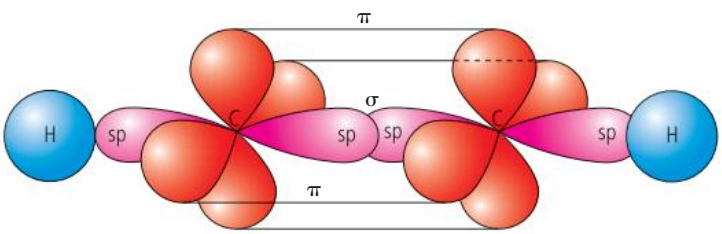
Molecular model of ethene, C_2H_2, showing the linear shape around each carbon. The triple bond between the two sp hybridized carbon atoms consists of one sigma bond and two pi bonds.



S2.2 Figure 26 sp hybridization

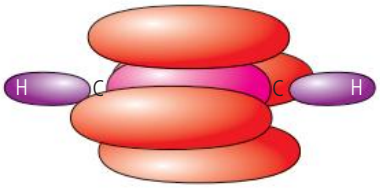
These orientate themselves at 180°, giving a linear shape. Overlap of the two hybrid orbitals with other atomic orbitals forms two sigma bonds.

For example, ethyne, C_2H_2 (Figure 27).



S2.2 Figure 27 Structure of ethyne. The two sp hybrid orbitals on each carbon atom form a linear shape, overlapping to form one C–C bond and one C–H sigma bond. The unhybridized p orbitals on each carbon atom overlap to form two pi bonds.

Each carbon has two unhybridized p orbitals that are orientated at 90° to each other. As these combine laterally, two pi bonds form representing four lobes of electron density around the atoms (Figure 28). These coalesce into a cylinder of negative charge around the atom, making the molecule susceptible to attack by **electrophilic reactants** (those that are attracted to electron-dense regions). This is discussed in Reactivity 3.4.



S2.2 Figure 28 Molecular orbitals formed in ethyne. The three sigma bonds are shown in pink (C–C) and purple (C–H) and the two pi bonds are shown as four red lobes above, below and to either side of the carbon–carbon bond axis.

Challenge yourself

10. Molecules with expanded octets require more than four hybrid orbitals around the central atom. This involves the use of d orbitals in addition to s and p orbitals. What type of hybrid orbitals would be formed by the phosphorus atom in PCl_5 and the sulfur atom in SF_6?

Lone pairs can also be involved in hybridization

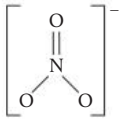
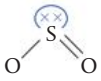
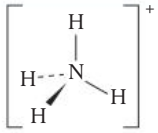
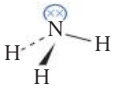
The examples earlier in this section all use orbitals with bonding electrons in the hybridization process. But non-bonding pairs of electrons can also take part in hybridization. For example, in ammonia, NH_3, the non-bonding pair on the N atom resides in an sp^3 hybrid orbital.

Hybridization can be used to predict molecular geometry

Although we have focused mostly here on examples from organic chemistry (those involving carbon), this concept of hybridization can be used to explain the shape of any molecule or ion. Conversely, the shape of a molecule can be used to determine the type of hybridization that has occurred. The relationship is as follows:

- tetrahedral arrangement ↔ sp^3 hybridized
- triangular planar arrangement ↔ sp^2 hybridized
- linear arrangement ↔ sp hybridized

Now we can look again at the geometric arrangement of the electron domains predicted by the VSEPR model on page 231 and deduce the hybridization involved.

Number of electron domains	Electron domain geometry	Molecular geometry	Example	Hybridization of central atom
2	linear	linear	CO_2 O=C=O	sp
3	planar triangular	planar triangular	NO_3^- 	sp^2
3	planar triangular	V-shaped	SO_2 	sp^2
4	tetrahedral	tetrahedral	NH_4^+ 	sp^3
4	tetrahedral	triangular pyramidal	NH_3 	sp^3
4	tetrahedral	V-shaped	H_2O 	sp^3

TOK

Electron orbitals do not exist as physical entities, but their description as a volume of space provides a convenient basis to explain electron properties and bonding. Their true definition depends on a mathematical equation describing the electron's wave function. Hybridization, for the purposes of explanations of bonding, is termed a mixing process, but in reality is likewise based on complex mathematical manipulation. In the world of electronic communication we similarly use familiar terms to describe entities which do not really exist as such – cyberspace, viruses, firewalls, and so on. To what extent do you think this use of language and imagery enhances or masks our understanding of what is represented?

VSEPR theory, applied to hybridized orbitals in the same way as to electron domains, explains the geometry of the hybrid atomic orbitals. It therefore relates the shape of the molecule or ion to the hybridization and to the number of electron domains.

number of electron domains ↔ **shape of molecule or ion** ↔ hybridization

Nature of Science

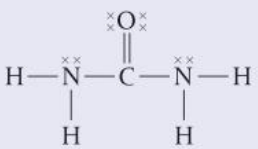
Hybridization has a sound mathematical foundation, based on combining wave functions to produce new wave functions in quantum mechanical approaches. But this is a relatively complex study and so hybridization is often presented as a model involving an imaginary mixing process. Use of this model is validated by its effectiveness in explaining molecular geometries that are consistent with observation.

Worked example

Urea $H_2N-\overset{\overset{O}{\|}}{C}-NH_2$ is present in solution in animal urine. What is the hybridization of C and N in the molecule, and what are the approximate bond angles?

Solution

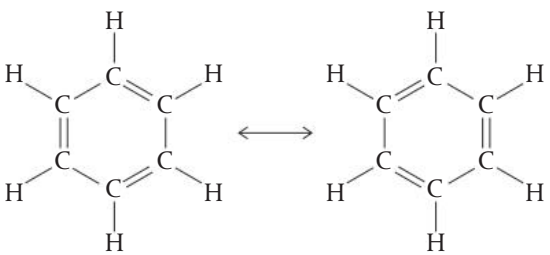
Start with the Lewis formula.



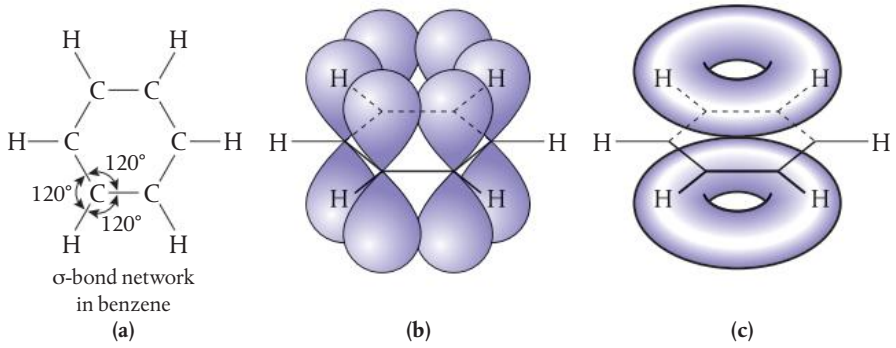
Because there are three electron domains around the C atom, they are arranged in a triangular planar shape with angles of approximately 120°. The C atom must be sp^2 hybridized to give this shape. There are four electron domains around each N atom, so they are arranged tetrahedrally. The N atoms must be sp^3 hybridized to give this shape.

Hybridization in benzene

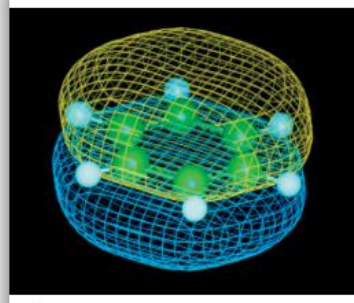
Recall from earlier in this chapter that benzene exists as a combination of two Lewis formulas.



Each of the six carbon atoms is sp^2 hybridized, and forms three σ bonds with angles of 120°, making a planar shape (Figure 29a). This leaves one unhybridized p electron on each carbon atom with its dumb-bell shape perpendicular to the plane of the ring (Figure 29b). But instead of pairing up to form discrete alternating π bonds, the p orbitals effectively overlap in both directions, spreading themselves out evenly to be shared by all six carbon atoms. This forms a **delocalized π electron cloud** in which electron density is concentrated in two donut-shaped rings above and below the plane of the ring (Figure 29c).



S2.2 Figure 29 The bonding in benzene. This is a symmetrical arrangement where all the p electrons are shared equally by all of the bonded carbon atoms. It is a very stable structure and lowers the internal energy of the molecule. **(a)** The σ-bond framework. **(b)** The unhybridized p orbitals before overlapping sideways. **(c)** The delocalized π electrons form regions of high electron density above and below the planar benzene ring.

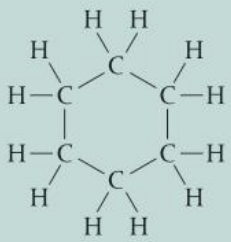
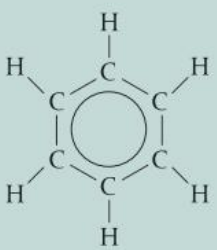


Computer graphics representation of the structure of benzene showing the delocalized electron clouds which confer great stability on the molecule. They appear as the blue and yellow cages above the flat plane of the molecule. Carbon atoms are shown in green and hydrogen atoms in white.

Exercise

Q55. What hybridization would you expect for the red coloured atom in each of the following?

(a) $H_2C{=}O$ **(b)** BH_4^- **(c)** SO_3 **(d)** $BeCl_2$ **(e)** CH_3COOH

Q56. Cyclohexane, C_6H_{12},  has a puckered, non-planar shape whereas benzene, C_6H_6,  is planar.

Explain this difference by making reference to the C–C–C bond angles and the type of hybridization of carbon in each molecule.

HL end

Guiding Question revisited

What determines the covalent nature and properties of a substance?

In this chapter we have used the covalent model of bonding to show:

- A covalent bond is formed by the electrostatic attraction between a shared pair of electrons and the positively charged nuclei. Atoms can share one, two or three pairs of electrons to form a single, double or triple bond respectively.
- A covalent bond in which one atom provides both shared electrons is called a coordination bond.
- The octet rule is a useful tool for predicting the arrangement of atoms in covalent molecules and network structures but has many exceptions. An atom with less than four valence pairs of electrons has an incomplete octet.
- Lewis formulas can be used to represent all of the valence electrons in a covalently bonded species.
- The Valence Shell Electron Pair Repulsion (VSEPR) model can be used to accurately predict the shape of molecules by considering the repulsions between electron domains. These can be bonding domains, containing shared pairs of electrons, or non-bonding domains (lone pairs of electrons).
- The electron geometry describes the arrangement of electron domains around a central atom:
  - 2 electron domains → linear
  - 3 electron domains → triangular planar
  - 4 electron domains → tetrahedral
- The molecular geometry describes the position of bonding domains around a central atom. We can predict the bond angles in a molecule knowing its geometry and considering any addition repulsion caused by non-bonding pairs and multiple bonds.
- Bond polarity results from the difference in electronegativities of the bonded atoms. This causes an unequal distribution of electron density, a bond dipole, which can be represented with partial charges ($\delta+$ and $\delta-$) and/or a vector.
- Molecular polarity depends on both bond polarity and molecular geometry. If bond dipoles cancel out on a molecule then it will be non-polar. If there is a net dipole across a molecule, then it will be polar.
- Carbon and silicon are able to form network structures with distinct chemical and physical properties. Examples include silicon, silicon dioxide and the allotropes of carbon.
- Intermolecular forces are determined by the size and polarity of a molecule. In increasing order of strength, they include London dispersion forces, dipole-induced dipole, dipole–dipole and hydrogen bonding. Intermolecular forces can influence physical properties such as melting and boiling point, volatility, electrical conductivity and solubility.

- Paper chromatography and thin layer chromatography are techniques used to separate the components of a mixture based on their relative attractions to the mobile and stationary phases. For a given solvent, the retardation factor value for a component can be calculated using $R_f = \frac{\text{distance moved by component}}{\text{distance moved by solvent}}$.
  This value is compared to known values in order to identify the compound.

HL

- Resonance structures occur when there is more than one possible position for a double bond in the Lewis formula of a molecule or ion. The true structure of the species can be represented as a resonance hybrid which indicates where delocalized electrons from a double bond are shared between multiple bonding positions. Resonance can explain experimental data that shows intermediate bond lengths and strengths between a single and double bond.
- Resonance in the cyclic compound benzene, C_6H_6, can explain its distinct physical and chemical properties such as bond length and strength, energy changes during hydrogenation and the types of reaction it undergoes.
- An atom with more than four valence pairs of electrons has an expanded octet. The electron domain geometry around a central atom with an expanded octet is as follows:
  - 5 electron domains → triangular bipyramidal
  - 6 electron domains → octahedral
- Formal charge is a useful tool to identify preferred structures in a molecule when there are multiple possibilities. Low formal charges, and therefore less charge transfer in the molecule, indicates the most stable structure.
- When atomic orbitals combine head-on along the bond axis they form a sigma (σ) bond and when p-orbitals combine laterally (sideways) they form pi (π) bonds.
  - A single bond is always a σ bond.
  - A double bond contains one σ bond and one π bond.
  - A triple bond contains one σ bond and two π bonds.
- Hybrid orbitals can be formed by the mixing of atomic orbitals in a process called hybridization. The number of electron domains around an atom, identified from a Lewis formula, is related to the type of hybridization and electron domain geometry as follows:
  - 2 electron domains ↔ sp hybridization ↔ linear geometry
  - 3 electron domains ↔ sp^2 hybridization ↔ triangular planar geometry
  - 4 electron domains ↔ sp^3 hybridization ↔ tetrahedral geometry

HL end

Practice questions

1. Which bonds are arranged in order of increasing polarity?

A H–F < H–Cl < H–Br < H–I
B H–I < H–Br < H–F < H–Cl
C H–I < H–Br < H–Cl < H–F
D H–Br < H–I < H–Cl < H–F

2. Which row correctly describes the bonding type and melting point of carbon and carbon dioxide?

	Carbon		Carbon dioxide	
A	covalent bonding	high melting point	covalent bonding	low melting point
B	ionic bonding	low melting point	ionic bonding	high melting point
C	ionic bonding	high melting point	ionic bonding	low melting point
D	covalent bonding	low melting point	covalent bonding	high melting point

3. What is the correct order of increasing boiling points?

A $CH_3CH_3 < CH_3CH_2Cl < CH_3CH_2Br < CH_3CH_2I$

B $CH_3CH_2Cl < CH_3CH_2Br < CH_3CH_3 < CH_3CH_2I$

C $CH_3CH_2I < CH_3CH_2Br < CH_3CH_2Cl < CH_3CH_3$

D $CH_3CH_2Br < CH_3CH_2Cl < CH_3CH_2I < CH_3CH_3$

4. Which compound forms hydrogen bonds in the liquid state?

A C_2H_5OH **B** $CHCl_3$ **C** CH_3CHO **D** $(CH_3CH_2)_3N$

5. Which molecule has a non-bonding (lone) pair of electrons around the central atom?

A BF_3 **B** SO_2 **C** PCl_5 **D** SiF_4

6. Which species contain a coordination bond?

I. HCHO II. CO III. H_3O^+

A I and II **B** I and III **C** II and III **D** I, II and III

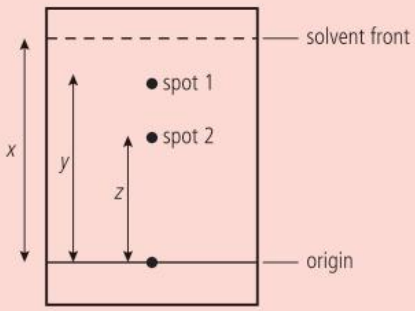
7. Which molecule has an octahedral shape?

A H_2O **B** CH_4 **C** AlF_3 **D** SF_6

8. Which substance can form intermolecular hydrogen bonds in the liquid state?

A CH_3OCH_3 **B** CH_3CH_2OH **C** CH_3CHO **D** $CH_3CH_2CH_3$

9. Which calculation would be required to calculate the retardation factor value, R_f, for spot 1 in this chromatogram?



A $\frac{x}{y}$ **B** $\frac{y}{x}$ **C** $\frac{y}{z}$ **D** $\frac{z}{x}$

10. Based on the types of intermolecular force present, explain why butan-1-ol has a higher boiling point than butanal. (2)

(Total 2 marks)

11. **(a)** For each of the species BH_3 and PCl_3:

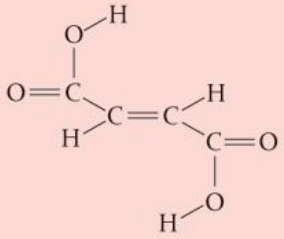
(i) deduce the Lewis formula (2)

(ii) predict the shape and bond angle (4)

(iii) predict and explain the molecular polarity. (2)

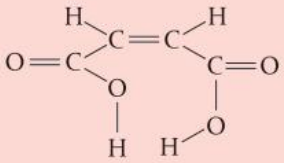
(b) **(i)** HL Compare the formation of sigma (σ) and pi (π) bonds between the carbon atoms in a molecule of ethyne, C_2H_2. (2)

(ii) Identify the number of sigma and pi bonds present in *trans*-but-2-ene-1,4-dioic acid shown below.



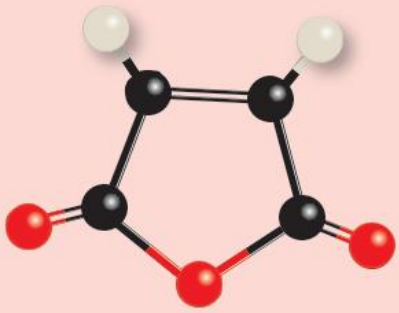
(1)

(iii) Explain why the melting point of *trans*-but-2-ene-1,4-dioic acid is higher than that of *cis*-but-2-ene-1,4-dioic acid shown below.



(1)

(iv) Explain why *cis*-but-2-ene-1,4-dioic acid forms *cis*-but-2-ene-1,4-dioic anhydride (shown below) when heated, whereas no cyclic anhydride forms when *trans*-but-2-ene-1,4-dioic acid is heated. (1)



(c) Deduce the hybridization of each oxygen atom in *cis*-but-2-ene-1,4-dioic acid. (1)

(Total 14 marks)

12. Carbon and silicon belong to the same group of the periodic table.

(a) Describe and compare three features of the structure and bonding in the three allotropes of carbon: diamond, graphite and C_{60} fullerene. (6)

(b) Both silicon and carbon form oxides.

(i) Describe the structure and bonding in SiO_2. (2)

(ii) Explain why silicon dioxide is a solid and carbon dioxide is a gas at room temperature. (2)

(c) Describe the bonding within the carbon monoxide molecule. (2)

(d) HL Describe the delocalization of pi (π) electrons and explain how this can account for the structure and stability of the carbonate ion, CO_3^{2-}. (3)

(e) HL Explain the meaning of the term 'hybridization'. State the type of hybridization shown by the carbon atoms in carbon dioxide, diamond, graphite and the carbonate ion. (5)

(Total 20 marks)

13. Methoxymethane, CH_3OCH_3, and ethanol, C_2H_5OH, have the same relative molecular mass. Explain why methoxymethane has a much lower boiling point than ethanol. (3)

(Total 3 marks)

14. (a) Draw the Lewis formulas, state the shape, and predict the bond angles for the following species.

(i) NH_3 (3)

(ii) NH_2^- (3)

(iii) NH_4^+ (3)

(b) (i) HL Compare the formation of the sigma (σ) and pi (π) bonds between the carbon atoms in a molecule. (2)

(ii) Identify how many sigma and pi bonds are present in propene, C_3H_6. (2)

(iii) Deduce all the bond angles present in propene. (2)

(iv) Explain how the concept of hybridization can be used to explain the bonding in the triple bond present in propyne. (3)

(Total 18 marks)

15. (a) Draw the Lewis formulas, state the molecular geometry, and predict the bond angles for the following species.

(i) Cl_2O (3)

(ii) NO_2^+ (3)

(b) Explain, using diagrams, why NO_2 is a polar molecule but CO_2 is a non-polar molecule. (3)

(c) Describe the structure and bonding in silicon dioxide. (2)

(d) HL Consider the molecule $HCONH_2$.

(i) Draw a Lewis formula for this molecule. (2)

(ii) Describe how sigma and pi bonds form. (2)

(iii) State the type of hybridization of the carbon and nitrogen atoms in $HCONH_2$. (2)

(Total 17 marks)

16. Ethyne, C_2H_2, and ethene, C_2H_4, are both examples of hydrocarbons.

(a) Draw the Lewis formulas of C_2H_2 and C_2H_4. (2)

(b) Compare, giving a reason, the length of the bond between the carbon atoms in ethyne and ethene. (1)

(c) Identify the type of interaction that must be overcome when liquid ethyne vaporizes. (1)

(Total 4 marks)

17. Paper chromatography is a simple method used to separate and identify the components in a mixture.

(a) State the meaning of the term 'retardation factor value R_f' for a component spot on a chromatogram. (1)

(b) Paper chromatography was used to analyse a sample containing two substances. The following data were collected from the chromatogram.

Compound	Distance travelled / mm
A	32
B	75
solvent	96

Calculate the R_f value of compound A. (1)

(c) Outline how the R_f value of a spot can be used to identify a compound. (1)

(d) Explain why the R_f value for the same component can be very different if different solvents are used for the mobile phase. (2)

(e) State one other type of chromatography that can be used to separate the components of a mixture. (1)

(Total 6 marks)

HL

18. Which statements about hybridization are correct?

I. The hybridization of carbon in diamond is all sp^3.

II. The hybridization of carbon in graphite is all sp^2.

III. The hybridization of carbon in C_{60} fullerene is all sp^3.

A I and II **B** I and III **C** II and III **D** I, II and III

19. How many σ and π bonds are present in a molecule of propyne, CH_3CCH?

	σ	π
A	5	3
B	6	2
C	7	1
D	8	0

20. Which species does not have delocalized electrons?

A NO_3^- **B** NO_2^- **C** O_3 **D** C_3H_6

21. Which statements about σ and π bonds are correct?

I. σ bonds result from the axial overlap of orbitals.

II. σ bonds only form from s orbitals.

III. π bonds result from the lateral overlap of parallel p orbitals.

A I and II **B** I and III **C** II and III **D** I, II and III

22. In which substance does a carbon atom have sp^2 hybridization?

A 2-methylbutan-1-ol, $CH_3CH_2CH(CH_3)CH_2OH$

B propyne, CH_3CCH

C fullerene, C_{60}

D diamond

23. The Lewis formula of XeF_2 contains two bonding pairs of electrons and three non-bonding pairs of electrons (lone pairs) around the central xenon atom. What is the shape of the XeF_2 molecule?

A bent

B trigonal bipyramidal

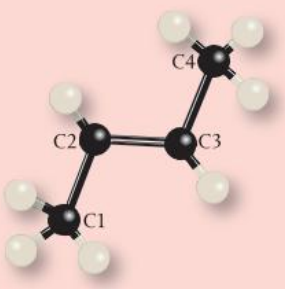
C square planar

D linear

24. What is the type of hybridization of the silicon and oxygen atoms in silicon dioxide?

	Silicon	Oxygen
A	sp^3	sp^3
B	sp^3	sp^2
C	sp^2	sp^3
D	sp^2	sp^2

25. But-2-ene is a straight-chain alkene with formula C_4H_8. The molecule contains both sigma and pi bonds.



(a) Explain the formation of the pi bond. (2)

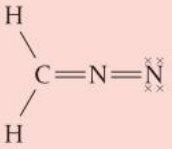
(b) For each of the carbon atoms, C1 and C2, identify the type of hybridization shown. (1)

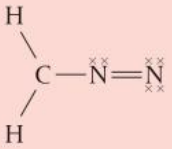
(Total 3 marks)

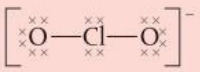
26. SF_2, SF_4 and SF_6 have different shapes. Draw their Lewis formulas and use the VSEPR model to predict the name of the shape of each molecule. (6)

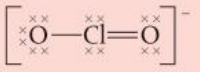
(Total 6 marks)

27. Assign formal charges to the atoms in the following structures. In each case, which of the two do you think is the more important contributor to the resonance hybrid and why?

(a) **(i)** 

(ii) 

(b) **(i)** 

(ii) 

(6)

(Total 6 marks)

28. Molecular oxygen, O_2, and ozone, O_3, are allotropes of oxygen found as gases in the atmosphere.

(a) Draw the Lewis formulas of O_2 and O_3. (2)

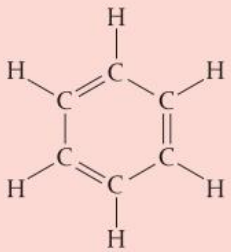
(b) Outline why both bonds in the ozone molecule are the same length and predict, with reference to Section 1 of the data booklet, the oxygen–oxygen bond length. (2)

(c) State the electron domain geometry and the molecular geometry, and predict the bond angle in the ozone molecule. (3)

(Total 7 marks)

29. The structure of an organic molecule can help predict the type of reaction it can undergo.

The Kekulé structure of benzene suggests it should readily undergo addition reactions.



Discuss two pieces of evidence, **one** physical and **one** chemical, which suggest this is not the structure of benzene. (2)

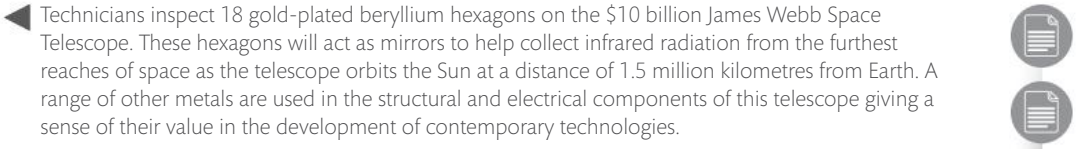
(Total 2 marks)

HL end



STRUCTURE

2.3 The metallic model



Technicians inspect 18 gold-plated beryllium hexagons on the $10 billion James Webb Space Telescope. These hexagons will act as mirrors to help collect infrared radiation from the furthest reaches of space as the telescope orbits the Sun at a distance of 1.5 million kilometres from Earth. A range of other metals are used in the structural and electrical components of this telescope giving a sense of their value in the development of contemporary technologies.

Nature of Science

As the scope for the application of metals continues to grow alongside the development of technology, scientists have a responsibility to consider the impact of their use. The implications of metal extraction and processing raise ethical questions that must be considered in social, political, economic and environmental domains.

Guiding Question

What determines the metallic nature and properties of an element?

The names of historical periods such as the Bronze Age and the Iron Age hint towards the significant role that metals have played in the transformation of human societies. Gold, for example, has seen its uses develop from art, jewellery and trade in ancient times, to applications as wide-ranging as dentistry, electronics and aerospace in contemporary society.

Given their distinct properties in comparison with both ionic and covalent substances, metals require a separate explanatory model of bonding. This model describes the structure of a metallic element as a **lattice of cations** surrounded by **delocalized electrons** and explains the characteristic physical and chemical properties observed in experimentation. This chapter will explore some of the applications of metals that stem from their characteristic properties and consider explanations for trends in their behaviour by considering the **charge** and **radius of metal cations**.

HL We will also investigate the transition elements, found in the d-block of the periodic table, in particular detail, given their integral role in developing technologies.

Structure 2.3.1 and 2.3.2 – The metallic bond

Structure 2.3.1 – A metallic bond is the electrostatic attraction between a lattice of cations and delocalized electrons. Explain the electrical conductivity, thermal conductivity and malleability of metals.	
Relate characteristic properties of metals to their uses.	Tool 1, Inquiry 2, Structure 3.1 – What experimental data demonstrate the physical properties of metals, and trends in these properties in the periodic table? Reactivity 3.2 – What trends in reactivity of metals can be predicted from the periodic table?

Structure 2.3.2 – The strength of a metallic bond depends on the charge of the ions and the radius of the metal ion.	
Explain trends in melting points of s and p block metals.	
A simple treatment in terms of charge of cations and electron density is required.	Structure 2.4 – What are the features of metallic bonding that make it possible for metals to form alloys?

Metallic bonding occurs between a lattice of cations and delocalized electrons

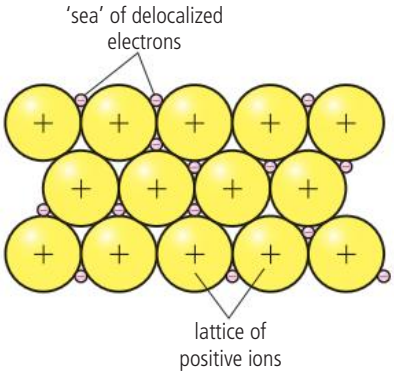
Metals are found on the left side of the periodic table and have a small number of electrons in their outer shell. These are atoms with low ionization energies, and so typically react with other elements by losing their valence electrons and forming positive ions. This loss of control over their outer shell electrons is what we are referring to when describing the **metallic character** of these elements.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.01						Atomic number / Element / Relative atomic mass											2 He 4.00
2	3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.90
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.96	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
6	55 Cs 132.91	56 Ba 137.33	57 † La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.20	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89 ‡ Ac (227)	104 Rf (267)	105 Db (268)	106 Sg (269)	107 Bh (270)	108 Hs (269)	109 Mt (278)	110 Ds (281)	111 Rg (281)	112 Cn (285)	113 Uut (286)	114 Uuq (289)	115 Uup (288)	116 Uuh (293)	117 Uus (294)	118 Uuo (294)

†	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97
‡	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

▲ The periodic table. Metals are shown in yellow, non-metals in red and metalloids in blue.

In the elemental state, when there is no other element present to accept the electrons and form an ionic compound, the outer electrons are held only loosely by the metal atom's nucleus and so tend to 'wander off' or, more correctly, become **delocalized**. As shown in Structure 2.2, delocalized electrons are not fixed in one position. This means that in metals the valence electrons are no longer associated closely with any one metal nucleus but instead can spread themselves through the metal structure. The metal atoms without these electrons have become **cations** (positively charged ions) and form a regular **lattice structure** through which these electrons can move freely.



The metallic model of bonding. It is often described as a lattice of cations surrounded by a sea of electrons.

You can think of it like a close neighbourhood of families where the children do not belong specifically to any one set of parents but are free to wander between the homes. This arrangement causes a close association between the families. Likewise in metals, there is a force of electrostatic attraction between the lattice of cations and the delocalized electrons, and this is known as **metallic bonding**.

A metallic bond is the electrostatic attraction between a lattice of cations and delocalized electrons.

The uses of metals are related to their characteristic properties

Experimental data on melting and boiling points, as well as electrical and thermal conductivity, show that metals share a number of characteristic physical properties. These properties and their trends in the periodic table can be explained using the metallic model of bonding. They are summarized on the following page.

Tool 1, Inquiry 2, Structure 3.1 – What experimental data demonstrate the physical properties of metals, and trends in these properties in the periodic table?



Pile of ancient Roman copper coins. Due to its relative ease of extraction, copper was one of the first metals used to make tools by humans. The Bronze Age was a historical period named after the alloy *bronze*, made by mixing copper and tin.

SKILLS

Investigating the properties of metals. Full details of how to carry out this experiment with a worksheet are available in the eBook.



Copper wire. Copper is malleable, ductile, and a good conductor of heat and electricity.

Metallic property	Explanation	Application
good electrical conductivity	delocalized electrons are highly mobile, and so can move through the metal structure in response to an applied voltage	electrical circuits use copper
good thermal conductivity	delocalized electrons and closely packed ions enable efficient transfer of thermal energy	pots and pans used for cooking
malleable, can be shaped under pressure	movement of delocalized electrons is **non-directional** and essentially random through the cation lattice, so the metallic bond remains intact while the conformation changes under applied pressure	moulded into many forms including machinery and structural components of buildings and vehicles
ductile, can be drawn out into threads		electric wires and cables
high melting points	a lot of energy is required to overcome the strong electrostatic forces of attraction in the metallic bond and separate the atoms	high-speed tools and turbine engines
shiny, lustrous appearance	delocalized electrons in metal crystal structure reflect light	ornamental structures and jewellery

Structure 2.4 – What are the features of metallic bonding that make it possible for metals to form alloys?

The non-directional nature of metallic bonding allows us to enhance the properties of a metallic substance by mixing a metal with other metal or non-metal elements in the molten state. The resulting mixture is known as an **alloy**. Steel, for example, is made by the addition of small amounts of carbon to molten iron. Although the carbon atoms sit within the lattice of cations, the cations themselves continue to experience electrostatic attraction to the delocalized electrons in all directions. Steel has a greater tensile strength than pure iron making it a more suitable material for construction. This is discussed in more depth in Structure 2.4.

Nature of Science

Atomic theory enables scientists to explain the distinct properties of metals. This is applied in the development of new materials such as alloys that combine the characteristics of different metals. The ability to explain natural phenomena such as metallic properties through the application of theory is an important feature of science.

The strength of a metallic bond depends on the charge and radius of the metal ions

The strength of a metallic bond depends on the charge and radius of the metal ions.

The strength of the metallic bond is determined by:

- the number of delocalized electrons
- the charge on the cation
- the radius of the cation.

The greater the delocalized electron density and the smaller the cation, the greater the electrostatic attraction between them. For example, if we compare:

- sodium, Na, Group 1, electron configuration $1s^2 2s^2 2p^6 3s^1$ and
- magnesium, Mg, Group 2, electron configuration $1s^2 2s^2 2p^6 3s^2$

we can deduce that Na will have one delocalized electron per atom and will form the Na^+ ion, whereas Mg will have two delocalized electrons per atom and form the Mg^{2+} ion. In addition, the radius of Mg^{2+} is slightly smaller than that of Na^+. These factors all indicate that Mg should have stronger metallic bonding than Na, which can be confirmed by a comparison of their melting points.

	Na	Mg
Melting point / °C	98	650

The strength of metallic bonding tends to decrease down a group as the size of the cation increases, reducing the attraction between the delocalized electrons and the positively charged protons in the nucleus. Again, melting points confirm this.

	Na	K	Rb
Melting point / °C	98	63	39

Given the tendency for metals to lose electrons during chemical reactions, the trends in melting point across a period and down a group can be used to predict their relative reactivity. These can be summarized as follows:

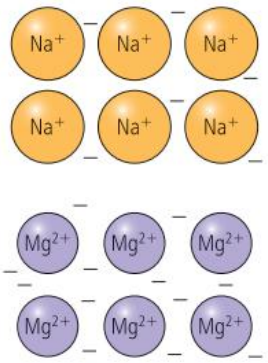
Left to right across a period

Increasing melting point ⟷ Greater attraction between ions and delocalized electrons ⟷ Lower degree of reactivity

Down a group

Decreasing melting point ⟷ Weaker attraction between ions and delocalized electrons ⟷ Higher degree of reactivity

Specific examples of these predictions are explored in Reactivity 3.2.



▲ Metallic model of the bonding in sodium and magnesium. Mg has a greater charge on its cations, more delocalized electrons and a smaller ionic radius, leading to stronger metallic bonds and a higher density.

Reactivity 3.2 – What trends in reactivity of metals can be predicted from the periodic table?

The extraction of metals from their ores is a major part of industry and development in many countries, but is associated with some complex environmental issues. These include the destruction of landscapes by strip mining, the 'tailings' or waste material that accumulate in spoil tips, and the release of toxic materials that leach out of waste and pollute the environment. An important step to reduce the impact of these effects is to maximize the reuse and recycling of all metal objects, and avoid metal dumping. Despite their apparent abundance, metals are a precious resource, available only at considerable cost.

Exercise

Q1. Which is the best definition of metallic bonding?

A the attraction between cations and anions

B the attraction between cations and delocalized electrons

C the attraction between nuclei and electron pairs

D the attraction between nuclei and anions

Q2. Explain, with reference to the features of the metallic model of bonding, the following properties:

(a) electrical conductivity

(b) thermal conductivity

(c) malleability

Q3. Aluminium is a widely used metal. What properties make it suitable for the following applications?

(a) baking foil **(b)** aircraft bodywork

(c) cooking pans **(d)** tent frames

Q4. Explain the difference in the melting points of lithium and beryllium, which melt at 180.5 °C and 1287 °C respectively.

Q5. Use the periodic table to identify the predicted trend in melting points of sodium (Na), potassium (K) and rubidium (Rb).

A Rb > K > Na **B** K > Na > Rb

C Na > K > Rb **D** Na > Rb > K

Q6. Explain the general trend of decreasing melting point down group 2 metals.

HL

Structure 2.3.3 – Transition elements

Structure 2.3.3 – Transition elements have delocalized d-electrons.	
Explain the high melting point and electrical conductivity of transition elements.	
Chemical properties of transition elements are covered in Reactivity 3.4.	Structure 3.1 – Why is the trend in melting points of metals across a period less evident across the d-block?

Transition elements are elements whose atoms have an incomplete d sublevel, or can give rise to cations with an incomplete d sublevel.

Transition elements have delocalized d-electrons

Transition elements are elements whose atoms have an incomplete d sublevel, or can give rise to cations with an incomplete d sublevel. This leads to a number of characteristic properties that are discussed further in Structure 3.1.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr

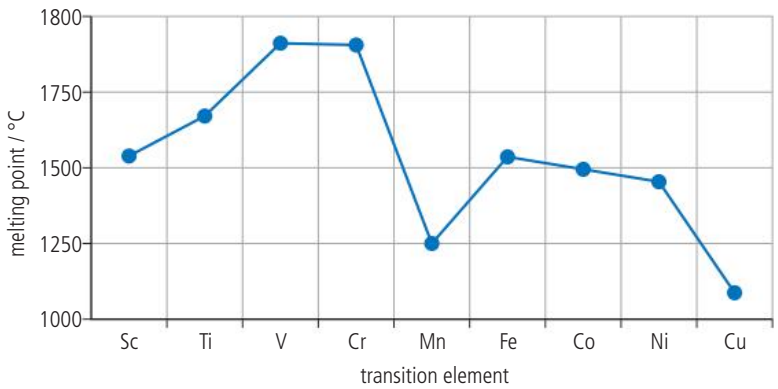
The transition elements of the 4th period are highlighted in yellow here. Note that elements are only considered to be transition elements if their atom has an incomplete d sublevel, or can give rise to cations with an incomplete d sublevel. For this reason, zinc is not considered a transition element and there is some debate over the inclusion of scandium as discussed in Structure 3.1.

In a similar way to other metals, the bonding in transition elements can be explained by the metallic model. However, given the proximity in energy between the outer occupied sublevels (for example, the 3d and 4s sublevels in period 4 transition elements) they are also able to delocalize d-electrons to form metallic bonds. This leads to particularly high melting points and electrical conductivity.

Transition metals have high melting points

The attraction between the large number of delocalized electrons and the large positive charge on the metal cations leads to very strong metallic bonding and high melting points. Rhenium, Re, for example, has a melting point of 3453 °C. This is one of the highest melting points of all the elements in the periodic table.

Unlike the s and p block metals, the trends in the melting points of transition elements are less evident as shown in the graph below.



Graph showing the melting points of the period 4 transition elements.

The lack of a clear trend in the melting point of transition elements relates to the ability of all transition elements to delocalize a large number of electrons in addition to having similar ionic radii. This makes it more difficult to accurately predict trends compared with s block elements.

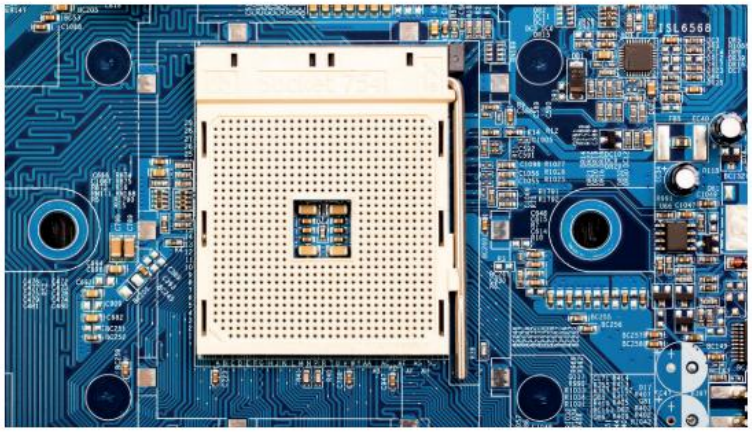
Transition metals have high electrical conductivity

The large number of delocalized electrons in the metallic structure of transition elements makes them particularly good at conducting electricity. Copper, for example, is the most common metal used in electrical cables.

Challenge yourself

1. Silver is the most electrically conductive metal but is used primarily in small amounts and only on the interior of electronic devices. Suggest why this might be the case.

Structure 3.1 – Why is the trend in melting points of metals across a period less evident across the d-block?



Laptop motherboard. The edge of most components in a motherboard will have gold contacts and connectors. Other transition elements such as nickel, platinum and palladium are commonly found in small amounts on circuit boards.

Exercise

Q7. Which of the following are transition elements?

I. Zirconium (Zr) II. Palladium (Pd) III. Lead (Pb)

A I and II only **B** I and III only **C** II and III only **D** I, II and III

Q8. Explain why transition elements tend to have higher melting points than s and p block metals.

Q9. Explain, with reference to the metallic model of bonding, why transition elements have high electrical conductivity.

HL end

Guiding Question revisited

What determines the metallic nature and properties of an element?

In this chapter we have used the metallic model to show:

- Metallic elements contain delocalized electrons and a lattice of cations. The electrostatic attraction between these electrons and cations is the metallic bond.
- The metallic model helps explain a number of characteristic properties:
  - Electrical conductivity – due to the mobility of delocalized electrons across the metal structure.
  - Thermal conductivity – due to the efficient transfer of heat energy via delocalized electrons and closely packed cations.
  - Malleability – related to the non-directional nature of delocalized electron movement which allows for conformation changes without the breaking of the metallic bond.
- Trends in the properties of metals can be explained by the charge and radius of cations. A stronger metallic bond, caused by ions with smaller radii and greater magnitudes of charge, will have a higher melting point and lower degree of reactivity.
- HL Transition elements, whose atoms have an incomplete d sub-shell, have particularly high melting points as well as being excellent conductors of electricity. This is due to the additional delocalization of d-electrons in the formation of metallic bonds.

Practice questions

1. Which combination would produce the strongest metallic bond?

	Charge on cations	Ionic radius
A	small	small
B	small	large
C	large	small
D	large	large

2. Which metal has the strongest metallic bonding?

A Na **B** K

C Mg **D** Al

3. Which of the following elements is most likely to be metallic?

	Electrical conductivity	
	Molten	**Solid**
A	good	good
B	good	poor
C	poor	good
D	poor	poor

4. Which series shows the correct order of metallic bond strength from strongest to weakest?

A Rb > K > Na > Li **B** Li > Na> K > Rb

C Rb > Na > K > Li **D** Li > K > Na > Rb

5. Calcium, Ca, and strontium, Sr, are both group 2 elements that contain metallic bonding.

(a) Describe the metallic model of bonding and explain how it contributes to electrical conductivity. (3)

(b) Explain why calcium has a higher melting point than strontium. (2)

(Total 5 marks)

6. Explain, with reference to the metallic model of bonding, why metals are generally malleable and good thermal conductors. (4)

(Total 4 marks)

7. HL The transition element gold, Au, is used in electrical circuits due to its high electrical conductivity.

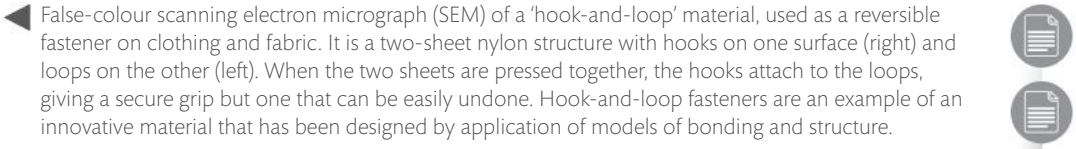
Explain why transition elements are generally better electrical conductors than s and p block metals. (2)

(Total 2 marks)



STRUCTURE

2.4 From models to materials



False-colour scanning electron micrograph (SEM) of a 'hook-and-loop' material, used as a reversible fastener on clothing and fabric. It is a two-sheet nylon structure with hooks on one surface (right) and loops on the other (left). When the two sheets are pressed together, the hooks attach to the loops, giving a secure grip but one that can be easily undone. Hook-and-loop fasteners are an example of an innovative material that has been designed by application of models of bonding and structure.

Guiding Question

What role do bonding and structure have in the design of materials?

From early history, humans have worked to transform readily available natural resources into more useful materials. Civilizations are sometimes characterized by the technology they have developed to accomplish this. The Bronze Age, for example, marks the time when copper was first produced from smelted ores. The extraction of iron from its ores in the blast furnace is probably one of the most significant developments in the Industrial Revolution of the 18th century. These technological advances, however, were largely based on empirical discovery and usually came without a full understanding of the underlying scientific principles.

As the models we use to explain chemical structure and bonding have advanced, so has our ability to predict the properties of materials. This has enabled us to design structures for specific purposes. Materials that have transformed everyday life, such as superconductors, breathable fabrics and liquid crystals, are only in existence because we have been able to apply advanced bonding theory to their synthesis.

In this chapter, we first develop a more holistic model of bonding from the three discrete models of ionic, covalent and metallic bonding discussed earlier. This gives us a tool, the bonding triangle, which helps to predict the properties of unknown and new substances. We describe alloys, which are mixtures of metals, as an example of how changing the bonding within a structure can enhance the resulting properties and uses of a material. Finally, we consider the structure of polymers, which include all plastics. These materials have made such a significant impact, both in terms of convenience in our lives and with respect to some of their damaging environmental effects, that it is suggested the current age may become known as the Plastic Age.

As the models we use to explain structure and bonding will continue to evolve, so will our ability to develop materials fit for purpose. This innovation in material science must be accompanied by the application of Green Chemistry principles to control the wider impact of these developments on health and the environment.

Structure 2.4.1 – The bonding triangle

Structure 2.4.1 – Bonding is best described as a continuum between the ionic, covalent and metallic models, and can be represented by a bonding triangle. Use bonding models to explain the properties of a material.	
A triangular bonding diagram is provided in the data booklet.	Structure 3.1 – How do the trends in properties of period 3 oxides reflect the trend in their bonding? Nature of Science, Structure 2.1, 2.2 – What are the limitations of discrete bonding categories?

SKILLS

Properties of ionic and covalent compounds. Full details of how to carry out this experiment with a worksheet are available in the eBook.

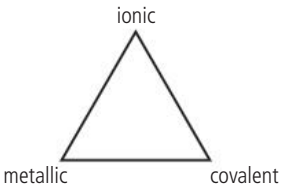
TOK

To what extent do the classification systems we use in the pursuit of knowledge affect the conclusions that we reach?

Chemical bonding is best described as a continuum rather than as discrete bonding types

In Structure 2.1, 2.2 and 2.3 we discussed the three models of bonding – ionic, covalent and metallic – as separate categories. Although there are materials that can be described by one of these models alone, often such a classification is an over-simplification as most materials are an intermediate between these three bonding types, and so show intermediate properties. We have already encountered this concept in Structure 2.2 with the description of polar bonds, which show some ionic character present in covalent bonds.

Therefore, a more accurate picture of bonding is a **continuum** where the different bonding types are present to different degrees. The simplest representation of this is a triangle where each vertex represents one of the three models of bonding. Different materials are then scattered through the triangle, positioned according to the relative amount of each type of bonding they contain.



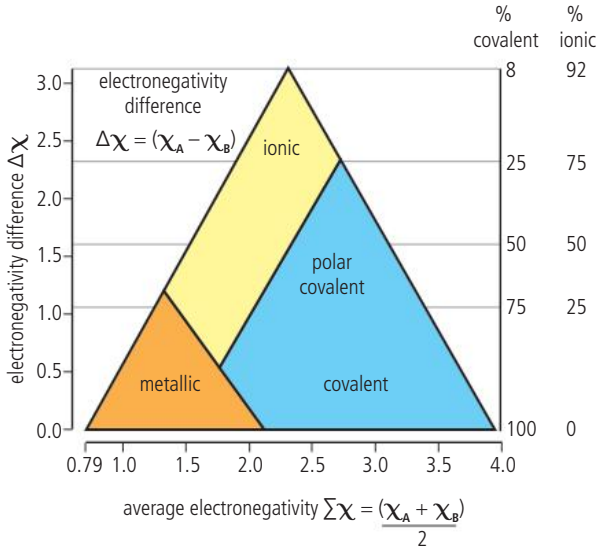
A simple bonding triangle showing the three main types of bonding.

i

The bonding triangle is fully described as the 'van Arkel–Ketelaar triangle of bonding' after the two Dutch chemists credited with its development in the mid-20th century. Anton van Arkel first proposed the triangle and applied it mostly to elements. Jan Ketelaar extended his ideas to more compounds. Others worked in this field and used various parameters to describe the properties of the bonded atoms, but electronegativity values became the established basis for determining positions in the triangle.

The position of an element or compound in the bonding triangle is determined from its electronegativity values, as these give a measure of the tendency of an atom to gain electrons, and therefore the type of bond it will form. Electronegativity values are given in Section 8 of the data booklet and are shown with the symbol χ. The bonding triangle uses the following axes:

- *x*-axis: average electronegativity of bonded elements A and B: $\Sigma\chi = \frac{\chi_A + \chi_B}{2}$
- *y*-axis: electronegativity difference of bonded elements A and B: $\Delta\chi = \chi_A - \chi_B$



The bonding triangle. Calculations of the electronegativity difference and the average electronegativity of the bonded atoms determine the position of a material in the triangle. In turn, this position helps to predict the properties of a material.

Elements have zero electronegativity difference between their atoms, and so are positioned on the *x*-axis, metals on the left (low electronegativity) and non-metals on the right (high electronegativity). Ionic compounds with high electronegativity differences are found at the top centre, while covalent compounds with low electronegativity differences are found in the lower right corner. Polar covalent compounds occupy the intermediate position.

From these positions in the triangle and knowledge of the characteristics of each bonding type, we are able to deduce the expected properties of a material.

Nature of Science

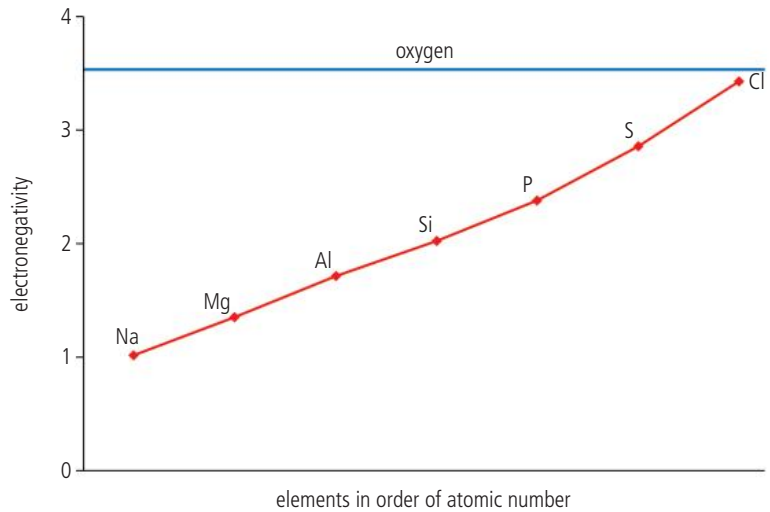
The bonding triangle is a tool that has predictive power for the properties of a substance.

SKILLS

Cement and mortar: investigating the parameters that affect their properties. Full details of how to carry out this experiment with a worksheet are available in the eBook.

Structure 3.1 – How do the trends in properties of period 3 oxides reflect the trend in their bonding?

We can illustrate the importance of electronegativity values in determining the type of bonding by looking at the oxides of the elements in period 3. Oxygen has an electronegativity value of 3.4, and as we move from left to right across period 3, the electronegativity of the elements increases and approaches this value, as shown in Figure 1.

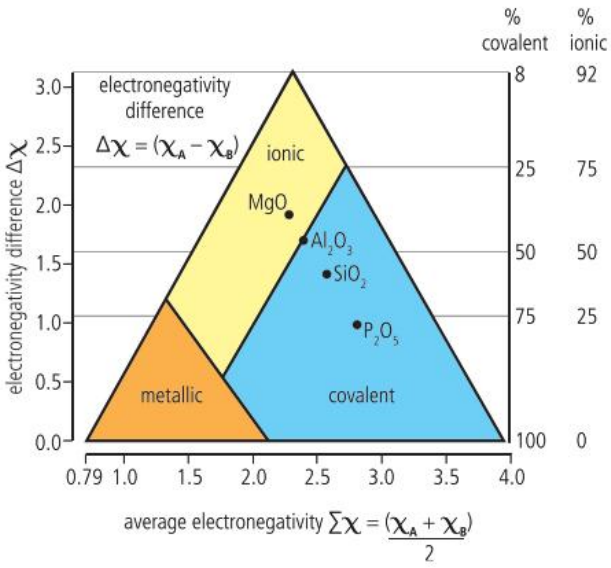


S2.4 Figure 1 Electronegativity values of the elements of period 3 increase across the period, approaching the value of oxygen.

As the *difference* in electronegativity values decreases, so too does the ionic character of the oxides, while the covalent character increases. This trend in bonding explains the trend in physical properties of the period 3 oxides as summarized below.

	Na_2O, MgO and Al_2O_3	SiO_2	P_4O_{10}, SO_2 and Cl_2O
properties	high melting and boiling points, electrical conductors when molten	high melting and boiling points, non-conductor of electricity	low melting and boiling points, non-conductors of electricity
bonding	ionic metallic oxides	giant covalent oxide of the metalloid silicon	covalent non-metallic oxides

This periodic trend could be predicted by considering the positions of the oxides in the bonding triangle, as shown in Figure 2.



S2.4 Figure 2 The bonding triangle showing the positions of the oxides of period 3 elements. These positions reflect the trend in their bonding, and enable us to predict and explain the trend in their properties.

Nature of Science, Structure 2.1, 2.2 – What are the limitations of discrete bonding categories?

We have described the classification of bonds into ionic, covalent or metallic as an over-simplification as it can lead to incorrect predictions of physical properties. For example, aluminium chloride, $AlCl_3$, containing a metal and a non-metal might be classified as ionic, which would suggest a high melting point. Yet the melting point of $AlCl_3$ is significantly lower than that of a similar-sized ionic compound such as NaCl.

- NaCl mp 801 °C
- $AlCl_3$ mp 192 °C

Electronegativity values → position of a material in the bonding triangle → prediction and explanation of many properties.

When we determine the positions of these compounds in the bonding triangle (see page 266), we find that $AlCl_3$ has significant covalent character, and this explains its relatively low melting point. The model of a bonding continuum in the bonding triangle allows us to make more accurate predictions of properties.

Structure 2.4.2 – Application of the bonding triangle

Structure 2.4.2 – The position of a compound in the bonding triangle is determined by the relative contributions of the three bonding types to the overall bond.	
Determine the position of a compound in the bonding triangle from electronegativity data. Predict the properties of a compound based on its position in the bonding triangle.	
To illustrate the relationship between bonding type and properties, include example materials of varying percentage bonding character. Only binary compounds need to be considered. Calculations of percentage ionic character are not required. Electronegativity data are given in the data booklet.	Structure 2.1, 2.2, 2.3 – Why do composites such as reinforced concretes, which are made from ionic and covalently bonded components and steel bars, have unique properties?

Electronegativity data are used to determine the position of a compound in the bonding triangle

We can calculate the position of elements and binary compounds (those containing only two elements) in the bonding triangle from electronegativity values. For example, consider caesium, fluorine and the compound they react together to form caesium fluoride.

Substance	$\chi_{average}$	$\Delta\chi$	Position in triangle
Cs	0.8	0.8 − 0.8 = 0.0	bottom left as 100% metallic; Cs has the lowest absolute electronegativity
F_2	4.0	4.0 − 4.0 = 0.0	bottom right corner as 100% molecular covalent
CsF	$\frac{4.0 + 0.8}{2} = 2.4$	4.0 − 0.8 = 3.2	top of the triangle as 100% ionic compound; made up of the most electropositive metal and most electronegative non-metal

The position of an element or compound in the bonding triangle is determined by the magnitude and difference of the electronegativities of the constituent elements.

Worked example

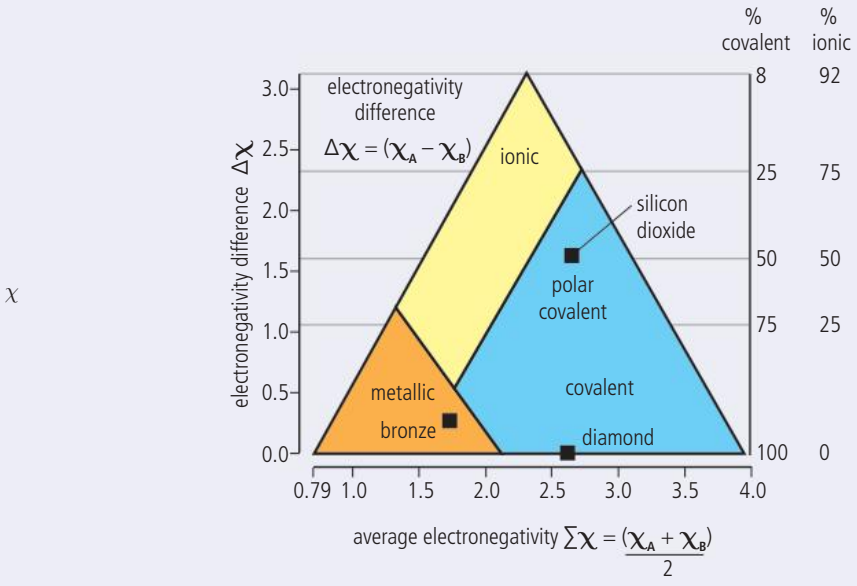
Locate the position of the following substances in the bonding triangle:

(a) diamond **(b)** silicon dioxide

(c) bronze (an alloy of copper and tin)

Solution

	Substance	$\chi_{average}$ (x-axis)	$\Delta\chi$ (y-axis)
(a)	diamond	2.6	0.0
(b)	silicon dioxide	$\frac{1.9 + 3.4}{2} = 2.65$	3.4 − 1.9 = 1.5
(c)	Cu/Sn	$\frac{1.9 + 2.0}{2} = 1.95$	2.0 − 1.9 = 0.1



Composite materials have been made by humans for thousands of years. One of the earliest examples is adobe bricks, which are made from a combination of mud and an organic material such as straw or dung. Dried mud alone is brittle, straw is very strong but difficult to hold in place. The combination produces a material which is strong and easy to shape.

In the previous section, we considered the bonding in $AlCl_3$ and NaCl. We can determine the positions of these compounds in the bonding triangle, and estimate their percentages of bonding type from the right-hand scale of the triangle.

Substance	$\chi_{average}$	$\Delta\chi$	Position in triangle	Bonding
NaCl	$\frac{0.9 + 3.2}{2} = 2.05$	$3.2 - 0.9 = 2.3$	upper centre	ionic compound, approximately 75% ionic
$AlCl_3$	$\frac{1.6 + 3.2}{2} = 2.4$	$3.2 - 1.6 = 1.6$	centre, close to the ionic and covalent border	polar covalent, approximately 50% covalent

Composite materials, such as fibreglass and concrete, are heterogeneous mixtures of at least two different materials, which are present as separate phases. As these are mixtures, each component retains its individual properties. The result is a material with enhanced properties designed for specific purposes.

Structure 2.1, 2.2, 2.3 – Why do composites such as reinforced concretes, which are made from ionic and covalently bonded components and steel bars, have unique properties?

Adobe bricks drying in the sun in Peru.



Construction of a stadium. Reinforcing metal bars (rebar) are fitted before pouring concrete. Concrete is strong in compression but weak in tension. The rebar significantly improves the tensile strength and ductility of concrete structures.



Exercise

Q1. Use data from Section 9 and Section 17 of the data booklet to classify the bonding in the following materials:

(a) Cl_2O **(b)** $PbCl_2$ **(c)** Al_2O_3 **(d)** HBr **(e)** NaBr

Q2. Copper(II) oxide can be added to give glass a green or blue colour. Deduce the position of copper oxide in the bonding triangle and describe the nature of its structure and bonding.

Q3. Silicon dioxide and aluminium oxide are important minerals in the Earth's crust. Use the bonding triangle to deduce their positions and so determine which has the greater covalent character.

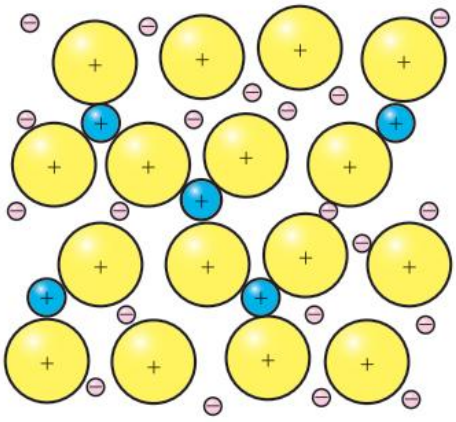
Structure 2.4.3 – Alloys

Structure 2.4.3 – Alloys are mixtures of a metal and other metals or non-metals. They have enhanced properties. Explain the properties of alloys in terms of non-directional bonding.	
Illustrate with common examples such as bronze, brass and stainless steel. Specific examples of alloys do not have to be learned.	Structure 1.1 – Why are alloys more correctly described as mixtures rather than as compounds?

Alloys are solutions of metals with enhanced properties

Alloys are produced by adding one metal element to another metal (or carbon) in the liquid state, so that the different atoms can mix. As the mixture solidifies, ions of the different metals are scattered through the lattice forming a structure of uniform composition. Alloys contain metallic bonds as the delocalized electrons bind the lattice. The production of alloys is possible because of the non-directional nature of the delocalized electrons and the fact that the lattice can accommodate ions of different size.

Alloys are homogeneous mixtures containing at least one metal, and held together by metallic bonding.



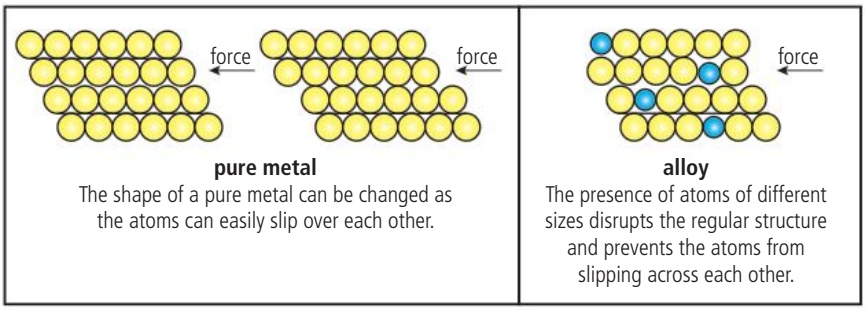
▲ Alloys consist of different metal ions and a sea of delocalized electrons. The smaller cations (blue) are able to fit in the spaces between the larger cations (yellow) in the lattice structure.



◀ Molten metal being poured from a vat at the Magnitogorsk iron and steel works, one of the largest metal-working plants in Russia. The production of alloys depends on mixing metals in the molten state.

Alloys have some properties that are distinct from their component elements due to the different packing of the cations in the lattice. The regular arrangement of atoms in a pure metal is interrupted in the alloy by the presence of different cations, making it more difficult for atoms to slip over each other and so change the shape. The alloy is often stronger, more chemically stable, and more resistant to corrosion than its component elements. For example, steel, which is an alloy of iron with less than 2% carbon and 1% manganese and other trace elements, can be 1000 times stronger than iron.

Changing the regular packing in the lattice gives alloys enhanced properties compared with the pure metal.



pure metal
The shape of a pure metal can be changed as the atoms can easily slip over each other.

alloy
The presence of atoms of different sizes disrupts the regular structure and prevents the atoms from slipping across each other.

You do not need to learn these examples, but you should be able to use examples you choose to explain why the structures of alloys give them enhanced properties compared with their component metals.

Some examples of common alloys are given below.

Name of alloy	Component metals	Properties and uses
steel	iron with carbon and other elements	high tensile strength but corrodes, used as a structural material
stainless steel	iron with other elements such as nickel and chromium	widely used in domestic and industrial appliances due to strength and corrosion resistance
brass	copper and zinc	variety of plumbing fittings
bronze	copper and tin	coins, medals, tools, heavy gears
pewter	tin, antimony and copper	decorative objects
duralumin	aluminium, copper and manganese	aircraft, boats and machinery due to high strength and resistance to corrosion
nichrome	nickel and copper	heating elements in toasters, electric heaters
solder	lead and tin	joining two metals together, especially in electric circuitry
sterling silver	silver and copper	jewellery, art objects

Alloys, in common with other mixtures, have no fixed composition. For example, 'steel' is the general name for a mixture of iron and carbon and other metals in different proportions. So, unlike compounds, alloys cannot be represented by a chemical formula. Alloys form by mixing liquid metals without chemical reaction, and so the components retain metallic properties such as thermal and electrical conductivity, and magnetism in the case of iron-containing alloys.



Nichrome wire, an alloy of nickel and copper, is used when carrying out flame tests in the laboratory. It is a convenient material because it is resistant to oxidation at high temperatures. The lilac colour here indicates that the sample contains potassium.



Swedish steel-making company SSAB has plans to eliminate its use of coal in its plants by 2045. The company uses hydrogen, produced using clean-energy powered electrolysis, in place of coal – dramatically reducing carbon pollution. The first fossil-fuel-free steel was produced in 2020, and will be brought to market in 2026.

Structure 1.1 – Why are alloys more correctly described as mixtures rather than as compounds?

Steel manufacture is one of the world's largest industries and is sometimes used as a measure of a country's development and economic progress. Global steel production has tripled in the last 50 years, with China and India becoming the world's top steel-producing nations. Steel is the foundation of buildings, vehicles and industries, including sustainable energy technologies. Plans for sustainability of steel production include moving towards a fossil-fuel-free industry by removing coal from the process. Steel is infinitely recyclable with no loss of quality, and it is estimated that new steel products contain on average 30% recycled steel.

Challenge yourself

1. The components of a mixture can usually be separated by physical means. What might be the challenges of trying to separate the metals from an alloy?

Exercise

Q4. An alloy is a mixture of metal with which of the following?

A a second metal or other non-metal material
B a non-metal material only
C a second metal only
D none of the above

Q5. Which of the following is not an alloy?

A solder **B** silver **C** bronze **D** brass

Q6. Explain how alloying can modify the structure and properties of metals.

Q7. What is the difference between an alloy and a composite?

Structure 2.4.4 – Polymers

Structure 2.4.4 – Polymers are large molecules, or macromolecules, made from repeating subunits called monomers.	
Describe the common properties of plastics in terms of their structure.	
Examples of natural and synthetic polymers should be discussed.	Structure 2.3 – What are the structural features of some plastics that make them biodegradable?

SKILLS

Making polymers. Full details of how to carry out this experiment with a worksheet are available in the eBook.

The polymers described in this chapter are organic compounds, based on the covalent chemistry of carbon and its unique ability to form stable bonds with itself, with hydrogen and with other elements. To understand these structures, you may find it helpful to first study an introduction to organic chemistry in Structure 3.2.

Polymers are large molecules made up of repeating subunits

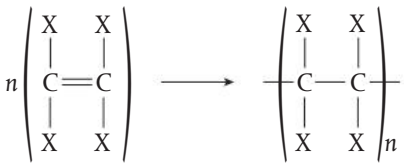


We can think of polymer formation as similar to making a chain of paper clips.

Some small molecules, known as **monomers,** are able to react together to form a linked chain held together by covalent bonds, known as a **polymer**.

Polymers are also known as **macromolecules,** as they are composed of thousands of atoms and so are relatively large compared with other molecules. Polymers vary in the nature of the monomer, and the length and the amount of branching in the chain, and so have a wide range of different properties.

As polymers are such large molecules, we show their structure as a **repeating unit**, which has open bonds at each end. It is put in a bracket with *n*, the number of monomers in the polymer, as a subscript.



monomer the repeating unit

This is an example of an addition polymer, described in Structure 2.4.5 on page 276.

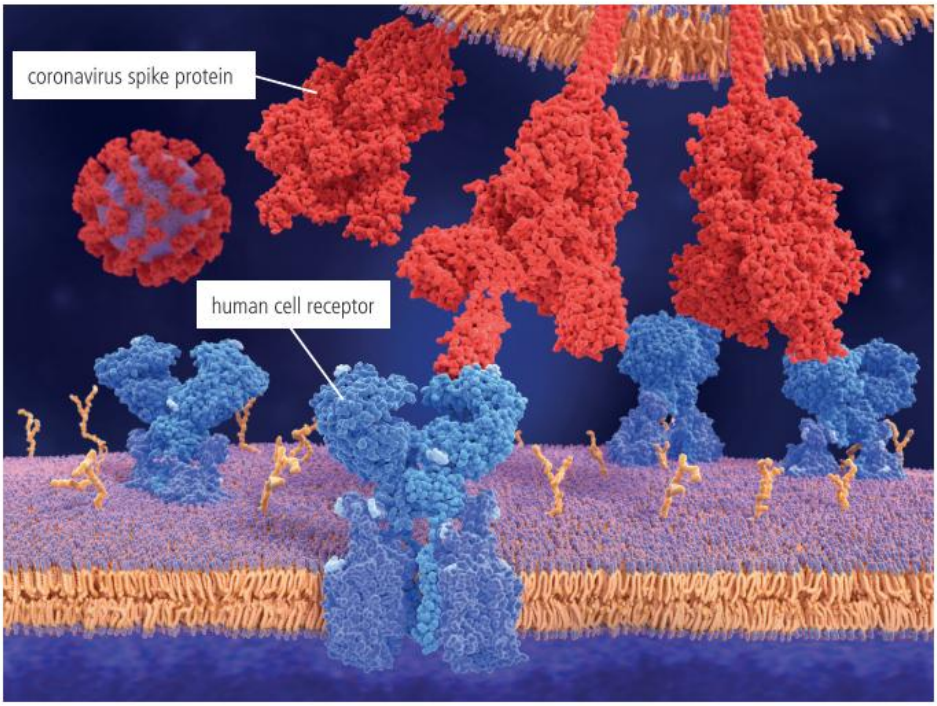
Nature of Science

Although plastics were one of the key materials of the 20th century, the notion of very large molecules was not widely accepted by the scientific community until 1929. Hermann Staudinger, a German organic chemist, pushed forward his idea of macromolecules, which he characterized as polymers. He experienced widespread resistance from his academic peers who thought that the newly invented plastics and natural materials such as rubber, starch, and cellulose were bundles of small molecules held together by unknown intermolecular forces. Staudinger's idea that there was a covalent bond between the units had little support. He was told by one of his colleagues to 'drop the idea of large molecules.' The eventual acceptance of Staudinger's theory was a key step in our understanding that led to the practical development of polymer chemistry. Science is a human activity and it sometimes takes courage to challenge the accepted models of the time.

Hermann Staudinger was the first polymer chemist to be awarded the Nobel Prize in Chemistry in 1953 *'for his discoveries in the field of macromolecular chemistry'.*

Does competition between scientists help or hinder the production of knowledge?

Polymers are widespread in living things. Molecules such as protein, starch and DNA are examples of **natural polymers**. Understanding the relationship between the structure and function of these molecules has been a major focus of biochemical research over the last 100 years. Many advances in medicine, such as vaccines and drugs, have been developed from knowledge of the detailed structure and interaction of these polymers.



Molecular model of a coronavirus spike protein (shown in red) bound to human cell receptors (shown in blue). Binding between the spike protein and the receptor enables the virus to enter the human cell, where it replicates itself and can cause disease. Analysis of the structure of the viral protein, a natural polymer, is critical in enabling researchers to develop vaccines against diseases such as Covid-19.

Human-made polymers, known as **synthetic polymers**, first appeared in the 1930s when raw materials from the petroleum industry became available. This rapidly led to the development of a wide range of new materials known as **plastics**, a trend which continues to this day. Plastics are synthetic polymers that have widespread uses due to their light weight, low reactivity, water resistance and in some cases their strength. We use plastics in almost every aspect of daily life including packaging, construction, clothing, transportation and machinery. As a result, plastics have become widely distributed in both terrestrial and marine environments.

The very features that make plastics so useful, such as their unreactivity and water repellency, mean they are often **non-biodegradable,** that is, they cannot be broken down by natural processes, and so remain in the environment for indefinite periods of time. Accumulation of plastics in natural environments is one of the largest and most pressing environmental concerns of our time.



Plastic waste washed up on beach in Ireland. Common plastics include polythene, PVC, nylon, polystyrene and Kevlar®.

Global production of plastics has increased exponentially since 1950 and continues to rise. It is suggested that fossilized plastics may form a distinctive stratal layer, possibly marking the start of the proposed geological epoch the 'Anthropocene', the time of significant human impact on Earth's geology and ecosystems. A high proportion of plastics end up in the oceans where they have a widespread impact on the ecosystem. It is estimated that by 2030 there could be 300 million tonnes of accumulated plastic in the oceans. While measures to try to address this include more efficient recycling processes, biodegradable plastics, and plastic-feeding microorganisms, the urgent need is to reduce the source. We can all share some responsibility for decreasing our use of disposable plastics.

Properties of polymers. Full details of how to carry out this experiment with a worksheet are available in the eBook.

Structure 2.3 – What are the structural features of some plastics that make them biodegradable?

A biodegradable compound can undergo breakdown by microorganisms into end products that are found in nature and therefore not harmful to the environment. Biodegradable plastics may be plant-based, containing starch, lignin or cellulose, and are often produced from corn. The breakdown products are carbon dioxide and water. Swelling of the starch grains in water can help to break down the plastic. Other biodegradable plastics are based on petroleum derivatives and contain catalysts for the breakdown process. **Compostable** plastics break down along with food and garden waste in the specific conditions found in a compost pile.



Clear plastic pellets made from corn. The plastic is biodegradable and can be used for both food and non-food packaging as well as textiles and other materials.

There is growing evidence that some microorganisms are evolving to break down plastic in their habitat. Genetic analysis of bacteria from different environments has found enzymes that can degrade different types of plastic, where the number and type of enzymes match the amount and type of plastic pollution in different locations. For example, in ocean studies, higher levels of degrading enzymes were found at levels of 200–600 m below the surface, matching the higher levels of plastic pollution known to exist at these depths. There is potential to develop these microbial communities for targeted degradation of specific polymers.

Nature of Science

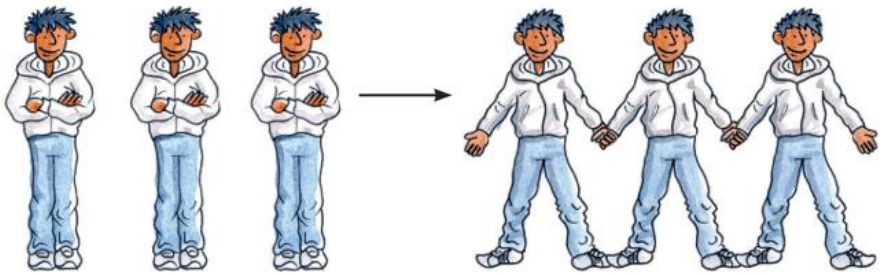
It is hard to assess the scale of the impact that plastics have had on society. The manufacture of diverse plastics has brought innovation and progress to our global food supply, clothing, health care and infrastructure. Yet these innovations have come at a significant cost to the environment, and the long-term consequences are still being determined. While scientific progress is responsible for both the intended and unintended consequences, it is scientists who must respond to the problems.

Structure 2.4.5 – Addition polymers

Structure 2.4.5 – Addition polymers form by the breaking of a double bond in each monomer. Represent the repeating unit of an addition polymer from given monomer structures.	
Examples should include polymerization reactions of alkenes. Structures of monomers do not have to be learned but will be provided or will need to be deduced from the polymer.	Structure 3.2 – What functional groups in molecules can enable them to act as monomers in addition reactions? Reactivity 3.1 – Why is the atom economy 100% for an addition polymerization reaction?

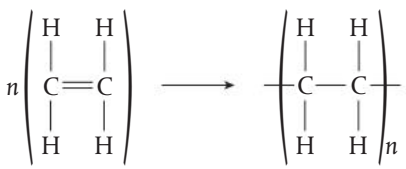
Monomers with double bonds can be used to make addition polymers

Addition reactions occur when a multiple bond in a molecule breaks and creates new bonding positions. Alkenes and alkynes are organic compounds that have double and triple carbon–carbon bonds respectively, and so readily undergo addition reactions, as described in Reactivity 3.4. This reactivity also means they can act as monomers in forming **addition polymers**.



People cannot form a chain until they unfold their arms to release their hands. Similarly, alkenes must break their double bonds in order to join together to form the polymer.

Addition polymerization reactions lead to the synthesis of many common plastics. For example, the reaction of ethene, C_2H_4, undergoing polymerization to form poly(ethene) can be shown as follows.

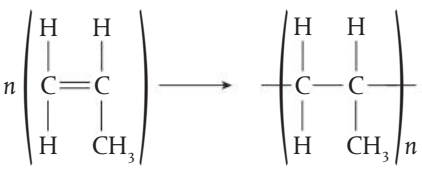


monomer
ethene

polymer
polyethene

An addition polymer is formed when the double bonds of monomer molecules break and make new covalent bonds with neighbouring molecules to form a chain. No other product is formed.

Similarly, propene polymerizes to form polypropene, often called polypropylene.

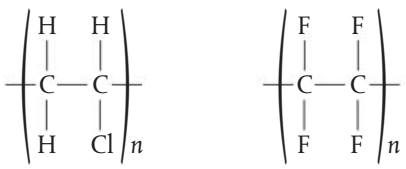


propene

polypropene

Structure 3.2 – What functional groups in molecules can enable them to act as monomers in addition reactions?

Other common addition polymers include polychloroethene, also known as PVC, and PTFE, polytetrafluoroethene, often marketed as Teflon®. Their repeating units are shown below.



PVC

PTFE

The example with propene shows that it is helpful to draw the structure of the monomer with the double bond in the *middle* and the other groups off at 90°. Then it is easy to see how the monomers link together when the double bond breaks.

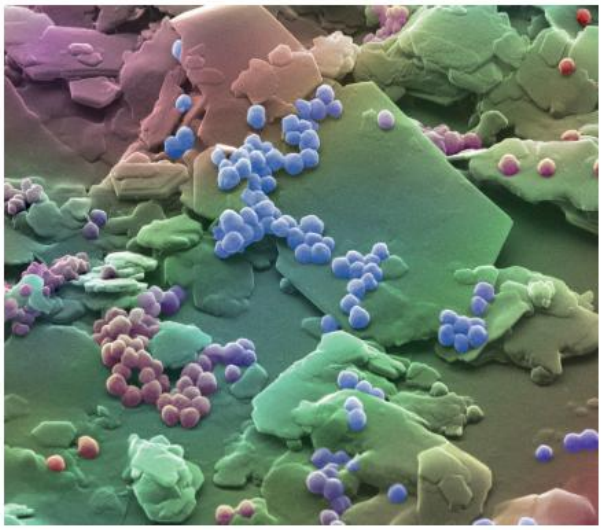
Atom economy is a measure of the proportion of reactant that ends up in the desired product, based on the reaction's stoichiometry.

$$\%\ \text{atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100$$

Addition polymerization reactions do not generate a by-product and so convert 100% of reactants into product. This does not mean, however, that there is no waste or environmental impact of these reactions. A reaction yield of less than 100% means there will be unreacted monomer at the end of the process. Also, many polymerization reactions use solvents and conditions of high temperature, pressure and/or catalysts – all of which must be considered as part of an environmental assessment of the process.

Reactivity 2.1 – Why is the atom economy 100% for an addition polymerization reaction?

Microplastics are small plastic pieces less than 5 mm long, which harm marine life and enter the food chain. Microplastics come from a variety of sources, including larger plastic debris that degrades into smaller and smaller pieces. **Microbeads** are a type of microplastic, mostly derived from health and beauty products that pass through water filtration systems.



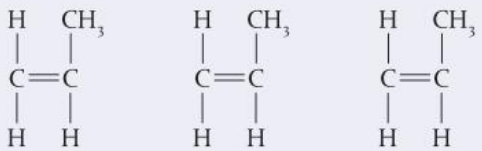
Coloured scanning electron micrograph (SEM) of particles found within a cosmetic facial scrub. A single shower can result in 100 000 plastic particles entering the ocean. Legislation to ban the use of microbeads is currently under discussion in many countries.

Worked example

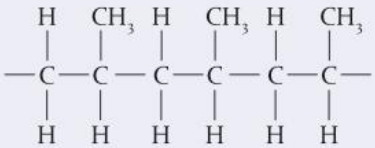
Deduce the structure of the addition polymer formed from methylpropene. You should include three repeating units in the structure.

Solution

1. Draw three structures with the alkene double bond in the middle:



2. Open the double bond in each molecule so that single bonds extend in both directions:



Challenge yourself

2. Draw the repeating unit in polystyrene, given that the formula of the monomer is $C_6H_5CHCH_2$.

Exercise

Q8. What do poly(ethene) and ethene have in common?

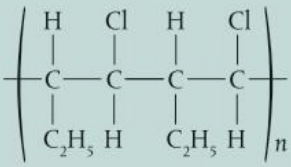
A same molecular formula

B same empirical formula

C same physical properties

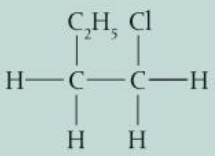
D same chemical properties

Q9. The repeating unit of a polymer is shown:

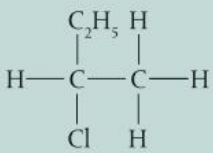


Which structure shows the monomer used to make this polymer?

A



B



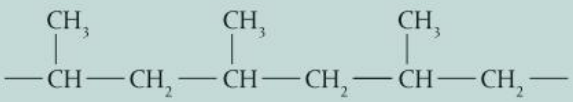
C



D



Q10. Part of the structure of a polymer is shown:



Which is the formula of the monomer used to make this polymer?

A C_3H_6 **B** C_6H_{12} **C** C_3H_8 **D** C_6H_{14}

Q11. Distinguish between the terms recyclable, biodegradable and reusable as applied to plastics. What are the advantages and disadvantages of each of these in helping to reduce the environmental impact of plastics? What other ways can we help to reduce the amount of plastic waste accumulating in the oceans?

Addition polymers are found almost universally in daily life. Poly(ethene) has excellent insulating properties and is commonly used in household containers, water tanks, and piping. Polypropylene is used in the manufacture of clothing, especially thermal wear for outdoor activities. PVC is used in all forms of construction materials, packaging, electrical cable sheathing etc. There is controversy regarding its use, linked to health and environmental concerns, because of its high chlorine content which makes it difficult to recycle. Some countries are banning the use of PVC in packaging. PTFE has a very low surface friction so it is widely used in non-stick pans. It also makes up one of the layers in waterproof, breathable fabrics such as GoreTex®. The resistance of PTFE to van der Waals' forces means that it is the only known surface to which a gecko cannot stick.

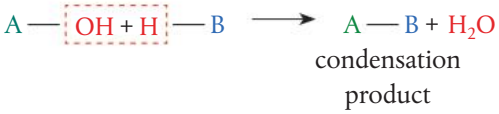
HL

Structure 2.4.6 – Condensation polymers

Structure 2.4.6 – Condensation polymers form by the reaction between functional groups in each monomer with the release of a small molecule.	
Represent the repeating unit of polyamides and polyesters from given monomer structures.	
All biological macromolecules form by condensation reactions and break down by hydrolysis.	Structure 3.2 – What functional groups in molecules can enable them to act as monomers in condensation reactions?

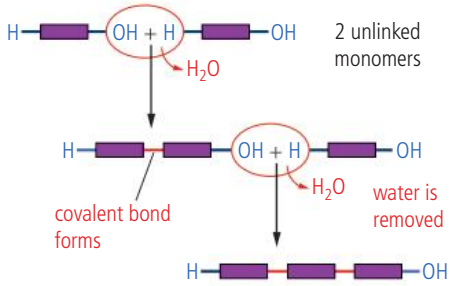
Monomers with two functional groups can be used to make condensation polymers

Condensation reactions occur when two functional groups react to form a new covalent bond, with the release of a small molecule, such as H_2O.



In order to form condensation polymers, monomers must each have *two functional groups*, which we can think of as 'active ends' where condensation reactions can occur. This allows them to form new covalent bonds with neighbours on both sides. It is similar to the way in which people can only form a human chain when they have two available hands to link with neighbours. A small molecule such as H_2O, HCl or NH_3 is released as each new bond forms.

Condensation polymers form between monomers which each have two functional groups to react. A small molecule is released for each covalent bond that forms between the monomers.



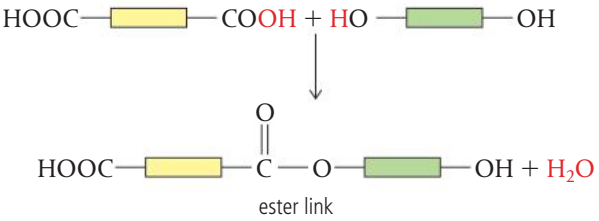
▲ Condensation reactions involve the loss of a small molecule for every covalent bond formed.

To take part in condensation reactions, the functional groups in neighbouring molecules must be able to react together. Two common examples are considered here.

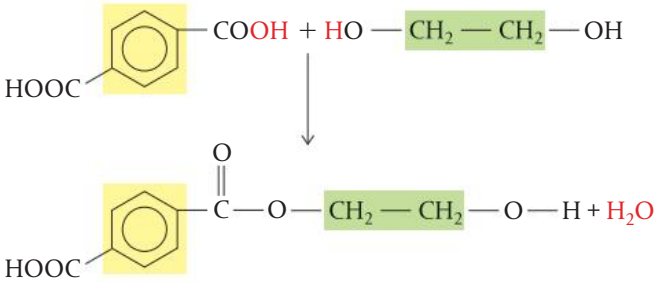
1. Carboxylic acid and alcohol react to form polyester

When one monomer has two carboxylic acid, –COOH, groups, and the other monomer has two alcohol, –OH, groups, an **ester link** forms between them. The chain extends in both directions and is therefore known as a **polyester**. When describing these reactions it is sometimes helpful to think about the functional groups sticking out in both directions as if from a box, which represents the rest of the molecule.

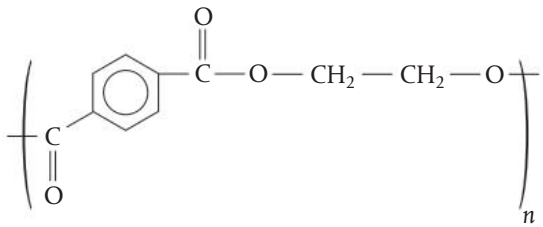
For example:



When we focus on the functional groups in this way, it is easier to deduce the repeating unit from any specified monomers. For example, formation of a polyester from the monomers benzene-1,4-dicarboxylic acid and ethane-1,2-diol is shown below.



The repeating unit of this polyester is:



This polyester, polyethylene terephthalate, is often abbreviated to PET and is widely used in synthetic fibres, plastic bottles and other containers. Other polyesters include the natural polymers in fats and oils, and phosphodiester links in the nucleic acids, DNA and RNA.

When we recognize the linkage between two monomers, we can work backwards to deduce the monomers that combined by condensation.



Bottles being processed at a PET recycling plant. PET is the most common plastic used in drink bottles and food containers and can be fully recycled through washing and remelting. Recycled PET is used to make new containers, carpets and fleece clothing.

You can learn more about naming and representing organic molecules in Structure 3.2, Functional groups.

Make sure when you draw a repeating unit of a polymer that you show open bonds extending through the brackets on each end of the molecule, as this shows the ability of the molecule to link with additional monomers.

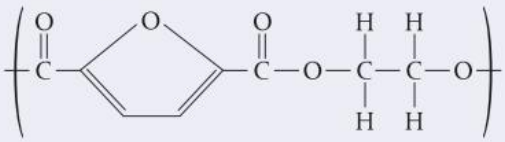
Commercial production of nylon began in 1939, just before the start of the Second World War. Its discovery in 1935 was the result of research by American chemists, notably Wallace Carothers working for the DuPont company. He was looking for a synthetic fibre to replace silk because the supply of silk from Japan was vulnerable to the worsening trade relations with America. When nylon was first produced, it was heralded as being 'as strong as steel, as fine as a spider's web.' One of the earliest major products was women's stockings – 64 million pairs were sold during the first year. Nylon was used in the Second World War in parachutes and tents as well as in surgical sutures. Nearly 100 years later, nylon in its various forms is still one of the most common polymers in use worldwide.



Coloured scanning electron micrograph (SEM) of the weave of a nylon stocking or tights. Nylon is a polyamide with fibres that are stronger and more elastic than silk, and relatively insensitive to moisture. Nylon is used in the manufacture of textiles, moulded objects and medical sutures.

Worked example

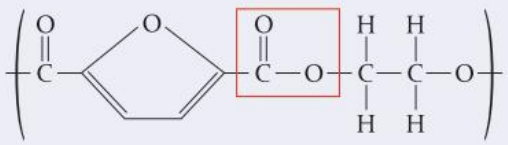
Poly(ethylene furanoate) (PEF) is a polyester made from bio-based monomers.

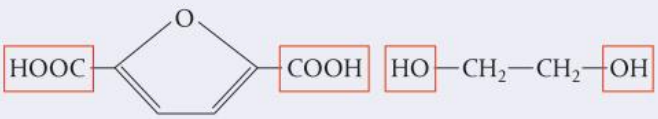


Deduce the structure of the two monomers from which it is made.

Solution

Find the ester link and break it to form an acid and an alcohol. Note that a molecule of water is added as the bond breaks.

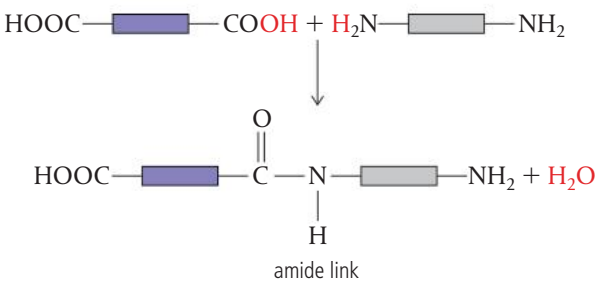




2. Carboxylic acid and amine react to form polyamide

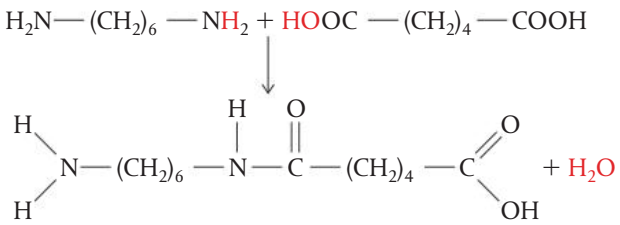
When one monomer has two carboxylic acid, –COOH, groups and another monomer has two amine, $–NH_2$, groups, an **amide link** forms between them. As the monomers can link with neighbours on both sides, this forms a polymer known as a **polyamide**. Polyamides can also form when monomers each have one acid and one amino group, known as amino acids.

Again, focusing on the functional groups, we can represent these reactions as follows.

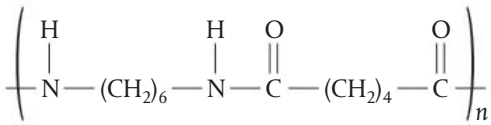


Polyamides include many synthetic polymers such as nylon and Kevlar®. They are widely used in the textile industry for clothing and carpets, as well as machine parts, tyre cords and ropes. Proteins, one of the most important and diverse types of molecules in biology, are polyamides formed by condensation reactions between amino acids.

There are several forms of nylon; the most common is called 6,6-nylon because both its monomers have six carbon atoms. The monomers are 1,6-diaminohexane and hexanedioic acid.



Therefore the repeating unit of 6,6-nylon is:



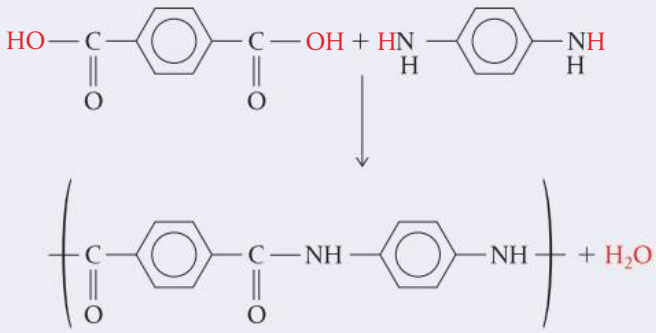
Structure 3.2 – What functional groups in molecules can enable them to act as monomers in condensation reactions?

Worked example

Use structural formulas to illustrate the reaction that occurs between benzene-1,4-dicarboxylic acid and 1,4-diaminobenzene to form the condensation polymer Kevlar®. Include the repeating unit of Kevlar® in your answer.

Solution

1. First draw the structures of the two monomers, positioned so that the functional groups stick out from the centre of the molecules and lie close to the functional groups on the neighbouring molecule.
2. Then deduce how the reaction between these two groups leads to the loss of H_2O and the formation of a new covalent bond.

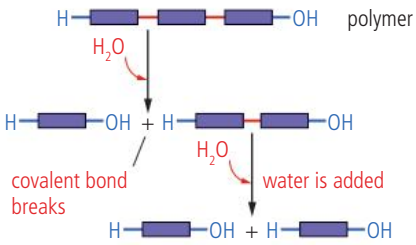


(a) Use brackets to surround the structure and ensure that you have shown open bonds in the unreacted positions.

(b) Include one molecule of H_2O as the product for each bond formed.

All biological macromolecules are condensation polymers synthesized in cells by condensation reactions between monomers. For example, starch is produced by linking glucose molecules into long chains. The reverse reaction, known as **hydrolysis**, breaks the polymers down into their monomers. A molecule of water is used for each bond broken.

Hydrolysis reactions involve addition of a molecule of water for every covalent bond broken.





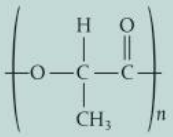
When a bulb germinates, it breaks down its food store of insoluble polymers into monomers by hydrolysis reactions. For example, the polymer starch is hydrolyzed to glucose which makes energy available for growth.

These hydrolysis reactions happen during digestion, decomposition and when stored materials need to be mobilized. Both condensation and hydrolysis reactions are controlled by biological catalysts called **enzymes**.

Exercise

Q12. Nylon-6,10 is made from the monomers 1,6-diaminohexane and decanedioic acid. Draw the repeating unit of this polymer.

Q13. Polylactic acid is a plastic made from fermented plant starch. It has the structure below.



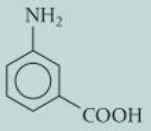
Deduce the structure of the monomer.

Q14. Draw the structures of the polymers and any by-products formed from the following pairs of monomers.

(a) $HO-CH_2-CH_2-CH_2-OH + HO-CO-CH_2-CH_2-CO-OH$

(b) $H_2N-CH_2-(CH_2)_4-CH_2-NH_2 + Cl-CO-CH_2-CH_2-CO-Cl$

Q15. This compound is a monomer for a condensation polymer.



(a) Identify the functional groups in the monomer which allow it to act as a monomer.

(b) Deduce the by-product of the polymerization reaction.

(c) Deduce the structure of the resulting polymer. You should include at least three monomer units in your answer.

(d) Kevlar® is a polymer produced from monomers which have functional groups in the 1,4 positions of the benzene ring. Explain the strength of the polymer in terms of the orientation of the two functional groups.

(e) Explain why Kevlar® has a lower density than steel.

HL end

Guiding Question revisited

What role do bonding and structure have in the design of materials?

In this chapter we used models of bonding to describe and explain the properties of some important materials.

- Bonding in materials is best described as a continuum rather than as discrete types, and can be represented as a triangle of bonding.
- The position of an element or compound in the bonding triangle is determined from electronegativity values.
- From the position of a substance in the bonding triangle, we can deduce its bonding and predict its properties.
- Alloys are homogeneous mixtures of metals with enhanced properties.
- Metals are able to form alloys because of the non-directional nature of metallic bonding.
- Polymers are macromolecules composed of subunits called monomers held together by covalent bonds.
- Addition polymers form from monomers that possess a double bond which can break to create new bonding positions for the attachment of neighbouring monomers.
- Addition polymerization reactions do not yield a by-product.
- Plastics are polymers with properties that give them widespread uses in almost all aspects of society.
- The distinct properties of plastics also cause them to accumulate in the environment without being broken down.
- Use of biodegradable plastics and recycling programmes are important steps to improve the processing of plastic waste, but the urgent need is to reduce the global production of plastic.

HL

- Condensation polymers form from monomers with two functional groups which can react with the functional groups on neighbouring monomers.
- Condensation polymerization reactions release a small molecule for each covalent bond formed.
- Condensation polymers break down by hydrolysis reactions in which a small molecule is added for each bond broken in the polymer.

HL end

Practice questions

1. What are alloys with two components called?

A binary alloy
B binary compound
C ternary alloy
D metallic compound

2. Which of the following **cannot** be deduced from the position of an unknown substance X in the bonding triangle?

A the chemical formula of X
B the type of bonding in X
C the physical properties of X
D whether X is an element or a compound

3. Which of the following is not an addition polymer?

A polyester **B** polystyrene
C poly(ethene) **D** poly(tetrafluoroethene)

4. In the bonding triangle, substance X is found in the top right, substance Y is found in the bottom left and substance Z is found in the bottom right. Answer the following, giving reasons for your answers:

(a) Which of these substances is likely to be an element? (2)
(b) For substances X and Y, give a physical property you would expect them to have in common. (2)
(c) Which substance will be the most brittle? (2)
(d) Which substance is likely to have the lowest boiling point? (2)

(Total 8 marks)

5. Use electronegativity values from Section 9 in the data booklet to complete this table for the five substances given.

Substance	$\chi_{average}$	$\Delta\chi$	Position in triangle and type of bonding	Predicted properties	
Sn					(2)
P_4O_{10}					(2)
Cd_3Mg					(2)
MgO					(2)
NCl_3					(2)

(Total 10 marks)

6. Justify why, in terms of atom economy, the polymerization reactions of polypropylene could be considered 'Green Chemistry'. (2)

(Total 2 marks)

7. Alloys of aluminium with nickel are used to make engine parts. With reference to the model of metallic bonding, explain why this alloy is used rather than pure aluminium. (3)

(Total 3 marks)

8. Lanthanum, La, and antimony, Sb, form compounds with bromine that have similar formulas, $LaBr_3$ and $SbBr_3$.

(a) Determine the type of bond present in $SbBr_3$, showing your method. Use Sections 9 and 17 of the data booklet. (2)

(b) Lanthanum has a similar electronegativity to group 2 metals. Explain, in terms of bonding and structure, why crystalline lanthanum bromide is brittle. (2)

(Total 4 marks)

9. Polymers are made up of repeating monomer units which can be manipulated in various ways to give structures with desired properties.

(a) Deduce the repeating unit of poly(2-methylpropene). (1)

(b) Deduce the percentage atom economy for polymerization of 2-methylpropene. (1)

(c) Suggest why incomplete combustion of plastics, such as polyvinyl chloride, is common in industrial and house fires. (1)

(Total 3 marks)

10. **(a)** Predict the predominant type of bonding for a binary substance AB in which the electronegativity of both atoms is low. Use Section 17 of the data booklet. (1)

(b) The type of bonding in a compound is sometimes used to classify materials. Outline why this type of classification has limitations by using magnesium diboride, MgB_2, as an example. Refer to Sections 9 and 17 of the data booklet. (2)

(Total 3 marks)

HL

11. A polyamide is broken down by hydrolysis. What are the two products formed?

A a dicarboxylic acid and a diammonium salt

B an amine and a carboxylic acid

C a diamine and a dicarboxylic acid

D a dialcohol and an amine

12. A dipeptide forms by a condensation reaction between two amino acids. Which statement describes the reaction?

A The reaction has an atom economy of 100%.

B The reaction forms an ester link and releases a molecule of water.

C The reaction involves the breaking of carbon–carbon double bonds.

D The reaction forms an amide link and releases a molecule of water.

HL end



STRUCTURE

3

Classification of matter

One of the broadest classifications of materials is to divide them into inorganic and organic substances. Here we have the periodic table, which is the great simplifying concept of inorganic chemistry. We also have the molecular model, which is our guide to organic chemistry. Organic chemistry covers most of the compounds of just one element, carbon, shown as black spheres in the model.

If you have ever visited a large supermarket, you will appreciate the importance of a classification system. Similar products are grouped together to help you find what you want. Classification is an important aspect of all scientific work but is fundamental to chemistry. Chemistry is not the study of a random collection of substances but the trends and patterns in their chemical and physical properties.

The broadest classification is to divide substances into inorganic and organic materials. Inorganic chemistry deals with the chemistry of over 100 elements with different properties, whereas organic chemistry is concerned with the compounds of only one element, carbon. The periodic table is the great simplifying concept of inorganic chemistry because it shows that the elements are related to each other. Elements with similar properties can be put into families or groups. These relations are all ultimately explained by the electron configurations of the atoms as discussed in Structure 1.3. The periodic table has only a limited role, however, in guiding our understanding of organic chemistry. Instead, we use a different classification system based on the groups of atoms or functional groups present in different molecules. Homologous series are the families of organic compounds.

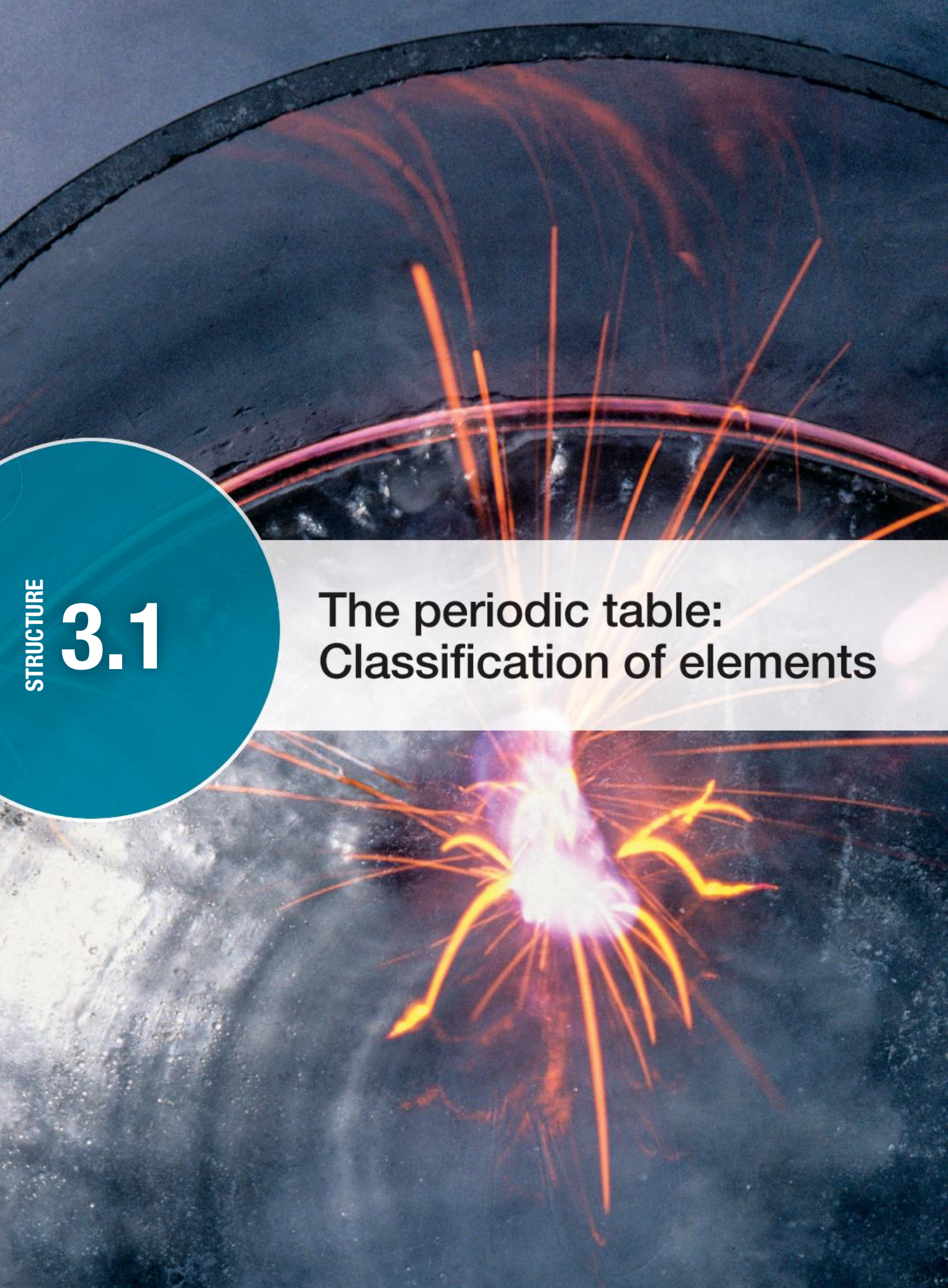
TOK

'Science is built of facts the way a house is built of bricks: but an accumulation of facts is no more science than a pile of bricks is a house.' Henri Poincaré, 1854–1912.

Do you agree with this description of science?

Nature of Science

Scientists classify observations and search for patterns and discrepancies as first steps to understanding. The identification of patterns, however, does not explain phenomena. These patterns lead to an underlying mechanism that explains the patterns. We see in Structure 1.3 that the patterns in the periodic table can be traced back to patterns in electron configuration.



STRUCTURE

3.1 The periodic table: Classification of elements

Potassium reacts with water to produce potassium hydroxide (soluble) and hydrogen gas. The heat of the reaction ignites the hydrogen gas, which burns and sparks with a pink-lilac flame due to the presence of the potassium. The heat of the reaction also melts the potassium, which forms a molten ball that floats on the water's surface.

Guiding Question

How does the periodic table help us to predict patterns and trends in the properties of elements?

The periodic table has been referred to as the most meaningful and compact system of knowledge that humans have devised. It reveals the organizing principles of matter and without it, inorganic chemistry in particular would be a meaningless compilation of random facts. Instead of studying elements individually, we can class them together in groups. The chemistry of potassium can be accurately predicted from the chemistry of lithium and sodium. Elements at opposite sides of the periodic table show opposing properties: the most reactive metal, francium, is on the bottom left of the table, whereas the most reactive non-metal, fluorine, is found near the top right. The periodic table has guided us to our understanding of the atom. The patterns in the periodic table reflect deeper patterns in electron configuration. The periodic table is the 'map' of chemistry. It suggests new avenues of research for the professional chemist and is a guide for students – because it disentangles a mass of observations and reveals hidden order.

TOK

What organizing systems exist in other areas of knowledge? To what extent do the classification systems we use in the pursuit of knowledge affect the conclusions that we reach?

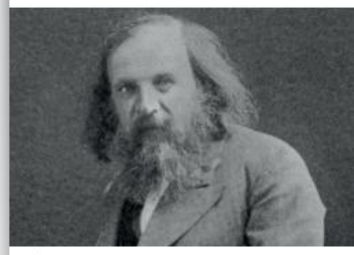
Structure 3.1.1 – Periods, groups and blocks

Structure 3.1.1 – The periodic table consists of periods, groups and blocks. Identify the positions of metals, metalloids and non-metals in the periodic table.	
The four blocks associated with the sublevels s, p, d, f should be recognized. A copy of the periodic table is available in the data booklet.	

Periodicity is the regular repetition of properties of the elements arising from patterns in their electron configuration.

The development of the periodic table

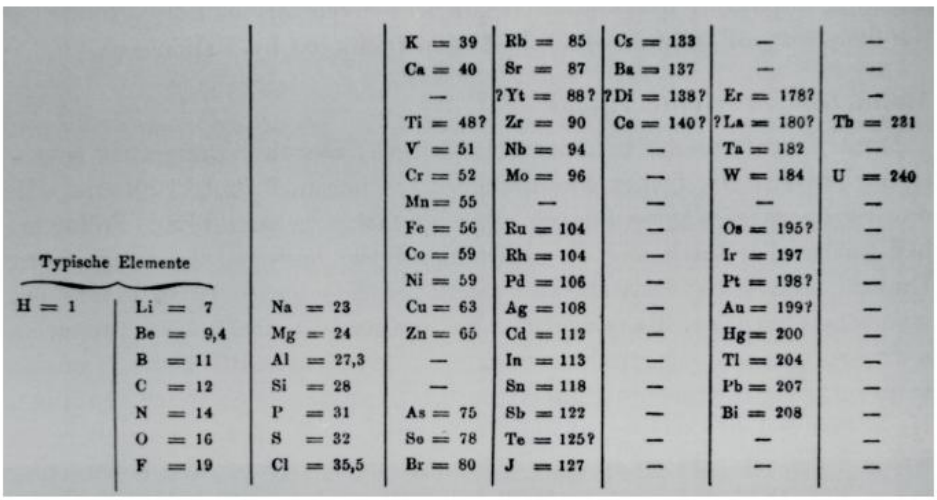
The periodic law states that after certain regular but varying intervals, the chemical elements show an approximate repetition in their properties. This **periodicity** in the physical and chemical properties was the basis of the periodic table first proposed in 1869 by the Russian chemist Dmitri Mendeleev. Previous attempts had been made to impose order on the then known 62 elements, but Mendeleev had the insight to realize that each element has its allotted place, so he left gaps where no known elements fitted into a position. As a scientific idea it was extremely powerful as it made predictions about the unknown elements that fitted these gaps, predictions which could be tested. When these elements were later discovered, the agreement between the predicted properties and the actual properties was remarkable.



Mendeleev grouped the known elements into families, leaving gaps corresponding to elements that he thought should exist but which had not yet been discovered.

Nature of Science

The periodicity among the elements is not constant like days of the week. Is the periodic 'law' equal in status to other scientific laws?



Typische Elemente								
			K = 39	Rb = 85	Cs = 133	—	—
			Ca = 40	Sr = 87	Ba = 137	—	—
			—	?Yt = 88?	?Di = 138?	Er = 178?	—
			Ti = 48?	Zr = 90	Ce = 140?	?La = 180?	Th = 231
			V = 51	Nb = 94	—	Ta = 182	—
			Cr = 52	Mo = 96	—	W = 184	U = 240
			Mn = 55	—	—	—	—
			Fe = 56	Ru = 104	—	Os = 195?	—
			Co = 59	Rh = 104	—	Ir = 197	—
			Ni = 59	Pd = 106	—	Pt = 198?	—
H = 1	Li = 7	Na = 23	Cu = 63	Ag = 108	—	Au = 199?	—
	Be = 9,4	Mg = 24	Zn = 65	Cd = 112	—	Hg = 200	—
	B = 11	Al = 27,3	—	In = 113	—	Tl = 204	—
	C = 12	Si = 28	—	Sn = 118	—	Pb = 207	—
	N = 14	P = 31	As = 75	Sb = 122	—	Bi = 208	—
	O = 16	S = 32	Se = 78	Te = 125?	—	—	—
	F = 19	Cl = 35,5	Br = 80	J = 127	—	—	—

Mendeleev's periodic table of 1869. The noble gas elements had not been discovered. Reading from top to bottom and left to right, the first four gaps were waiting for scandium (1879), gallium (1875), germanium (1886) and technetium (1937). The later discovery of these elements, with properties that matched their periodicity, helped to confirm Mendeleev's ideas.

Mendeleev had no knowledge of the structure of the atom, which is discussed in Structure 1. With the benefit of hindsight, it is clear that the periodicity of the elements is a direct consequence of the periodicity of the electron configurations within the atom. The position of an element in the periodic table is based on the sublevel of the highest-energy electron in the ground-state atom.

Mendeleev is said to have made his discovery after a dream. When he awoke he set out his chart in virtually its final form. He enjoyed playing a form of patience (solitaire) and wrote the properties of each element on cards which he arranged into rows and columns.

Periods and groups

In the periodic table, the elements are placed in order of increasing atomic number (Z), the number of protons in the nucleus of its atoms. As there are no gaps in the sequence of atomic numbers, we can be confident that the search for new elements in nature is over.

The only way to extend the periodic table is by making elements artificially. In 2022, the International Union of Pure and Applied Chemistry (IUPAC) recognized 118 elements, but more may be discovered in the future.

The discovery of the elements was an international endeavour. This is illustrated by some of their names. Some derive from the place where they were found, some from the origins of their discoverers, and some from the geographical origins of the minerals from which they were first isolated. The periodic table hangs in chemistry classrooms and science laboratories throughout the world.

The columns of the table are called **groups** and the rows are called **periods**.

Challenge yourself

1. Four elements derive their name from a small town called Ytterby, just outside Stockholm, Sweden. Try to find their names.

Metals and non-metals

Metallic elements are found on the left-hand side of the table in the **s block**, in the central **d block**, and in the island of the **f block**. A small number of metals, such as aluminium and lead, are also found on the left of the **p block** (see Figure 1).

	s^1	s^2	d^1	d^2	d^3	d^5s^1	d^5	d^6	d^7	d^8	$d^{10}s^1$	d^{10}	p^1	p^2	p^3	p^4	p^5	p^6
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H hydrogen 1																	He helium 2
2	Li lithium 3	Be beryllium 4											B boron 5	C carbon 6	N nitrogen 7	O oxygen 8	F fluorine 9	Ne neon 10
3	Na sodium 11	Mg magnesium 12											Al aluminium 13	Si silicon 14	P phosphorus 15	S sulfur 16	Cl chlorine 17	Ar argon 18
4	K potassium 19	Ca calcium 20	Sc scandium 21	Ti titanium 22	V vanadium 23	Cr chromium 24	Mn manganese 25	Fe iron 26	Co cobalt 27	Ni nickel 28	Cu copper 29	Zn zinc 30	Ga gallium 31	Ge germanium 32	As arsenic 33	Se selenium 34	Br bromine 35	Kr krypton 36
5	Rb rubidium 37	Sr strontium 38	Y yttrium 39	Zr zirconium 40	Nb niobium 41	Mo molybdenum 42	Tc technetium 43	Ru ruthenium 44	Rh rhodium 45	Pd palladium 46	Ag silver 47	Cd 48	In indium 49	Sn tin 50	Sb antimony 51	Te tellurium 52	I iodine 53	Xe xenon 54
6	Cs caesium 55	Ba barium 56	57–71 see below	Hf hafnium 72	Ta tantalum 73	W tungsten 74	Re rhenium 75	Os osmium 76	Ir iridium 77	Pt platinum 78	Au gold 79	Hg mercury 80	Tl thallium 81	Pb lead 82	Bi bismuth 83	Po polonium 84	At astatine 85	Rn radon 86
7	Fr francium 87	Ra radium 88	89–103 see below	Rf rutherfordium 104	Db dubnium 105	Sg seaborgium 106	Bh bohrium 107	Hs hassium 108	Mt meitnerium 109	Ds darmstadtium 110	Rg roentgenium 111	Cp copernicium 112	Uut ununtrium 113	Fl flerovium 114	Uup Ununpentium 115	Lv Livermorium 116	Uus Ununseptium 117	Uuo Ununoctium 118

La lanthanum 57	Ce cerium 58	Pr praseodymium 59	Nd neodymium 60	Pm promethium 61	Sm samarium 62	Eu europium 63	Gd gadolinium 64	Tb terbium 65	Dy dysprosium 66	Ho holmium 67	Er erbium 68	Tm thulium 69	Yb ytterbium 70	Lu Lutetium 71
Ac actinium 89	Th thorium 90	Pa protactinium 91	U uranium 92	Np neptunium 93	Pu plutonium 94	Am americium 95	Cm curium 96	Bk berkellium 97	Cf californium 98	Es einsteinium 99	Fm fermium 100	Md mendelevium 101	No nobelium 102	Lr Lawrencium 103

S3.1 Figure 1 The periodic table. The colours show the blocks formed by the elements with their outer electrons in the same electron sublevel: s block (blue), d block (yellow), p block (red), f block (green).

Challenge yourself

2. State the electron configuration of europium.



A sample of europium (Eu), one of the lanthanides or rare earth elements. Europium is a hard silvery-white metal. Its compounds, such as its oxides, are used in fluorescent light bulbs and television screens.

The non-metals are found on the upper right-hand side of the p block.



Metals include, clockwise from left, copper, aluminium, zinc, iron and lead.

The element europium is used in the security marking of euro notes and other banknotes. When placed in ultraviolet (UV) radiation, europium compounds fluoresce, making the security markers visible.

SKILLS

Redesigning the periodic table. Full details of how to carry out this activity with a worksheet are available in the eBook.



Some non-metallic elements. Clockwise from top left, sulfur (S), bromine (Br), phosphorus (P), iodine (I) and carbon (C). Non-metals are generally poor conductors of both heat and electricity. Graphite, an allotrope of carbon, is unusual in that it is a non-metal that does conduct electricity.

The metalloid elements have the characteristics of both metals and non-metals. Their physical properties and appearance most resemble the metals, although chemically they have more in common with the non-metals. In the periodic table, the metalloid elements silicon, germanium, arsenic, antimony, tellurium and polonium form a diagonal staircase between the metals and non-metals.

Challenge yourself

3. How many elements in the periodic table are liquids and how many are gases?
4. Distinguish between the terms 'metalloid' and 'semiconductor'.



Silicon is a metalloid used in computers.

Nature of Science

'Theories' and 'laws' are terms that have a special meaning in science and it is important to distinguish these from their everyday use. Scientific laws are descriptive statements derived from observations of regular patterns of behaviour. They do not necessarily explain a phenomenon. Mendeleev's periodic law, for example, tells us that there is a pattern in the properties of the elements but it does not attempt to explain these patterns. This had to wait for the discovery of the electron by Thomson in 1897 and the work of Rutherford and Bohr at the beginning of the 20th century.

Exercise

Q1. What increases **in equal steps of one** from left to right in the periodic table for the elements sodium to argon?

A the relative atomic mass

B the number of occupied electron energy levels

C the number of neutrons in the most common isotope

D the number of electrons in the atom

Q2. Which of the following elements is a metalloid?

A calcium **B** manganese **C** germanium **D** carbon

Q3. Which of the following materials is the best conductor of electricity in the solid state?

A silicon **B** graphite **C** phosphorus **D** antimony

Q4. Use the IB periodic table to identify the position of the following elements.

	Element	Period	Group
(a)	helium		
(b)	chlorine		
(c)	barium		
(d)	francium		

Structure 3.1.2 – Periodicity and electron configuration

Structure 3.1.2 – The period number shows the outer energy level that is occupied by electrons. **Elements in a group have a common number of valence electrons.** Deduce the electron configuration of an atom up to Z = 36 from the element's position in the periodic table and vice versa.	
Groups are numbered from 1 to 18. The classifications 'alkali metals', 'halogens', 'transition elements' and 'noble gases' should be known.	Nature of Science, Structure 1.2 – How has the organization of elements in the periodic table facilitated the discovery of new elements?

The position of an element is related to the electron configuration of its atoms, as discussed in Structure 1.3. The groups are numbered from 1 to 18. Elements whose valence electrons occupy an s sublevel make up the s block, which includes the **alkali metals** in group 1. Elements with valence electrons in p orbitals make up the p block, which includes the **halogens** in group 17 and the **noble gases** in group 18. The d block and f block are similarly made up of elements with outer electrons in d and f orbitals.

HL The d block includes the **transition metals**. As explained later in this chapter, not all d block elements are transition metals.

The alkali metals are in group 1, the halogens are in group 17, the transition elements are in the d block and the noble gases are in group 18.

The period of an element gives the number of occupied energy levels. The element sodium, for example, is in period 3 because it has three occupied principal energy levels, and is in group 1 of the s block because there is one electron in the valence energy level [Ne] $3s^1$. Bromine is in period 4 and in group 17 of the p block because it has 7 electrons in the fourth principal energy level, and 17 more electrons than the previous noble gas, argon: [Ar] $4d^{10}5s^25p^5$.

The rows in the periodic table are called periods. The period number gives the number of occupied electron principal energy levels. The columns in the periodic table are called groups. The group number is related to the number of valence electrons in the outer energy level. Elements in a group have the same number of valence electrons.

How can the production of artificial elements give us more knowledge of the natural world?

TOK

Nature of Science, Structure 1.2 – How has the organization of elements in the periodic table facilitated the discovery of new elements?

Worked example

How many electrons are in the valence energy level of iodine?

Solution

Find the element in the periodic table. It is in period 5, so has the noble gas core of Kr, with electrons added to 5s, then 4d, and then 5p.

As it is in group 17 it has the configuration: [Kr] $5s^24d^{10}5p^5$ or [Kr] $4d^{10}5s^25p^5$ and so has seven electrons in its valence energy level.

Nature of Science

Oganesson (Og), element 118, is one of the most recently added elements to the periodic table. Whereas the discovery of the early elements involved the practical steps of extraction and isolation often performed by one individual, later elements are made by teams of scientists working together. New elements are as much invented as discovered, but their existence provides further knowledge about the natural world. Claims of a new element's existence have to be verified by the IUPAC in a process called peer review.

Exercise

Q5. Phosphorus is in period 3 and group 15 of the periodic table.

(a) Distinguish between the terms 'period' and 'group'.

(b) State the electron configuration of phosphorus and relate it to its position in the periodic table.

Q6. How many valence electrons are present in the atoms of the element with atomic number 51?

Q7. Which of the following properties is used to arrange the elements in the modern periodic table?

A relative atomic mass

B number of valence electrons

C atomic number

D effective nuclear charge

Q8. The only isotope of oganesson to be synthesized is $^{294}_{118}Og$ with a half-life of 700 μs. Which of the following statements is correct?

I. The nucleus of the atom has a relative charge of +118.

II. Og has the outer electron configuration $7p^6$.

III. Oganesson is a stable element.

A I and II only **B** I and III only

C II and III only **D** I, II and III

Q9. Mendeleev left a space in his table for the element now known as gallium. He was able to predict many properties for the then unknown element.

(a) The densities of some group 13 elements are shown in the table.

Atomic number	Element	Density / g cm^{-3}
5	boron	2.34
13	aluminium	2.70
31	gallium	
49	indium	7.30
81	thallium	11.85

Plot a graph of density against atomic number to predict the density of gallium.

Originally, when gallium was first discovered by the French chemist, Paul-Emile Lecoq, its density did not correspond to the value predicted by Mendeleev. Mendeleev suggested to Lecoq that he needed to prepare a purer sample. When this was done the density matched the value predicted.

Structure 3.1.3 – Periodicity in properties of elements

Structure 3.1.3 – Periodicity refers to trends in properties of elements across a period and down a group.

Explain the periodicity of atomic radius, ionic radius, ionization energy, electron affinity and electronegativity.

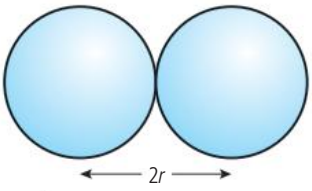
Properties

The periodicity of the elements is reflected in their properties. The atomic and ionic radii, electronegativity, ionization energy and electron affinity are of particular interest.

The concept of effective nuclear charge discussed in Structure 2.1 is helpful in explaining trends in both physical and chemical properties. The effective nuclear charge experienced by an atom's outer electrons increases across a period but remains approximately the same down a group.

The effective nuclear charge experienced by an atom's outer electrons increases across a period but remains approximately the same down a group.

Atomic radius increases down a group and decreases across a period



S3.1 Figure 2 The atomic radius *r* is measured as half the distance between neighbouring nuclei in a covalent bond.

The concept of atomic radius is not as straightforward as you may think. We see in Structure 1.3 that electrons occupy atomic orbitals, which give a probability description of the electrons' locations, but do not have sharp boundaries. The atomic radius *r* is measured as half the distance between neighbouring nuclei (Figure 2). For many purposes, however, it can be considered as the distance from the nucleus to the outermost electrons in the atom.

The data booklet shows that the (covalent) atomic radii increase down a group and decrease across a period. Consider, for example, the group 1 elements – as shown in the table below.

Element	Period	Electron configuration	No. of occupied principal energy levels	Atomic radius / 10^{-12} m
Li	2	$1s^2 2s^1$	2	130
Na	3	$1s^2 2s^2 2p^6 3s^1$	3	160
K	4	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	4	200
Rb	5	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^1$ = [Kr] $5s^1$	5	215
Cs	6	[Rn] $6s^1$*	6	238

*The condensed electron configuration is shown for Cs.

The atomic radii increase down a group, as the number of occupied electron levels (given by the period number) increases.

The trend across a period is illustrated by the period 3 elements, as shown below.

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Atomic radius / 10^{-12} m	160	140	124	114	109	104	100	101

All these elements have three occupied principal energy levels. The attraction between the nucleus and the outer electrons increases as the nuclear charge increases so there is a general decrease in atomic radius across the period.

The decrease in radius across a period is significant; a chlorine atom, for example, has a radius that is about 60% that of a sodium atom.

Ionic radius increases down a group and decreases across a period

The atomic and ionic radii of the period 3 elements are shown in the table below.

Element	Na	Mg	Al	Si	P	S	Cl
Atomic radius / 10^{-12} m	160	140	124	114	109	104	100
Ionic radius / 10^{-12} m	102 (Na^+)	72 (Mg^{2+})	54 (Al^{3+})	40 (Si^{4+}) 271 (Si^{4-})	38 (P^{5+}) 212 (P^{3-})	184 (S^{2-})	181 (Cl^-)

Five trends can be identified.

- Positive ions are smaller than their parent atoms. The formation of positive ions involves the loss of the outer energy level.
- Negative ions are larger than their parent atoms. The formation of negative ions involves the addition of electrons into the outer energy level. The increased electron repulsion between the electrons in the outer principal energy level causes the electrons to move further apart and so increases the radius of the outer energy level.
- The ionic radii decrease from groups 1 to 14 for the positive ions due to the increase in nuclear charge with atomic number across the period. The increased attraction between the nucleus and the electrons pulls the outer energy level closer to the nucleus.
- The ionic radii decrease from groups 14 to 17 for the negative ions due to the increase in nuclear charge across the period, as explained above. The positive ions are smaller than the negative ions, as the former have only two occupied electron principal energy levels and the latter have three. This explains the big difference between the ionic radii of the Si^{4+} and Si^{4-} ions and the discontinuity in the middle of the table.
- The ionic radii increase down a group as the number of electron energy levels increases.

Worked example

Describe and explain the trend in radii of the following atoms and ions:

O^{2-}, F^-, Ne, Na^+, and Mg^{2+}.

Solution

The ions and the Ne atom have 10 electrons and the electron configuration $1s^2 2s^2 2p^6$.

The nuclear charges increase with atomic number:

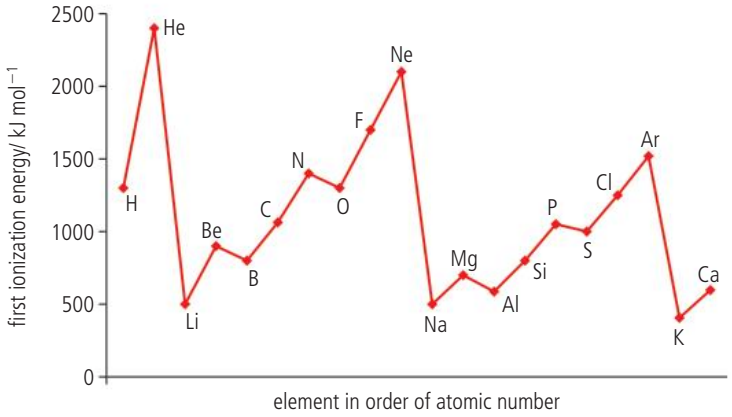
O: Z = +8 F: Z = +9 Ne: Z = +10 Na: Z = +11 Mg: Z = +12

The increase in nuclear charge results in increased attraction between the nucleus and the outer electrons. The ionic radii decrease as the atomic number increases.

Ionization energies decrease down a group and increase across a period

First ionization energies are a measure of the attraction between the nucleus and the outer electrons. They are defined in Structure 1.3, where they provide evidence for the electron configuration of the atoms of different elements (Figure 3).

The first ionization energy of an element is the energy required to remove one mole of electrons from one mole of gaseous atoms in their ground state.



S3.1 Figure 3 First ionization energies of the first 20 elements.

Two general trends can be identified from Figure 3:

- Ionization energies increase across a period. The increase in effective nuclear charge increases the attraction between the outer electrons and the nucleus and makes the electrons more difficult to remove.
- Ionization energies decrease down a group. The electron removed is from the energy level furthest from the nucleus. Although the nuclear charges increase, the effective nuclear charge is about the same, owing to shielding by the inner electrons, and so the increased distance between the electron and the nucleus reduces the attraction between them.

HL The small departures from these trends provide evidence for the division of energy levels into sublevels, as is discussed in Structure 1.3. Discontinuities in the trend of increasing first ionization energy across a period are discussed further on page 320.

The trend in ionization energy is the reverse of the trend in atomic radii. Both trends are an indication of the attraction between the nucleus and the outer electrons.

Electron affinity decreases down a group and increases across a period

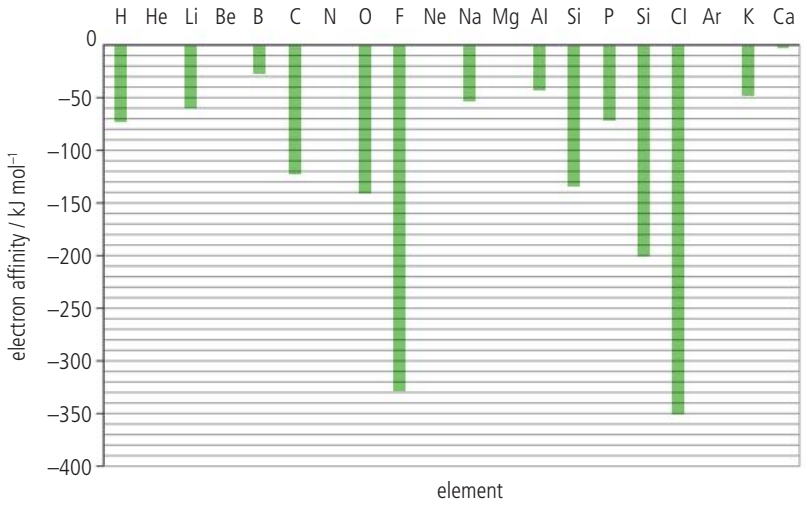
The first **electron affinity** of an element ($\Delta H^{\ominus}_{ea}$) is the energy change that occurs when one mole of electrons is added to one mole of gaseous atoms to form one mole of gaseous ions:

$$X(g) + e^- \rightarrow X^-(g)$$

As the added electron is attracted to the positively charged nucleus, the process generally gives out energy and is exothermic.

Values are tabulated in the data booklet. The noble gases do not generally form negatively charged ions so electron affinity values are not available for these elements.

The electron affinities of the first 18 elements are shown on the following page.



The electron affinities of the first 18 elements. Note there are no values assigned to the noble gases, or to Be, N and Mg.

The group 17 elements have incomplete outer energy levels and a high effective nuclear charge of approximately +7 and so attract electrons the most.

The electron affinities for some group 2 and group 5 elements are not included in the graph. Group 2 elements have an electron configuration ns^2, so the added electron must be placed into a 2p orbital which is further from the nucleus and so experiences reduced electrostatic attraction due to shielding from electrons in the *n*s orbital.

The value of the electron affinity for beryllium in some sources is positive as there is electrostatic repulsion between the electrons of the Be atom and the added electron. The electrons in the 1s and 2s orbitals of Be shield the added electron from the positively charged nucleus.

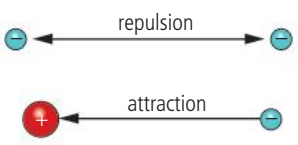
A similar effect occurs with nitrogen with the configuration $2s^2\mathbf{2}p_x^1 2p_y^1 2p_z^1$ as the added electron must occupy a p orbital already occupied by a single electron: the attraction between the electron and atom is less than expected as there is increased inter-electron repulsion. Some sources give the electron affinity of nitrogen as zero but there is some uncertainty about its precise value.

The electron affinity of an atom is the energy change that occurs when one mole of electrons is added to one mole of gaseous atoms.

The second and third electron affinities are defined similarly. The second electron affinity for oxygen, for example, corresponds to the change:

$$O^-(g) + e^- \rightarrow O^{2-}(g)$$

This process is endothermic as the added electron is repelled by the negatively charged oxide (O^-) ion, and energy needs to be available for the electron to be added to the negatively charged ion.



Energy is needed to bring two particles of the same charge closer together because they repel each other. This is an endothermic process. Particles of the opposite charge attract each other. They will spontaneously move closer together. It is an exothermic process.

Electronegativity decreases down a group and increases across a period

The **electronegativity** of an element is a measure of the ability of its atoms to attract electrons in a covalent bond (see Structure 2.2). It is related to ionization energy as it is also a measure of the attraction between the nucleus and its outer electrons – in this case *bonding electrons*. The concept does not apply to the group 18 elements, as they do not generally form covalent bonds.

An element with a high electronegativity has strong electron pulling power and an element with a low electronegativity has weak pulling power. The concept was originally devised by the American chemist Linus Pauling and his values are given in the data booklet. Pauling proposed an electronegativity scale in 1932, which depends on bond energies. The general trends are the same as those for ionization energy.

- Electronegativity increases from left to right across a period owing to the increase in nuclear charge, resulting in an increased attraction between the nucleus and the bond electrons.
- Electronegativity decreases down a group. The bonding electrons are furthest from the nucleus and so there is reduced attraction.

Electronegativity is the ability of an atom to attract electrons in a covalent bond.

The most electronegative element, fluorine, on the top right of the periodic table, has an electronegativity of 4 and francium on the bottom left has an electronegativity of 0.6.

Although the general trends in ionization energy and electronegativity are the same, they are distinct properties. Ionization energies can be measured directly and are a property of gaseous atoms. Electronegativities are a measure of the atoms' attraction for electrons in a covalent bond.

Linus Pauling has the unique distinction of winning two *unshared* Nobel Prizes – one for Chemistry in 1954 and one for Peace in 1962. His Chemistry Prize was for improving our understanding of the chemical bond and his Peace Prize was for his campaign against nuclear weapons testing.

TOK

The structure of the periodic table was first discovered by observing patterns in the chemical and physical properties of the elements. We now realize that it is determined by the electron configuration of the elements. What roles did inductive and deductive reasoning play in the development of the periodic table? What role does inductive and deductive reasoning have in science in general?

Exercise

Q10. Which properties of the period 3 elements increase from sodium to argon?

A nuclear charge and atomic radius

B atomic radius and electronegativity

C nuclear charge and electronegativity

D nuclear charge, atomic radius, and electronegativity

Q11. Which of the following are properties of gaseous atoms?

I. ionization energy
II. electron affinity
III. electronegativity

A I and II **B** I and III **C** II and III **D** I, II and III

Q12. Which of the following changes are endothermic?

I. $Ca(g) \rightarrow Ca^{+}(g) + e^{-}$
II. $I(g) + e^{-} \rightarrow I^{-}(g)$
III. $O^{-} + e^{-} \rightarrow O^{2-}(g)$

A I and II **B** I and III **C** II and III **D** I, II and III

Q13. Identify the element which is likely to have an electronegativity value most similar to that of sodium.

A beryllium **B** calcium **C** magnesium **D** hydrogen

Q14. The graph represents the variation of a property of the group 2 elements.



Identify the property.

A ionic radius

B atomic radius

C neutron/proton ratio

D first ionization energy

Q15. Which physical property generally increases down a group but decreases from left to right across a period?

A electron affinity

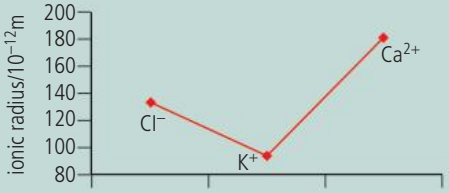
B electronegativity

C ionization energy

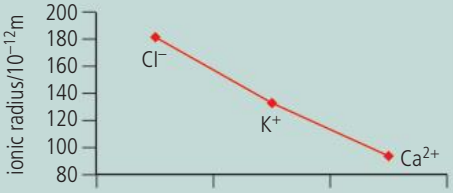
D atomic radius

Q16 Identify the graph which shows the correct ionic radii for the isoelectronic ions Cl^-, K^+, and Ca^{2+}.

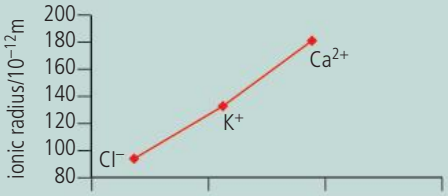
A



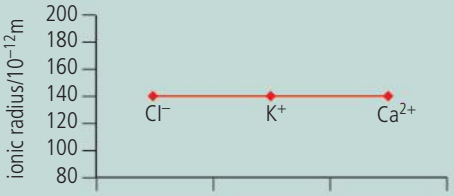
B



C



D



Q17. **(a)** Explain what is meant by the atomic radius of an element.

(b) The atomic radii of the elements are given in Section 10 of the data booklet.

(i) Explain why no values for atomic radii are given for the noble gases.

(ii) Describe and explain the trend in atomic radii across the period 3 elements.

Q18. Si^{4+} has an ionic radius of 4.2×10^{-11} m and Si^{4-} has an ionic radius of 2.71×10^{-10} m.

Explain the large difference in size between the Si^{4+} and Si^{4-} ions.

Q19. Atomic radii and ionic radii are given in the data booklet.

Explain why:

(a) the potassium ion is much smaller than the potassium atom.

(b) there is a large increase in ionic radius from silicon (Si^{4+}) to phosphorus (P^{3-}).

(c) the ionic radius of Na^+ is less than that of F^-.

Q20. What is the order of decreasing radii for the species Cl, Cl^+, and Cl^-?

Structure 3.1.4 – Periodicity in reactivity

Structure 3.1.4 – Trends in properties of elements down a group include the increasing metallic character of group 1 elements and the decreasing non-metallic character of group 17 elements. Describe and explain the reactions of group 1 metals with water, and of group 17 elements with halide ions.	
	Inquiry 2, Tool 2 – Why are simulations and online reactions often used in exploring the trends in chemical reactivity of group 1 and group 17 elements?

Trends in chemical properties

Chemical properties of an element are largely determined by the number of valence electrons in their outer energy level.

The chemical properties of an element are determined by the electron configuration of its atoms. Elements of the same group have similar chemical properties as they have the same number of valence electrons in their outer energy level. The alkali metals in group 1, for example, all have one electron in their outer energy level and the halogens in group 17 all have seven outer electrons.

Group 18: The noble gases

To understand the reactivity of the elements, it is instructive to consider group 18, which contains the least reactive elements – the noble gases.

The reactivity of elements in other groups can be explained by their unstable incomplete electron energy levels. They lose or gain electrons to achieve the electron configuration of their nearest noble gas.

Group 18 used to be called the 'inert gases' as it was thought that they were completely unreactive. Xenon, which has the lowest ionization energy, is the most reactive element in the group as reactions involve the withdrawal of electrons from the parent atom. The first compound of xenon was made in 1962.

Group 1: The alkali metals

All the group 1 elements are silvery metals and are too reactive to be found in nature. They are usually stored in oil to prevent contact with air and water. The properties of the first three elements are summarized in the table below.

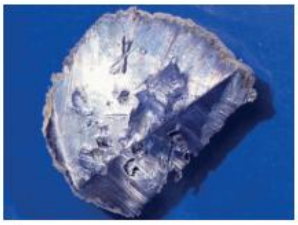
Physical properties	Chemical properties
• They are good conductors of electricity and heat. • They have low densities. • They have shiny grey surfaces when freshly cut with a knife.	• They are very reactive metals. • They form ionic compounds with non-metals.



Lithium is a soft reactive metal. When freshly cut, it has a metallic lustre. However, it rapidly reacts with oxygen in the air, giving it a dark oxide coat.



A piece of sodium. The shiny surface has been exposed by a knife cutting the soft metal. Sodium is softer and more reactive than lithium.



Freshly cut shiny surface of potassium metal. Potassium is softer and more reactive than sodium.

As discussed in Structure 2.1, group 1 metals form single charged ions, M^+, with the stable octet of the noble gases when they react. Their low ionization energies give an indication of the ease with which the outer electron is lost. Reactivity increases down the group as the elements with higher atomic numbers have the lowest ionization energies. Their ability to conduct electricity and heat is also due to the mobility of their outer electron.

Reaction with water

The alkali metals react with water to produce hydrogen and the metal hydroxide. When you drop a piece of one of the first three group 1 elements into a small beaker containing distilled water, the following happens.

- Lithium floats and reacts slowly. It releases hydrogen but keeps its shape.
- Sodium reacts with a vigorous release of hydrogen. The heat produced is sufficient to melt the unreacted metal, which forms a small ball that moves around on the water surface.
- Potassium reacts even more vigorously to produce sufficient heat to ignite the hydrogen produced. It produces a lilac flame and moves excitedly on the water surface.

SKILLS

Simulations and online reactions are available to explore the trends in the dangerously reactive group 1 elements.

They are called alkali metals because the resulting solution is alkaline owing to the presence of the hydroxide ion formed. For example, for potassium:

$$2K(s) + 2H_2O(l) \rightarrow 2KOH(aq) + H_2(g)$$

As KOH is an ionic compound (Structure 2.1) which dissociates in water (see chapter opener image), it is more appropriate to write the equation as:

$$2K(s) + 2H_2O(l) \rightarrow 2K^+(aq) + 2OH^-(aq) + H_2(g)$$

Note that the metal hydroxide is produced when group 1 elements are added to water. A common mistake is to give the oxide as the product. Observations must be something that can be observed. You cannot usually identify chemicals by simple observations. If you are asked to describe what you would *see*, saying 'a gas was produced' would gain more marks than 'hydrogen was produced'.

The reaction becomes more vigorous as you go down the group. The most reactive element, caesium, has the lowest ionization energy and so forms positive ions most readily.

Group 17: The halogens

The group 17 elements exist as diatomic molecules, X_2. Their physical and chemical properties are summarized in the table below.

Physical properties	Chemical properties
• They are coloured. • They show a gradual change from gases (F_2 and Cl_2), to liquid (Br_2), and solids (I_2 and At_2).	• They are very reactive non-metals. • Reactivity decreases down the group. • They form ionic compounds with metals and covalent compounds with other non-metals.

The names of diatomic elements all end in *-ine* or *-gen*.



From left to right: chlorine (Cl_2), bromine (Br_2), and iodine (I_2). These are toxic and reactive non-metals. Chlorine is a green gas at room temperature. Bromine is a dark liquid, although it readily produces a brown vapour. Iodine is a crystalline solid.

Two halogens are named by their colours: *chloros* means 'yellowish green' and *ioeides* is 'violet' in Greek. One is named by its smell: '*bromos*' is the Greek word for 'stench'.

The word halogen means salt maker.

Simulations and online reactions are available to explore the reactivity of the group 17 elements.

The group 17 trend in reactivity can be explained by their readiness to accept electrons, as illustrated by their very exothermic electron affinities discussed earlier. The nuclei have a high effective charge, of approximately +7, and so exert a strong pull on any electron from other atoms. This electron can then occupy the outer energy level of the halogen atom and complete a stable octet. The attraction is greatest for the smallest atom fluorine, which is the most reactive non-metal in the periodic table. Non-metal reactivity decreases down the group as the atomic radius increases and the attraction for outer electrons decreases.

Inquiry 2, Tool 2 – Why are simulations and online reactions often used in exploring the trends in chemical reactivity of group 1 and group 17 elements?

TOK Chlorine was used as a chemical weapon during the First World War. Should scientists be held morally responsible for the applications of their discoveries? Should scientific research be subject to ethical constraints or is the pursuit of all scientific knowledge intrinsically worthwhile?

Displacement reactions

The *relative* reactivity of the group 17 elements can be seen by placing them in direct competition for an extra electron. When chlorine is bubbled through a solution of potassium bromide, the solution changes from colourless to orange owing to the production of bromine:

$$2KBr(aq) + Cl_2(aq) \rightarrow 2KCl(aq) + Br_2(aq)$$

$$2Br^-(aq) + Cl_2(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$$

A chlorine nucleus has a stronger attraction for an electron than a bromine nucleus does because of its smaller atomic radius and so it takes the electron from the bromide ion. The chlorine has gained an electron and so forms the chloride ion, Cl^-. The bromide ion loses an electron to form bromine.

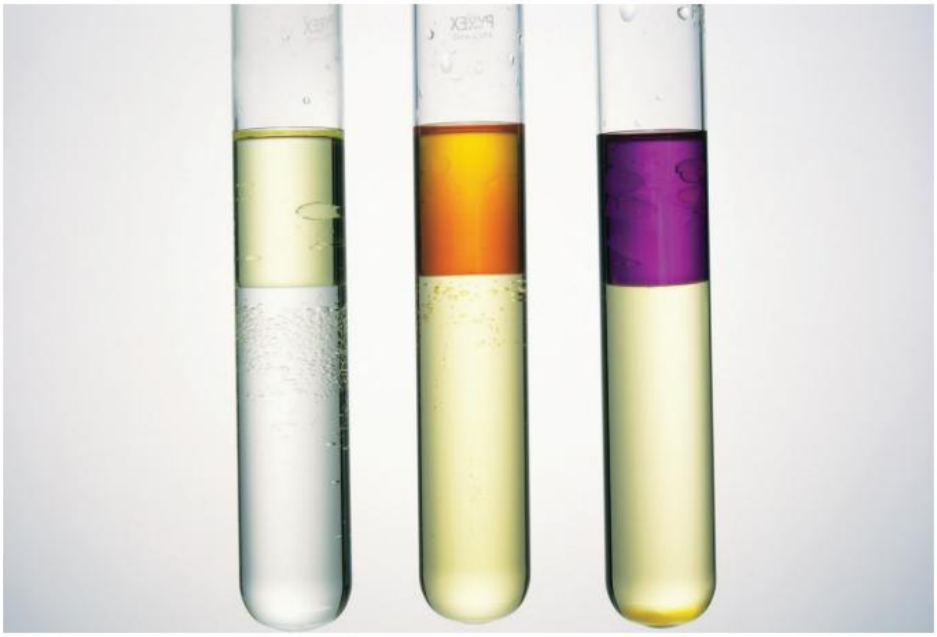
Other reactions are:

$$2I^-(aq) + Cl_2(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$$

The colour changes from colourless to dark orange/brown owing to the formation of iodine.

$$2I^-(aq) + Br_2(aq) \rightarrow 2Br^-(aq) + I_2(aq)$$

To distinguish between bromine and iodine more effectively, the final solution can be shaken with a hydrocarbon solvent. Iodine forms a violet solution and bromine forms a dark orange solution as shown in the photo below.



Solutions of chlorine (left), bromine (middle), and iodine (right) in water (lower part) and cyclohexane (upper part). Chlorine dissolves in water, but the halogens are generally more soluble in non-polar solvents such as cyclohexane.

The halides

The halogens form insoluble salts with silver. Adding a solution containing the halide to a solution containing silver ions produces a **precipitate** that is useful in identifying the halide ion.

$$Ag^+(aq) + X^-(aq) \rightarrow AgX(s)$$



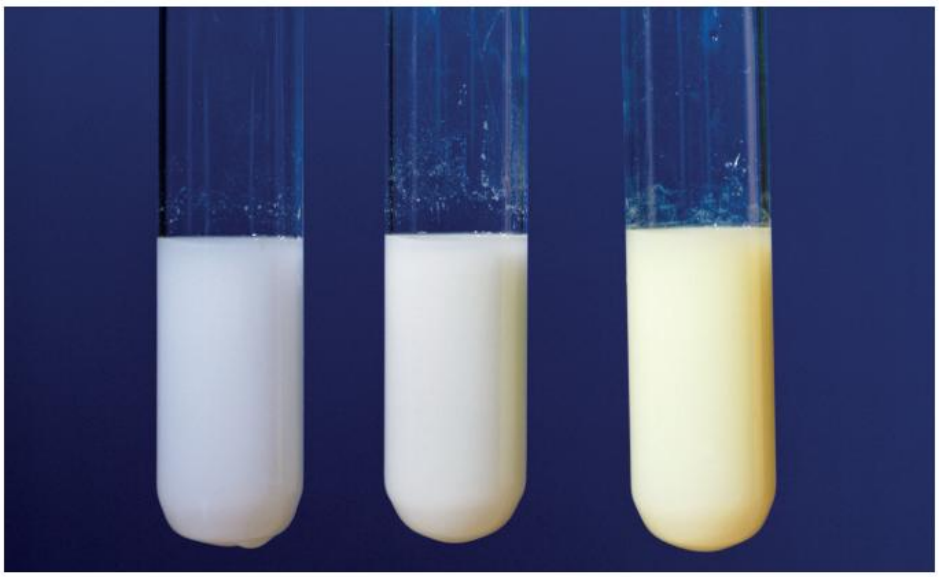
When chlorine water is added to the colourless potassium bromide solution, bromine (yellow/orange) is formed. Bromine is displaced from solution by the more reactive chlorine.

The more reactive halogen displaces the ions of the less reactive halogen from its compounds.

SKILLS

Determining the properties of the halogens. Full details of how to carry out this experiment with a worksheet are available in the eBook.

This is shown in the photo below.



Silver halide precipitates formed by reacting silver nitrate ($AgNO_3$) with solutions of the halides. From left to right, these are silver chloride (AgCl), silver bromide (AgBr), and silver iodide (AgI).

SKILLS

The reaction between silver nitrate solution and the different halide solutions can be investigated in the lab.

Exercise

Q21. Which pair of elements reacts most readily?

A $Li + Br_2$ **B** $Li + Cl_2$ **C** $K + Br_2$ **D** $K + Cl_2$

Q22. Chlorine is a greenish-yellow gas, bromine is a dark red liquid, and iodine is a dark grey solid. Identify the property which most directly causes these differences in volatility.

A the halogen–halogen bond energy

B the number of neutrons in the nucleus of the halogen atom

C the number of outer electrons in the halogen atom

D the number of electrons in the halogen molecule

Q23. Caesium is an element in group 1 of the periodic table. Which is the best description of its melting point and reactivity with water?

A low melting point and reacts slowly with water

B low melting point and reacts vigorously with water

C high melting point and reacts slowly with water

D high melting point and reacts vigorously with water

Q24. State two observations you could make during the reaction between sodium and water. Give an equation for the reaction.

Q25. How do the reactivities of the alkali metals and the halogens vary down the group?

Q26. Explain the trend in reactivity of the alkali metals in terms of their valence electron configuration.

Q27. Explain the trend in reactivity of the halogens in terms of their valence electron configuration.

Structure 3.1.5 – Metal and non-metal oxides

Structure 3.1.5 – Metallic and non-metallic properties show a continuum. This includes the trend from basic metal oxides through amphoteric to acidic non-metal oxides.

Deduce equations for the reactions with water of the oxides of group 1 and group 2 metals, carbon and sulfur.

Include acid rain caused by gaseous non-metal oxides, and ocean acidification caused by increasing CO_2 levels.	Structure 2.1, 2.2 – How do differences in bonding explain the differences in the properties of metal and non-metal oxides?

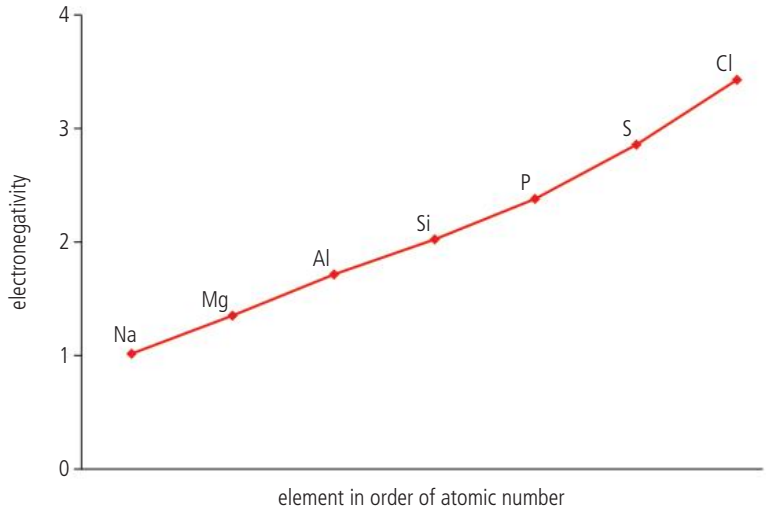
Bonding of period 3 oxides

SKILLS

Oxides of period 3. Full details of how to carry out this experiment with a worksheet are available in the eBook.

The transition from metallic to non-metallic character is illustrated by the bonding of the period 3 oxides. Ionic compounds are generally formed between metal and non-metal elements and so the oxides of elements Na to Al have **giant ionic** structures. Covalent compounds are formed between non-metals, so the oxides of phosphorus, sulfur, and chlorine are **molecular covalent**. The oxide of silicon, which is a metalloid, has a **giant covalent** structure. The different types are explored more fully in Structure 2.

The ionic character of a compound depends on the *difference* in electronegativity between its elements. Oxygen has an electronegativity of 3.4, so the ionic character of the period 3 oxides decreases from left to right, as the electronegativity values of the elements approach this value (Figure 4).



S3.1 Figure 4 Electronegativities increase across the period and approach 3.4, the value for oxygen.

The oxides become more ionic down a group as the electronegativity decreases. The conductivity of the molten oxides gives an experimental measure of their ionic character, as is shown in the table on the next page. Oxides only conduct electricity in the liquid or aqueous state when the ions are free to move.

Note that the maximum oxidation state of a period 3 element is related to the group number. It is +1 for elements in group 1, +2 for elements in group +2, +3 for elements in group 13, +4 for elements in group 14, and so on. Oxidation states are discussed further on page 315.

Formula of oxide	$Na_2O(s)$	$MgO(s)$	$Al_2O_3(s)$	$SiO_2(s)$	$P_4O_{10}(s)$ / $P_4O_6(s)$	$SO_3(l)$ / $SO_2(g)$	$Cl_2O_7(l)$ / $Cl_2O(g)$
Oxidation number	+1	+2	+3	+4	+5 / +3	+6 / +4	+7 / +1
Electrical conductivity in molten state	high	high	high	very low	none	none	none
Structure	giant ionic			giant covalent	molecular covalent		

High melting points are associated with ionic or covalent giant structures, and low melting points with molecular covalent structures.

Acid–base character of the period 3 oxides

Oxides of metals are ionic and basic. Oxides of the non-metals are covalent and acidic. Amphoteric oxides show both acidic and basic properties. Aluminium oxide is amphoteric.

The acid–base properties of the oxides are closely linked to their bonding and structure. Metallic elements, which form ionic oxides, are basic; non-metal oxides, which are covalent, are acidic. Aluminium oxide, which can be considered as an ionic oxide with some covalent character, shows amphoteric properties – reacting with both acids and bases. The acid–base properties of period 3 oxides are shown in the table below.

Formula of oxide	$Na_2O(s)$	$MgO(s)$	$Al_2O_3(s)$	$SiO_2(s)$	$P_4O_{10}(s)$ / $P_4O_6(s)$	$SO_3(l)$ / $SO_2(g)$	$Cl_2O_7(l)$ / $Cl_2O(g)$
Acid–base character	basic		amphoteric	acidic			

SKILLS

The pH of aqueous solutions of metal and non-metal oxides can be investigated in the lab.



Aqueous solutions of the oxides of some elements with universal indicator. Sulfur trioxide forms sulfuric acid in water, which is highly acidic. Sodium oxide forms sodium hydroxide, which is a strong alkali. Non-metal oxides have pHs below 7 and are acidic. Metal oxides have high pHs above 7 and are basic.

Basic oxides

Sodium oxide and magnesium oxide dissolve in water to form alkaline solutions owing to the presence of hydroxide ions:

$$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$$

$$MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(aq)$$

A basic oxide reacts with an acid to form a salt and water. The oxide ion combines with two H^+ ions to form water:

$$O^{2-}(s) + 2H^+(aq) \rightarrow H_2O(l)$$

$$Li_2O(s) + 2HCl(aq) \rightarrow 2LiCl(aq) + H_2O(l)$$

$$MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l)$$

Non-metallic oxides are acidic

The non-metallic oxides react readily with water to produce acidic solutions.

Carbon dioxide dissolves in water to form the weak acid, carbonic acid, H_2CO_3.

$$H_2O(l) + CO_2(g) \rightleftharpoons H_2CO_3(aq)$$

Sulfur trioxide reacts with water to produce sulfuric(VI) acid:

$$SO_3(l) + H_2O(l) \rightarrow H_2SO_4(aq)$$

Sulfur dioxide reacts with water to produce sulfuric(IV) acid:

$$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$$

Amphoteric oxides

Aluminium oxide does not affect the pH when it is added to water as it is essentially insoluble. It has amphoteric properties, however, as it shows both acid and base behaviour. For example, it behaves as a base when it reacts with sulfuric acid:

$$Al_2O_3(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2O(l)$$

$$Al_2O_3(s) + 3H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 3H_2O(l)$$

and behaves as an acid when it reacts with alkalis such as sodium hydroxide:

$$Al_2O_3(s) + 3H_2O(l) + 2OH^-(aq) \rightarrow 2Al(OH)_4^-(aq)$$

Acid rain and acid deposition are produced by non-metal oxides

All rainwater is naturally acidic due to the presence of dissolved carbon dioxide. The minimum pH of carbonic acid solutions is 5.6. Acid rain refers to solutions with a lower pH owing to the presence of sulfur and nitrogen oxides.

Acid deposition is a broader term than acid rain and includes all processes by which acidic components as precipitates or gases leave the atmosphere. There are two main types of acid deposition:

- wet acid deposition: rain, snow, sleet, hail, fog, mist and dew fall to the ground as aqueous precipitates;
- dry acid deposition: acidifying particles and gases fall to the ground as dust and smoke, and later dissolve in water to form acids.

Alkalis are bases that are soluble in water. They form hydroxide ions in aqueous solution.

Structure 2.1, 2.2 – How do differences in bonding explain the differences in the properties of metal and non-metal oxides?

TOK Although all rainwater is acidic, the term 'acid rain' only applies to some rainwater. How does language as a way of knowing influence communication in science?

Rainwater is naturally acidic due to dissolved CO_2. Acid rain has a pH < 5.6.

Sulfur oxides produce acid rain

Sulfur dioxide, SO_2, is produced from the burning of fossil fuels, particularly coal and heavy oil in power plants used to generate electricity. It is also released in industrial processes of smelting where metals are extracted from their ores. It is estimated that about 50% of annual global emissions of sulfur dioxide come from coal.

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

Challenge yourself

5. What is the source of sulfur in fossil fuels? Consider why some fuels such as coal contain higher amounts of sulfur.

Sulfur dioxide dissolves in rainwater to form sulfuric(IV) or sulfurous acid, $H_2SO_3(aq)$.

$$H_2O(l) + SO_2(g) \rightarrow H_2SO_3(aq)$$

Sulfur dioxide can be oxidized to sulfur trioxide, SO_3, in the atmosphere, which then dissolves in rainwater to form sulfuric (VI) acid, H_2SO_4.

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

$$H_2O(l) + SO_3(g) \rightarrow H_2SO_4(aq)$$

Nitrogen oxides produce acid rain

Several other oxides of nitrogen exist, and the term NOx is used somewhat variably. But in atmospheric chemistry it refers specifically to the total of the two oxides of nitrogen, NO and NO_2, present.

Nitrogen monoxide, NO, is produced mainly from internal combustion engines, where the burning of the fuel releases heat energy that causes nitrogen and oxygen from the air to combine.

$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$

A similar reaction gives rise directly to the brown gas, nitrogen dioxide, NO_2.

$$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$$

Nitrogen dioxide also forms from the oxidation of nitrogen monoxide.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

One of the most controversial aspects of acid deposition is that its effects often occur far from the source of the pollutants, due to atmospheric weather patterns. In many cases, this means countries are suffering the impact of other countries' industrial processes. Legislation to reduce the impact of acid deposition has therefore been the subject of intense political debate, and several international protocols have developed.

Nitrogen dioxide dissolves in rainwater to form a mixture of nitric(III) or nitrous acid (HNO_2) and nitric (V) acid (HNO_3).

$$H_2O(l) + 2NO_2(g) \rightarrow HNO_2(aq) + HNO_3(aq)$$

Alternatively, nitrogen dioxide can be oxidized to form nitric(V) acid.

$$2H_2O(l) + 4NO_2(g) + O_2(g) \rightarrow 4HNO_3(aq)$$

Nature of Science

Intense scientific research into the formation and impacts of acidic rainfall has led to policy responses at the national and local level. The implications of science within environmental, political, and economic domains can be profound and illustrate the importance of local, national and international scientific bodies that engage with the public understanding of science.

Challenge yourself

6. Acid rain damages building materials.



The effects of acid rain on a limestone lion outside Leeds Town Hall, England.

Limestone is a form of calcium carbonate. Deduce an equation for the reaction that accounts for the damage to the stone lion.

Ocean acidification occurs as carbon dioxide dissolves in the oceans

About 50% of the carbon dioxide produced by the combustion of fossil fuels is dissolved by the oceans. The carbon dioxide reacts with the water to form carbonic acid.

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

The carbonic acid then reacts to form hydrogencarbonates or carbonates.

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$$

This leads to higher ocean acidity, mainly near the surface, where the carbon dioxide is absorbed. This higher acidity inhibits shell growth in marine animals and is suspected to be a cause of reproductive disorders in some fish.



Ocean acidity dissolving sea snail shell. The shell is being dissolved by increasing ocean acidity due to carbon dioxide released into the atmosphere from human sources. Ocean acidification is predicted to have a disastrous effect on marine ecosystems.

Exercise

Q28. An oxide of a period 3 element is a solid at room temperature and forms a basic solution. Identify the element.

A Mg **B** Al **C** P **D** S

Q29. Identify the oxide which forms an acidic solution when added to water.

A $Na_2O(s)$ **B** $MgO(s)$ **C** $SiO_2(s)$ **D** $SO_3(g)$

Q30. Identify the oxides that produce an acidic solution when added to water.

I. SiO_2 II. N_2O_5 III. SO_2

A I and II only **B** I and III only **C** II and III only **D** I, II and III

Q31. The melting and boiling points of four oxides are shown.

Oxides	Melting point / K	Boiling point / K
MgO	3125	3873
SiO_2 (quartz)	1883	2503
P_4O_{10}	297	448
SO_2	200	263

(a) Identify the state of the four oxides listed under standard conditions.

(b) Explain the difference in melting points by referring to the bonding and structure in each case.

(c) The oxides are added to separate samples of pure water. State whether each resulting liquid is acidic, neutral, or alkaline. Describe all chemical reactions by giving chemical equations.

(d) Use chemical equations to describe the reactions of aluminium oxide with:

(i) hydrochloric acid

(ii) sodium hydroxide.

Q32. Describe the acid–base character of the oxides of the period 3 elements, Na to Ar. For sodium oxide and sulfur trioxide, write balanced equations to illustrate their acid–base character.

Q33. Acid rain has a pH of less than 5.6.

(a) Explain why natural rain has a pH of around 5.6. Give a chemical equation to support your answer.

(b) Acid rain may be 50 times more acidic than natural rain. One of the major acids present in acid rain originates mainly from burning coal. State the name of the acid and give equations to show how it is formed.

(c) The second major acid responsible for acid rain originates mainly from internal combustion engines. State the name of this acid and state two different ways in which its production can be reduced.

Structure 3.1.6 – Oxidation states

Structure 3.1.6 – The oxidation state is a number assigned to an atom to show the number of electrons transferred in forming a bond. It is the charge that the atom would have if the compound were composed of ions. Deduce the oxidation states of an atom in an ion or a compound. Explain why the oxidation state of an element is zero.

Oxidation states are shown with a + or – sign followed by the Arabic symbol for the number, e.g. +2, –1. Examples should include hydrogen in metal hydrides (–1) and oxygen in peroxides (–1). The terms 'oxidation number' and 'oxidation state' are often used interchangeably, and either term is acceptable in assessment. Naming conventions for oxyanions use oxidation numbers shown with Roman numerals, but generic names persist and are acceptable. Examples include NO_3^- nitrate, NO_2^- nitrite, SO_4^{2-} sulfate and SO_3^{2-} sulfite.	Reactivity 3.2 – How can oxidation states be used to analyse redox reactions?

The oxidation state is the charge the atom would have if the compound were composed of ions

Oxidation can involve elements other than oxygen

When magnesium reacts with oxygen it is oxidized and forms the ionic compound magnesium oxide.

$$Mg(s) + \tfrac{1}{2}O_2(g) \rightarrow MgO\ (s)$$

If this reaction is considered from the perspective of magnesium, we see that a magnesium atom has been converted into an ion and lost two electrons:

$$\underset{\text{atom}}{Mg} \rightarrow \underset{\text{ion}}{Mg^{2+}} + 2e^-$$

As magnesium loses electrons when it reacts with other non-metals such as chlorine, it makes sense to extend the term oxidation to other reactions which do not necessarily involve oxygen:

$$Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$$

As discussed in detail in Reactivity 3.2, the term 'oxidation' is applied to any electron transfer reaction. Magnesium has changed from a neutral atom to an ion with a charge of 2+. We say its oxidation state has increased from 0 to +2. Oxidation has led to an increase in oxidation state.

These points can be summarized as follows.

Oxidation is:

- the addition of oxygen
- the removal of hydrogen
- electron loss
- an increase in oxidation state.

Oxidation states are a measure of how electrons are distributed

An increase in oxidation state means the atom has lost electron control and is oxidized. A decrease in oxidation states means that an atom has gained electron control and is reduced.

The oxidation state of an element is zero as the atoms have no charge and the electrons are distributed equally between the atoms. In binary ionic compounds such as magnesium oxide, the oxidation states are the same as the ionic charges. The oxidation state of sodium in sodium chloride is +1 as it has lost one electron, and that of chlorine is –1 as it has gained an electron.

In covalent substances, the electron distribution depends on the polarity of the bond and the relative electronegativities of the bonding atoms. If an atom is bonded to a more electronegative atom, it loses some control over its electrons and has a positive oxidation state. When bonded to a less electronegative atom, it gains control over more electrons and has a negative oxidation state.

Reactivity 3.2 – How can oxidation states be used to analyse redox reactions?

Rules to assign oxidation states

Here are some rules to follow when assigning the oxidation state of an atom in any species.

	Rule	Example
1.	Atoms in the free (uncombined) element have an oxidation state of zero.	The oxidation states of Mg, O_2, N_2, and Ar are all 0.
2.	In simple ions, the oxidation state is the same as the charge on the ion.	The oxidation state of Mg in Mg^{2+} is +2, oxygen in O^{2-} is –2, and nitrogen in N^{3-} is –3.
3.	The oxidation states of all the atoms in a neutral (uncharged) compound must add up to zero.	The sum of oxidation states in H_2SO_4 = 0.
4.	The oxidation states of all the atoms in a polyatomic ion must add up to the charge on the ion.	In SO_4^{2-} the sum of oxidation states = –2.
5.	The usual oxidation state for an element in a compound is the same as the charge on its most common ion.	In compounds: group 1 metals are +1; group 2 metals are +2.
6.	F has the oxidation state of –1 in all its compounds as it is the most electronegative element.	
7.	O has the oxidation state of –2 except when in peroxides such as H_2O_2, where it is –1; when bonded to fluorine it is positive as it is less electronegative than fluorine.	Oxidation number of O is: –1 in H_2O_2 +2 in OF_2
8.	Cl has the oxidation state of –1 except when bonded to the more electronegative F and O.	Oxidation number of Cl is: +1 in ClF +1 in OCl_2 +7 in ClO_4^-
9.	H has the oxidation state of +1 except when bonded to the group 1 and 2 metals when it forms ionic hydrides.	Oxidation number of H is –1 in NaH and in MgH_2.
10.	HL The oxidation state of a transition metal in a complex ion can be worked out from the charge on the ligands.	HL Common ligands include: H_2O, NH_3, Cl^-, CN^-, OH^-

Worked example

Assign oxidation states to all the elements in **(a)** H_2SO_4 and **(b)** SO_3^{2-}.

Solution

(a) H_2SO_4:

The H atoms can be given a value of +1 and the O atoms a value of –2.

As H_2SO_4 is electrically neutral, the sum of all oxidation states = 0.

$$H_2SO_4 \rightarrow 2 \times (+1) + S + 4 \times (-2) = 0$$

$\therefore S = +8 - 2 = +6$

(b) SO_3^{2-}:

We can start by assigning O = –2.

Note that here the oxidation states must add up to –2, the charge on the ion.

Therefore, $S + (3 \times -2) = -2$

$S = -2 + 6 = +4$

HL Worked example

Assign oxidation states to all the transition elements in **(a)** $[Fe(CN)_6]^{4-}$ and **(b)** $[FeCl_4]^-$.

Solution

(a) The ligand is CN^-

$Fe + 6(-1) = -4$

$Fe = -4 + 6 = +2$

(b) The ligand is Cl^-

$Fe + 4(-1) = -1$

$Fe = -1 + 4 = +3$

Worked example

Identify the elements which are oxidized and reduced in the reaction between hydrogen and chlorine to produce hydrogen chloride:

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

Solution

Assign oxidation states to the elements in the reactants and products:

	$H_2(g)$	+ $Cl_2(g)$	→ $2HCl(g)$
Oxidation states	0	0	(H)+1 (Cl)–1

The oxidation state of hydrogen increases: it is oxidized.

The oxidation state of chlorine decreases: it is reduced.

Worked example

Nitrogen dioxide dissolves in rainwater to form a mixture of nitrous acid (HNO_2) and nitric acid (HNO_3).

$$H_2O(l) + 2NO_2(g) \rightarrow HNO_2(aq) + HNO_3(aq)$$

Identify the element that is oxidized and reduced in the reaction.

Solution

Assign oxidation states to the elements in the reactants and products:

	$H_2O(l)$ +	$2NO_2(g)$ →	$HNO_2(aq)$ +	$HNO_3(aq)$
Oxidation states	(H) +1	(N) +4	(H) +1	(H) +1
	(O) –2	(O) –2	(N) +3	(N) +5
		(O) –2	(O) –2	

The oxidation state of nitrogen increases and decreases. Nitrogen is both oxidized and reduced. This is an example of a disproportionation reaction.

A disproportionation reaction is a redox reaction in which the same element both increases and decreases its oxidation state.

Systematic names of compounds use oxidation numbers

In the worked example on page 317, we can see that sulfur exhibits different oxidation states in different compounds. We also discussed sulfuric acid ($H_2SO_4(aq)$) and sulfurous acid ($H_2SO_3(aq)$) in acid rain in the last section. Although these traditional names for the acid are acceptable, IUPAC introduced a nomenclature using oxidation numbers to make the names more recognizable and unambiguous. This system uses Roman numerals corresponding to the oxidation state, which are inserted in brackets after the name of the element. As we have seen in the worked example, S is +6 in H_2SO_4, so it is called sulfuric(VI) acid, and the corresponding oxyanion SO_4^{2-} is the sulfate(VI) ion. Using the same rules, H_2SO_3 is sulfuric(IV) acid and the SO_3^{2-} ion is the sulfate(IV) ion.

Worked example

Deduce the names of the following compounds using oxidation numbers.

(a) N_2O_5 **(b)** NO_2 **(c)** HNO_2

Solution

1. Deduce the oxidation state of N:

N_2O_5	NO_2	HNO_2
As O = –2	As O = –2	As H = +1 and O = –2
2N + (5 × –2) = 0	N + (2 × –2) = 0	+1 + N + (2 × –2) = 0
2N = +10	N = +4	N = +4 – 1
N = +5		= +3

2. Insert the corresponding Roman numeral after the reference to nitrogen in the name. There is no space between the name and the number, and the number is placed in brackets.

N_2O_5	NO_2	HNO_2
nitrogen(V) oxide	nitrogen(IV) oxide	nitric(III) acid

Oxidation state is shown with a '+' or '–' sign and an Arabic numeral, e.g. +2. Oxidation number is shown by inserting a Roman numeral in brackets after the name or symbol of the element.

The terms 'oxidation number' and 'oxidation state' are often used interchangeably in some sources. Either term is acceptable in assessment.

Exercise

Q34. Identify the pair of compounds in which chromium is in the same oxidation state.

A Cr_2O_3 and CrO_3 **B** CrO_3 and $CrCl_3$

C K_2CrO_4 and $K_2Cr_2O_7$ **D** Cr^{2+} and CrO_2

Q35. Deduce the oxidation number of sulfur in $Na_2S_4O_6$.

A +6 **B** +3 **C** +2.5 **D** +2

Q36. Assign oxidation states to all elements in the following compounds:

(a) NH_4^+ **(b)** $SnCl_2$ **(c)** H_2O **(d)** NO_3^-

(e) PbO_2 **(f)** PO_4^{3-} **(g)** ClO_4^- **(h)** HOCl

Q37. Deduce the names of the following compounds, using their oxidation numbers.

(a) HNO_3 **(b)** HNO_2 **(c)** H_3PO_4 **(d)** PbO_2 **(e)** $PbSO_4$

Q38. Deduce the formulas of the following compounds, using their oxidation numbers.

(a) copper(I) oxide **(b)** iron(III) oxide

(c) tin(IV) oxide **(d)** sodium bromate(V)

Q39. Use oxidation states to deduce which element is oxidized and which is reduced in the following reactions.

(a) $Cl_2(aq) + 2NaI(aq) \rightarrow I_2(aq) + 2NaCl(aq)$

(b) $2H_2O(l) + 2F_2(g) \rightarrow 4HF(aq) + O_2(g)$

(c) $P_4(s) + 10F_2(g) \rightarrow 4PF_5(g)$

(d) $H_2(g) + 2Na(s) \rightarrow 2NaH(s)$

HL

Structure 3.1.7 – Discontinuities in patterns of first ionization energy

Structure 3.1.7 – Discontinuities occur in the trend of increasing first ionization energy across a period. Explain how these discontinuities provide evidence for the existence of energy sublevels.	
Explanations should be based on the energy of the electron removed, rather than on the 'special stability' of filled and half-filled sublevels.	

Trends and discontinuities in first ionization energy (IE) in period 4

The trends and discontinuities in first ionization energy (IE) across period 3 are discussed in Structure 1.3.

Looking back to Figure 3 earlier in this chapter, we can see that the group 13 elements (e.g. B), with the electron configuration ns^2np^1, have lower first ionization energies than group 2 elements (e.g. Be), with the configuration ns^2, because p orbitals have higher energy than s orbitals. The drop between groups 15 (e.g. N) and 16 (e.g. O) occurs as the electron removed from a group 16 element, unlike a group 15 element, is taken from a doubly occupied p orbital. The group 16 electron is easier to remove because it is repelled by its partner.

Exercise

Q40. First ionization energies increase for consecutive elements E1, E2 and E3 in the third period of the periodic table. Identify E1, E2 and E3.

	E1	E2	E3
A	Na	Mg	Al
B	Mg	Al	Si
C	Al	Si	P
D	Si	P	S

Q41. Which ions have the electron configuration $1s^22s^22p^63s^23p^6$?

I. Ca^{2+} II. Ti^{4+} III. Cu^{2+}

A I and II **B** I and III **C** II and III **D** I, II and III

Q42. Identify the electron configuration of the V^{2+} ion in its ground state.

A [Ar] $3d^3$ **B** [Ar] $3d^4$ **C** [Ar] $3d^24s^1$ **D** [Ar] $3d^14s^2$

Q43. The first ionization energies for the first 20 elements are shown on page 81.

(a) State the equation that corresponds to the *first ionization energy* of an element.

(b) The first ionization energies show periodicity. Suggest what is meant by the term *periodicity*.

(c) Explain the drop in ionization energies that occurs between beryllium and boron.

(d) Explain the drop in ionization energies that occurs between nitrogen and oxygen.

Structure 3.1.8 – Characteristic properties of transition elements

Structure 3.1.8 – Transition elements have incomplete d-sublevels that give them characteristic properties.

Recognize properties, including variable oxidation state, high melting points, magnetic properties, catalytic properties, formation of coloured compounds and formation of complex ions with ligands.

Knowledge of different types of magnetism will not be assessed.	Nature of Science, Structure 2.3 – What are the arguments for and against including scandium as a transition element?

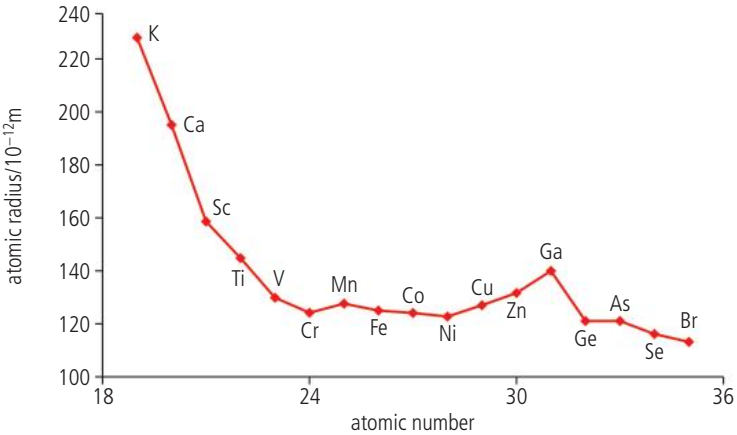
Electron configuration and atomic radii of the d block metals

The electron configuration of the elements in the first row of the d block is summarized in the table below. The unusual electron configurations of chromium (Cr) and copper (Cu) are discussed in Structure 1.3.

Element	Core	3d					4s
Sc	[Ar]	↑					↑↓
Ti	[Ar]	↑	↑				↑↓
V	[Ar]	↑	↑	↑			↑↓
Cr	[Ar]	↑	↑	↑	↑	↑	↑
Mn	[Ar]	↑	↑	↑	↑	↑	↑↓
Fe	[Ar]	↑↓	↑	↑	↑	↑	↑↓
Co	[Ar]	↑↓	↑↓	↑	↑	↑	↑↓
Ni	[Ar]	↑↓	↑↓	↑↓	↑	↑	↑↓
Cu	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Zn	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

As an inner d sublevel is being filled along the series, these elements have similar physical and chemical properties. This is illustrated by the relatively small range in atomic radii.

Atomic radii across period 4.



The relatively small decrease in atomic radii across the d block is due to the correspondingly small increase in effective nuclear charge experienced by the outer 4s electrons. The increase in nuclear charge due to the added proton is largely offset by the addition of an electron in an *inner* 3d sublevel. This similarity in atomic radii explains the ability of the d block metals to form alloys: the atoms of one d-block metal can be replaced by atoms of another without too much disruption of the solid structure discussed in Structure 2.4. The small increase in effective nuclear charge also accounts for the small range in first ionization energies across the first d block elements.

Zinc is not a transition metal

Transition metals are elements whose atoms have an incomplete d sublevel, or which can give rise to cations with an incomplete d sublevel.

Zinc is a d-block element but not a transition metal as it does not show the characteristic properties outlined in the chapter. It does not form coloured compounds, for example, and exists in only the +2 oxidation state in its compounds. The reason for its exclusion can be traced to the electronic configuration of its atom and the Zn^{2+} ion – the d sublevel is complete in both species. The electron configurations of some ions including Sc^{2+} and Zn^{2+} are shown for comparison.

Ion	Core	3d					4s
Sc^{2+}	[Ar]	↑					
Ti^{2+}	[Ar]	↑	↑				
Cu^{2+}	[Ar]	↿⇂	↿⇂	↿⇂	↿⇂	↑	
Zn^{2+}	[Ar]	↿⇂	↿⇂	↿⇂	↿⇂	↿⇂	

Nature of Science, Structure 2.3 – What are the arguments for and against including scandium as a transition element?

There are arguments for and against including scandium as a transition element. Its most stable ion Sc^{3+} does not have any electrons in d orbitals but $Sc^{2+}(aq)$, although not common, has a single d electron.

Physical properties of the transition metals

The transition metals have the following general physical properties:

- high electrical and thermal conductivity
- high melting point
- malleable – they are easily beaten into shape
- high tensile strength – they can hold large loads without breaking
- ductile – they can be easily drawn into wires
- iron, cobalt and nickel are ferromagnetic.

These properties can be explained in terms of the strong metallic bonding found in the elements. As the 3d electrons and 4s electrons are close in energy, they are all involved in bonding, and form part of the delocalized sea of electrons, which holds the metal lattice together (Structure 2.3). This large number of delocalized electrons accounts for the strength of the metallic bond and the high electrical conductivity. The smaller atomic radii of the transition metals compared to their s-block neighbours also account, in part, for their higher densities.

The properties and uses of the transition metals make them important commodities on the international stock exchange. The mining and extraction of these elements is an important industrial process in the economic development of some countries.

The magnetic properties of the transition metals and their compounds

Iron, nickel and cobalt show strong magnetic properties

The magnetic properties of the transition metal elements and compounds are due to the presence of unpaired electrons in the d orbitals. Every spinning electron in an atom or molecule can behave as a tiny magnet. Electrons with opposite spins behave like small bar magnets with opposing orientation and so have no net magnetic effect. Most substances have paired electrons that pair up and so are non-magnetic. Some transition metals and their compounds are unusual in having some electrons that remain unpaired, which when aligned lead to magnetic properties.

The term 'magnetic' derives from the mineral magnetite, which has been widely used as a compass because of its magnetic properties. The origin of the term 'ferromagnetism' derives from iron's magnetic properties.



Iron can be separated from sulfur using a magnet. Iron is magnetic due to the unpaired electrons in its d orbitals.

The action at a distance of invisible magnetic forces mystified early thinkers, who drew parallels between magnetism and other areas of human experiences – such as infection and love. Remnants of this confusion are reflected in our language; the French word for 'magnet' is *aimant* which means 'loving'. Language allows knowledge to be passed on to others and to be accumulated over time for future generations. This is how knowledge is 'shared', but outdated ideas and theories can be communicated in the same way. How does the vocabulary we use help and hinder the pursuit of knowledge?

TOK

Nature of Science

Magnetism was used in navigation long before it was explained scientifically. Historically, technology emerged before science. Materials were often used practically long before there was an understanding of why they possessed their properties.

In today's world, the reverse is often the case, with scientific understanding leading to technological developments, which in turn drive further developments in scientific ideas.

Chemical properties of the transition metals

The chemical properties of the transition metals are very different from those of the s-block metals. Transition metals:

- form compounds with more than one oxidation state
- form a variety of complex ions
- form coloured compounds
- act as catalysts when either elements or compounds.

These properties are discussed in more detail in the next section.



Transition element ions are coloured in aqueous solutions. From left to right, the solutions are compounds of: titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni) and copper (Cu).

Preparing a coloured coordination complex. Full details of how to carry out this experiment with a worksheet are available in the eBook.

SKILLS

Transition metals and their ions are important catalysts

A catalyst is a substance that alters the rate of reaction by providing an alternative reaction pathway with a lower activation energy (see Reactivity 2.2). Catalysts play an essential role in the chemical industry as they allow chemical processes to proceed at an economical rate.

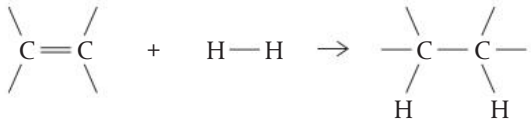
Examples of transition metals as catalysts include the following.

- Iron (Fe) in the Haber process:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Ammonia (NH_3) is the raw material for a large number of other useful chemical products such as fertilizers, plastics, drugs and explosives.

- Nickel (Ni) in the conversion of alkenes to alkanes:



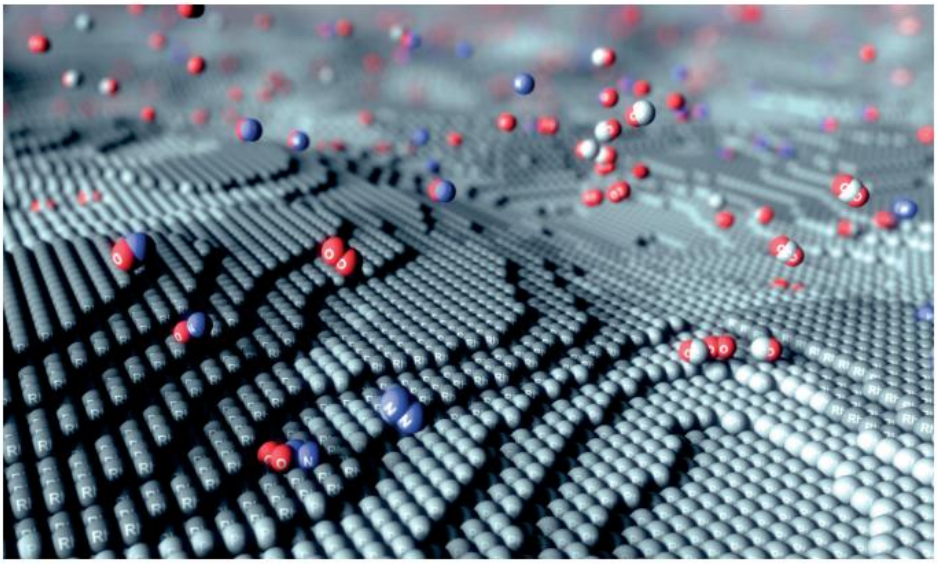
This reaction allows unsaturated vegetable oils with a carbon–carbon double bond to be converted to margarine.

- Palladium (Pd), rhodium(Rh) and platinum (Pt) in catalytic converters:

$$2CO(g) + 2NO(g) \rightarrow 2CO_2(g) + N_2(g)$$

This reaction removes harmful primary pollutants from a car's exhaust gases.

Palladium and platinum are very expensive materials, but only minimal amounts of the metals are needed as they do not chemically change when they act as catalysts.



A catalytic converter converts harmful polluting gases from a motor vehicle's engine into relatively harmless ones. The surface is lined with the catalyst, which is a combination of rhodium (Rh) and platinum (Pt) metals. Nitrogen, oxygen and carbon are represented as blue, red and grey spheres.

Exercise

Q44. Identify the property/properties which are characteristic of **all** elements found in the d block of the periodic table.

A All the compounds of the elements are ionic.

B The elements exhibit a variety of oxidation states and colours in their compounds.

C The elements have low melting points.

D The elements are good conductors of heat and electricity.

Q45. Which of the following atoms would be expected to be attracted by a magnetic field?

A Ca **B** Zn **C** He **D** Mn

Q46. Zinc is a d block metal that is not a transition metal.

(a) State the full electron configuration of zinc (Zn).

(b) State the full electron configuration of Zn^{2+}.

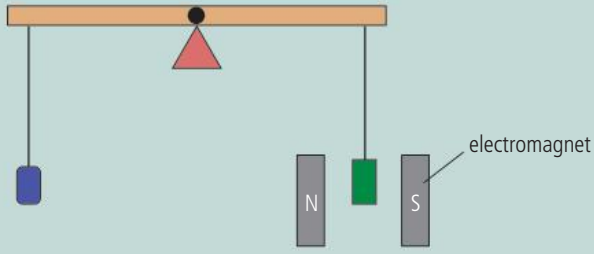
(c) Explain why zinc is not classed as a transition metal.

Q47. State the electron configurations of the following metal ions by filling in the boxes below. Use arrows to represent the electron spin.

Ion	3d					4s
Sc^{3+}						
Ti^{3+}						
Ni^{2+}						
Zn^{2+}						

Q48. Explain why chromium atoms experience the strongest attraction toward a magnetic field of all elements in the first transition series and why zinc atoms experience no attraction.

Q49. A solution of $[Fe(H_2O)_6]^{2+}$ ions is divided into two parts of equal mass which are placed on both sides of the balance with the electromagnet turned off.



Predict what happens when the electromagnet is turned on and justify your answer.

Structure 3.1.9 – Variable oxidation states

Structure 3.1.9 – The formation of variable oxidation states in transition elements can be explained by the fact that their successive ionization energies are close in value.

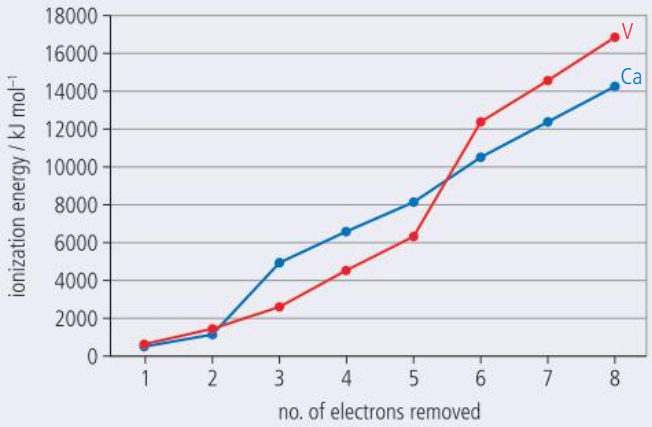
Deduce the electron configurations of ions of the first-row transition elements.

The variable oxidation number of transition elements

One of the key features of transition metal chemistry is the wide range of oxidation states that the metals display in their compounds. This should be contrasted with the s block metals, which show only the oxidation state corresponding to their group number in their compounds. The difference in behaviour can be related to patterns in successive ionization energies and is discussed in Structure 1.3 and Structure 2.1.

Worked example

The graph shows successive ionization energies of calcium and vanadium.



(a) Deduce the ground-state electron configuration of the V atom and the V^{3+} ion.

(b) Predict the stable oxidation states of calcium and vanadium.

Solution

(a) The V atom has 23 electrons.

The electron configuration of the atom:

Remember from Structure 1.3 that the 4s is filled before 3d:
$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$

But the 3d sublevel is below the 4s level for elements after calcium, so we write this as $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$

The electron configuration of V^{3+}:

Now remove the two electrons from the 4s sublevel and one electron from the 3d sublevel.

The electron configuration of V^{3+} is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$

(b) Calcium is stable in the +2 state. The Ca^{3+} ion is energetically unstable because there is a large jump in ionization energy as the third electron is removed from the inner 3p orbital.

The increase in successive energies for vanadium is more gradual as the 3d and 4s orbitals are close in energy. Vanadium shows the +2, +3, +4 and +5 oxidation states. A large jump occurs between the fifth and sixth ionization energies, as the inner 3p electron is removed, so it does not form the +6 state.

The following points should be noted.

- All the transition metals show both the +2 and +3 oxidation states. The M^{3+} ion is the stable state for the elements from scandium to chromium, but the M^{2+} state is more common for the later elements. The increased nuclear charge of the later elements makes it more difficult to remove a third electron.
- The maximum oxidation state of the elements increases in steps of +1 and reaches a maximum at manganese. These states correspond to the use of both the 4s and 3d electrons in bonding. Thereafter, the maximum oxidation state decreases in steps of –1.
- Oxidation states above +3 generally show covalent character. Ions of higher charge have such a large charge density that they polarize negative ions and increase the covalent character of the compound (see Structure 2.1).
- Compounds with higher oxidation states tend to be oxidizing agents. The use of potassium dichromate(VI) ($K_2Cr_2O_7$), for example, in the oxidation of alcohols is discussed in Reactivity 3.2.

Exercise

Q50. Identify the oxidation state which is the most common among the first-row transition elements.

A +1 **B** +2 **C** +4 **D** +6

Q51. An element has the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$. Identify the oxidation states the element could show.

A +2 and +3 **B** +2 and +4 **C** +3 and +4 **D** +2, +3 and +4

Q52. State the oxidation states shown by aluminium and chromium and explain the difference in their behaviour.

Structure 3.1.10 – Coloured complexes

Structure 3.1.10 – Transition element complexes are coloured due to the absorption of light when an electron is promoted between the orbitals in the split d sublevels. The colour absorbed is complementary to the colour observed.

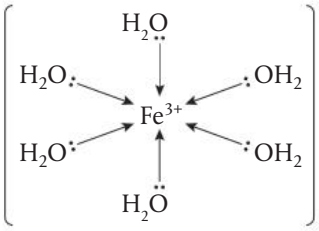
Apply the colour wheel to deduce the wavelengths and frequencies of light absorbed and/or observed.

Students are not expected to know the different splitting patterns and their relation to the coordination number. The colour wheel and the equation $c = \lambda f$ are given in the data booklet.	Reactivity 3.4 – What is the nature of the reaction between transition element ions and ligands in forming complex ions? Tool 1, Inquiry 2 – How can colorimetry or spectrophotometry be used to calculate the concentration of a solution of coloured ions?

Transition metals form complex ions

Transition metal ions in solution have a high charge density and attract water molecules which form coordination bonds with the positive ions to form a **complex ion**. The complex ion $[Fe(H_2O)_6]^{3+}$, for example, is formed when Fe^{3+} ions form

coordination bonds with six water molecules. The square brackets indicate that the Fe^{3+} ion and water molecule form one distinct unit with the charge delocalized on both the water molecules and the central ion.



The complex ion $[Fe(H_2O)_6]^{3+}$. The water molecules are ligands as they form coordination bonds to the central ion.

More generally, a complex is formed when a central ion is surrounded by molecules or ions which possess a lone pair of electrons. These surrounding species (**ligands**) are attached via a coordination bond. All ligands have at least one atom with a lone pair of electrons which is used to form a coordination bond with the central metal ion. The formation of a complex ion is an example of an electron-pair sharing reaction explored in more detail in Reactivity 3.4.

The number of coordination bonds from the ligands to the central ion is called the **coordination number**.

Transition metal complex ions are coloured as the 3d sublevel splits into two energy levels

The colour of transition metal ions (shown in the table below) can be related to the presence of partially filled d orbitals. The ion Sc^{3+} is colourless because the 3d sublevel is empty; Sc^{3+} is colourless because the 3d sublevel is full.

Ion	Electron configuration	Colour	Ion	Electron configuration	Colour
$Sc^{3+}(aq)$	[Ar]	colourless	$Fe^{3+}(aq)$	[Ar] $3d^5$	yellow
$Ti^{3+}(aq)$	[Ar] $3d^1$	violet	$Fe^{2+}(aq)$	[Ar] $3d^6$	green
$V^{3+}(aq)$	[Ar] $3d^2$	green	$Co^{2+}(aq)$	[Ar] $3d^7$	pink
$Cr^{3+}(aq)$	[Ar] $3d^3$	violet	$Ni^{2+}(aq)$	[Ar] $3d^8$	green
$Mn^{2+}(aq)$	[Ar] $3d^5$	pink	$Cu^{2+}(aq)$	[Ar] $3d^9$	blue

The visible spectrum

The visible spectrum ranges from 400 nm to about 700 nm. The colour we see depends on the wavelength.

Colour	Wavelength range / nm
Red	630–700
Orange	590–630
Yellow	560–590
Green	490–560
Blue	450–490
Violet	400–450

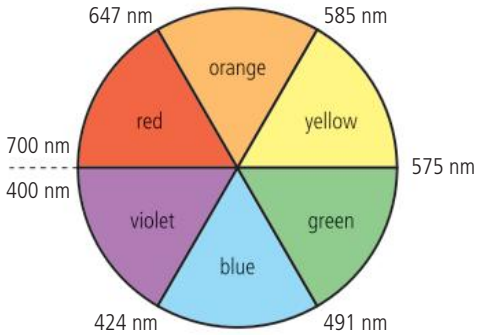
A coordination bond uses a lone pair of electrons to form a covalent bond.

A ligand is a species that uses a lone pair of electrons to form a coordination bond with a metal ion.

The word 'ligand' is derived from *ligandus*, the Latin word for 'to bind'.

Reactivity 3.4 – What is the nature of the reaction between transition element ions and ligands in forming complex ions?

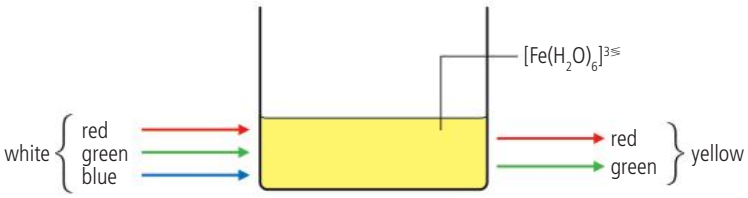
The colour of a substance is determined by which colour(s) of light it absorbs and which colour(s) it transmits or reflects (the complementary colour(s)). Copper sulfate, for example, appears turquoise because it absorbs orange light. Orange and turquoise are complementary colours; they are opposite each other in the colour wheel (Figure 5).



S3.1 Figure 5 The colour wheel. There is a colour wheel in Section 15 of the data booklet.

Transition metals appear coloured because they absorb visible light

As discussed in Structure 1.3, white light is composed of all the colours of the visible spectrum. Transition metal compounds appear coloured because their ions absorb some of these colours. $[Fe(H_2O)_6]^{3+}$, for example, appears yellow (see photo on page 332) because it absorbs light in the blue region of the spectrum (see Figure 6 and Figure 7).



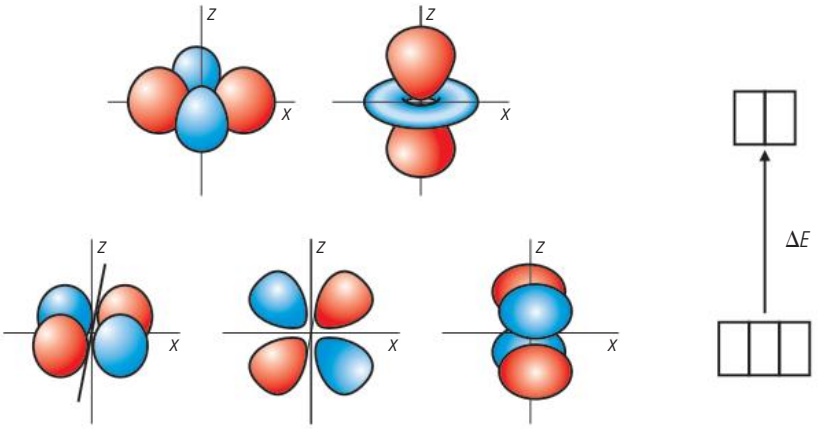
S3.1 Figure 6 The ion Fe^{3+} appears yellow because it absorbs blue light. Yellow is the complementary colour to blue.



S3.1 Figure 7 Complementary colours. Yellow light (a mixture of red and green light) appears when blue is removed from white light.

Transition metals absorb light because the d sublevel splits into two levels

The d orbitals in an isolated transition metal atom are said to be *degenerate* because they all have the same energy. However, in the electric field produced by the ligand's lone pair of electrons, the orbitals split into two levels. Consider, for example, the octahedral complex $[Ti(H_2O)_6]^{3+}$ with the water molecules placed along the *x*-, *y*-, and *z*-axes (Figure 8).



S3.1 Figure 8 An electron in a d orbital orientated *along* the bond axis has a higher energy than an electron in one of the three orbitals which point *between* the axes.

When light passes through a solution of $[Ti(H_2O)_6]^{3+}$, one 3d electron is excited from the lower to the higher energy sublevel (Figure 9). A photon of green light is absorbed and light of the complementary colour (purple) is transmitted, which accounts for the purple colour of a solution of $[Ti(H_2O)_6]^{3+}$.



S3.1 Figure 9 Green light of energy *hf* excites an electron from a d orbital of lower energy to a d orbital of higher energy. The transmitted light is purple, which is complementary to the green light absorbed.

Worked example

Copper(II) sulfate forms a blue aqueous solution. Estimate a wavelength of light absorbed by this solution, using Section 15 of the data booklet.

Solution

Copper appears blue because it absorbs the complementary colour orange.

From the colour wheel in the data booklet, we can predict that it absorbs in the range 585–647 nm.

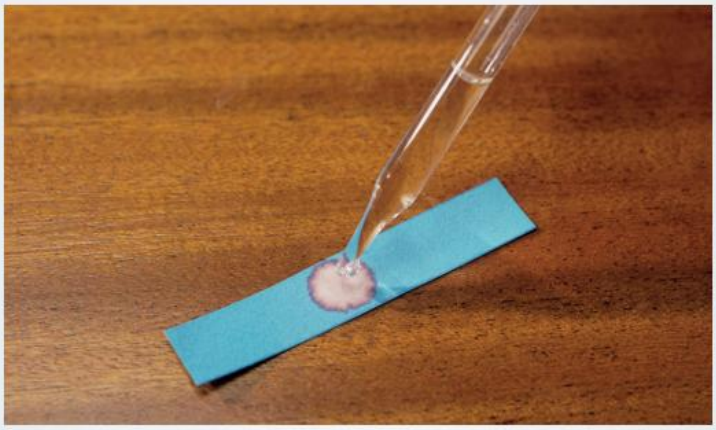
SKILLS

Qualitative observation of coordination bond formation. Full details of how to carry out this experiment with a worksheet are available in the eBook.

When predicting the colour absorbed be sure to use the data booklet as different colour wheels may give different colours.

Challenge yourself

7. Cobalt chloride paper is used to indicate the presence of water. The colour changes from blue to pink as the ligands change from Cl^- ions to H_2O molecules.



Cobalt chloride ($CoCl_2$) paper with a drop of water.

Suggest why the two cobalt complex ions $[Co(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$ are different colours.

8. Explain why the absorption spectra of gaseous atoms are made up of a series of lines whereas complex ions produce broad absorption bands.

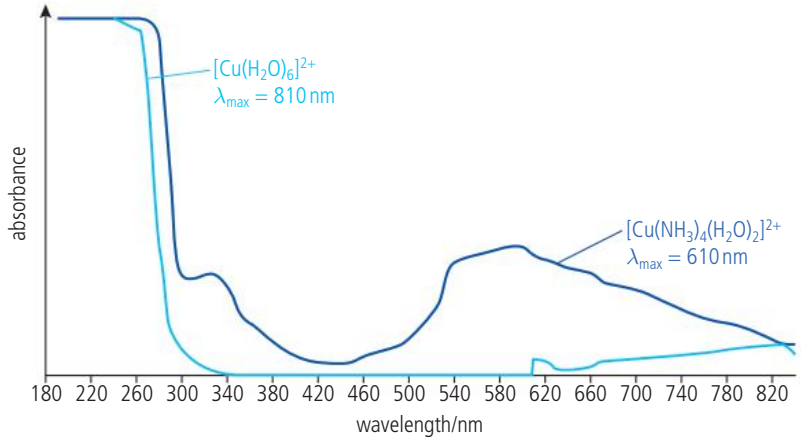
Do not confuse the colour of transition metals ions, produced as a result of light being absorbed as electrons jump between the split d sublevels, with the emission of colour produced when excited electrons return to the ground state.



The energy difference between d orbitals and the colour of a complex depends on the nuclear charge of the central ion. $[Mn(H_2O)_6]^{2+}$ (on the left) is pale pink and $[Fe(H_2O)_6]^{3+}$ (on the right) is yellow/brown. Both have the same electron configuration.

Charge density of the ligand

The spectrum of the copper complex formed when four of the water molecule ligands are replaced by four ammonia molecules is shown in Figure 10. The $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex absorbs the shorter wavelength yellow light, therefore, the complex has a deep blue colour. Ammonia has a greater charge density than water and so produces a larger split in the d orbitals.



S3.1 Figure 10 The electronic UV–vis absorption spectrum of two copper complexes. $[Cu(H_2O)_6]^{2+}$ absorbs light in the orange region of the spectrum and so appears turquoise. $[Cu(NH_3)_4(H_2O)_2]^{2+}$ absorbs light in the yellow region of the spectrum and so appears dark blue.

The absorbance of light depends on the concentration

As we can see from Figure 6, substances that appear coloured absorb certain wavelengths of light in the visible region and transmit the remaining wavelengths. The amount of light absorbed at a particular wavelength can be used to measure the concentration of the substance as there is a proportional relationship between the absorbance and concentration of a compound at a fixed wavelength.

The absorbance of a compound at a fixed wavelength is directly proportional to its concentration.

Once it is clear that a substance absorbs at a particular wavelength, a **calibration curve** is produced by measuring the absorbance at the selected wavelength for a range of standard solutions with known concentrations. Typically, at least five dilutions of a standard of known concentration are prepared. The absorbance is measured and plotted on a graph to obtain the calibration curve. The absorbance of the solution to be analysed is then measured at the same wavelength as the standard solutions, and its concentration is determined from the calibration curve. When calibration curves have been generated by data logging, appropriate software can often be used for this calculation.



Beakers showing the colour change in a test for the iron(III) ion. The complex ion ($[Fe(H_2O)_6]^{3+}$) on the left has a yellow/orange colour. This reacts with the colourless potassium thiocyanate solution (centre) to form a distinctive blood-red colour (right); one of the water ligands (H_2O) is replaced with a thiocyanate ion (SCN^-). The resulting complex ion has a formula $[Fe(SCN)(H_2O)_5]^{2+}$.

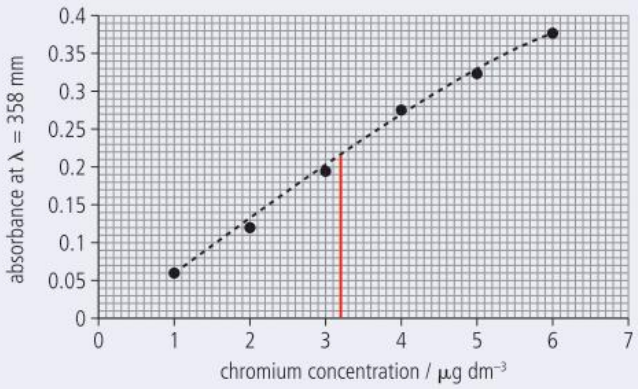
Worked example

The amount of light absorbed by seawater at a wavelength of $\lambda = 358\,nm$ can be used to measure the concentration of the chromium in seawater. A sample was analysed along with six standard solutions. Determine the concentration of chromium in the seawater by plotting a graph of the data.

Chromium concentration / $\mu g\,dm^{-3}$	Absorbance at $\lambda = 358\,nm$
1.00	0.062
2.00	0.121
3.00	0.193
4.00	0.275
5.00	0.323
6.00	0.376
Sample	0.215

Solution

Plot the points with labelled axes.



Draw the best-fit straight line and find the point on the line with an absorbance of 0.205. This corresponds to a concentration of 3.2 μg dm^{-3}.

Concentration of chromium = 3.2 μg dm^{-3}.

Tool 1, Inquiry 2 – How can colorimetry or spectrophotometry be used to calculate the concentration of a solution of coloured ions?

Exercise

Q53. Explain why $Fe^{2+}(aq)$ is coloured whereas $Zn^{2+}(aq)$ is not coloured.

Q54. $[Fe(H_2O)_6]^{3+}$ forms a yellow solution. Estimate a wavelength of light absorbed by this complex, using Section 15 of the data booklet.

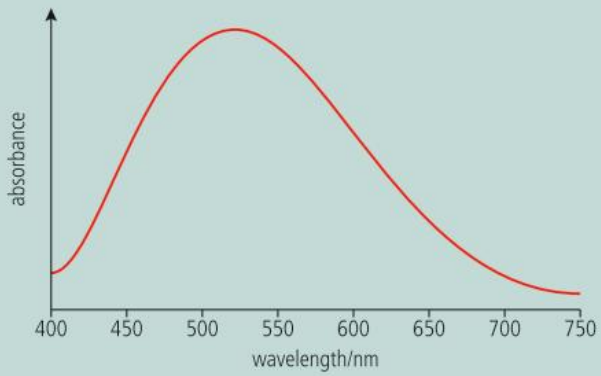
Q55. The colour of transition metal complexes depends on several factors.

(a) Suggest why the colour of $[Cr(H_2O)_6]^{3+}$ is different from the colour of $[Fe(H_2O)_6]^{3+}$.

(b) Suggest why the colour of $[Fe(H_2O)_6]^{2+}$ is different from the colour of $[Fe(H_2O)_6]^{3+}$.

(c) Suggest why the colour of $[Fe(NH_3)_6]^{2+}$ is different from the colour of $[Fe(H_2O)_6]^{3+}$.

Q56. The absorption spectrum of $[Ti(H_2O)_6]^{3+}$ is shown below. Use the colour wheel in the data booklet to suggest a colour for the complex.



Q57. Draw a diagram to show how the electrons are arranged in Fe^{2+} when it is present in the $[Fe(H_2O)_6]^{2+}$ ion.

HL end

Guiding Question revisited

How does the periodic table help us to predict patterns and trends in the properties of elements?

In this chapter, we have seen how the periodic table highlights the patterns and trends in the properties of the elements.

- The periodicity in the physical and chemical properties of elements is due to the periodicity of their electron configuration.
- Metals are on the left of the table, non-metals are on the upper right-hand side and metalloids are in a diagonal area between.
- The columns of the table are called groups and the rows are called periods. Elements in the same group show similar chemical properties as they have the same number of electrons in their valence energy level.
- The group 1 or alkali metals react with water to produce hydroxides and hydrogen. Melting points decrease down the group and metal reactivity increases down the group. They react by losing electrons.
- The group 17 elements or halogens are reactive non-metals. Melting and boiling points increase down the group and non-metal reactivity decreases down the group. They react by gaining electrons.
- Group 1 and group 17 elements are on opposite sides of the table and show opposite trends in reactivities and melting points.
- The group 18 elements or noble gases are unreactive as they have complete outer energy levels.

HL

- The transition metals are found in the d block. Zinc is not a transition metal as both the Zn atom and the Zn^{2+} ion have a complete d sublevel.
- Transition metals show variable oxidation states, act as catalysts and form coloured complex ions. The colour is due to electron transitions between d orbitals of different energy. The d sublevel is split into orbitals of different energy due to the electric field created by lone pair of electrons of the ligand.

HL end

Practice questions

1. Which property generally decreases across period 3?

A atomic number
B electronegativity
C atomic radius
D first ionization energy

2. Which statements about period 3 are correct?

I. The electronegativity of the elements increases across period 3.

II. The atomic radii of the elements decrease across period 3.

III. The oxides of the elements change from acidic to basic across period 3.

A I and II only **B** I and III only **C** II and III only **D** I, II and III

3. Which property decreases down group 17 in the periodic table?

A melting point **B** electronegativity

C atomic radius **D** ionic radius

4. Which oxides produce an acidic solution when added to water?

I. P_4O_{10} II. MgO III. SO_3

A I and II only **B** I and III only **C** II and III only **D** I, II and III

5. Which is the best definition of *electronegativity*?

A Electronegativity is the energy required for a gaseous atom to gain an electron.

B Electronegativity is the attraction of an atom for a bonding pair of electrons.

C Electronegativity is the attraction between the nucleus and the valence electrons of an atom.

D Electronegativity is the ability of an atom to attract electrons from another atom.

6. What happens when sodium is added to water?

I. A gas is evolved.

II. The temperature of the water increases.

III. A clear, colourless solution is formed.

A I and II only **B** I and III only **C** II and III only **D** I, II and III

7. Which species could be oxidized to form $S_2O_3^{2-}$?

A S **B** SO_2 **C** H_2SO_3 **D** H_2SO_4

8. Which statements are correct for the complex ion $[CuCl_4]^{2-}$?

I. The oxidation number of Cu in the complex ion is +2.

II. The coordination number of the copper ion is 4.

III. Chloride ions are behaving as ligands.

A I and II only **B** I and III only **C** II and III only **D** I, II and III

9. In which complexes does iron have an oxidation number of +3?

I. $[Fe(H_2O)_6]^{3+}$

II. $[Fe(H_2O)_5(CN)]^{2+}$

III. $[Fe(CN)_6]^{3-}$

A I and II only **B** I and III only **C** II and III only **D** I, II and III

10. Which processes could result in acid rain?

I. burning coal

II internal combustion engines

III. burning methane

A I and II only **B** I and III only **C** II and III only **D** I, II and III

11. Which process is responsible for the colour of a transition metal complex?

A the absorption of light when electrons move between s orbitals and d orbitals

B the emission of light when electrons move between s orbitals and d orbitals

C the absorption of light when electrons move between different d orbitals

D the emission of light when electrons move between different d orbitals

12. Deduce the oxidation numbers of iron in $[Fe(OH)_2(H_2O)_4]^+$ and in $[FeCl_4]^-$.

	$[Fe(OH)_2(H_2O)_4]^+$	$[FeCl_4]^-$
A	+2	+2
B	+2	+3
C	+3	+2
D	+3	+3

13. **(a)** Define the term *first ionization energy*. (2)

(b) Explain why the first ionization energy of magnesium is higher than that of sodium. (2)

(Total 4 marks)

14. Samples of sodium oxide and sulfur trioxide are added to separate beakers of water. Deduce the equation for each reaction and identify each oxide as acidic, basic, or neutral. (3)

(Total 3 marks)

15. Describe and explain what you will see if chlorine gas is bubbled through a solution of:

(a) potassium iodide (2)

(b) potassium fluoride (1)

(Total 3 marks)

16. The periodic table shows the relationship between electron configuration and the properties of elements and is a valuable tool for making predictions in chemistry.

(a) Identify the property used to arrange the elements in the periodic table. (1)

(b) Outline two reasons why electronegativity increases across period 3 in the periodic table and one reason why noble gases are not assigned electronegativity values. (3)

(Total 4 marks)

17. **(a)** Outline two reasons why a sodium ion has a smaller radius than a sodium atom. (2)

(b) Explain why the ionic radius of P^{3-} is greater than the ionic radius of Si^{4+}. (2)

(Total 4 marks)

18. Sodium oxide, Na_2O, is a white solid with a high melting point.

(a) Explain why solid sodium oxide is a non-conductor of electricity. (1)

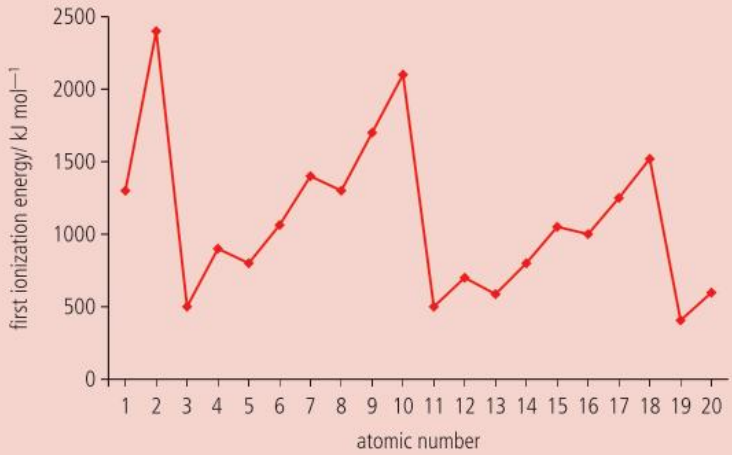
(b) Molten sodium oxide is a good conductor of electricity. State the half-equation for the reaction occurring at the positive electrode during the electrolysis of molten sodium oxide. (1)

(c) **(i)** State the acid/base nature of sodium oxide. (1)

(ii) State the equation for the reaction of sodium oxide with water. (1)

(Total 4 marks)

19. The graph of the first ionization energy plotted against atomic number for the first 20 elements shows periodicity.



(a) State what is meant by the term *periodicity*. (1)

(b) State the electron arrangement of argon and explain why the noble gases, helium, neon and argon, show the highest first ionization energies for their respective periods. (3)

(c) A graph of atomic radius plotted against atomic number shows that the atomic radius decreases across a period. Explain why chlorine has a smaller atomic radius than sodium. (1)

(d) Explain why a sulfide ion, S^{2-}, is larger than a chloride ion, Cl^-. (1)

(e) Explain why the melting points of the group 1 metals (Li to Cs) decrease down the group whereas the melting points of the group 17 elements (F to I) increase down the group. (3)

(Total 9 marks)

HL

20. When concentrated hydrochloric acid is added to a solution containing hydrated copper(II) ions, the colour of the solution changes from light blue to green. The equation for the reaction is:

$$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightarrow [CuCl_4]^{2-}(aq) + 6H_2O(l)$$

(a) Explain what the square brackets around the copper-containing species represent. (1)

(b) Explain why the $[Cu(H_2O)_6]^{2+}$ ion is coloured and why the $[CuCl_4]^{2-}$ ion has a different colour. (2)

(Total 3 marks)

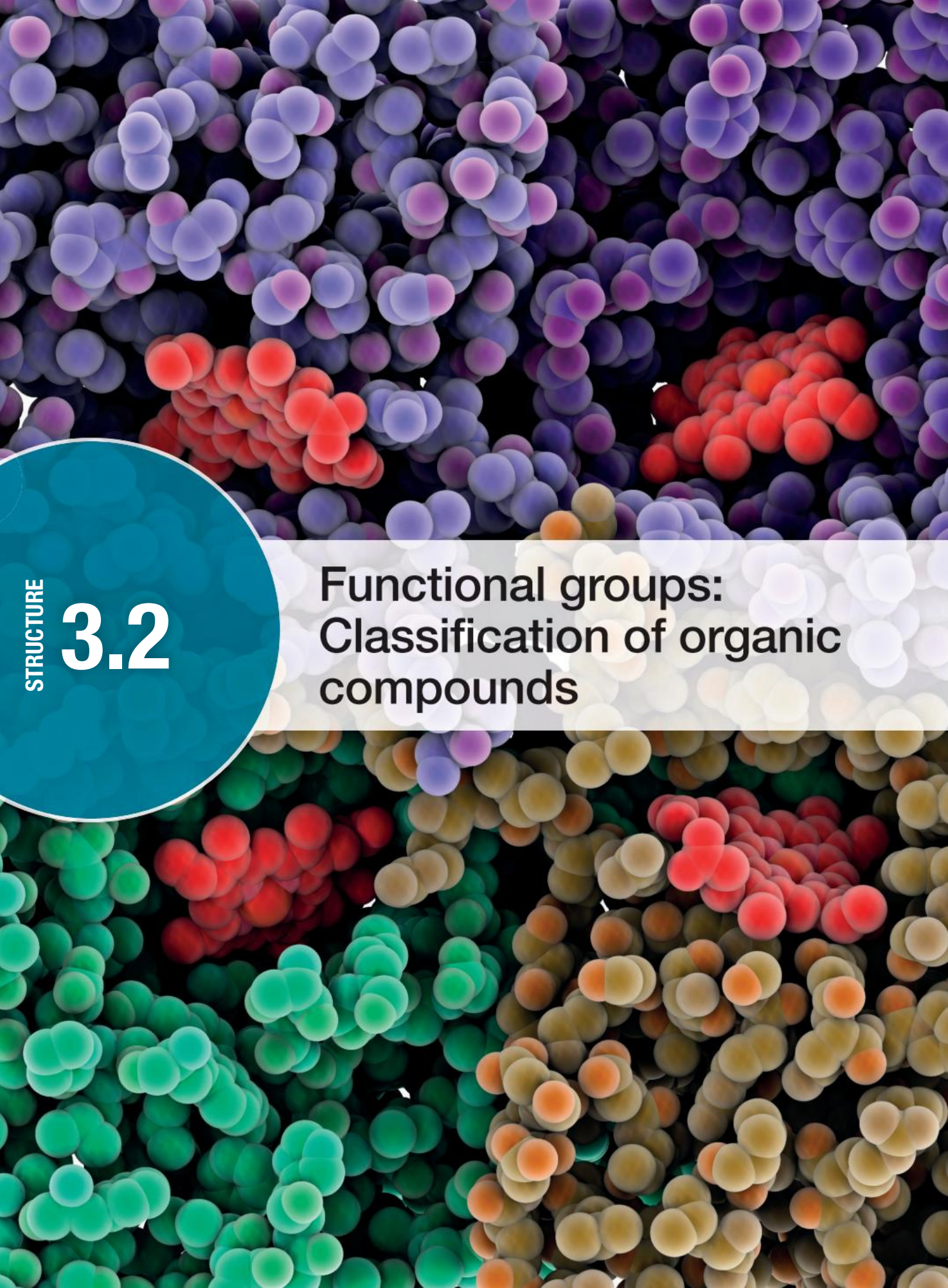
21. $Fe^{2+}(aq)$ ions form green solutions and $Fe^{3+}(aq)$ ions are orange/yellow.

(a) Estimate a wavelength of light absorbed by these solutions, using Section 15 of the data booklet. (2)

(b) Compare the magnetic property of $Fe^{2+}(aq)$ ions and $Fe^{3+}(aq)$ ions. (2)

(Total 4 marks)

HL end



STRUCTURE

3.2

Functional groups: Classification of organic compounds

The development of organic chemistry as a field of study has allowed chemists to investigate increasingly complicated organic compounds, gaining new insights into their physical properties and chemical reactivity. Since the first applications of computerized molecular modelling in the 1960s, the steady growth in computing power has allowed for the modelling of increasingly complex molecules, utilizing current knowledge of chemical bonding and the intramolecular forces associated with different functional groups. With modern computers and software, the 3D structures of extremely complex biological compounds, such as proteins and enzymes, are now able to be modelled, giving new insights into the dynamics of protein folding and enzyme catalysis. The picture shown is a computer-generated model of the human catalase enzyme that shows the shape and folding of the enzyme.

Guiding Question

How does the classification of organic molecules help us to predict their properties?

The total number of organic compounds that exists on Earth is so large that it is impossible to give a definite number. In any case, it is increasing all the time as new materials are synthesized. It is currently estimated that there are over 20 million different organic molecules on the planet and every one of them is unique in its chemical structure and specific properties.

With such a large number of organic compounds, it is necessary to have a system for classifying and naming them. In this chapter, we will learn how the presence of specific **functional groups** allows for the classification of organic compounds into **classes** of compounds with similar properties.

A functional group is usually a small group of atoms attached to a carbon atom in a molecule, and it gives the characteristic properties to the compound. The properties of any individual compound can therefore be predicted and explained by what functional groups are present and the class it belongs to.

Given the incredible diversity of organic compounds, it is possible for compounds with the same molecular formula to have different structures along with different physical and chemical properties. Applying the rules for **IUPAC nomenclature** allows unique names to be obtained for each individual compound, which also assists in their classification.

HL The presence of functional groups makes it possible to determine the identity of an unknown organic compound, using analytical techniques such as **mass spectrometry**, **infrared spectroscopy** and **proton nuclear magnetic resonance spectrometry**. While each individual technique can provide insights into the bonding and functional groups present in a compound, a full determination of its structure typically requires information from more than one technique.

The international, non-governmental organization IUPAC (International Union of Pure and Applied Chemistry), is best known for its system of nomenclature, and is now recognized as the world authority in this field. IUPAC terminology enables precise communication between scientists across international boundaries.

Structure 3.2.1 – Structural representations of organic compounds

Structure 3.2.1 – Organic compounds can be represented by different types of formulas. These include empirical, molecular, structural (full and condensed), stereochemical and skeletal. Identify different formulas, and interconvert molecular, skeletal and structural formulas. Construct 3D models (real or virtual) of organic molecules.	
Stereochemical formulas are not expected to be drawn, except where specifically indicated.	Structure 2.2 – What is unique about carbon that enables it to form more compounds than the sum of all the other elements' compounds? Nature of Science, Structure 2.2 – What are the advantages and disadvantages of different depictions of an organic compound (e.g. structural formula, stereochemical formula, skeletal formula, 3D models)?

Different types of formulas can provide different information about organic compounds

Structure 1.4 shows that chemical compounds can be represented by empirical and molecular formulas which give the identities of the elements present in the compound. However, for organic compounds, an understanding of *how* the atoms within the compound are linked is often required in order to predict and explain their properties and reactivity. Structural and skeletal formulas that illustrate the connections and spatial arrangements between atoms are commonly used in organic chemistry.

The **empirical formula** of a compound is the simplest whole-number ratio of the atoms it contains (see Structure 1.4). For example, the empirical formula of ethane, C_2H_6, is CH_3. This formula can be derived from percentage composition data obtained from combustion analysis. It is, however, of rather limited use on its own, as it does not tell us the actual number of atoms in the molecule.

The **molecular formula** of a compound is the actual number of atoms of each element present. For example, the molecular formula of ethane is C_2H_6. It is therefore a multiple of the empirical formula, and so can be deduced if we know both the empirical formula and the molar mass *M*. The relationship can be expressed as:

$$M = (\text{molar mass of empirical formula})_n$$

where n is an integer.

So, for example, if we know that the empirical formula of ethane is CH_3, and its molar mass $M = 30\,\text{g mol}^{-1}$, using the formula above:

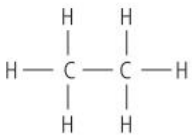
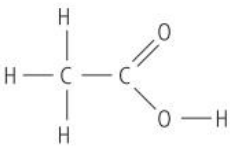
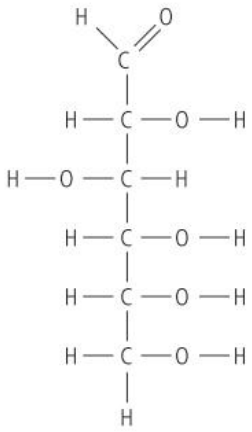
$$30\,\text{g mol}^{-1} = (\text{mass of } CH_3) \text{ so } 30 = (12 + (3 \times 1)), \text{ which gives } n = 2$$

Therefore, the molecular formula of ethane is $(CH_3)_2$ or C_2H_6.

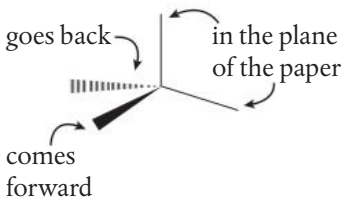
However, the molecular formula is also of quite limited value as the properties of a compound are determined not only by the atoms it contains, but also by how those atoms are arranged in relation to each other and in space.

The **structural formula** is a representation of the molecule showing how the atoms are bonded to each other. There are variations in the amount of detail this shows.

- A **full structural formula** (graphic formula or displayed formula) shows every bond and atom. Usually 60°, 90° and 180° angles are used to show the bonds because this is the clearest representation on a two-dimensional page, although it is not the true geometry of the molecule.
- A **condensed structural formula** often omits bonds where they can be assumed, and groups atoms together. It contains the minimum information needed to describe the molecule unambiguously – in other words there is only one possible structure that could be described by this formula.
- The table below shows empirical and structural formulas applied to three compounds.

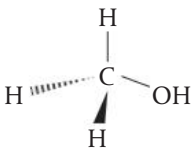
Compound	Ethane	Ethanoic acid	Glucose
Empirical formula	CH_3	CH_2O	CH_2O
Molecular formula	C_2H_6	$C_2H_4O_2$	$C_6H_{12}O_6$
Full structural formula			
Condensed structural formula	CH_3CH_3	CH_3COOH	$CHO(HCOH)_4CH_2OH$

A **stereochemical formula** attempts to show the relative positions of atoms and groups around a central carbon in three dimensions. The convention is that a bond sticking forwards from the page is shown as a solid wedge, whereas a bond sticking behind the page is shown as a dashed wedge. A bond in the plane of the paper is a solid line.

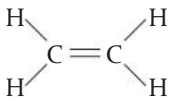


When carbon forms four single bonds, the arrangement is tetrahedral with bond angles of 109.5°. When it forms a double bond, the arrangement is triangular planar with bond angles of 120°.

methanol, CH_3OH



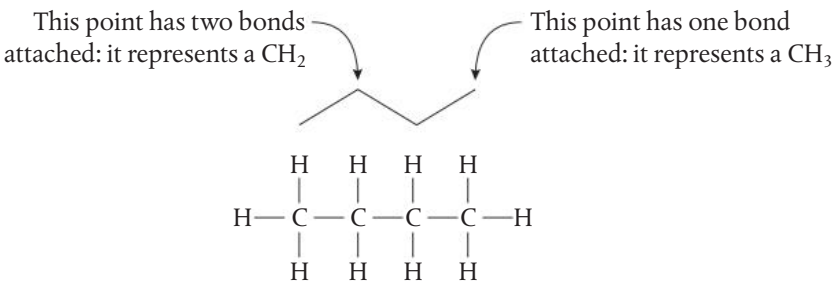
ethene, C_2H_4



A **skeletal formula** can be regarded as a shorthand representation of a structural formula. It shows all the bonds present in the molecule, except C–H bonds, and omits the element symbols for carbon and hydrogen atoms. The symbols of all atoms other than C and H are included along with the condensed formula of any functional groups present.

This results in a simpler visualization but it requires the user to become proficient with identifying the positions of carbon atoms, along with the numbers of hydrogens attached to each carbon, as this information is not readily apparent in the skeletal formula.

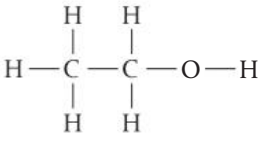
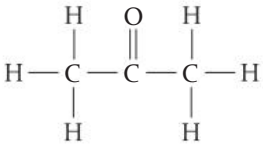
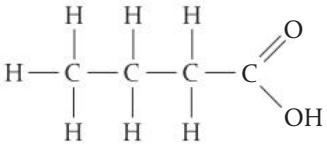
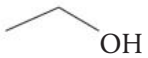
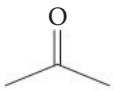
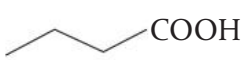
The skeletal structure of butane, C_4H_{10}, is compared to its full structural formula below:



C–C bonds in a carbon chain are represented as offset lines in a skeletal formula. The positions and numbers of carbon atoms present are identified by the points where bond lines meet or end.

Each carbon atom in an organic compound has four bonds. The number of hydrogen atoms attached to each carbon can therefore be determined by subtracting the number of bonds drawn to that atom from four. In the example of butane above, the point at the end of the skeletal structure has one bond drawn to it, therefore it has three H attached and represents a CH_3 group.

The table on the next page compares the condensed structural and skeletal formulas for three organic compounds.

Compound	Ethanol	Propanone	Butanoic acid
Molecular formula	C_2H_5OH	C_3H_6O	C_3H_7COOH
Full structural formula			
Condensed structural formula	CH_3CH_2OH	CH_3COCH_3	$CH_3CH_2CH_2COOH$
Skeletal formula			

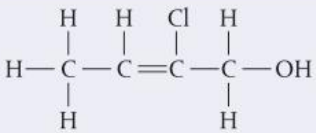
Sometimes we do not need to show the exact details of the hydrocarbon, or alkyl, part of the molecule in a structure, so we can abbreviate this to R. For molecules which contain a benzene ring, C_6H_6 (page 222), known as **aromatic compounds**, we use  to show the ring.

If you can identify primary, secondary and tertiary carbons (page 364) in a skeletal formula, this should help you to determine the number of hydrogens bonded to each carbon.

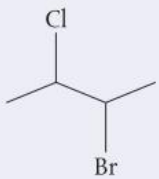
Be careful not to confuse structural and skeletal formulas. When a full structural formula is required, the element symbols of all carbon and hydrogen atoms must be included, along with the bonds between them.

Worked example

(i) Convert the following full structural formula to a skeletal formula.

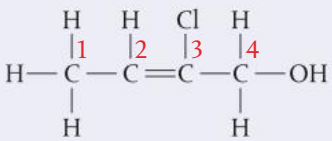


(ii) Convert the following skeletal formula to a condensed structural formula.

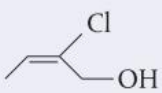


Solution

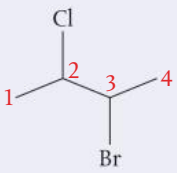
(i)



- Carbon 1 has only one bond that is not to a hydrogen atom so it can be represented as a point connected by a line to another point representing carbon 2.
- The double bond between carbons 2 and 3 must be represented as a double line.
- Carbon 3 has a bond to a non-hydrogen atom, Cl, which must be shown.
- Carbon 4 has an OH group attached so this also must be shown.



(ii)



- The point labelled 1 represents a carbon that has only one C–C bond so it must have three hydrogens attached.
- Point 2 represents a carbon with two C–C bonds and a C–Cl bond so it must have one hydrogen attached.
- Point 3 represents a carbon with two C–C bonds and a C–Br bond so it must also have one hydrogen attached.
- Point 4 is similar to point 1 and also represents a carbon that has one C–C bond and three hydrogens attached.

1 2 3 4
$CH_3CHClCHBrCH_3$

Construction of 3D models and working with virtual models online are important experiences that help in gaining an understanding of the structural concepts described in this chapter. Full details of a modelling activity are available in the eBook.

SKILLS

The use of physical and computer models can assist organic chemists in visualizing the three-dimensional shapes of compounds, which can also help explain their physical properties and chemical reactivity.

As we learn in Structure 1.3, common representations of atoms tend to be misleading as they do not accurately depict the true scale of the nucleus compared to the overall size of the atom. This is also true of modelling kits, along with ball-and-stick computer models, where nuclei are depicted as spheres or balls with relatively small distances between them.

Nature of Science, Structure 2.2 – What are the advantages and disadvantages of different depictions of an organic compound (e.g. structural formula, stereochemical formula, skeletal formula, 3D models)?

Challenge yourself

1. Based on experimental evidence, the bond length of a carbon–carbon single bond is 154 pm (1 pm = 10^{-12} m) and the radius of a carbon nucleus is 2.7×10^{-15} m. If modelling kits were made to scale, how long would the plastic stick representing a single bond need to be if the carbon nucleus was represented as a plastic ball with a 0.5 cm radius?



Students practising their chemistry can find modelling kits very useful in visualizing the shapes of molecules they encounter in class.



The two images above are different computer-generated models of dexamethasone, a drug used to treat arthritis. The *ball-and-stick* model on the left shows the nuclei of the atoms as 'balls' and the covalent bonds as 'sticks'. The *space-filling model* on the right shows the atoms as overlapping spheres whose sizes correspond to the atomic radii of each atom.

HL In Structure 2.2, we learn that carbon atoms are able to sp, sp^2 or sp^3 hybridize.

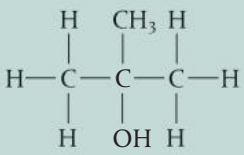
This allows carbon to form a variety of different compounds containing single, double or triple bonds. From the examples on previous pages illustrating the different structural representations of organic compounds, it should become apparent that carbon is unique among the elements for its ability to link to itself and form chains of bonded carbon atoms, as well as ring structures such as benzene. This ability, known as **catenation**, is one of the main reasons for the vast number of organic compounds that exist. As we continue through this chapter, we will see that the possibility for carbon chains to be branched, and for compounds to contain one or more functional groups or substituents, further increases the incredible variety of organic compounds that are possible.

Structure 2.2 – What is unique about carbon that enables it to form more compounds than the sum of all the other elements' compounds?

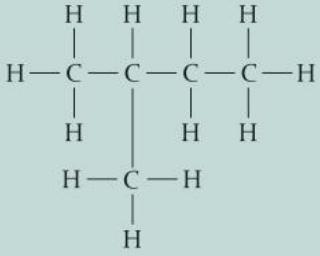
Exercise

Q1. Convert the following full structural formulas to condensed structural formulas.

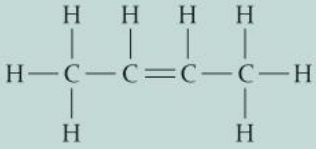
(a)



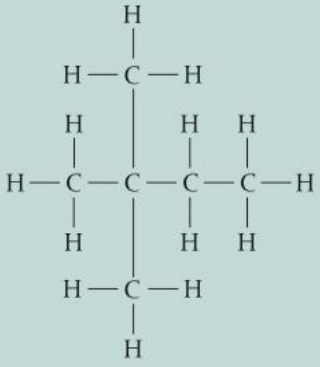
(b)



(c)



(d)



Q2. Convert the following condensed structural formulas to skeletal formulas.

(a) $CH_3CH(CH_3)CH_3$

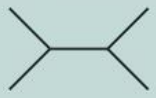
(b) $CH_2OHCH_2CH_2CH_2Cl$

(c) $CHClCHCH_3$

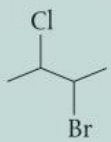
(d) $CH_3C(CH_3)_2CH_2CH_3$

Q3. Convert the following skeletal formulas to condensed structural formulas.

(a)



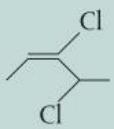
(b)



(c)



(d)



Structure 3.2.2 – Functional groups and classes of compounds

Structure 3.2.2 – Functional groups give characteristic physical and chemical properties to a compound. Organic compounds are divided into classes according to the functional groups present in their molecules.

Identify the following functional groups by name and structure: halogeno, hydroxyl, carbonyl, carboxyl, alkoxy, amino, amido, ester, phenyl.

The terms 'saturated' and 'unsaturated' should be included.

HL Structure 2.4 – What is the nature of the reaction that occurs when two amino acids form a dipeptide?

Nature of Science, Reactivity 3.2, 3.4 – How can functional group reactivity be used to determine a reaction pathway between compounds, e.g. converting ethane into ethanoic acid?

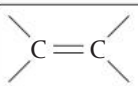
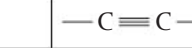
Different classes of organic compounds contain different functional groups

Functional groups are atoms, or groups of atoms, that are present in organic compounds and are responsible for a compound's physical properties and chemical reactivity. Compounds that contain the same functional group belong to the same **class**. For example, the class of organic compounds called **carboxylic acids** contain the **–COOH** functional group.

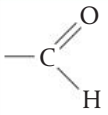
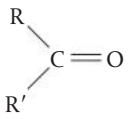
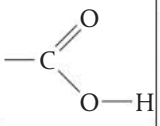
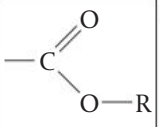
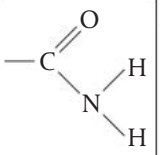
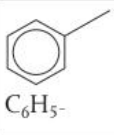
The table below gives common classes of organic compounds along with the formula and name of the functional group that defines each class. The table also includes the suffix (or prefix) specific to each class when using IUPAC nomenclature to name a compound as well as the general formula that describes the compounds belonging to each class.

For certain classes, the general formula has been given as $C_xH_yO_z$ to show the overall chemical formula and also using R and R′ to represent alkyl chains that are linked by functional groups. This format can help distinguish between classes such as aldehydes and ketones that have the same overall formula.

3.2 Table 1 Important classes of organic compounds along with their associated functional groups, IUPAC suffixes and general formulas. The table is continued on the next page.

Class	Functional group	Name of functional group	Suffix in IUPAC name	Example of compound	General formula
alkane			-ane	C_2H_6, ethane	C_nH_{2n+2}
alkene		alkenyl	-ene	$H_2C{=}CH_2$, ethene	C_nH_{2n}
alkyne		alkynyl	-yne	HC≡CH, ethyne	C_nH_{2n-2}
alcohol	**–OH**	hydroxyl	-anol	C_2H_5OH, ethanol	$C_nH_{2n+1}OH$
ether	**R–O–R′**	alkoxy	-oxyalkane	$H_3C–O–C_2H_5$, methoxyethane	$C_nH_{2n+2}O$ R–O–R′

continued

Class	Functional group	Name of functional group	Suffix in IUPAC name	Example of compound	General formula
aldehyde		carbonyl (aldehyde)	-anal	C_2H_5CHO, propanal	$C_nH_{2n}O$ R–CHO
ketone		carbonyl (ketone)	-anone	CH_3COCH_3, propanone	$C_nH_{2n}O$ R–CO–R′
carboxylic acid		carboxyl (acid)	-anoic acid	C_2H_5COOH, propanoic acid	$C_nH_{2n+1}COOH$
ester		carboxyl (ester)	-anoate	$C_2H_5COOCH_3$, methyl propanoate	$C_nH_{2n}O_2$ R–COO–R′
amide		amido	-anamide	$C_2H_5CONH_2$, propanamide	$C_nH_{2n+1}CONH_2$
amine	**–NH_2**	amino	-anamine	$C_2H_5NH_2$, ethanamine	$C_nH_{2n+1}NH_2$
halogenoalkane*	**–F, –Cl, –Br, –I**	halogeno	fluoro, chloro, bromo, iodo (prefixes, not suffixes. See below)	C_2H_5Cl, chloroethane $CH_3CH_2BrCH_3$, 2-bromopropane	$C_nH_{2n+1}X$ X = F, Cl, Br, I
arene**	 C_6H_5-	phenyl	-benzene	$C_6H_5CH_3$, methylbenzene	

* For halogenoalkane compounds, the halogen atoms are regarded as **substituents** as they have taken the position of a hydrogen atom.

When applying IUPAC nomenclature, substituents such as halogens are typically identified using prefixes: chloroethane, 2-bromopropane etc.

** The syllabus does not require knowledge of arenes as a class of compounds, but you are expected to recognize the phenyl group when it is present in a structure. The naming of compounds containing a phenyl group is also not required knowledge.

Although there will only be one systematic IUPAC name, compounds containing phenyl groups often have alternative names. Methylbenzene (IUPAC name) consists of a methyl group (–CH_3) attached to a phenyl group (–C_6H_5) and it is therefore also known as phenylmethane. Historically, it was known as toluene and this name is still in common use.



Methylbenzene is used as a solvent in many applications, including markers, paint thinners, industrial cleaners and glues.

Quickly sketching the full structural formula can sometimes make it easier to identify the functional groups and structural features of an organic compound.

One important way of classifying organic compounds is by their **saturation**. Compounds that are **saturated** only contain single bonds whereas **unsaturated** compounds contain double or triple bonds. As we see in Reactivity 3.3 and 3.4, saturated and unsaturated compounds undergo different types of reactions.



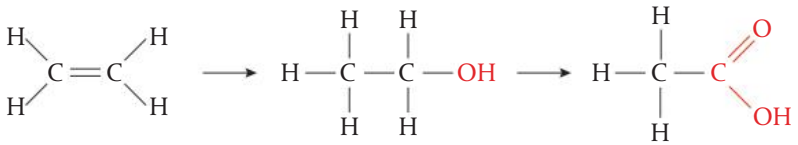
Food sources rich in unsaturated fats. Fats are biological compounds that contain long carbon chains which, in unsaturated fats, include multiple double bonds. The World Health Organization and other health agencies recommend diets higher in unsaturated fats than saturated fats due to a decreased risk of cardiovascular disease.

Functional groups influence the chemical reactivity of organic compounds

Nature of Science, Reactivity 3.2, 3.4 – How can functional group reactivity be used to determine a reaction pathway between compounds, e.g. converting ethene into ethanoic acid?

In Reactivity 3.2–3.4, we learn in more detail about different chemical reactions that occur for compounds with specific functional groups. Synthetic organic chemists can use their knowledge of these reactions to synthesize target compounds from readily available starting materials. This often requires organizing several reactions in sequence so that the product of one reaction is the reactant of the next. Each step will typically involve a functional group interconversion and the series of discrete steps is known as a **reaction pathway**.

For example, ethene (C_2H_4) can be converted into ethanoic acid (CH_3COOH) via a two-step reaction pathway where ethanol (CH_3CH_2OH) is formed as a product in the first step and then used as a reactant in the second step.



ethene ethanol ethanoic acid

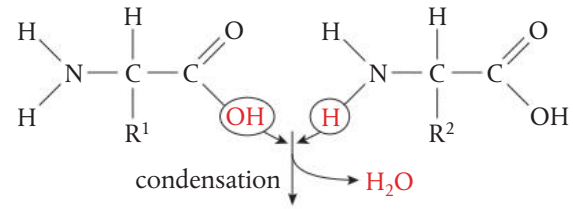
Amino acids link together when condensation reactions occur between their functional groups

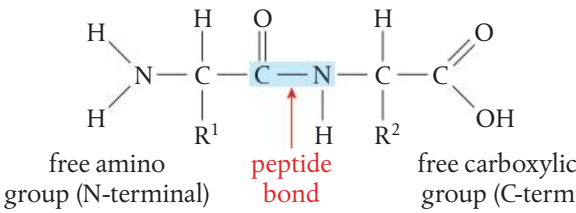
The reaction of two amino acids with each other provides a specific example of how functional groups on different molecules can react via a specific type of reaction to give a new class of product.

Amino acids each contain two functional groups, an amine group ($–NH_2$) and a carboxylic acid group (–COOH). As shown on the next page, these two groups are able to react together in a **condensation reaction** in which a molecule of water is eliminated and a new bond is formed between the acid group of one amino acid and the amino group of the other. This bond is a substituted **amide link** known as a **peptide bond**, and two amino acids linked in this way form an amide product known as a **dipeptide**.



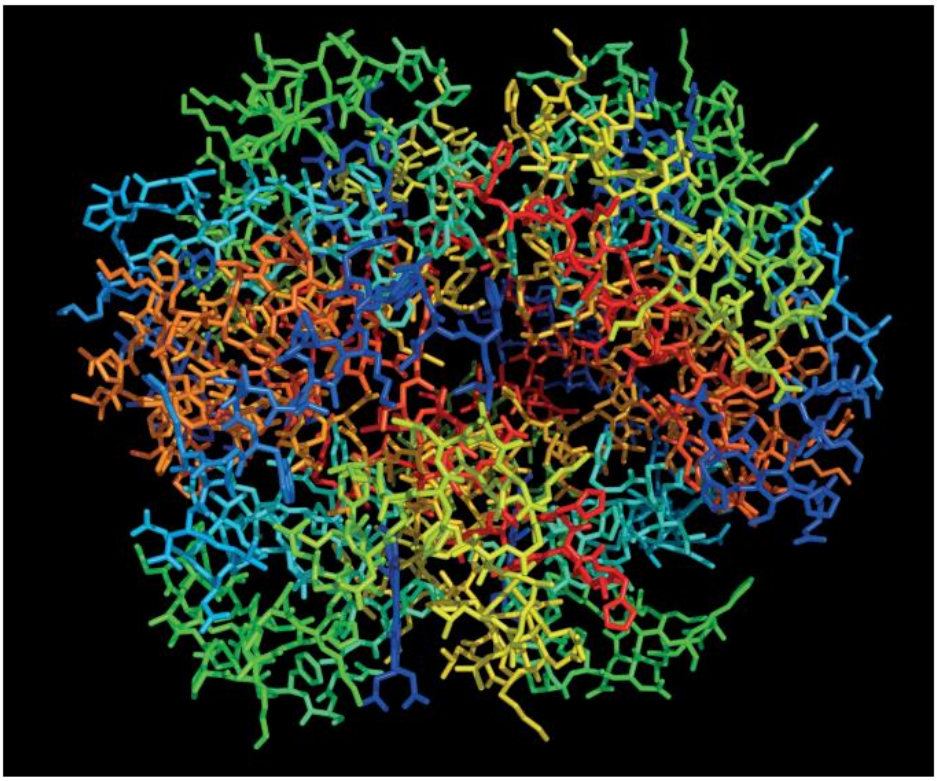
Ethanoic acid is an important industrial chemical. One major use involves its conversion to vinyl acetate and the production of polymers, such as polyvinyl acetate (PVA) which is used in many glues. A fun home use of PVA glue is making artificial slime.





We can see that the dipeptide still has a functional group at each end of the molecule, with $-NH_2$ at one end and –COOH at the other. So it can react again by another condensation reaction, forming a **tripeptide** and eventually a chain of many linked amino acids known as a **polypeptide**.

HL Structure 2.4 – What is the nature of the reaction that occurs when two amino acids form a dipeptide?



Haemoglobin is a metalloprotein that transports oxygen in the bloodstream. The structure of haemoglobin includes four subunits which are folded polypeptide chains.

Exercise

Q4. For each of the following molecules, give its class and the name of its functional group:

(a) CH_3CH_2COOH
(b) $CH_3CHCHCH_3$
(c) $CH_2OHCH_2CH_2CH_3$
(d) CH_3COOCH_3
(e) CH_3CH_2CHO
(f) $CH_3NH(CH_3)$

Q5. Which of the following is an amide?

A $CH_3NH(CH_3)$ **B** CH_3CONH_2

C $CH_3CH_2NH(CH_3)$ **D** $CH_3CH_2COOCH_3$

Q6. Which of the following is an ester?

A CH_3COCH_3 **B** $CH_3COCH_2NH_2$

C $CH_3CH(OH)CH_3$ **D** $CH_3COOCH_2CH_3$

Structure 3.2.3 and 3.2.4 – Homologous series

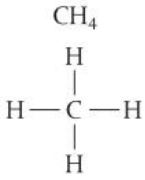
Structure 3.2.3 – A homologous series is a family of compounds in which successive members differ by a common structural unit, typically CH_2. Each homologous series can be described by a general formula. Identify the following homologous series: alkanes, alkenes, alkynes, halogenoalkanes, alcohols, aldehydes, ketones, carboxylic acids, ethers, amines, amides and esters.	
	Nature of Science, Tool 2 – How useful are 3D models (real or virtual) to visualize the invisible?

Structure 3.2.4 – Successive members of a homologous series show a trend in physical properties. Describe and explain the trend in melting and boiling points of members of a homologous series.	
	Structure 2.2 – What is the influence of the carbon chain length, branching and the nature of the functional groups on intermolecular forces?

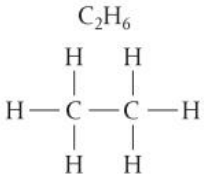
Homologous series differ by a CH_2 group

Organic compounds are classified into 'families' of compounds known as **homologous series**. The members of each such series possess certain common features, as described below.

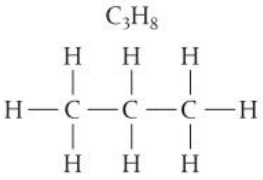
Consider the following compounds of carbon and hydrogen where the carbons are all bonded by single covalent bonds.



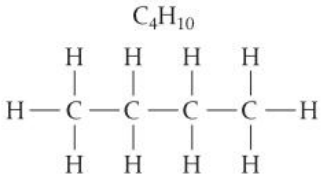
methane



ethane



propane



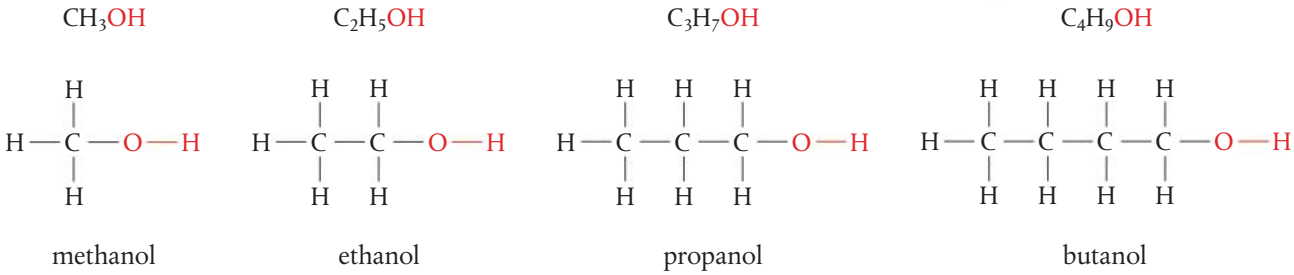
butane

These are members of a homologous series known as the **alkanes**. It can be seen that neighbouring members differ from each other by $-CH_2-$. This same increment applies to successive members of each homologous series, and means that the molecular mass increases by a fixed amount as we go up a series.

Members of a homologous series can be represented by the same general formula

The four alkanes shown on the previous page can all be represented by the general formula C_nH_{2n+2}

Other homologous series are characterized by the presence of a particular functional group, and this will be shown in the general formula for the series. For example, the homologous series known as the **alcohols** possesses the functional group –OH as shown below.



The four alcohols shown above can all be represented by the general formula $C_nH_{2n+1}OH$.

General formulas for the homologous series of other classes of organic compounds have been provided in Table 1 on pages 348–349.

Members of a homologous series show a trend in physical properties

As successive members of a homologous series differ by a $–CH_2–$ group, they have successively longer carbon chains. This is reflected in a gradual trend in the physical properties of the members of the series. For example, the effect of the length of the carbon chain on the boiling point of three classes of compounds, alkanes, chloroalkanes and alcohols is shown in the table below.

3.2 Table 2 Boiling points for the first eight members in the homologous series of alkanes, chloroalkanes and alcohols.

Alkane		Boiling point / °C	Chloroalkane		Boiling point / °C	Alcohol		Boiling point / °C
methane	CH_4	−164	chloromethane	CH_3Cl	−24	methanol	CH_3OH	65
ethane	C_2H_6	−89	chloroethane	C_2H_5Cl	12	ethanol	C_2H_5OH	78
propane	C_3H_8	−42	1-chloropropane	C_3H_7Cl	46	propan-1-ol	C_3H_7OH	97
butane	C_4H_{10}	−0.5	1-chlorobutane	C_4H_9Cl	78	butan-1-ol	C_4H_9OH	118
pentane	C_5H_{12}	36	1-chloropentane	$C_5H_{11}Cl$	108	pentan-1-ol	$C_5H_{11}OH$	138
hexane	C_6H_{14}	69	1-chlorohexane	$C_6H_{13}Cl$	135	hexan-1-ol	$C_6H_{13}OH$	156
heptane	C_7H_{16}	98	1-chloroheptane	$C_7H_{15}Cl$	159	heptan-1-ol	$C_7H_{15}OH$	176
octane	C_8H_{18}	125	1-chlorooctane	$C_8H_{17}Cl$	182	octan-1-ol	$C_8H_{17}OH$	194

The compounds shaded in yellow exist as gases at room temperature and those shaded in green exist as liquids at room temperature.

The trend in boiling points of the alkanes is of great significance in the oil industry, as it makes it possible to separate the many components of crude oil into **fractions** that contain molecules of similar molecular mass on the basis of their boiling points. As the crude oil is heated, the smaller hydrocarbons boil off first while larger molecules distil at progressively higher temperatures in the fractionating column. The different fractions are used as fuels, industrial lubricants, and as starting molecules in the manufacture of synthetic compounds.

The data for each class of compound in Table 2 show that boiling point increases with increasing carbon number. This is because a longer chain length increases both the instantaneous and induced dipoles occurring, which then results in stronger London dispersion forces, and therefore stronger overall intermolecular forces, between the molecules.

Other physical properties that show this predictable trend with increasing carbon number are melting point, density and viscosity.

Functional groups affect the physical properties of organic compounds

For the alkanes listed in Table 2, the increase in boiling point is not linear, but steeper near the beginning as the influence of the increased chain length is proportionally greater for small molecules. For the chloroalkanes and alcohols, there is a more consistent increase in boiling point with carbon chain length. This is because the strongest intermolecular forces present are associated with their functional groups rather than carbon chain length.

Owing to their different polarities and resulting differences in intermolecular forces, functional groups have a significant effect on physical properties. One such property is volatility and the effect of different functional groups on volatility can be summarized as follows.

Volatility is a term used to describe the tendency of a substance to vaporize. Substances with strong intermolecular forces have a high boiling point and a low volatility.

most volatile **least volatile**

alkane > **halogenoalkane** > **aldehyde** > **ketone** > **alcohol** > **carboxylic acid**

London (dispersion) force → dipole–dipole interaction → hydrogen bonding

increasing strength of intermolecular attraction →

increasing boiling point →

If we look across any row in Table 2, the compounds listed have the same number of carbons but their boiling points increase in the order: alkane < chloroalkane < alcohol. This is consistent with the strength of the intermolecular forces present due to the different functional groups in these compounds: London dispersion forces (alkane) < dipole–dipole (chloroalkane) < hydrogen bonding (alcohol). As Table 2 shows, the hydrogen bonding present in alcohols is so strong that even the smallest alcohol, methanol (CH_3OH), is a liquid at room temperature.

Structure 2.2 – What is the influence of the carbon chain length, branching and the nature of the functional groups on intermolecular forces?

In this section we have seen that both chain length and the functional groups present affect the nature of the intermolecular forces in a compound. Longer chains result in increased London dispersion forces and polar functional groups result in dipole–dipole interactions or hydrogen bonding. In the next section we will see that branching of the carbon chain in a compound also affects intermolecular forces as it results in weaker London dispersion forces.

Exercise

Q7. Which of the following is a member of the same homologous series as butanoic acid, $CH_3CH_2CH_2COOH$?

A $CH_3CH_2COOCH_3$ **B** $CH_3CH_2CH_3$

C $CH_3OCH_2CH_3$ **D** CH_3COOH

Q8. Which of the following pairs of compounds belong to the same homologous series?

I. CH_3CH_2Cl, $CH_2ClCH_2CH_2CH_3$

II. CH_3CH_2Br, $CH_2ClCH_2CH_3$

III. CH_3CH_2Br, CH_2BrCH_2Br

A I only **B** I and III **C** III only **D** I, II and III

Q9. Which option ranks the compounds in order of increasing boiling point?

A $CH_3CH_2COOH < CH_3CH_2CH_3 < CH_3CH_2CH_2F$

B $CH_3CH_3 < CH_3COOH < CH_3CH_2COOH$

C $CH_3COOH < CH_3COOCH_3 < CH_3COCH_3$

Q10. Rank the following compounds in order of increasing volatility and provide an explanation for your answer.

bromopropane ($CH_3CH_2CH_2Br$); propanoic acid (CH_3CH_2COOH); propane ($CH_3CH_2CH_3$)

Q11. Predict how the aqueous solubility of the alcohols changes with increasing chain length and provide a reason for your answer.

Structure 3.2.5 – IUPAC nomenclature

Structure 3.2.5 – 'IUPAC nomenclature' refers to a set of rules used by the International Union of Pure and Applied Chemistry to apply systematic names to organic and inorganic compounds.	
Apply IUPAC nomenclature to saturated or mono-unsaturated compounds that have up to six carbon atoms in the parent chain and contain one type of the following functional groups: halogeno, hydroxyl, carbonyl, carboxyl.	
Include straight and branched-chain isomers.	

Unique names for organic compounds are derived using IUPAC nomenclature

For over a hundred years, chemists have recognized the need for a specific set of rules for the naming of organic compounds. Rules developed by the IUPAC generate names that are logically based on the chemistry of the compounds, and so give information about the functional groups present and the size of the molecules.

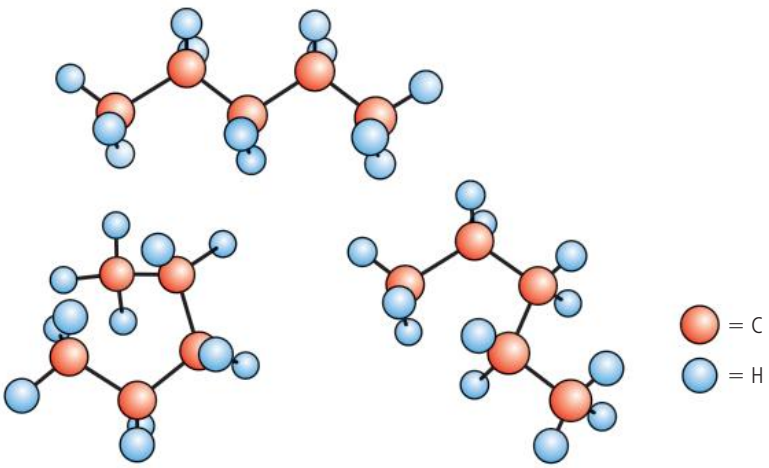
Some guidelines for applying the IUPAC nomenclature are discussed below.

Rule 1: Identify the longest straight chain of carbon atoms

The longest chain of carbon atoms gives the **stem** of the name as follows.

Number of carbon atoms in longest chain	Stem in IUPAC name	Example of compound
1	meth-	CH_4, methane
2	eth-	C_2H_6, ethane
3	prop-	C_3H_8, propane
4	but-	C_4H_{10}, butane
5	pent-	C_5H_{12}, pentane
6	hex-	C_6H_{14}, hexane

Note that 'straight chain' refers to continuous or unbranched chains of carbon atoms – it does not mean angles of 180°. Be careful when identifying the longest straight chain not to be confused by the way the molecule may appear on paper, because of the free rotation around carbon–carbon single bonds. For example, in Figure 1 all three structures are the same straight-chain molecule pentane, C_5H_{12}, even though they may look different.



S3.2 Figure 1 Different representations of the same molecule, C_5H_{12}, pentane. These can all be interconverted by rotating the carbon–carbon bonds.

Rule 2: Identify the functional group

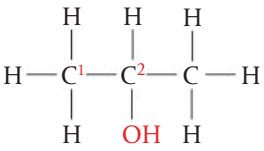
The functional group usually determines the specific ending or **suffix** to the name, which replaces the '-ane' ending in the parent alk*ane*. The suffixes used for some common functional groups are shown in Table 1 on pages 348–349. Note the distinction between class, which refers to the type of compound, and functional group, which refers to the site of reactivity in the molecule.

You are expected to be familiar with the nitrogen-containing functional groups at the bottom of Table 1 on page 349 (amine and amide), but nomenclature of these classes of compounds will not be assessed.

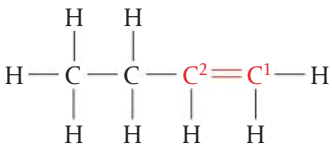
Remember that the name for the stem is derived from the ***longest*** carbon chain, which may include the carbon of the functional group. Look at Table 1 on pages 348–349 and see how this applies to carboxylic acids and their derivatives (esters and amides).

The position of a functional group is shown by a number between dashes inserted before the functional group ending. The number refers to the carbon atom to which the functional group is attached. *The chain is always numbered starting at the end that will give the smallest number to the group.*

For example:



propan-2-ol

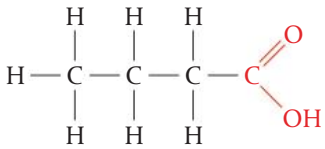


but-1-ene

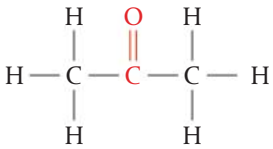
As shown in the structure of but-1-ene above, here we number the carbon chain starting from the right-hand side so that the number of the group will be 1 and not 3.

Sometimes a functional group can only be in one place; in these cases we do not need to give a number to show its position.

For example, the carboxylic acid group must always be at the end of a chain so it does not need a number assigned. A ketone with three carbons has only one possible position for the carbonyl group so it also does not need a number assigned.



butanoic acid



propanone

Rule 3: Identify the side chains or substituent groups

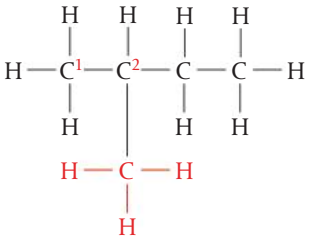
Side chains, or functional groups in addition to the one used as the suffix, are known as **substituents** and are given as the first part or **prefix** of the name. Some common examples are shown in the table below.

Class	Functional group	Name of functional group	Prefix in IUPAC name	Example of compound
alkane			methyl, ethyl, propyl etc.	$CH_3CH(CH_3)C_2H_5$, 2-methylbutane $CH(C_2H_5)_3$, 3-ethylpentane $CH(C_3H_7)_3$, 4-propylheptane
halogenoalkane	–F, –Cl, –Br, –I	halogeno	fluoro, chloro, bromo, iodo	C_2H_5Cl, chloroethane $CH_3CH_2BrCH_3$, 2-bromopropane
amine	$–NH_2$	amine	amino	$CH_2(NH_2)COOH$, 2-aminoethanoic acid

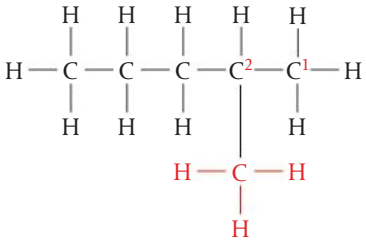
You will notice that $–NH_2$ appears as both a possible suffix in Table 1 on pages 348–349and a prefix in the table above. Usually when it is the only functional group it will take the suffix, but if there are two or more functional groups in the molecule it will be a prefix, as for example in *amino* acids.

As shown in the table on the previous page, the position of the substituent groups is given by a number followed by a dash in front of its name showing the carbon atom to which it is attached, again numbering the chain to give the smallest number to the group.

For example:



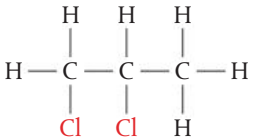
2-methylbutane



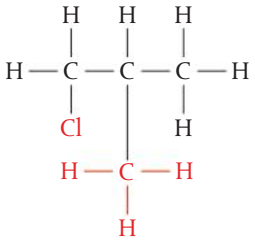
2-methylpentane

If there is more than one substituent group of the same type, we use commas between the numbers and the prefixes di-, tri-, or tetra- before the name. Substituents are given in order of the number of the carbon atom to which they are attached; if there is more than one group on the same atom they are put in alphabetical order.

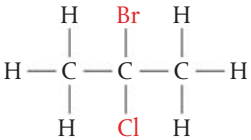
For example:



1,2-dichloropropane



1-chloro-2-methylpropane



2-bromo-2-chloropropane

When carboxylic acids lose H^+ they become **alkanoate ions.** In naming esters this also applies to the parent acid the ester is made from: methanoic acid (HCOOH) becomes methanoate ($HCOO^-$) in the ester; propanoic acid (CH_3CH_2COOH) becomes propanoate ($CH_3CH_2COO^-$) etc.

Naming esters and ethers

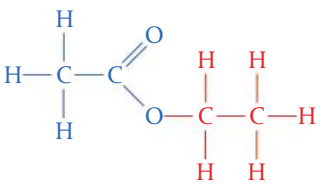
Esters

Esters form when the alkyl group of an alcohol replaces the hydrogen of a carboxylic acid in a condensation reaction:

$$R–COOH + R'OH \rightarrow R–COO–R' + H_2O$$

Esters are named in a similar way to salts, which form when a metal has replaced the hydrogen of a carboxylic acid. Salts take the stem of the name from the parent acid and the prefix is the cation. For example, CH_3COONa is sodium ethanoate.

In esters, the stem still comes from the parent acid but the alkyl group of the alcohol is the prefix. The ester made from the reaction of ethanol with ethanoic acid will be ethyl ethanoate, $CH_3COOCH_2CH_3$.



ethyl ethanoate



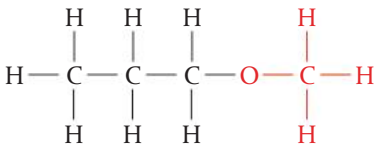
A selection of fresh fruits. The distinctive tastes and smells of fruits and berries are typically caused by ester compounds.

Ethers

Ethers consist of two alkyl chains linked by an oxygen atom (R–O–R′).

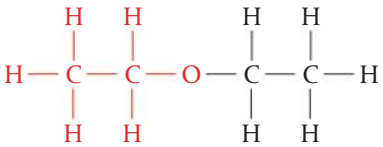
When naming ethers:

- the longer chain will be the stem and retains its alkane name
- the shorter chain is regarded as a substituent and is given the prefix alkoxy.



methoxypropane

When the two chains are the same length, then one is assigned as the alkane stem and the other becomes the substituent.



ethoxyethane



A selection of foods rich in carbohydrates. Carbohydrates are complex sugars with individual sugar units (saccharides) joined by ether linkages.

Ethers are used commercially as solvents and in the production of polymers. They are also used for medicinal purposes such as antiseptics and some of the first anaesthetics were ethers.



The ether monument in Boston, USA. It commemorates the first use of ethoxyethane (diethyl ether) as an anaesthetic, as well as the many lives saved through surgical procedures only possible with the use of anaesthesia.

Nature of Science

Classification is an important aspect of many disciplines as it brings some order to large amounts of data, and helps in the recognition of patterns and trends. In organic chemistry, classification is particularly helpful given the almost infinite number of compounds. The IUPAC nomenclature system described earlier is broadly accepted by scientists because it provides effective communication. Yet, in common with most systems of classification, there are limits to its usefulness. One of these limits is in biochemistry, where IUPAC nomenclature can result in seemingly complex and extended names for relatively simple molecules. For example, sucrose, $C_{12}H_{22}O_{11}$, becomes (2*R*,3*R*,4*S*,5*S*,6*R*)-2-[(2*S*,3*S*,4*S*,5*R*)-3,4-dihydroxy-2,5-bis(hydroxymethyl) oxolan-2-yl]oxy-6-(hydroxymethyl)oxane-3,4,5-triol. Although there is a place for such terminology, it is not widely used. Classification and nomenclature are artificial constructs, and when not helpful need not be used. Throughout this book we will commonly use non-IUPAC names for biological molecules for this reason.

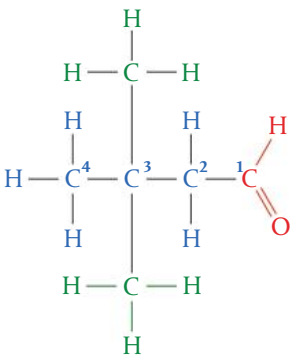
Nature of Science

As the study of organic chemistry has grown to include increasingly large and complex molecules, IUPAC nomenclature has had to adapt accordingly. New rules have been introduced with the identification of complex structural features that could not be named using earlier rules.

Summary of IUPAC nomenclature

In summary, IUPAC nomenclature has three possible parts, which are usually written together as a single word.

Prefix	.....	Stem	.....	Suffix
position, number and name of substituents		number of carbon atoms in longest chain		class of compound determined by functional group



3,3-dimethylbutanal

In the upcoming section on structural isomers you will encounter many examples of different organic compounds that have the same molecular formula (isomers). You should use these examples as an opportunity to confirm your ability to apply IUPAC rules and determine the correct systematic name for each isomer.

Exercise

Q12. For each of the following molecules, give its class and its IUPAC name.

(a) $CH_3CH_2CH(CH_3)CH_3$ **(b)** $CH_3CH(CH_3)COOH$

(c) $CH_3COCH_2CH_3$ **(d)** $CH_3COOCH_2CH_2CH_3$

(e) $CH_3CH_2CH_2OH$ **(f)** $CH_3CH_2CH_2CH_2CHO$

Q13. Give the structural formulas for the following molecules (condensed form is acceptable).

(a) methanoic acid
(b) hex-3-yne
(c) 3-ethylpentanal
(d) 3-methylbutan-2-one
(e) ethoxypropane
(f) 2-bromopropan-1-ol

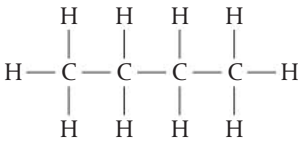
Q14. A student draws the structure of what they believe is 2-ethylpentane. Draw the structure that is consistent with this name and then determine the correct IUPAC name for this compound.

Structure 3.2.6 – Structural isomers

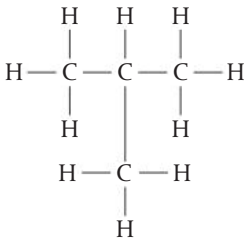
Structure 3.2.6 – Structural isomers are molecules which have the same molecular formula but different connectivities.	
Recognize isomers, including branched, straight-chain, position and functional group isomers.	
Primary, secondary and tertiary alcohols, halogenoalkanes and amines should be included.	HL Structure 2.2 – How does the fact that there are only 3 isomers of dibromobenzene support the current model of benzene's structure?

Organic compounds with the same molecular formula can have different structures

The molecular formula of a compound shows the atoms that are present in the molecule, but gives no information on how they are arranged. Consider for example the formula C_4H_{10}. There are two possible arrangements for these atoms that correspond to different molecules with different properties.



butane,
boiling point –0.5 °C



2-methylpropane,
boiling point –11.7 °C

Such molecules, having the same molecular formula but different arrangements of the atoms, are known as **structural isomers**.

Structural isomers are molecules that have the same molecular formula but different arrangements of the atoms. Because of their different structures, they also have different physical and chemical properties.



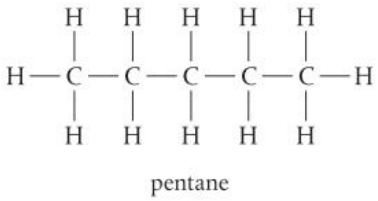
Molecular models of the two isomers of C_4H_{10}. On the left is butane (sometimes called *n*-butane to denote a straight chain), and on the right is 2-methylpropane.

The number of isomers that exist for a molecular formula increases as the molecular size increases. In fact, the increase is exponential; there are 75 possible isomers of $C_{10}H_{22}$ and 366 319 isomers of $C_{20}H_{42}$!

Each isomer is a distinct compound, having unique physical and chemical properties. As we will see, the number of isomers that exist for a molecular formula increases with the size of the molecule. This is one of the reasons for the vast number of compounds that can be formed from carbon.

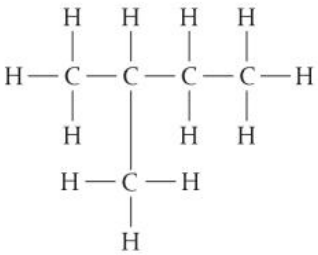
Alkanes can have straight chain or branched structural isomers

As we saw on the previous page, butane, C_4H_{10}, has two structural isomers, one that forms a straight chain and another that has a branched structure. Pentane, C_5H_{12}, has three structural isomers as shown below.



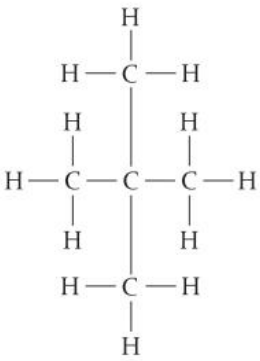
pentane

straight chain
boiling point 36.1 °C



2-methylbutane

one branch
boiling point 27.8 °C



2,2-dimethylpropane

two branches
boiling point 9.5 °C

From the examples of C_4H_{10} and C_5H_{12} we can see a trend in the boiling points of their isomers: *the more branching that is present in an isomer, the lower its boiling point.*

Branching of the hydrocarbon chain influences the strength of the London dispersion forces occurring between neighbouring molecules because it reduces the amount of surface contact. Think, for example, how tree logs with lots of branches sticking out cannot stack together as closely as a pile of logs which have no branches. In a similar way, branched-chain isomers have less contact with each other than their straight-chain isomers. This results in weaker attractions between instantaneous and induced dipoles on neighbouring molecules with weaker overall London dispersion forces and lower boiling points.

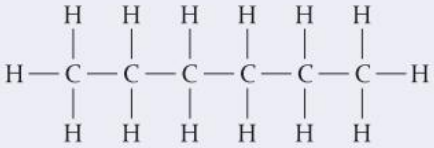
The existence of these different straight-chain and branched-chain isomers of the alkanes is of great significance in the petroleum industry. It has been found that branched-chain isomers generally burn more smoothly in internal combustion engines than straight-chain isomers, and so oil fractions with a higher proportion of these branched-chain isomers are considered to be of 'better grade'. This is often referred to as a higher 'octane number' and means that it fetches a higher price at the pump.

Worked example

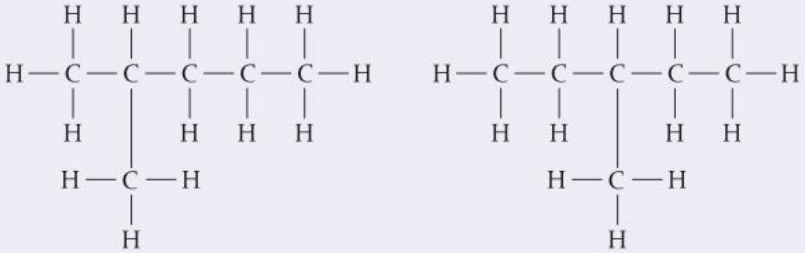
Draw full structural formulas for the five different structural isomers of hexane, C_6H_{14}.

Solution

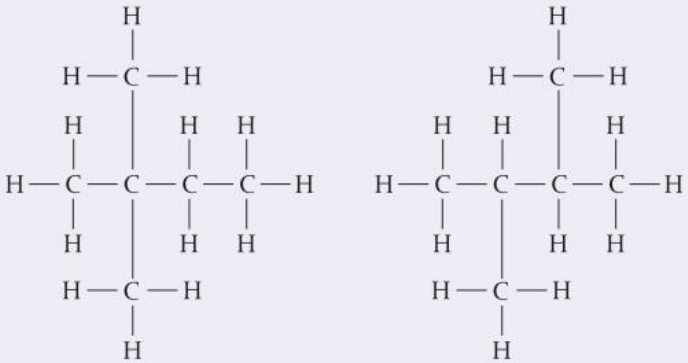
When identifying structural isomers for a given formula it is best to start with the longest possible chain and then progress through the possibilities with successively shorter chain lengths. C_6H_{14} has one straight chain isomer:



There are two isomers with a five-carbon longest chain and one methyl branch:



There are two isomers with a four-carbon longest chain and two methyl branches:



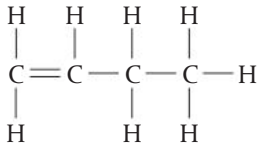
Challenge yourself

2. The Subject Guide only requires you to determine isomers for compounds containing up to six carbons in the longest chain. However, it can be beneficial to apply your knowledge to larger compounds. See if you can identify the nine structural isomers of heptane (C_7H_{16}).

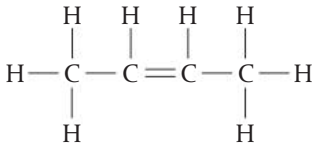
Alkenes can have positional structural isomers

Alkenes are a class of organic compounds that contain at least one carbon–carbon double bond. For alkanes, we saw that structural isomers can occur due to branching of the carbon chains. For alkenes, a different type of structural isomer can also occur, where the double bond is found in different positions.

C_4H_8 has the following straight-chain isomers:

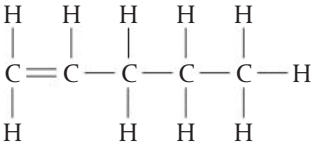


but-1-ene

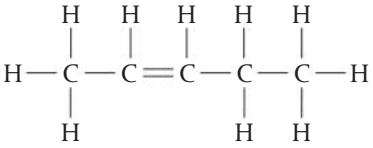


but-2-ene

C_5H_{10} has the following two straight-chain isomers:

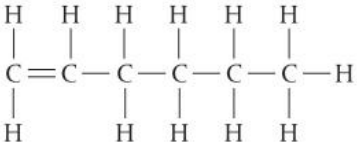


pent-1-ene

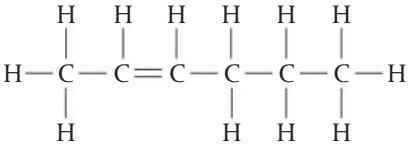


pent-2-ene

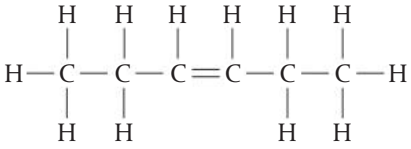
C_6H_{12} has the following three straight-chain isomers:



hex-1-ene



hex-2-ene



hex-3-ene

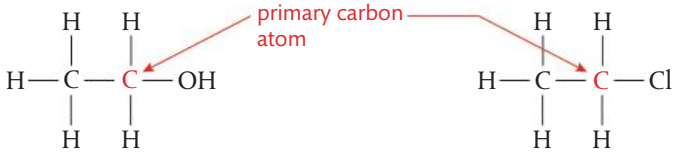
Similarly, the structures of the isomers of the alkynes, which contain at least one triple carbon–carbon bond, can be deduced by considering different possible positions for the triple bond.

Positional isomers for some classes of compounds can be classified as primary, secondary or tertiary compounds

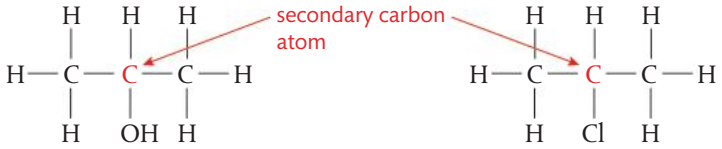
Structural isomers also occur in alcohols, halogenoalkanes and amines due to the position of their functional group. For these compounds, identifying different positional isomers is of particular importance as they can have significantly different chemical reactivity, as seen in Reactivity 3.2–3.4 for the oxidation reactions of alcohols and in Reactivity 3.4 for the substitution reactions of halogenoalkanes.

A **primary carbon atom** is attached to the functional group and also to at least two hydrogen atoms. Molecules with this arrangement are known as primary molecules.

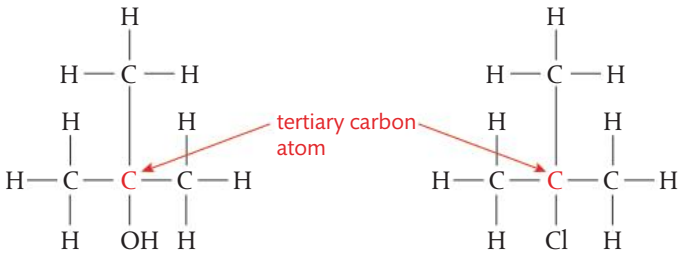
For example, ethanol, C_2H_5OH, is a primary alcohol and chloroethane, C_2H_5Cl, is a primary halogenoalkane.

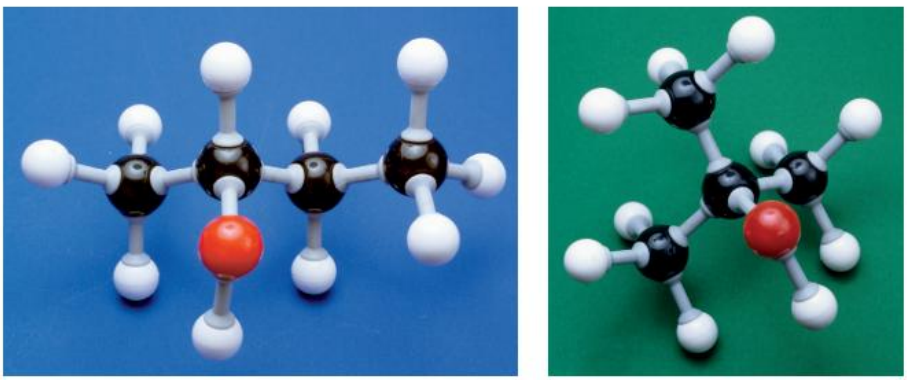


A **secondary carbon atom** is attached to the functional group and also to one hydrogen atom and two alkyl groups. These molecules are known as secondary molecules. For example, propan-2-ol, $CH_3CH(OH)CH_3$, is a secondary alcohol, and 2-chloroethane, $CH_3CHClCH_3$, is a secondary halogenoalkane.



A **tertiary carbon atom** is attached to the functional group and is also bonded to three alkyl groups and so has no hydrogen atoms. These molecules are known as tertiary molecules. For example, 2-methylpropan-2-ol, $C(CH_3)_3OH$, is a tertiary alcohol, and 2-chloro-2-methylpropane, $C(CH_3)_3Cl$, is a tertiary halogenoalkane.

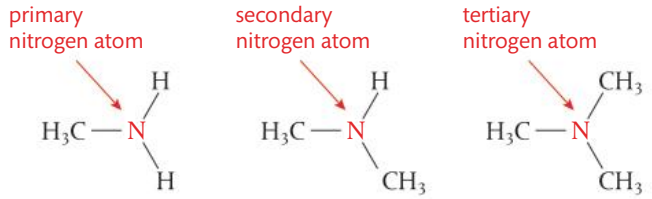




Butan-2-ol (left) and 2-methylpropan-2-ol (right) are two structural isomers with the formula C_4H_9OH. With molecular models it is easy to visualize their different structures and identify that butan-2-ol is a secondary alcohol and 2-methylpropan-2-ol is a tertiary alcohol. Carbon atoms are shown in black, hydrogen atoms are white and oxygen atoms are red.

In amines, a similar classification can be applied according to the number of alkyl groups and hydrogen atoms bonded to the nitrogen atom.

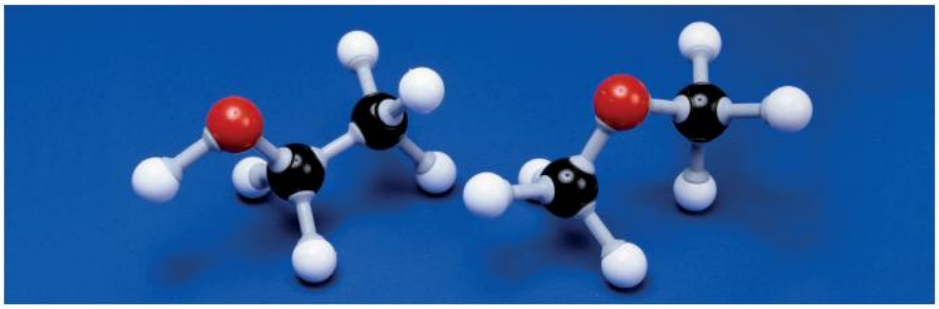
Type of amine	Primary	Secondary	Tertiary
Number of H atoms attached to central N	2	1	0
Number of C atoms attached to central N	1	2	3



Structural isomers can have different functional groups

There are many different types of isomers, including those in which the molecules have different functional groups and so are members of different classes of compounds with very different reactivities. For example, the molecular formula C_2H_6O describes both an alcohol and an ether, with models of these **functional group isomers** shown in the picture below.

Nature of Science, Tool 2 – How useful are 3D models (real or virtual) to visualize the invisible?



Methoxymethane (left) and ethanol (right) are functional group isomers, both with the molecular formula C_2H_6O. With the use of molecular models, it is easy to visualize the different functional groups in these molecules and explain their different physical and chemical properties. Ethanol is a liquid widely used in alcoholic drinks while methoxymethane is a gas used in aerosol propellants. Carbon atoms are represented here as black, hydrogen atoms are white and oxygen atoms are red.

HL

Disubstituted benzene compounds have structural isomers

The structure of benzene, C_6H_6, and its unique properties were introduced in Structure 2.2. Substituted benzene compounds are formed when hydrogen atoms in a benzene molecule are replaced by halogen atoms or a functional group including the amino (NH_2) or nitro groups (NO_2). The structures of some monosubstituted benzene compounds are shown below.



Intensely coloured azo-dye powders synthesized from phenylamine (aniline).



chlorobenzene



phenylamine



nitrobenzene

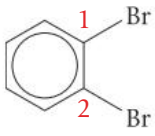
Phenylamine is also known as aminobenzene, aniline and benzenamine. The name phenylamine implies it consists of a phenyl group (C_6H_5) attached to an amine, aminobenzene implies it has an amino substituent (NH_2) attached to a benzene ring and aniline is its historical name. Benzenamine is the systematic IUPAC name but phenylamine is commonly preferred. Phenylamine is used in the manufacture of dyes and polyurethane, a widely used plastic.

One use of phenylamine (aniline) is in the production of synthetic azo-dyes. The first azo-dye was synthesized by William Perkin in 1856, but this was actually the result of an experiment that went wrong! Perkin had been attempting to convert phenylamine into quinine, a natural antimalarial drug, but instead he isolated an intensely purple-coloured product. Perkin recognized the significant potential of this product as a dye, which he subsequently called mauveine. He went on to synthesize and commercialize this and other azo-dyes, becoming a leading chemist in this field as well as a very wealthy man.

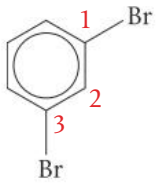
TOK

A common perception of scientific knowledge is that it develops through carefully planned experiments that test hypotheses and verify or refute currently accepted theories. In the example of William Perkin and mauveine, given on the previous page, his results were completely unexpected but led to the development of a new field of chemistry. What role does luck play in the advancement of science? Is there a single 'scientific method'?

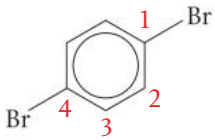
No structural isomers are possible for monosubstituted benzenes because all six positions in the hexagonal carbon ring are identical. However, three structural isomers are possible for disubstituted benzenes such as dibromobenzene, $C_6H_4Br_2$. These isomers differ due to the substituents occupying different positions on the benzene ring:



1,2-dibromobenzene



1,3-dibromobenzene



1,4-dibromobenzene

If benzene did exist as either a linear structure, containing double or triple bonds, or as 1,3,5-cyclohexatriene, with alternating single and double C–C bonds in the ring, then a large number of different structural isomers would be observed for its disubstituted compounds. The fact that only three distinct isomers are observed for disubstituted benzenes, shown above for dibromobenzene, provides additional support for the accepted model of benzene where it exists as a hexagonal ring with delocalized pi bonds and all C–C bonds having equal lengths.

Numbers are assigned to the ring positions of substituted benzenes so that the lowest possible numbers are obtained.

HL Structure 2.2 – How does the fact that there are only 3 isomers of dibromobenzene support the current model of benzene's structure?

Challenge yourself

3. Dimethylbenzene (xylene) has three structural isomers. Draw and name these isomers and predict which one would have the highest melting point.

HL end

Exercise

Q15. Which of the following pairs of compounds are structural isomers?

I. $CH_3CH_2CH_2CH_3$, $CH_3CH(CH_3)CH_3$

II. $CH_3CH_2CH_2CH_3$, $CH_3CH_2CH_3$

III. $CH_3CH_2CH_2CH_2OH$, $CH_3CH(CH_3)CH_2OH$,

A I only **B** I, II and III **C** III only **D** I and III

Q16. Pentyne, C_5H_8, contains a triple bond.

(a) Draw two positional isomers of pentyne.

(b) Draw a third structural isomer of pentyne that is not a positional isomer of the two isomers you drew for part **(a)**.

Q17. Which of the following compounds contains a secondary carbon.

A $CH_3CH_2CH_2CH_2OH$ **B** $CH_3CHF(CH_3)CH_2CH_3$

C $CH_2BrCH_2CH_2CH_2OH$ **D** $CH_3CH_2CHClCH_3$

Q18. Draw and name the structural isomers of bromobutane, C_4H_9Br, and identify each isomer as being primary, secondary or tertiary.

Q19. Draw and name two different functional group isomers that can have the following molecular formulas:

(a) C_3H_8O **(b)** C_3H_6O **(c)** $C_3H_6O_2$

HL

Structure 3.2.7 – Stereoisomers

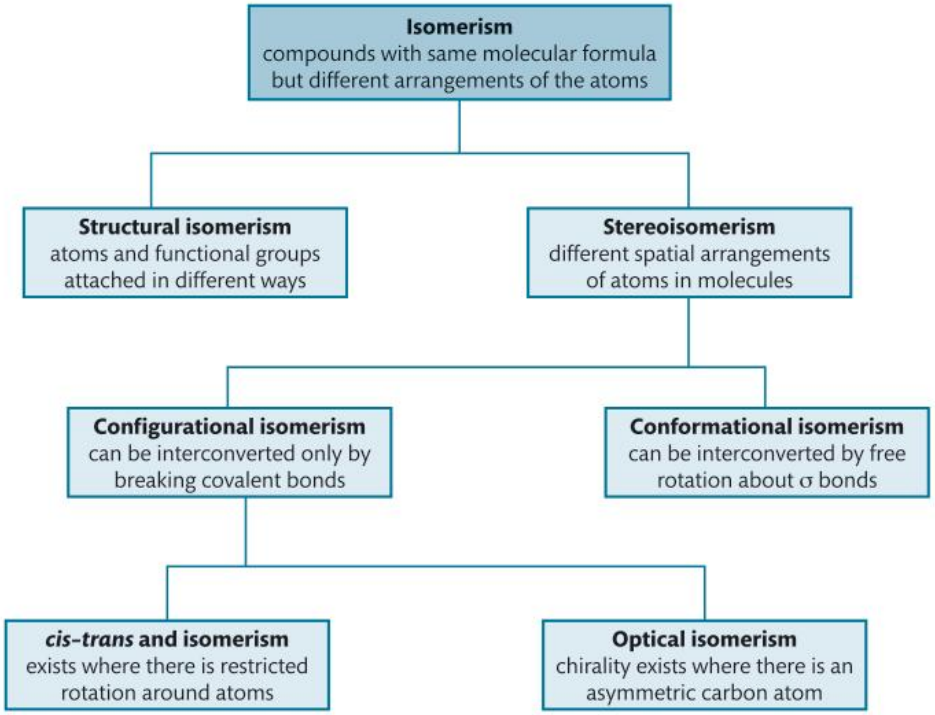
Structure 3.2.7 – Stereoisomers have the same constitution (atom identities, connectivities and bond multiplicities) but different spatial arrangements of atoms. Describe and explain the features that give rise to *cis–trans* isomerism; recognize it in non-cyclic alkenes and in C3 and C4 cycloalkanes. Draw stereochemical formulas showing the tetrahedral arrangement around a chiral carbon. Describe and explain a chiral carbon giving rise to stereoisomers with different optical properties. Recognize a pair of enantiomers as non-superimposable mirror images from 3D modelling (real or virtual).	
Nomenclature using the *E-Z* system will not be assessed. The terms 'chiral', 'optical activity', 'enantiomer' and 'racemic' mixture should be understood. Different chemical properties of enantiomers can be limited to the fact that they behave differently in chiral environments. Wedge-dash type representations involving tapered bonds should be used for the representation of enantiomers.	

Stereoisomers have different spatial arrangements

In this chapter we have learnt about different types of structural isomers which is where molecules contain the same atoms but arranged in different ways. This included straight chain versus branched isomers, positional isomers and functional group isomers.

Another type of isomerism, known as **stereoisomerism**, has molecules with atoms attached in the same order, but differing from each other in their spatial or three-dimensional arrangement. Although structural isomers can be represented relatively easily in two dimensions on paper, the study of stereoisomerism often requires three-dimensional representation.

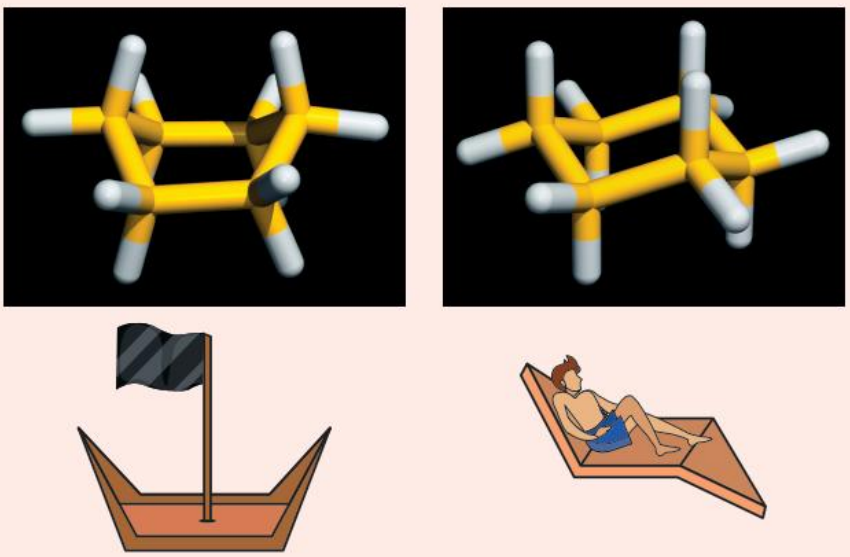
Stereoisomerism can be further broken down into different types, as shown in the chart on the next page.



Conformational isomers usually spontaneously interconvert through bond rotations and so, in most cases, cannot be isolated separately. Some conformers of a compound, though, may be more stable than others, and so are favoured and this may influence the reactivity of the compound. A knowledge of conformational isomers is not required for this course.

TOK

Cyclohexane, C_6H_{12}, is a compound that has two conformational isomers which are shown below. Bond rotation allows the ring structure to 'flip' between these two forms.



The two conformational isomers are known as the boat (left) and chair (right) forms of cyclohexane due to their distinctive shapes. What is the role of imagination and intuition in the creation of hypotheses in the natural sciences?

Configurational isomers have a permanent difference in their geometry. These isomers cannot be interconverted and they exist as separate compounds, with some distinct properties. We will study in turn the two main groups of configurational isomerism here.

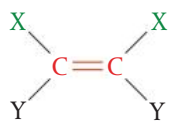
cis–trans isomers can occur with alkenes and cyclic molecules

When there is some constraint in a molecule that restricts the free rotation of substituted groups, they become fixed in space relative to each other. In these cases, the position of the groups must be described with respect to a reference plane.

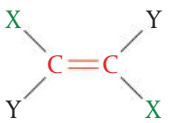
There are two circumstances where these isomers arise.

Double-bonded molecules

The double bond consists of one sigma (σ) bond and one pi (π) bond, with the π bond forming by sideways overlap of two p orbitals. Free rotation around this double bond is not possible as it would push the p orbitals out of position, and the π bond would break. The reference plane is perpendicular to the sigma bonds and passes through the double bond. When the molecule contains two or more different groups attached to the double bond, these can be arranged to give two different isomers. The simplest examples, involving only two different substituents, form what are known as ***cis*** and ***trans* isomers**.

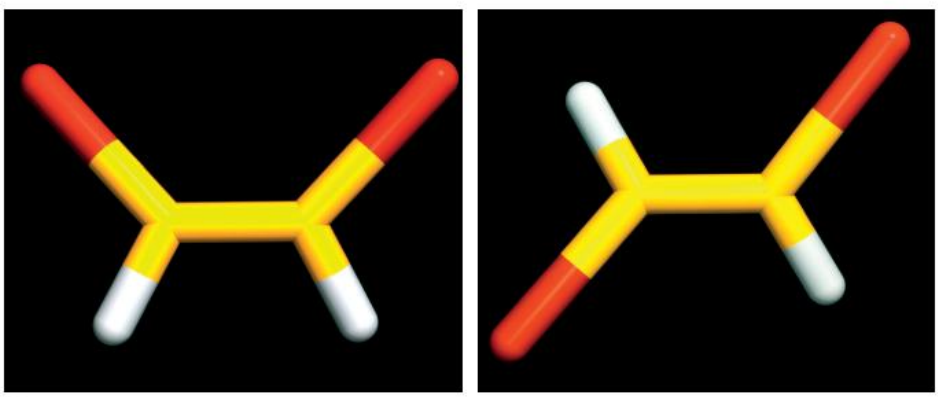


cis isomer



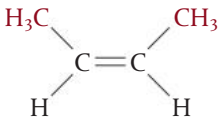
trans isomer

cis refers to the isomer that has the same groups on the same side of the double bond or ring, while *trans* is the isomer that has the same groups on opposite sides, or across the reference plane. These prefixes are given in italics before the name of the compound.

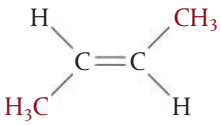


Molecular graphics of the geometric isomers of 1,2-dibromoethene. The atoms are shown as colour-coded cylinders, with carbon in yellow, hydrogen in white, and bromine in red. The *cis* form is on the left and the *trans* form is on the right. The molecule cannot alternate between the two forms as there is restricted rotation about the carbon–carbon double bond.

The examples of *cis*-but-2-ene and *trans*-but-2-ene are given below:



cis-but-2-ene

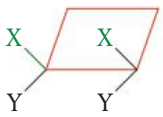


trans-but-2-ene

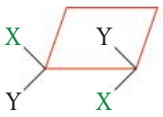
Cyclic molecules

Cycloalkanes contain a ring of carbon atoms that restricts rotation. The bond angles are strained from the tetrahedral angles in the parent alkane. For example, in cyclopropane, the carbon atoms form a triangle with bond angles of 60°, and in cyclobutane the atoms form a puckered square with approximate angles of 90°. The reference plane is the plane of the ring.

cis and *trans* isomers also occur for substituted cyclic molecules; *cis* isomers have the matching groups on the same side of the ring, *trans* isomers have the matching groups on the opposite side of the ring.

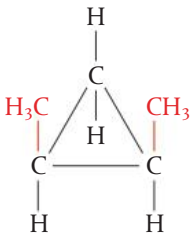


cis isomer

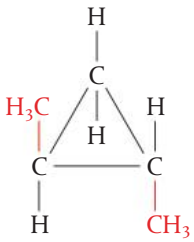


trans isomer

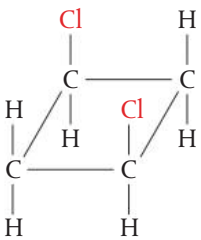
Examples of *cis* and *trans* isomers for two disubstituted cyclic compounds, 1,2-dimethylcyclopropane and 1,3-dichlorocyclobutane, are given below:



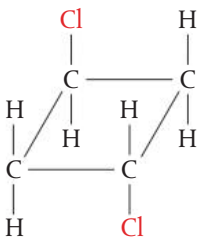
cis-1,2-dimethylcyclopropane



trans-1,2-dimethylcyclopropane



cis-1,3-dichlorocyclobutane



trans-1,3-dichlorocyclobutane

Note that, as in the example of 1,3-dichlorocyclobutane above, the substituted groups do not have to be on adjacent carbon atoms; it is their position relative to the plane of the ring that defines the isomer.

cis–trans isomerism plays an important role in the chemistry of vision, as light causes a photochemical transformation between the isomers of the pigment rhodopsin. This form of isomerism is a concern in the margarine industry, where partial hydrogenation of fats leads to the production of *trans* fats, associated with some negative health effects. A widely used chemotherapy drug used in the treatment of cancer is *cis*-platin, the activity of which is dependent on its stereochemistry and planar shape.

Worked example

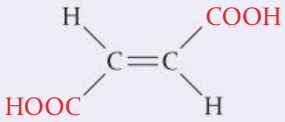
Draw and name the *cis–trans* isomers of butenedioic acid.

Solution

As the carboxylic acid groups must be in the terminal positions and cannot be attached to a double bond, the condensed structural formula must be HOOC–CH=CH–COOH. To identify the geometric isomers, we need to represent the geometry of the molecule.



cis-butenedioic acid



trans-butenedioic acid

You will not be able to demonstrate the presence of stereoisomers using a condensed formula of the compound. It is essential in this topic that you use the full structural formula or stereochemical formula to show the differences between the isomers.

Challenge yourself

4. *cis–trans* isomerism can occur in inorganic as well as in organic compounds. Think about why it can occur in square planar or octahedral complexes but not in tetrahedral complexes.
5. *cis*-butenedioic acid forms intramolecular hydrogen bonds at the expense of intermolecular bonds. Consider what impact this may have on the physical properties and acid strength of the two isomers.

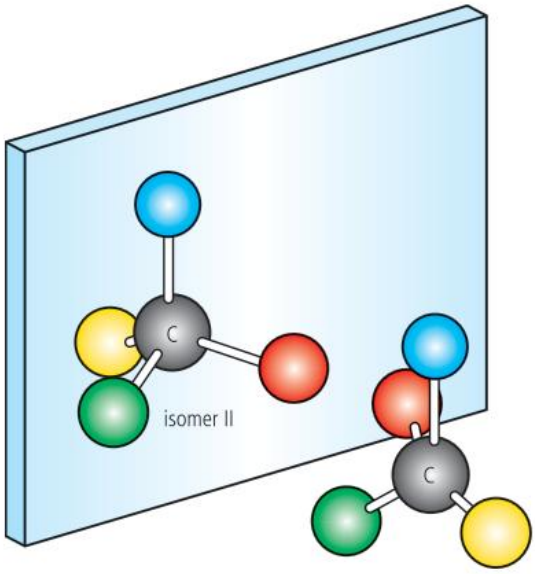
cis and *trans* isomers of the same compound may have different physical properties and chemical reactivity, depending on the influence of the substituted groups on polarity and the shape or symmetry of the molecules. Boiling points, melting points, and solubility data are therefore reported separately for each isomer.

Differences in the properties of the *cis* and *trans* isomers of butenedioic acid become very evident when examples of their roles in biology are compared. They are given distinct non-IUPAC names. Fumaric acid (*trans*) is an intermediate in the Krebs cycle, an essential part of the reactions of aerobic respiration for energy release in cells. By contrast, maleic acid (*cis*) is an inhibitor of reactions that interconvert amino acids, for example, in the human liver. Their different biological activities are a consequence of their different shapes affecting their binding to enzymes, the biological catalysts that control all these reactions.

Optical isomers

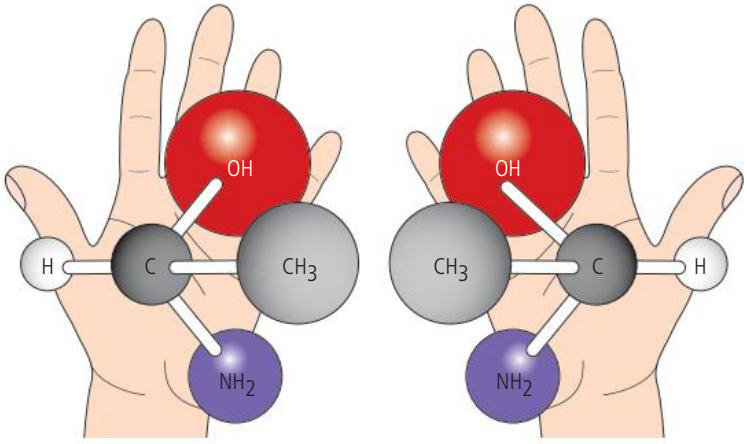
A carbon atom attached to four *different* atoms or groups is known as **chiral** (Figure 2). It is alternatively known as **asymmetric** or as a **stereocentre**. The four groups, arranged tetrahedrally around the carbon atom with bond angles of 109.5°, can be arranged in two different three-dimensional configurations which are mirror images of each other. This is known as **optical isomerism**. The term refers to the ways in which the isomers interact with plane-polarized light, which will be discussed below. The two optical isomers are also known as **enantiomers**. They are said to be **chiral molecules** and have no plane of symmetry.

Molecular modelling stereoisomers. Full details of how to carry out this activity with a worksheet are available in the eBook.



S3.2 Figure 2 An asymmetric, or chiral, carbon atom, shown in black, is bonded to four different atoms or groups – shown here in different colours. This gives rise to two configurations, called enantiomers or optical isomers, which are mirror images of each other.

If you look at your two hands you will see that they also are mirror images (Figure 3). When you put them on top of each other, with both palms up or both palms down, the fingers and thumbs do not line up – we say they are **non-superimposable**.



S3.2 Figure 3 Your two hands are non-superimposable mirror images.

Many molecules have more than one chiral centre, and so can give rise to different configurations at each position (Figure 4). Enantiomers have opposite configurations at *each* chiral centre, which is why the molecules are mirror images of each other. But when molecules have different configurations at one or more, *but not all*, chiral centres, they are known as **diastereomers** and are not mirror images of each other. Common sugars are often diastereomers of each other; examples are glucose and galactose.

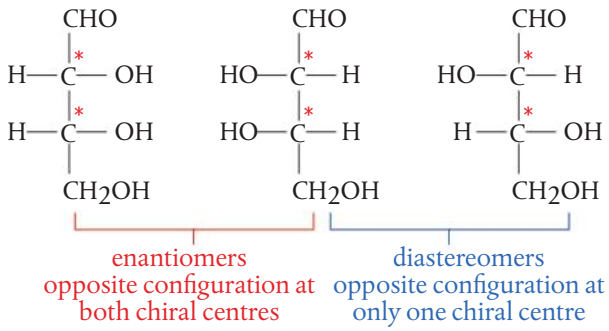
The word 'chiral' is derived from the Greek word for 'hand'. Lord Kelvin first introduced the term into science in 1904 with the now celebrated definition: 'I call any geometrical figure, or group of points, chiral, and say it has chirality if its image in a plane mirror, ideally realized, cannot be brought to coincide with itself.' His definition can therefore be applied much more generally to structures outside chemistry, such as knots.

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Computer simulations and technologies such as 3D printing may facilitate our understanding of stereochemistry. To what extent do these approaches involve a different way of knowing than studies based on two-dimensional representations? How do the tools we use shape the knowledge that we produce?

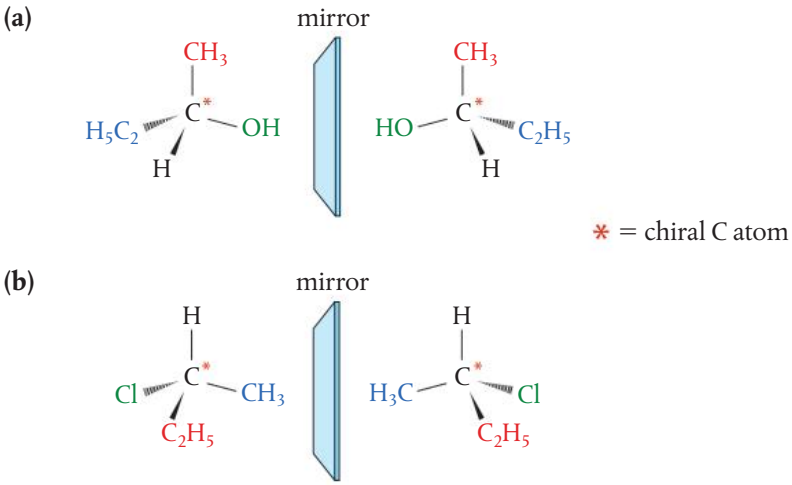
A single chiral centre in a molecule gives rise to two stereoisomers. In general, a molecule with *n* chiral centres has a maximum of 2^n stereoisomers, although some may be too strained to exist. For example, cholesterol has eight chiral centres and therefore a possible $2^8 = 256$ stereoisomers. However, only one is produced in biological systems, which is just one example of how incredibly specific biological reactions can be.

Enantiomers have opposite configurations at all chiral centres and are mirror images of each other. Diastereomers have opposite configurations at some, but not all, chiral centres, and are not mirror images of each other.



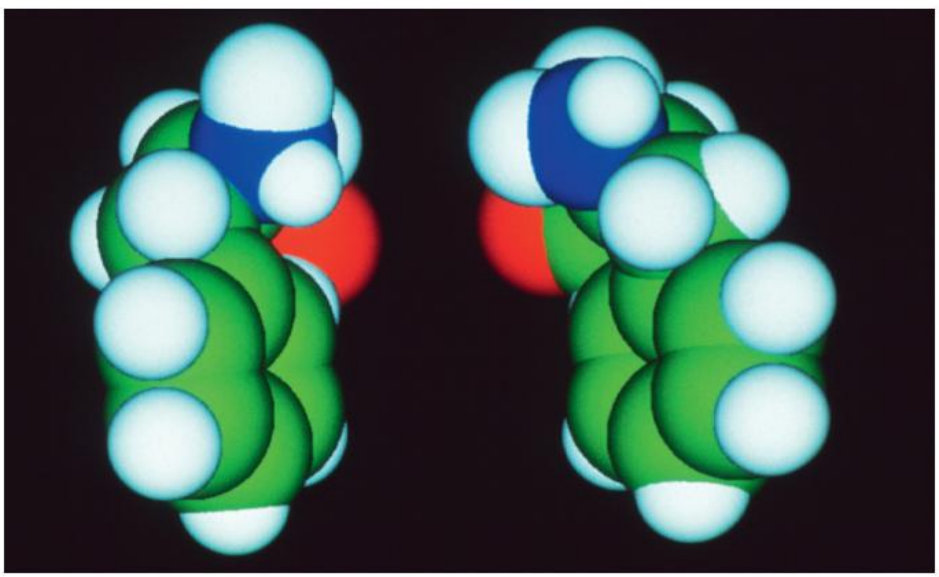
S3.2 Figure 4 Enantiomers have opposite configurations at each chiral centre, so the molecules are mirror images of each other. Diastereomers have different configurations at one or more, but not all, chiral centres, and are not mirror images of each other.

We can find optical activity in many of the molecules we have already encountered in this chapter. The clue is to look for any carbon atom that is bonded to four different groups. It is often useful to mark that carbon with a red asterisk (Figure 5).



S3.2 Figure 5 Enantiomers of **(a)** butan-2-ol and **(b)** 2-chlorobutane.

Molecular graphic of the two enantiomers of the amino acid phenylalanine, showing that they are mirror images of each other. Nearly all amino acids are chiral, but only one optical isomer, known as the L-form, occurs in biological systems.

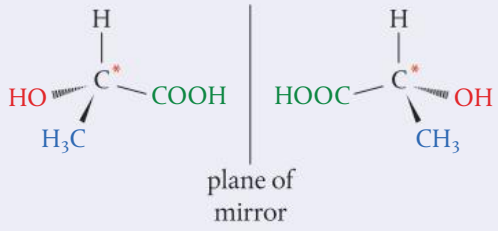


Worked example

Draw the enantiomers of 2-hydroxypropanoic acid (lactic acid). Mark the chiral carbon atom and show the plane of the mirror.

Solution

Identify the chiral carbon and draw a stereochemical structure showing the four different groups around this chiral carbon. Then add a mirror plane and use this to draw the mirror image of the first structure.



When drawing enantiomers, make sure that you use the wedge-dash type representation. It is best to draw in the plane of the mirror first and then ensure that the same groups in the two molecules are an equal distance from this plane.

Note that when you are looking for a chiral carbon atom in a molecule you must look at the whole group bonded to the carbon, not just the immediately bonded atom. For example, $-CH_3$ is a different group from $-C_2H_5$.

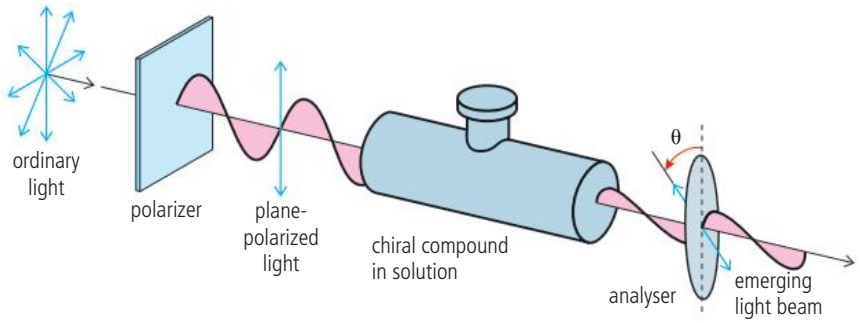
Properties of enantiomers

Diastereomers usually differ from each other in their physical and chemical properties. Enantiomers, on the other hand, have identical physical and chemical properties – with two important exceptions.

Optical activity

As their name suggests, optical isomers show a difference in a specific interaction with light. A beam of ordinary light consists of electromagnetic waves that oscillate in an infinite number of planes at right angles to the direction of travel. If, however, this light is passed through a device called a **polarizer**, only the light waves oscillating in a single plane pass through, while light waves in all other planes are blocked out. This is known as **plane-polarized light**. A similar effect is achieved in polarized sunglasses or windshields to reduce glare.

In the early 1800s, it was discovered that when a beam of plane-polarized light passes through a solution of optical isomers, they rotate the plane of polarization. The amount and direction of rotation can be measured with an instrument called a **polarimeter**, as shown in Figure 6.



S3.2 Figure 6 Schematic representation of a polarimeter.

The solution of isomers is placed in the sample tube through which plane-polarized light is passed. Rotation of the polarization plane occurs and the light then passes through a second polarizer called the **analyser**. This can be rotated until the light passes through it and so the angle of rotation (θ) can be deduced. In order to compare different solutions, the concentrations of the solutions, the wavelength of light used, and the sample path length must all be kept the same.



The two enantiomers of a chiral compound rotate plane-polarized light in equal and opposite directions.

Separate solutions of enantiomers, at the same concentration, rotate plane-polarized light in equal amounts but in opposite directions. This is what is meant by being **optically active**. A **racemic mixture** of a chiral compound contains equal concentrations of the two optical isomers. The rotation caused by each optical isomer cancels that of the other so a racemic mixture does not rotate polarized light and is said to be **optically inactive**. Naturally occurring chiral molecules are optically active, in other words, they exist as only one enantiomer. For example, morphine rotates plane-polarized light to the left so is said to be (–), whereas sucrose rotates it to the right and is said to be (+).



Nature of Science

The pioneer of polarimetry was Jean-Baptiste Biot (1774–1862) who was a French physicist and friend of the famous French bacteriologist Louis Pasteur (1822–1895). Biot showed that some crystals of quartz rotated the plane of polarized light while other crystals rotated it to the same extent in the opposite direction. Later, by showing the same effect in liquids such as turpentine, and in solutions of naturally occurring substances such as sugar, he realized it must be a molecular property and coined the term 'optical activity'. In 1848 Pasteur discovered that while tartaric acid shows optical activity, racemic acid with the same chemical composition does not, and deduced that this is because the racemic acid contains an equal mixture of two isomers. Pasteur saw the huge significance of this. He reasoned that reactions outside the cell always produce an optically inactive mixture whereas biological activity is specific to one isomer. In his later work on the origin of life, this became his guiding distinction between living and inanimate material.

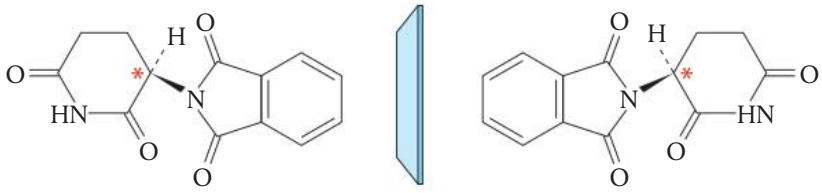


Different notations are used to distinguish between the two enantiomers of a pair. (+) and (–) refer to the direction in which the plane-polarized light is rotated, (+) for a clockwise direction and (–) for anticlockwise rotation. The lowercase d- (dextrorotatory) and l- (laevorotatory) respectively, are used as alternates for this but are becoming obsolete. Confusingly, small uppercase D- and L- are a different, unrelated notation based on spatial configurations in comparison with the reference molecule glyceraldehyde. This latter system is widely used in naming many biological molecules such as amino acids and sugars. Other molecules are described by their absolute configuration, using *R* (rectus) for right or clockwise and *S* (sinister) for left or anticlockwise. The rules for determining the absolute configuration are based on atomic number and mass. Happily, we will not adopt any particular system here and you will not be expected to identify the specific enantiomer in any of these examples.

Reactivity with other chiral molecules

When a racemic mixture is reacted with a single enantiomer of another chiral compound, the two components of the mixture, the (+) and (–) enantiomers, react to produce different products. These products have distinct chemical and physical properties and so can be separated from each other relatively easily. This is therefore a means by which the two enantiomers can be separated from a racemic mixture, a process known as **resolution**.

The different reactivity of a pair of enantiomers with another chiral molecule is of particular significance in biological systems because these *are* chiral environments. An infamous example of this occurred in the 1960s when the drug thalidomide was prescribed to pregnant women for morning sickness.



(*R*)-thalidomide
(sleep-inducing)

(*S*)-thalidomide
(teratogenic)

S3.2 Figure 7 The two enantiomers of the drug thalidomide. The chiral carbon atom is marked with a red asterisk(*).

As Figure 7 outlines, one enantiomer is therapeutic but the other is teratogenic and produces severe malformations in the fetus. This tragedy largely spearheaded research into chiral compounds, and the development of processes for the manufacture of a single enantiomer using a chiral catalyst. These processes, known as **asymmetric synthesis**, led to the Nobel Prize in Chemistry in 2001 and 2021.

TOK

The thalidomide drug was never marketed in the USA because of the intervention of Frances Kelsey, a pharmacologist working at the Food and Drug Administration (FDA). Despite pressure from thalidomide's manufacturer and the fact that it was already approved in over 20 countries, she registered concerns about the drug's ability to cross the placenta into the fetal blood. Her insistence that further tests be carried out was dramatically vindicated when the effects of thalidomide became known. For her insightful work in averting a similar tragedy in the USA, she was given a Distinguished Federal Service Award by President Kennedy.
Do the natural sciences provide us with good examples of people who approach knowledge in a rigorous and responsible way?



Close-up of the deformed hand and forearm of a 'thalidomide baby'. Thalidomide is a sedative drug that was administered to many pregnant women in the 1960s. It was withdrawn from the market after it was found to cause serious fetal abnormalities. This tragedy led to major changes in drug testing protocols.

The human senses of smell and taste are responsive to chiral influences. For example, D-amino acids all taste sweet, whereas L-amino acids are often tasteless or bitter. We can distinguish between the smells of oranges and lemons due to the presence of different enantiomers of the compound limonene. This is because taste buds on the tongue and sense receptors in the nose contain chiral molecules and so interact differently with the different enantiomers. As a result, stereochemistry is a major aspect of the food and perfume industries, as well as being a key factor in the pharmaceutical industry.

Many drugs are chiral and so exist as two forms – these forms should be considered as two separate drugs, with different properties, during research and development. Often only one form has the intended therapeutic effect so it is very important that the testing and approval process of any new chiral drug determines the biological effects for **each** enantiomer.

To what extent do you think consumers can be free from prejudice regarding the use of the thalidomide drug, given its dark history? Is opposition likely to be based on emotion or on rational distrust of the scientific research? Does knowledge always require some kind of rational basis?

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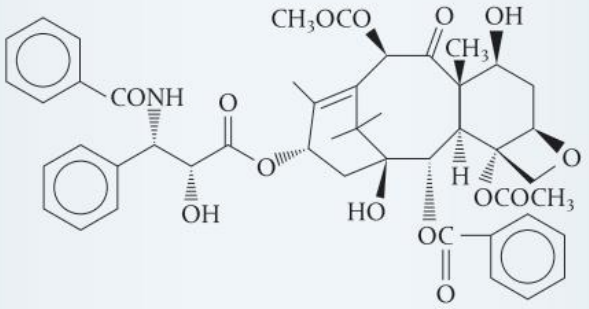
It is known that the two forms of the thalidomide drug interconvert under physiological conditions, so administering a pure isomer would not protect against the teratogenic effects. Nonetheless, the drug is still of some interest to researchers. It is thought that the action of the (*S*) form is to prevent the development of new blood vessels and this makes it an interesting agent for suppressing tumour growth in cancer and in treatment of HIV/AIDS and leprosy. Thalidomide is administered in some places for these purposes, but its marketing remains highly controversial.

TOK

All drugs carry risks as well as benefits. Who should ultimately be responsible for assessing the risk-to-benefit ratio of a drug in an individual – the pharmaceutical company, a government watchdog body, the doctor, or the patient? Do scientists or the societies in which scientists operate exert a greater influence on what is ethically acceptable in this area of knowledge?

Challenge yourself

6. The structure of taxol, an anti-cancer drug, is given below. Taxol contains 11 chiral carbons. Can you find them all?



Exercise

Q20. Draw the structural formulas for the following molecules:

(a) *trans*-but-2-ene

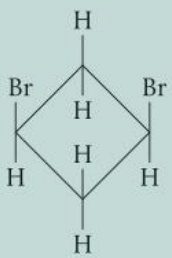
(b) *cis*-1,2-dichloropropene

(c) *cis*-1,3-dimethylcyclopentane

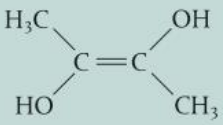
(d) *trans*-1,2-dibromocyclobutane

Q21. Name the following molecules:

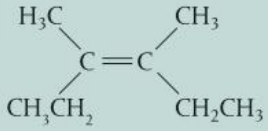
(a)



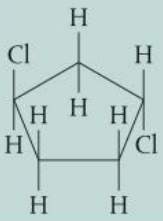
(b)



(c)



(d)



Q22. Draw the two optical isomers of 1-bromo-1-chloroethane using stereochemical structures.

Q23. Which of the following compounds can exist as optical isomers?

I. $CH_3CHBrCHClCH_2OH$

II. $CH_3CH_2CH(CH_3)COOH$

III. $CH_2ClCHBrCH_3$

A II only **B** II and III **C** III only **D** I, II and III

Q24. The first alkane to show optical isomerism is 3-methylhexane.

(a) Draw the condensed structural formula of 3-methylhexane and identify the chiral carbon.

(b) Determine the structure and name of the first alcohol that shows optical isomerism.

The structures of organic compounds can be determined using analytical techniques

Chemical analysts identify and characterize unknown substances, determine the composition of a mixture, and identify impurities. Their work can be divided into three types of analysis:

- **qualitative analysis**: the detection of the *presence* but not the quantity of a substance in a mixture; for example, forbidden substances in an athlete's blood
- **quantitative analysis**: the measurement of the *quantity* of a particular substance in a mixture; for example, the alcohol levels in a driver's breath
- **structural analysis**: a description of how the atoms are arranged in molecular structures; for example, the determination of the structure of a naturally occurring or artificial product.

Many instrumental techniques are available to provide structural analysis but we will focus on three of the most common.

- Mass spectrometry is used to determine relative atomic and molecular masses. The fragmentation pattern can be used as a fingerprint technique to identify unknown substances or for evidence for the arrangements of atoms in a molecule.
- Infrared spectroscopy is used to identify the bonds in a molecule.
- Nuclear magnetic resonance spectroscopy is used to show the chemical environment of certain isotopes (hydrogen, carbon, phosphorus and fluorine) in a molecule and so gives vital structural information.

No one method alone is definitive, but a combination of techniques can provide strong evidence for a particular structure.



The Spectra Database for Organic Compounds was opened in 1997 and has given the public free access to the spectra of more than 35 000 organic compounds. The total accumulated number of visits reached 550 million at the end of January 2015, and the database has sent information from Japan to all over the world. The open exchange of information is a key element of scientific progress.

Structure 3.2.8 – Mass spectrometry

Structure 3.2.8 – Mass spectrometry (MS) of organic compounds can cause fragmentation of molecules. Deduce information about the structural features of a compound from specific MS fragmentation patterns.	
Include reference to the molecular ion. Data on specific MS fragments are provided in the data booklet.	

Determining the molecular mass of a compound

The mass spectrometer was introduced in Structure 1.2 where we saw how it is used to find the mass of individual atoms and the relative abundances of different isotopes. The instrument can be used in a similar way to find the relative molecular mass of a compound. If the empirical formula is also known from compositional analysis, the molecular formula can be determined. The technique also provides useful clues about the molecular structure.



A mass spectrometer. The molecules are ionized and accelerated towards a detector. The sensor array can be seen through the round window (lower left).

Fragmentation patterns

The ionization process in the mass spectrometer involves an electron from an electron gun hitting the incident species and removing an electron:

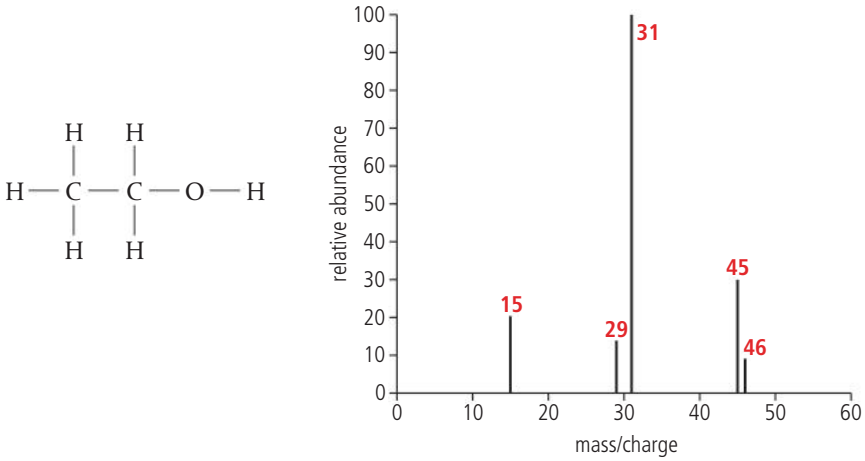
$$\underset{\text{molecule}}{X(g)} + e^- \rightarrow \underset{\text{molecular ion}}{X^+(g)} + 2e^-$$

The collision can be so energetic that it causes the molecule to break up into different fragments. The peak with the largest mass/charge value in the mass spectrum corresponds to the molecular ion which has passed through the instrument without fragmenting. Other ions, produced as a result of the molecular ion breaking up into smaller fragments, are also detected.

The molecular ion, or parent ion, is formed when a molecule loses one electron but otherwise remains unchanged.

The **fragmentation pattern** can provide useful evidence for the structure of the compound. A chemist pieces together the fragments to form a picture of the complete molecule in the same way that archaeologists find clues about the past from the pieces of artefacts discovered in the ground.

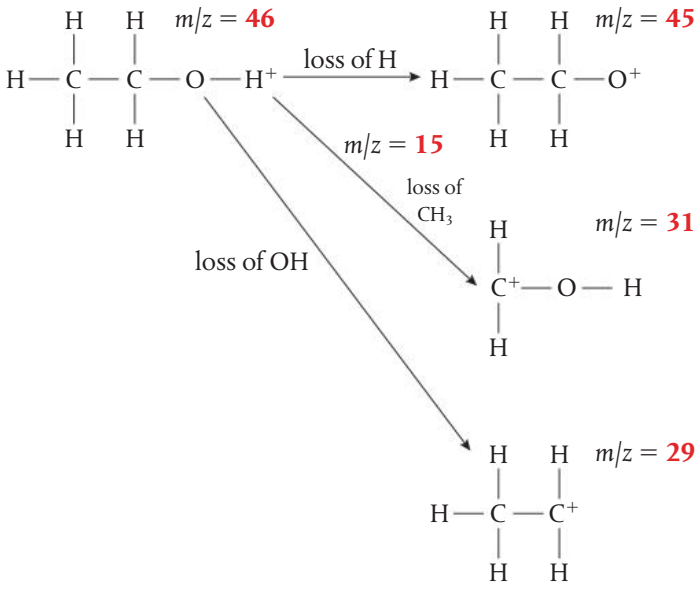
Consider Figure 8, which shows the mass spectrum of ethanol.



S3.2 Figure 8 The structure of ethanol and its mass spectrum.

The molecular ion corresponds to the peak at 46. The ion that appears at a relative mass of 45, one less than the molecular ion, corresponds to the loss of a hydrogen atom.

Figure 9 shows fragmentation paths that explain the rest of the spectrum.

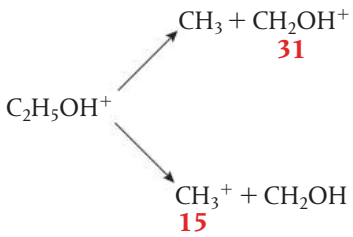


S3.2 Figure 9 Possible fragmentation pattern produced when ethanol is bombarded with high-energy electrons in a mass spectrometer.

The parent ion can break up into smaller ions in a mass spectrometer. A compound is characterized by this fragmentation pattern.

For each fragmentation, one of the products keeps the positive charge. So, for example, if the C–C bond breaks in the molecular ion formed from ethanol, two outcomes are possible, as seen in Figure 10.

The fragmentation shown in Figure 10 explains the presence of peaks at both $m/z = 15$ and $m/z = 31$. Generally, the fragment that gives the most stable ion is formed and subsequently observed in the mass spectrum.



S3.2 Figure 10 Two possible ways in which the C–C bond can break in the molecular ion of ethanol. Only the charged species can be detected, as electric and magnetic fields have no effect on neutral fragments.

The cleavage of the C–O bond leads to the formation of the $C_2H_5^+$ ion in preference to the OH^+ ion in the example above, so there is an observed peak at $m/z = 29$ but not at $m/z = 17$.

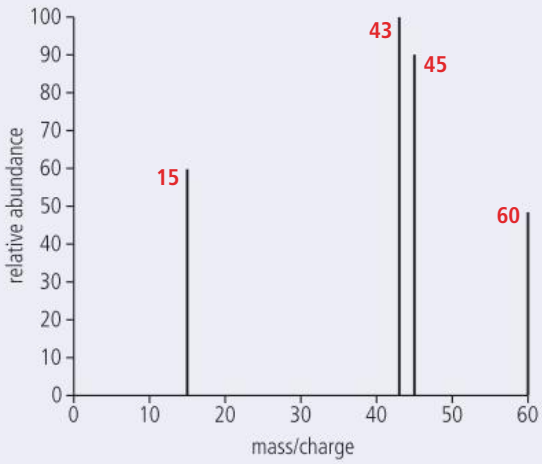
Do not forget to include the positive charge on the ions when identifying different fragments.

Full analysis of a mass spectrum can be a complex process. We make use of the mass difference between the peaks to identify the pieces that have fallen off. You are expected to recognize the mass fragments shown below. You are not expected to memorize the details as the data are given in Section 22 of the data booklet.

Mass lost	Fragment lost
15	$\cdot CH_3$
17	$\cdot OH$
18	H_2O
28	$CH_2{=}CH_2$, $C{=}O$
29	$\cdot CH_3CH_2$, $\cdot CHO$
31	$\cdot OCH_3$
45	$\cdot COOH$

Worked example

A molecule with an empirical formula CH_2O has the simplified mass spectrum shown below. Deduce the molecular formula and give a possible structure of the compound.



Solution

empirical formula = CH_2O; molecular formula = $C_nH_{2n}O_n$

We can see that the parent ion has a relative mass of 60.

$M_r = n(12.01) + 2n(1.01) + n(16.00) = 30.03n$

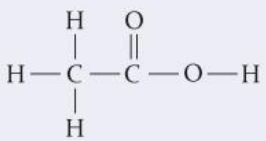
$$n = \frac{60}{30.03} = 2$$

molecular formula = $C_2H_4O_2$

From the spectrum, we can identify the following peaks:

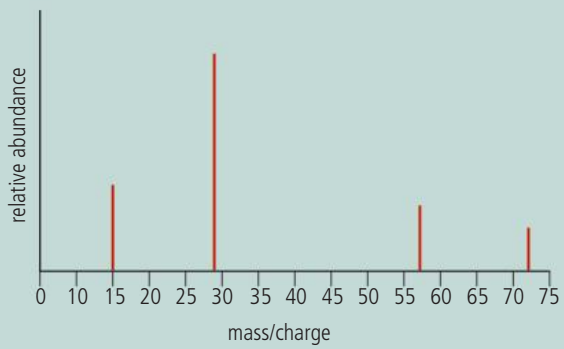
Peaks	Explanation
15 (60 – 45)	presence of CH_3^+ loss of COOH from molecule
43 (60 – 17)	presence of $C_2H_3O^+$ loss of OH from molecule
45 (60 – 15)	presence of $COOH^+$ loss of CH_3 from molecule

The structure consistent with this fragmentation pattern is:



Exercise

Q25. The mass spectrum shown below was produced by a compound with the formula $C_nH_{2n}O$.



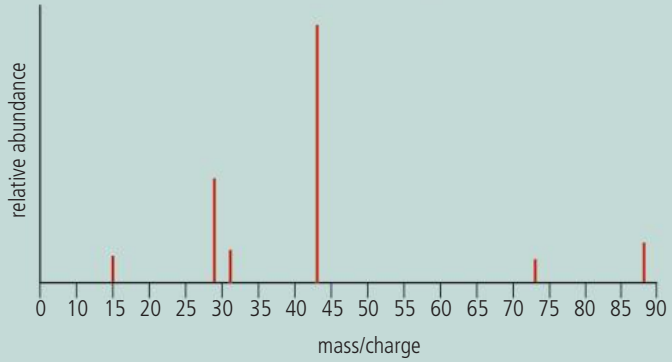
Which ions are detected in the mass spectrometer?

I. $C_2H_3O^+$ II. $C_3H_5O^+$ III. $C_4H_8O^+$

A I and II only **B** I and III only

C II and III only **D** I, II and III

Q26. While working on an organic synthesis, a student isolated a compound X, which they then analysed with a mass spectrometer.

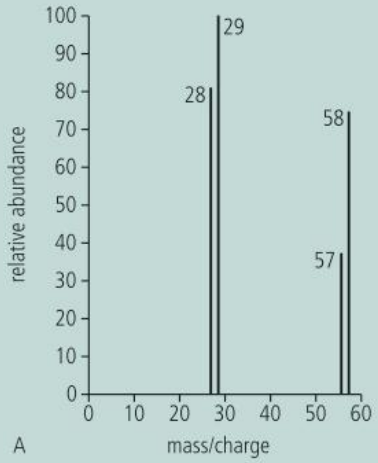


Identify X from the mass spectrum shown.

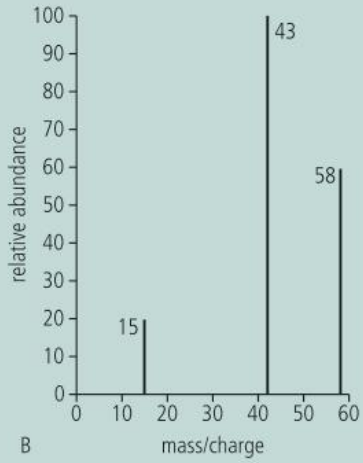
A $CH_3CH_2CH_3$ **B** $C_3H_7CO_2H$

C $C_2H_5CO_2CH_3$ **D** $(CH_3)_2CHCO_2H$

Q27. The mass spectra of two compounds, **A** and **B**, are shown below. One is propanone (CH_3COCH_3) and the other is propanal (CH_3CH_2CHO). Identify the compound in each case and explain the similarities and differences between the two spectra.



A

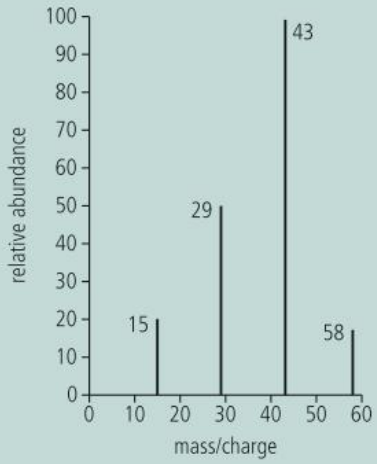


B

Q28. The simplified mass spectrum of a compound with empirical formula C_2H_5 is shown on the right.

(a) Explain which ions give rise to the peaks shown.

(b) Deduce the molecular structure of the compound.



Structure 3.2.9 – Infrared spectroscopy

Structure 3.2.9 – Infrared (IR) spectra can be used to identify the type of bond present in a molecule. Interpret the functional group region of an IR spectrum, using a table of characteristic frequencies (wavenumber / cm^{-1}).	
Include reference to the absorption of IR radiation by greenhouse gases. Data for interpretation of IR spectra are given in the data booklet.	Structure 2.2 – What features of a molecule determine whether it is IR active or not? Reactivity 1.3 – What properties of a greenhouse gas determine its 'global warming potential'?

Different regions of the electromagnetic spectrum give different information about the structure of organic molecules

Spectroscopy is the main method we have of probing into the atom and the molecule. There is a type of spectroscopy for each of the main regions of the electromagnetic spectrum. As discussed in Structure 1.3, electromagnetic radiation is a form of energy transferred by waves and characterized by its:

- **wavelength** (λ): the distance between successive crests or troughs
- **frequency** (f): the number of waves which pass a point every second.

The electromagnetic spectrum can be found in Section 5 of the data booklet. Typical wavelengths and frequencies for each region of the spectrum are summarized in the table below.

Type of electromagnetic radiation	Typical frequency (f) / s^{-1}	Typical wavelength (λ) / m
radio waves (low energy)	3×10^{6}	10^{2}
microwaves	3×10^{10}	10^{-2}
infrared	3×10^{12}	10^{-4}
visible	3×10^{15}	10^{-7}
ultraviolet	3×10^{16}	10^{-8}
x-rays	3×10^{18}	10^{-10}
gamma rays	greater than 3×10^{22}	less than 10^{-14}

It should be noted from the table that $f \times \lambda = 3.0 \times 10^{8}$ m $s^{-1} = c$, the speed of light. This gives $f = c/\lambda$.

In infrared spectroscopy, the frequency of radiation is often measured as the number of waves per centimetre (cm^{-1}), also called the **wavenumber**.

A wavenumber (cm^{-1}) is a measure of frequency commonly used in IR spectroscopy. The frequency of electromagnetic radiation is typically measured in units of s^{-1} which corresponds to the number of peaks that are observed per second. When measured in wavenumbers, the frequency of electromagnetic radiation instead corresponds to the number of peaks that occur within 1 cm.

TOK

The physical analytical techniques now available to us are due to advances in technology. To what extent are technologies, such as spectrometers, merely extensions to the human senses, or do they introduce radically new ways of seeing the world?

- The distance between two successive crests (or troughs) is called the wavelength.
- The frequency of the wave is the number of waves which pass a point in one second.

For electromagnetic waves, the wavelength and frequency are related by the equation

$$c = f\lambda$$

where c is the speed of light, f is frequency in s^{-1} and λ is wavelength in m.

Worked example

If an absorption occurs at a wavelength of 5556 nm, what would be the frequency of this absorption in units of cm^{-1}?

Solution

First, convert the wavelength into units of cm.

$5556\,nm = 5556 \times 10^{-9}\,m = 5.556 \times 10^{-6}\,m = 5.556 \times 10^{-4}\,cm$

$$\text{The frequency in } cm^{-1} = \frac{1}{\text{wavelength (cm)}}$$

$$= \frac{1}{5.556 \times 10^{-4}\,cm} = 1800\,cm^{-1}$$

TOK

All forms of spectroscopy involve the study of how electromagnetic radiation interacts with matter. However, scientists working with different regions of the electromagnetic spectrum tend to use different conventions and units to characterize the light absorbed. For example:

- Uultraviolet-visible spectroscopists use nm (10^{-9} m) to define a wavelength
- IR spectroscopists use wavenumbers (cm^{-1}) to define a frequency
- NMR spectroscopists working with radio waves use s^{-1} (Hz) to define a frequency.

If scientists work with more than one spectroscopic technique, they need to become proficient at working with the different conventions and units. Does the precision of the language used in the natural sciences successfully eliminate all ambiguity?

Microwave cookers heat food very quickly because the radiation penetrates deep into the food. The frequency used corresponds to the energy needed to rotate water molecules, which are present in most foods. The radiation absorbed by the water molecules makes them rotate faster. As they bump into other molecules, the extra energy is spread throughout the food and the temperature rises.

As well as transferring energy, electromagnetic radiation can also be viewed as a carrier of information. Different regions give different types of information, by interacting with substances in different ways.

- **Radio waves** can be absorbed by certain nuclei, causing them to reverse their nuclear spin. They are used in nuclear magnetic resonance (NMR) and can give information about the environment of certain atoms.
- **Microwaves** cause molecules to increase their rotational energy. This can give information about bond lengths.
- **Infrared radiation** is absorbed by certain bonds causing them to stretch or bend. This gives information about the bonds in a molecule.
- **Visible light** and **ultraviolet light** can produce electronic transitions and give information about the electronic energy levels within the atom or molecule.
- **X-rays** are produced when electrons make transitions between inner energy levels. They have wavelengths of the same order of magnitude as the inter-atomic distances in crystals and produce diffraction patterns which provide direct evidence of molecular and crystal structure.

Challenge yourself

7. Calculate the energy of a photon of visible light with a frequency of $3.0 \times 10^{14}\,s^{-1}$. Express your answer in $kJ\,mol^{-1}$.

As stated above, all regions of the electromagnetic spectrum can provide important information about the properties and structures of molecules. In this course we focus on the information that can be obtained from the use of infrared (IR) and radio waves in IR and NMR spectroscopy.

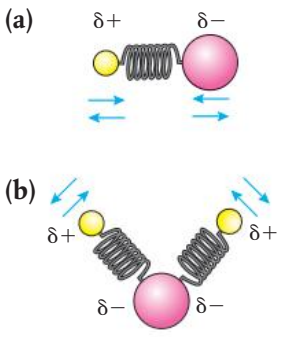
Infrared (IR) spectroscopy gives information about the bonds present in a molecule

The natural frequency of a chemical bond

A chemical bond can be thought of as a spring. Each bond vibrates and bends at a natural frequency, which depends on the bond strength and the masses of the atoms. Light atoms, for example, vibrate at higher frequencies than heavier atoms and multiple bonds, which are stronger, vibrate at higher frequencies than single bonds.

Simple diatomic molecules such as HCl, HBr and HI can only vibrate when the bond stretches (Figure 11a). The HCl bond has the highest frequency of these three as it has the largest bond energy and the halogen atom with the smallest relative atomic mass.

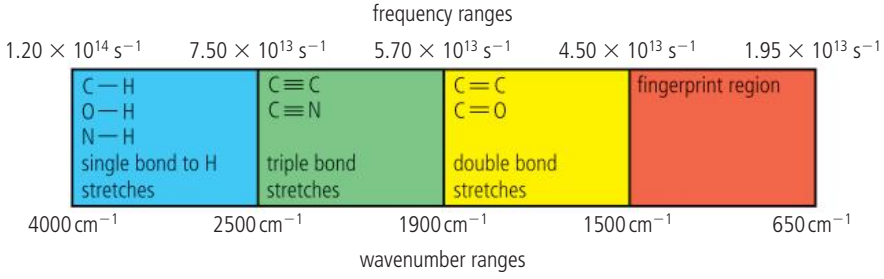
In more complex molecules, different types of vibration can occur, such as bending, so that a complex range of frequencies is present (Figure 11b).



S3.2 Figure 11 IR radiation can cause a bond to stretch or bend.

Absorbing infrared radiation excites the bonds in molecules

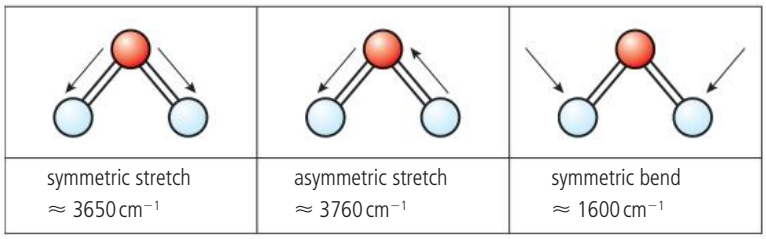
The energy needed to excite the bonds in a molecule, to make them vibrate with greater amplitude, occurs in the IR region (Figure 12). A bond in a diatomic molecule will only interact with the electromagnetic infrared radiation, however, if it is polar. The presence of separate areas of partial positive and negative charge in a molecule allows the electric field component of the electromagnetic wave to excite the vibrational energy of the molecule. The change in the vibrational energy produces a corresponding change in the dipole moment of the molecule. The intensity of the absorption depends on the polarity of the bond. Symmetrical non-polar bonds in N≡N and O=O do not absorb radiation, as they cannot interact with an electric field.



S3.2 Figure 12 The natural frequencies of some covalent bonds.

Stretching and bending in a polyatomic molecule

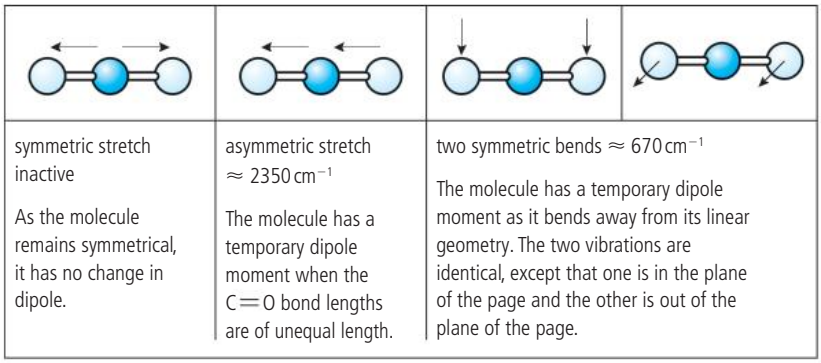
In a polyatomic molecule such as water, it is more correct to consider the molecule stretching and bending as a whole, rather than considering the individual bonds. Water, for example, can vibrate at three fundamental frequencies as shown in Figure 13. As each of the three modes of vibration results in a change in the dipole of the molecule, they can be detected with IR spectroscopy.



S3.2 Figure 13 The three vibrational modes of the water molecule are all IR active as they each produce a change in the dipole moment of the molecule.

Structure 2.2 – What features of a molecule determine whether it is IR active or not?

For a symmetrical linear molecule such as carbon dioxide, there are four modes of vibration (Figure 14). However, the symmetric stretch is IR inactive as it produces no change in dipole moment. The dipoles of both C=O bonds are equal and opposite throughout the vibration.



S3.2 Figure 14 Three of the vibrational modes of the carbon dioxide molecule are IR active. The symmetric stretch produces no change in dipole and so is IR inactive.

Nature of Science

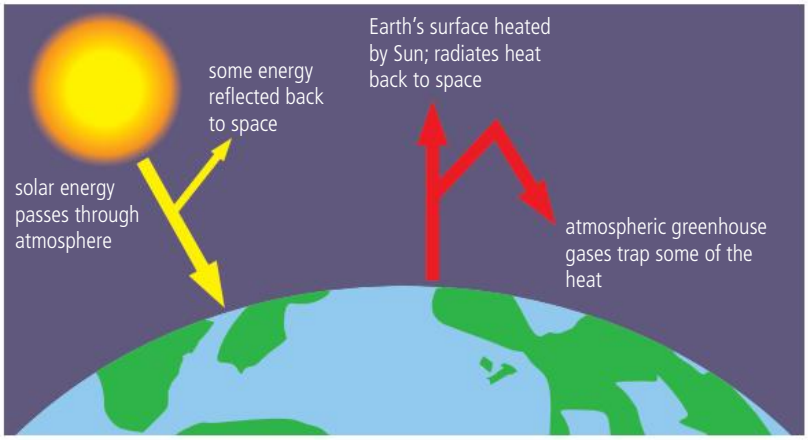
Scientists use models to clarify features and relationships that are not directly observable. These models can become more and more sophisticated but they can never become the real thing. Models are just a representation of reality. The IR spectra of organic molecules, for example, are based on the bond vibration model, in which the covalent bond between two atoms is compared to a spring, with its natural frequency depending on the bond strength and the masses of an atom in the same way that the natural frequency of a spring depends on its stiffness and mass. We often use our everyday experiences to help us construct models to understand processes that are occurring on a scale beyond our experience. This is the strength of such models as it helps our understanding; the same mass/spring model can be used to explain a float bobbing up and down in water for example. However, models also have limitations.

Scientists often take a complex problem and reduce it to a simpler, more manageable one that can be treated mathematically. We should not forget that the bond vibration model is a simplification – albeit an effective one. It is molecules, and not individual bonds, that are vibrating, as we saw on the previous page and above for the examples of water and carbon dioxide.

Greenhouse gases absorb long-wavelength IR radiation from the Earth

The temperature of the Earth is maintained by a steady-state balance between the energy received from the Sun and the energy leaving the Earth and going back into space. Incoming solar radiation is in the visible and ultraviolet region. Some of this radiation is reflected back into space and some is absorbed by gases in the atmosphere. Most of the solar radiation passes through the atmosphere, however, and warms the surface of the Earth. The warm Earth surface then **radiates** some of this energy as **longer wavelength infrared** radiation which is **absorbed** by **greenhouse molecules** such as carbon dioxide and water vapour in the lower atmosphere. This makes the air warmer, causing it to radiate heat in turn. Some of this radiation is **re-radiated** back to the Earth's surface and some is re-radiated back into space. This natural process is called the **greenhouse effect** because the Sun's energy is absorbed

in a way that is similar to the way light energy is trapped by the glass in a greenhouse. The glass lets light energy in but does not let heat energy out.



The ability of a molecule to absorb infrared radiation depends on the change in dipole moment that occurs as it vibrates. This means that some greenhouse gases are much more effective than others in absorbing infrared radiation and trapping heat in the atmosphere.

The **global warming potential** of a greenhouse gas compares the amount of infrared energy that one tonne of the gas would absorb to the amount that would be absorbed by one tonne of CO_2 over the same time period. This will depend upon:

- how effective the individual gas molecules are at absorbing IR radiation
- the atmospheric lifetime of the gas; i.e. how long it persists in the atmosphere before being removed through natural processes.

The global warming potentials for some greenhouse gases over a 100-year time period are given in the table below.

Greenhouse gas	Chemical formula	Global warming potential (100-year time period)
carbon dioxide	CO_2	1
methane	CH_4	28
nitrous oxide	NO_2	265
CFC-13	$CClF_3$	13 900
HFC-134a	CH_2FCF_3	1300

Reactivity 1.3 – What properties of a greenhouse gas determine its 'global warming potential'?

CFC-13 and HFC-134a are both synthetic compounds that have been used as refrigerants. CFC-13 is a chlorofluorocarbon that was banned under the Montreal Protocol due to it being an ozone depleting substance. HFC-134a is a hydrofluorocarbon that was regarded as a safer alternative as a refrigerant as it is not ozone depleting. Under the Kigali Amendment to the Montreal Protocol, it is also being phased out due to its high global warming potential.

Matching wavenumbers with bonds

The absorption of particular wavenumbers of IR radiation helps the chemist identify the bonds in a molecule. The precise position of the absorption depends on the environment of the bond, so a range of wavenumbers is used to identify different bonds.

You are not expected to remember the characteristic wavenumbers. A more complete list is given in Section 20 of the data booklet.

Characteristic infrared absorption bands are shown in the table below.

Bond	Wavenumber / cm^{-1}	Intensity
C–O	1050–1410	strong
C=C	1620–1680	medium-weak; multiple bands
C=O	1700–1750	strong
C≡C	2100–2260	variable
O–H, hydrogen bonded in carboxylic acids	2500–3000	strong, very broad
C–H	2850–3090	strong
O–H, hydrogen bonded in alcohols and phenols	3200–3600	strong
N–H	3300–3500	strong

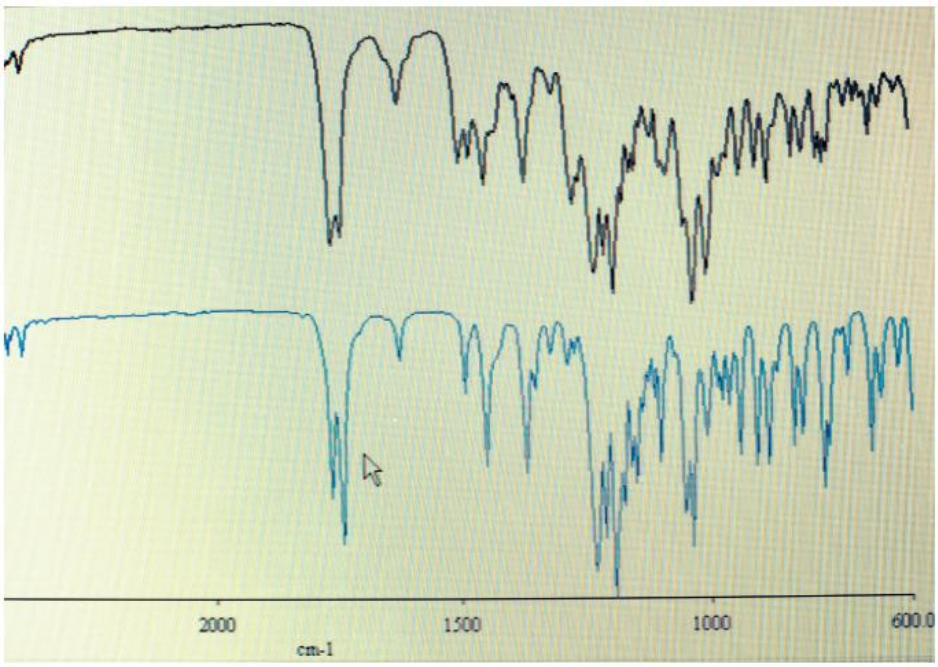
Some bonds can also be identified by the distinctive shapes of their signals: for example, the O–H bond gives a broad signal and the C=O bond gives a sharp signal.

Because hydrogen bonding broadens the IR absorptions, its presence can be detected. For example, hydrogen bonding between hydroxyl groups changes the O–H vibration; it makes the absorption much broader and shifts it to a lower frequency.

Molecules with several bonds can vibrate in many different ways and with many different frequencies. The complex pattern can be used as a 'fingerprint' to be matched against the recorded spectra of known compounds in a database (Figure 15). A comparison of the spectrum of a sample with that of a pure compound can also be used as a test of purity.

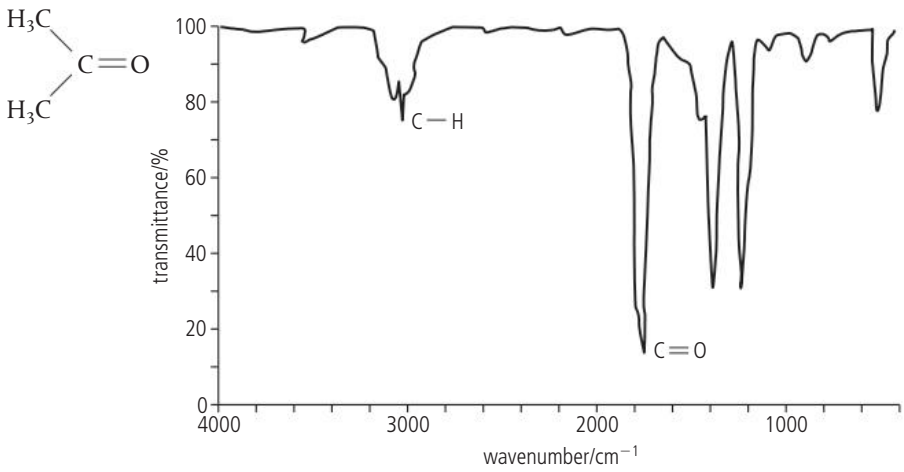


An illustration of the *Rosalind Franklin* rover used to explore the surface of Mars. An IR spectrometer on its mast measures reflected solar radiation and assists in the detection of water-bearing minerals and organic compounds.



S3.2 Figure 15 The IR spectrum of heroin (blue) compared with that of an unknown sample (black). The near-perfect match indicates that the sample contains a high percentage of heroin. Spectral analysis such as this can identify unknown compounds in mixtures or from samples taken from clothing or equipment. The technique is widely used in forensic science.

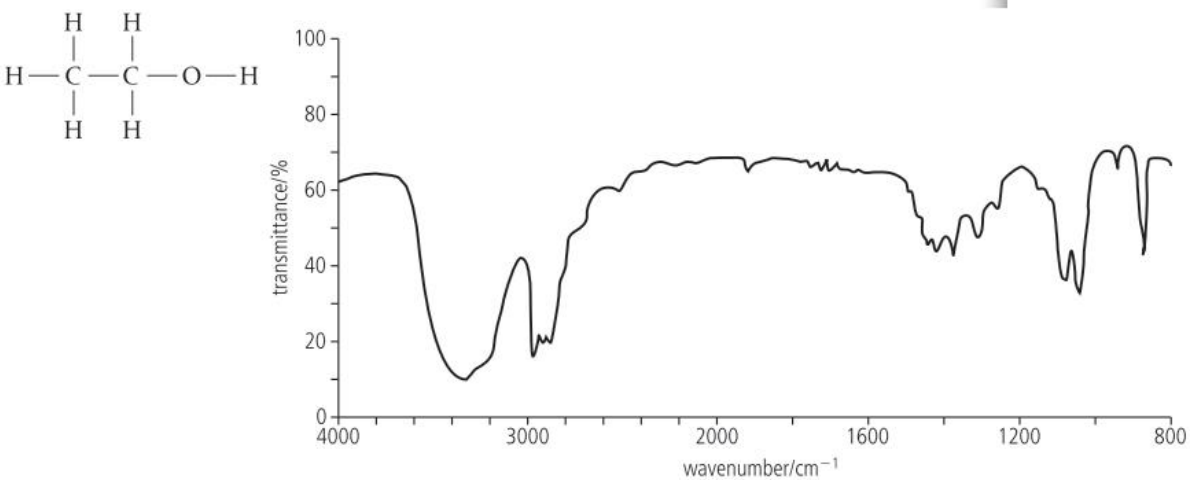
Consider the IR spectrum of propanone (Figure 16). The baseline at the top corresponds to 100% transmittance and the key features are the troughs which occur at the natural frequencies of the bonds present in the molecule.



S3.2 Figure 16 The molecular structure and IR spectrum of propanone.

The absorption at just below 1800 cm^{-1} shows the presence of the C=O bond and the absorption near 3000 cm^{-1} is due to the presence of the C–H bond. The more polar C=O bond produces the more intense absorption.

You can see the presence of the C–H bond again near 3000 cm^{-1} in the IR spectrum of ethanol (Figure 17). The broad peak at just below 3400 cm^{-1} shows the presence of hydrogen bonding which is due to the hydroxyl (OH) group.



S3.2 Figure 17 The IR spectrum of ethanol. Note that the horizontal axis has a non-linear scale. This is common for many instruments, so you should always take care when reading off values for the wavenumbers of the absorptions.





Early breath alcohol tests relied on qualitative data, observing the distinctive orange to green colour change that occurs when dichromate ions are reduced by ethanol (page 778). A method for breath testing that obtains quantitative data uses a small portable IR spectrometer to measure the amount of IR radiation absorbed by C–H bonds in ethanol.

Exercise

Q29. Which of the following types of bond is expected to absorb IR radiation of the longest wavelength?

	Bond order	Mass of atoms bonded together
A	1	small
B	1	large
C	2	small
D	2	large

Q30. For each pair of bonds, state which one would absorb IR radiation of the shortest wavelength and explain why.

(a) C–O and C=O **(b)** C–Cl and C–Br

Q31. Compounds A and B have the same molecular formula: $C_3H_6O_2$. Absorptions are observed in the IR spectra of the two compounds at the following frequencies:

Compound A: 3000 cm^{-1} (broad), 1730 cm^{-1}, 1230 cm^{-1}

Compound B: 1720 cm^{-1}, 1230 cm^{-1}

(a) Use this information to determine the structure and name of compound A.

(b) Compound B could be one of two possible isomers. Draw and name these two isomers.

Q32. The major components of the Earth's atmosphere are nitrogen (N_2) and oxygen (O_2). Explain why these gases do not contribute to the greenhouse effect.

Q33. Draw the structure of the sulfur dioxide molecule and identify its possible modes of vibration. Predict which of these is likely to absorb IR radiation.

Q34. Hexane and hex-1-ene are both colourless liquids. Explain how IR spectroscopy could be used to distinguish between the two compounds.

Q35. The intoximeter, used by police to test the alcohol levels in the breath of drivers, measures the absorbance at 2900 cm^{-1}. Identify the bond which causes ethanol to absorb at this wavenumber.

Challenge yourself

8. A bond has an IR absorption at 2100 cm^{-1}. Calculate the wavelength of the radiation absorbed and the natural frequency (s^{-1}) of the bond.

Structure 3.2.10 and 3.2.11 – Nuclear magnetic resonance spectroscopy

Structure 3.2.10 – Proton nuclear magnetic resonance (^{1}H NMR) spectroscopy gives information on the different chemical environments of hydrogen atoms in a molecule.

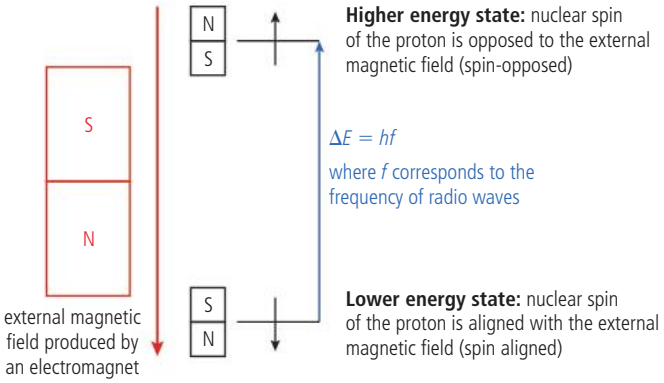
Interpret ^{1}H NMR spectra to deduce the structures of organic molecules from the number of signals, the chemical shifts, and the relative areas under signals (integration traces).

Structure 3.2.11 – Individual signals can be split into clusters of peaks.

Interpret ^{1}H NMR spectra from splitting patterns showing singlets, doublets, triplets and quartets to deduce greater structural detail.

Data for interpretation of ^{1}H NMR spectra are given in the data booklet.

Nuclear magnetic resonance (NMR) spectroscopy, a powerful technique for finding the structure and shape of molecules, depends on a combination of nuclear physics and chemistry. The nuclei of atoms with an odd number of nucleons such as ^{1}H, ^{13}C, ^{19}F and ^{31}P, have a property called nuclear spin and behave like tiny bar magnets. When placed in an external magnetic field, these nuclei can exist in two distinct energy levels depending on whether their magnetic field is aligned with or opposed to the external magnetic field. The energy gap between the two energy levels is very small and it only requires the absorption of low-energy radio waves for nuclei to move from the lower energy state to the higher energy state (Figure 18).



S3.2 Figure 18 A hydrogen nucleus (proton) that is spin-aligned with an external magnetic field can absorb radio waves and move to a higher energy state where it is spin-opposed to the external magnetic field.

As electrons shield the nucleus from the full effects of the external magnetic field, differences in electron distribution produce different energy separations between the two spin energy levels. The technique is a very useful analytical tool, as nuclei in different **chemical environments** produce different signals in the spectrum. Proton or ^{1}H NMR is particularly useful. The hydrogen nuclei, present in all organic molecules, effectively act as spies and give information about their position in a molecule.

A full explanation of how NMR spectroscopy works is beyond the scope of this course. Instead we will focus on how the spectra obtained using ^{1}H NMR can help determine the structures of organic compounds.

Note that a hydrogen nucleus consists of a single proton. The terms hydrogen nucleus and proton can therefore be used interchangeably when discussing proton, or ^{1}H, NMR spectroscopy and interpreting spectra, as you will see when we examine this topic in more detail.

Nature of Science

The development of many scientific techniques involves a steady process of refinement and improvement until physical or technological limits are reached. Breakthroughs in materials or technology may allow these limitations to be overcome with the subsequent development of improved techniques. The first nuclear magnetic spectrometers, developed in the 1950s, used iron magnets that generated field strengths of 4–30 MHz. The development of superconducting materials, and successive improvements in these materials, led to progressively stronger magnets and increased operating field strengths, with a 1 GHz spectrometer first being introduced in 2010. However, this proved to be the limit of the superconducting materials available at the time as no further increases in field strength were to occur until 2019 when the development of new high-temperature superconductors led to the first 1.1 GHz NMR spectrometer, with 1.2 GHz spectrometers following soon after in 2021.

TOK

As the operating frequencies of NMR spectrometers have increased, scientists have been able to determine the structures of larger, and more complex, molecules as well as to investigate more complicated reaction mechanisms. Will further improvements in NMR technology allow this trend to continue? Could there be scientific problems that are currently unknown because the technology needed to reveal them does not exist yet?

(a) (b)

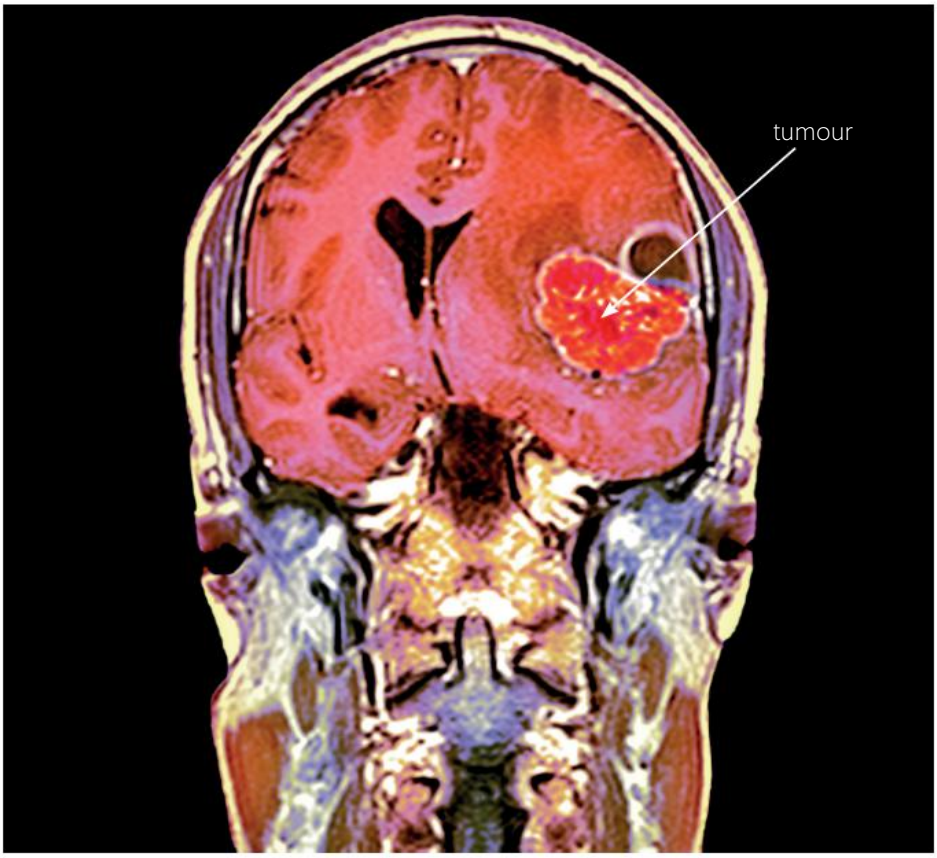


Advancements in NMR spectrometry have largely been determined by the strength of the magnetic field that can be generated by superconducting magnets. The photos show **(a)** a 500 MHz and **(b)** a 900 MHz spectrometer, which were the strongest magnetic fields available in the early 1980s and 2000s respectively.

In contrast to other imaging techniques, MRI does not use ionizing radiation, so is considered relatively non-invasive. Radio waves are low-energy waves and there are no known hazards of exposure of the body to the strength of magnetic fields applied. MRI scans give detailed images of almost any part of the body and are widely used in cancer detection, the diagnosis of soft tissue injuries, and in monitoring degenerative diseases.

Magnetic resonance imaging (MRI)

Since 1977, when MRI was first used to produce images of internal body organs and soft tissue, it has developed into one of the most widely used diagnostic techniques in modern medicine. MRI is an application of nuclear magnetic resonance (NMR) spectroscopy and so uses the fact that hydrogen atoms, ^1H, have a magnetic moment due to their odd number of nucleons. In the presence of a powerful magnet, radio waves are used to generate an electronic signal that can be decoded by a computer to produce two- or three-dimensional images. MRI is particularly useful in the diagnosis of living tissue because hydrogen atoms are present in water, which makes up about 70% of the body by mass.



Coloured MRI scan through the head of a male patient. A cancerous tumour is shown in bright red compressing the left side of the brain. Information from scans such as this can help doctors to determine the best treatments for disease.

TOK

The term *MRI* is used for the application of NMR technology in medicine, purposefully avoiding reference to the word nuclear and the negative associations with nuclear waste and harmful radiation. How do our expectations and assumptions have an impact on how we perceive things?

Structures of organic compounds can be deduced from ^{1}H NMR spectroscopy

The ^{1}H NMR spectra of organic molecules can range from very simple through to highly complex. Regardless of how complicated they may appear, each ^{1}H NMR spectrum provides four important pieces of information that can be used to deduce the structure of the compound being analysed:

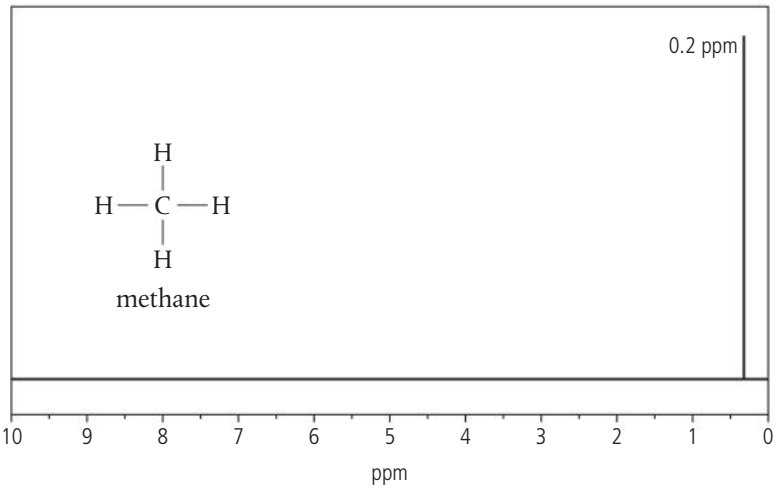
1. The **number of signals** in the spectrum.
2. The position, or **chemical shift**, of each signal.
3. The size, or **integrated area**, of each signal.
4. The **splitting pattern** observed for each signal.

Interpretation of each signal in the spectrum gives information about the chemical environment of the hydrogen nucleus generating that signal. Piecing together the information gained for the individual chemical environments allows the overall structure of the compound to be deduced.

Protons in different chemical environments have different chemical shifts

Hydrogen nuclei (protons) that have the same chemical environment are said to be **equivalent** as they give the same signal in the ^{1}H NMR spectrum. The number of signals observed in a spectrum therefore depends on the number of different chemical environments in the compound being analysed.

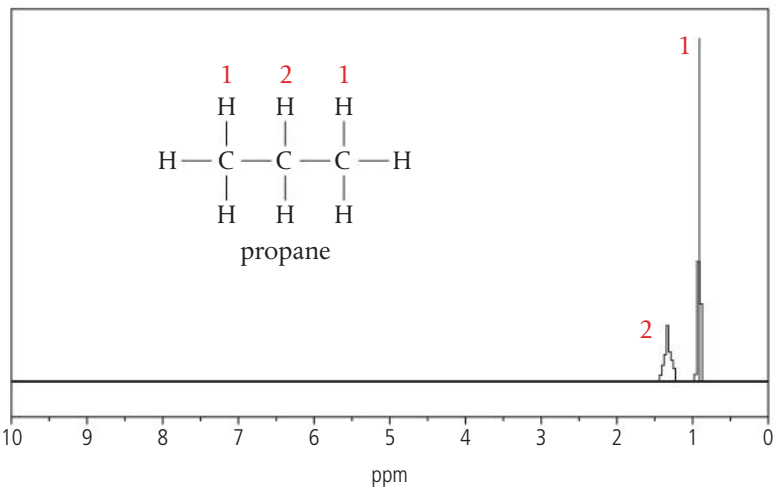
The ^{1}H NMR spectra of methane (CH_4) and ethane (C_2H_6) both give one signal as the hydrogen nuclei in both compounds are equivalent.



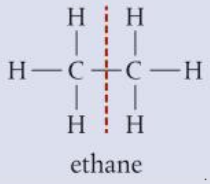
For methane it is readily apparent that the hydrogens are all equivalent; each is attached to a central carbon bonded to three other hydrogens.

For ethane a quick look would suggest two different chemical environments as the hydrogens are bonded to two different carbons. However, closer examination shows that all six hydrogens are actually equivalent; each is attached to a carbon atom that is bonded to two other hydrogens and a methyl group.

Propane (C_3H_8) is the first alkane that has an ^{1}H NMR spectrum containing more than one signal. It has a symmetrical structure so the protons in the two $-CH_3$ groups at each end of the chain are equivalent and generate the same signal. The protons in the central CH_2 group are in a different chemical environment so they produce a second signal.

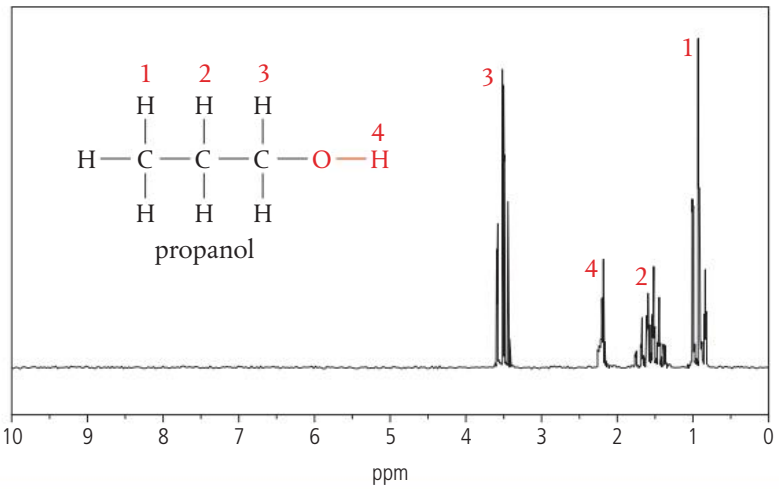


Equivalent hydrogens can often be identified by looking at the symmetry of the structure. If a compound is symmetrical and a mirror plane can be drawn, as shown here for ethane, any hydrogens that appear as reflections of each other will be equivalent.



Looking closely at the spectra of propane on the previous page, and propanol below, it can be observed that some of the individual signals are actually made up of a series of lines in distinctive patterns. These patterns also convey important information about the structure of a compound and this will be covered in more detail when we discuss splitting patterns.

Propan-1-ol (C_3H_7OH) is not a symmetrical molecule so the hydrogens on each carbon are in different chemical environments. This generates three distinct signals in the ^1H NMR spectrum. The hydrogen in the OH group occupies a fourth chemical environment so the ^1H NMR spectrum of propanol contains a total of four signals.



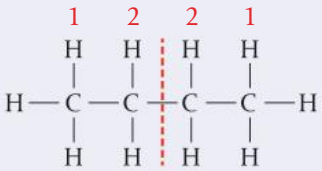
A hydrogen nucleus consists of a single proton. The terms hydrogen nucleus and proton are therefore used interchangeably when discussing ^1H NMR spectroscopy.

Worked example

How many signals would be observed in the ^1H NMR spectra of butane and butan-1-ol?

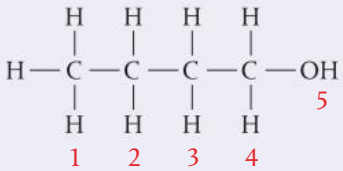
Solution

Butane is a symmetrical molecule with two different chemical environments: CH_3 and CH_2.



The ^1H NMR spectrum of butane will contain two signals.

Butan-1-ol is not a symmetrical molecule. It contains five different chemical environments as shown in the following structure:



So the ^1H NMR spectrum of butan-1-ol will contain five signals.

The chemical shifts observed for hydrogen nuclei are affected by neighbouring atoms

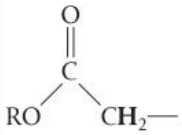
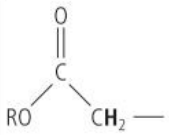
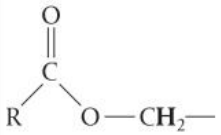
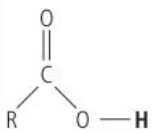
As shown in the spectra on the previous page, the position where a signal appears in an NMR spectrum is measured in terms of its **chemical shift** which has units of parts per million (ppm).

In the ^{1}H NMR spectrum of propanol, given on the previous page, we can observe a definite pattern in the chemical shifts for the hydrogen atoms in the molecule. The closer these hydrogen atoms are to the OH group, the higher the chemical shift observed. This happens because the high electronegativity of the oxygen atom effectively pulls electrons away from the hydrogen atoms, causing the nuclei to become deshielded. This makes these nuclei more susceptible to the effects of the external magnetic field and results in their signals occurring at a higher chemical shift. The closer a hydrogen nucleus is to an electronegative atom, the more pronounced the electron-withdrawing effect and the higher the chemical shift observed.

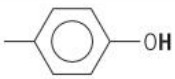
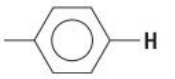
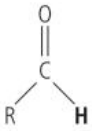
Hydrogen nuclei close to electronegative atoms, or electron-withdrawing groups, become deshielded and their ^{1}H NMR signals occur at higher ppm. The ^{1}H NMR signals of hydrogen nuclei that are shielded occur at low ppm.

Note that the signal observed for the OH proton itself does not follow this pattern. Even though the hydrogen atom is directly attached to the oxygen atom, other factors also influence the chemical shift for this signal. As shown in Section 21 of the data booklet chemical shifts for alcohol protons can occur within a wide range of values.

Hydrogen nuclei in particular environments have characteristic chemical shifts. Some examples are given in the table below (continued on the next page). A more complete list is given in Section 21 of the data booklet.

Type of proton	Chemical shift / ppm
—CH$_3$	0.9–1.0
	2.0–2.5
	2.2–2.7
—C≡C—H	1.8–3.1
R—O—CH$_2$—	3.3–3.7
	3.7–4.8
	9.0–13.0*
R—O—H	1.0–6.0*

continued

—HC ═ CH_2	4.5–6.0
	4.0–12.0*
	6.9–9.0
	9.4–10.0

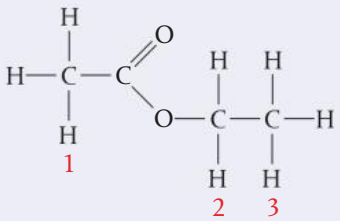
* Signals from the hydrogen atoms in the –OH groups are very variable owing to hydrogen bonding.

Worked example

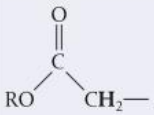
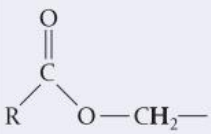
Determine the number of signals in the ^1H NMR spectrum of ethyl ethanoate and predict the chemical shift for each signal using the table of chemical shifts given on the previous page and above.

Solution

The structure of ethyl ethanoate and the number of different proton chemical environments are given below:

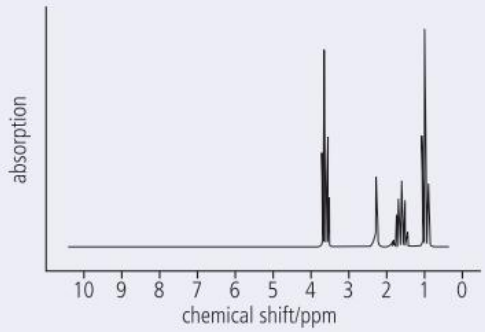


The chemical shifts for each signal can be determined by looking at the neighbouring atoms and using the table provided to identify the type of proton generating the signal.

Signal	Type of proton	Chemical shift
1		2.0–2.5
2		3.7–4.8
3	—CH_3	0.9–1.0

Worked example

The NMR spectrum of a compound that has the molecular formula C_3H_8O is shown here.



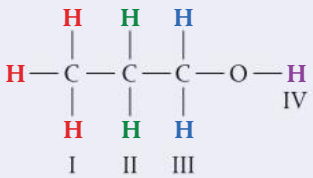
(a) Draw the full structural formulas and give the names of the three possible isomers of C_3H_8O.

(b) Identify the unknown compound from the number of signals in the spectrum.

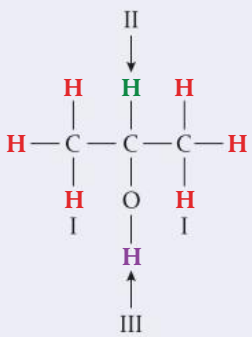
(c) Identify the group responsible for the signal at 0.9 ppm.

Solution

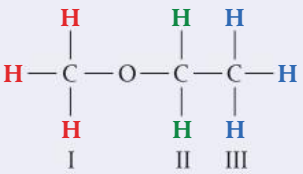
(a) The structures and names are:



propan-1-ol



propan-2-ol



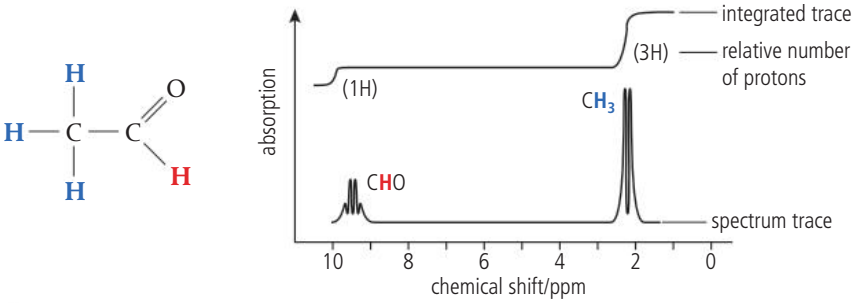
methoxyethane

(b) For each structure, I–IV identifies the different environments of the H atoms in the molecule. There are four signals observed in the spectrum and this is consistent with the number of different chemical environments predicted for the structure of propan-1-ol.

(c) From the table on page 398–99 we can determine that the peak at 0.9 ppm corresponds to the CH_3 group.

The area under a signal depends on the number of nuclei in that chemical environment

The ^{1}H NMR spectrum of ethanal is shown in Figure 19.



S3.2 Figure 19 The ^{1}H NMR spectrum of ethanal shows two signals because the hydrogen atoms are in two different environments. The **integrated trace** indicates the relative number of hydrogen atoms in the two environments.

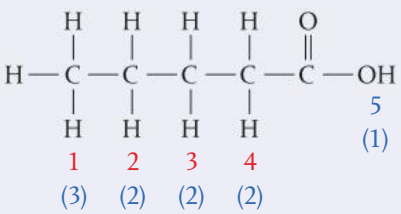
The spectrum has a signal at 9.7, which corresponds to the C**H**O proton, and a signal at 2.1 which corresponds to the three protons in the C**H**$_3$ group. The area under the CH_3 signal is three times larger than that under the CHO signal as it indicates the relative number of protons in each environment. The integrated trace gives this information more directly, as it goes up in steps which are proportional to the number of protons.

Worked example

Predict the number of signals, and their relative intensities, that will be observed in the ^{1}H NMR signal of pentanoic acid.

Solution

First draw the full structure of pentanoic acid.



Looking at the structure, it is evident that this is not a symmetrical molecule. Therefore, the hydrogens on each carbon will produce a unique signal, numbered 1 to 4 in the structure. The OH hydrogen will produce a 5th signal.

The relative intensity of each signal depends on the number of protons generating the signal and is given in brackets below each numbered signal.

The relative intensity of a NMR signal relates to its integrated area and is proportional to the number of hydrogen atoms present in that chemical environment.

Hydrogens on neighbouring carbons split an ^{1}H NMR signal into specific patterns

As observed in the various spectra shown earlier, individual signals in the NMR spectrum of an organic compound do not generally consist of a single peak. Instead, high-resolution NMR spectra reveal a much more detailed structure, with the signals split, or resolved, into distinctive patterns.

The splitting of the peaks occurs as the effective magnetic field, experienced by particular nuclei, is modified by the magnetic field produced by neighbouring protons. This effect is known as **spin–spin coupling**.

The numbers of lines in the splitting patterns caused by spin–spin coupling, and the relative intensities of the lines in a particular splitting pattern, are easily predicted based on the number of neighbouring hydrogens involved in the coupling.

Number of lines: this follows the ***n* + 1 rule:** If there are ***n*** hydrogens on the neighbouring carbons there will be ***n* + 1** lines observed in the splitting pattern. For example, the presence of three neighbouring hydrogens causes the signal to be split into four lines.

Intensity of lines: the intensities of the lines observed for a given splitting pattern follow the sequential pattern known as Pascal's triangle.

If a proton has *n* protons as nearest neighbours, its NMR signal is split into a group of (*n* + 1) peaks. Thus, for CH_3CH_2F, we would expect the CH_2 proton signal to be split into a quartet as it has three protons as nearest neighbours.

TOK

Mathematics has been described as the science of patterns. Pascal's triangle has been known independently for over a thousand years by a number of different cultures. Why is mathematics so important in other areas of knowledge, particularly the natural sciences?

The application of the *n* + 1 rule and Pascal's triangle to the splitting patterns and intensities of ^{1}H NMR signals are illustrated in the table below.

Number of hydrogen atoms on neighbouring carbons (*n*)	Number of peaks in signal (*n* + 1 rule)	Splitting pattern and intensities	Signal observed in ^{1}H NMR spectrum	Name of signal
0	1	1		singlet
1	2	1 1		doublet
2	3	1 2 1		triplet
3	4	1 3 3 1		quartet

This pattern will continue for each additional proton on neighbouring carbons: four adjacent protons gives a quintet with intensities 1:4:6:4:1; five adjacent protons gives a sextet with intensities 1:5:10:10:5:1. Larger splitting patterns can typically be difficult to resolve and are commonly referred to as multiplets.

When analysing high-resolution NMR spectra, the following additional points should be noted:

- protons bonded to the same atom do not interact with one another as they are equivalent and behave as a group
- protons on carbon atoms not adjacent to each other do not generally interact with one another as they are too far apart for their magnetic fields to interact through spin–spin coupling
- alcohol protons (O**H**) typically do not engage in spin–spin coupling with hydrogen atoms on neighbouring carbons. This means that:
  - the signals for O**H** protons are not split by other protons and appear as singlets in ^{1}H NMR spectra
  - O**H** protons are not counted when applying the $n + 1$ rule as they do not split the signals of other protons.

If we return to the example of ethanal, whose spectrum was presented in Figure 19, we can now recognize that:

- the signal generated by the C**H**O proton at 9.8 ppm is split into a **quartet** due to the **three** hydrogens on the neighbouring $-CH_3$ group
- the signal generated by the C**H**$_3$ protons at 9.8 ppm is split into a **doublet** due to the **one** hydrogen on the neighbouring CHO group.

Worked example

Predict the number and position of the signals, along with their associated splitting patterns, that would be observed in the ^{1}H NMR spectrum of propanoic acid, CH_3CH_2COOH.

Solution

Propanoic acid has three distinct chemical environments so the ^{1}H NMR spectrum will have three signals. The chemical shifts for these signals can be determined using Section 21 of the data booklet.

Chemical environment	Chemical shift / ppm	Number of hydrogen atoms on neighbouring carbons	Splitting pattern ($n + 1$ rule)
C**H**$_3$CH$_2$COOH	0.9–1.0	2 (CH_2)	triplet
CH$_3$C**H**$_2$COOH	2.0–2.5	3 (CH_3)	quartet
CH$_3$CH$_2$COO**H**	9.0–13.0	0	singlet

You need to be aware that the chemical shifts do not always exactly match the ones given in the data booklet.

The ethyl group pattern is easy to spot. The three-proton signal is split into a triplet and the two-proton signal is split into a quartet.

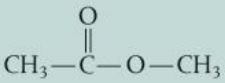
A shorthand notation that gives the type of signal and intensity can be applied when determining the NMR spectrum for a compound. For example:

3H s means the signal is a singlet generated by three protons
3H d means the signal is a doublet generated by three protons
1H t means the signal is a triplet generated by one proton

Exercise

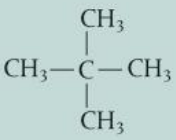
Q36. How many signals will the following compounds show in their ^{1}H NMR spectra?

(a)

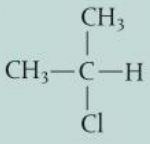


(b) $CH_3—O—CH_3$

(c)



(d)



Q37. Determine the number of signals, along with their chemical shifts, that will be observed in the ^{1}H NMR spectrum of 2-methylpropanoic acid, $CH_3CH(CH_3)COOH$.

Q38. The ^{1}H NMR spectrum of a compound exhibits three signals at 1.0 ppm, 2.2 ppm and 2.5 ppm.

Identify the compound using the table of chemical shifts given on pages 398 and 399.

A $CH_3CH_2CH_3$ **B** CH_3CH_2CHO

C $CH_3CH_2COCH_3$ **D** $CH_3CH_2CH_2CH_2CH_3$

Q39. **(a)** Draw the full structural formula of butanone.

(b) Use Section 21 of the data booklet to predict the high-resolution ^{1}H NMR spectrum of butanone. Your answer should include the chemical shift, the number of hydrogen atoms, and the splitting pattern for the different environments of the hydrogen atoms.

Q40. Compare the ^{1}H NMR spectra of ethanal and propanone. Your answer should refer to the number of signals, and the areas and splitting patterns of each signal.

Q41. The key features of the ^{1}H NMR spectrum of a compound with the molecular formula $C_3H_6O_2$ are summarized below.

Chemical shift / ppm	Number of H atoms	Splitting pattern
1.3	3	3
4.3	2	4
10	1	1

What is the structure of this compound?

Structure 3.2.12 – Combining analytical techniques

Structure 3.2.12 – Data from different techniques are often combined in structural analysis.

Interpret a variety of data, including analytical spectra, to determine the structure of a molecule.

Analytical chemistry depends on combining information

The techniques discussed in this chapter provide the analytical chemist with different types of information. The skill of the analyst is to combine these methods to give a complete description of the structure of the substance being studied. For example, infrared spectroscopy gives some information about the bonds present in a molecule, but often this information needs to be supplemented with data from other sources to give a complete structure of the molecule. Mass spectrometry can give information about the molar mass and the mass of fragment ions but does not necessarily give conclusive evidence on how the fragments are pieced together in the parent molecule. ^{1}H NMR is one of the most powerful analytical techniques and frequently a structure can be determined using this technique alone. However, analytical chemists will still look for supporting evidence from other techniques to ensure their results are consistent and conclusive when determining the structure of an organic compound.

SKILLS

Using spectra to confirm the structure of a compound. Full details of how to carry out this experiment with a worksheet are available in the eBook.

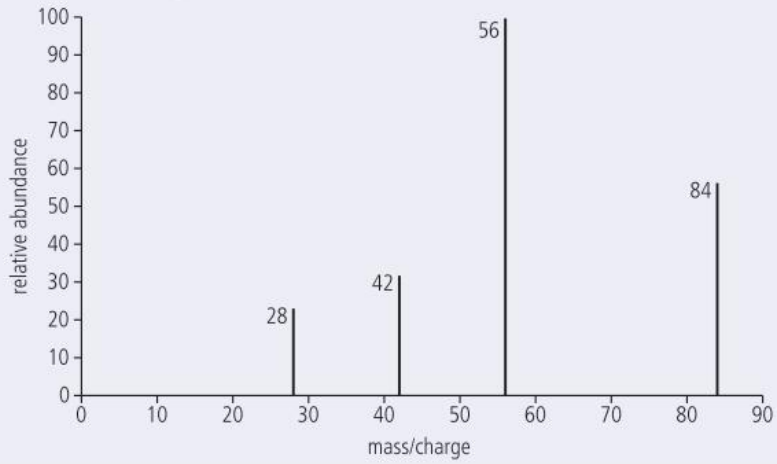
Worked example

(a) An unknown compound is found to have the following composition:

	% composition by mass
C	85.6
H	14.4

Deduce the empirical formula of the compound.

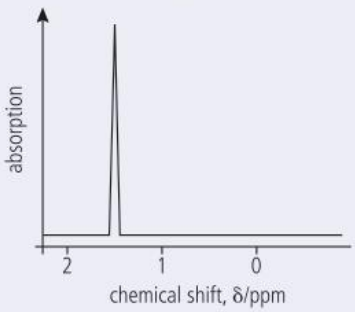
(b) The mass spectrum of the compound is shown below. Deduce the molecular formula of the compound.



(c) Is the molecule likely to contain a CH_3 group? Explain your answer.

(d) The infrared spectrum shows one absorption close to 2900 cm^{-1}, but there is no absorption close to 1600 cm^{-1}. State what can be deduced from this information.

(e) Deduce the molecular structure from the ^1H NMR spectrum shown.



Solution

To find the empirical formula, calculate the relative number of moles:

	C	H
mass / g	85.6	14.4
moles	$= \frac{85.6}{12.01}$ $= 7.13$	$= \frac{14.4}{1.01}$ $= 14.26$
simple ratio	$= \frac{7.13}{7.13}$ $= 1.00$	$= \frac{14.26}{7.13}$ $= 2.00$

The empirical formula is CH_2.

(b) The mass spectrum shows a parent ion at 84. The molecular formula is C_nH_{2n}.

$$n(12.01) + 2n(1.01) = 84$$

$$14.03n = 84$$

$$n = \frac{84}{14.03} = 5.99$$

The molecular formula is C_6H_{12}.

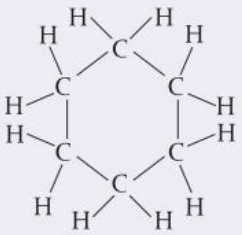
The saturated non-cyclic compound with six carbons is C_6H_{14}, so the molecule C_6H_{12} contains a C=C or a ring.

(c) The absence of peaks at 15 or 69 (84 − 15) suggests that the molecule probably does not contain a methyl group.

(d) The absorption close to 2900 cm^{-1} is due to the C–H bond.

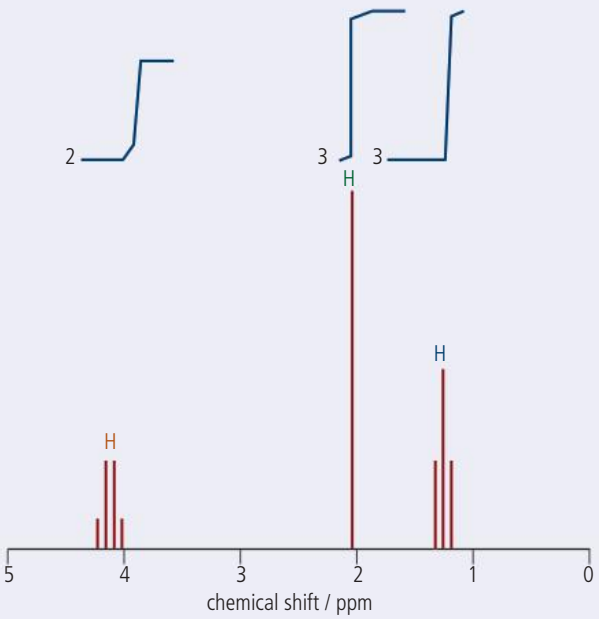
The absence of an absorbance at 1600 cm^{-1} suggests that the molecule does not contain a C=C bond. It must, therefore, have a ring structure.

(e) The NMR spectra shows only one peak, so all the hydrogen atoms are in the same chemical environment. This confirms that the molecule has a ring structure. It is cyclohexane.



Worked example

The ^1H NMR spectrum of a compound with the empirical formula C_2H_4O is shown.



(a) Deduce the molecular formula of the compound.

(b) Draw possible structures of molecules with this molecular formula.

(c) The IR spectrum of the compound shows distinctive peaks at 1730 cm^{-1} and 1210 cm^{-1}. No broad peaks are observed in the 2500–3000 cm^{-1} region. What does this information tell us about the possible structures for the compound?

(d) Use Section 21 of the data booklet to identify a structure which is consistent with the ^1H NMR spectrum and account for the number of peaks and the splitting patterns in the spectrum.

Solution

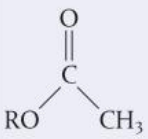
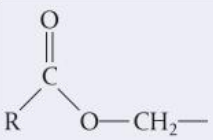
(a) The ^{1}H NMR spectrum shows the presence of eight hydrogens so the molecular formula is $C_4H_8O_2$. The hydrogens are in three different chemical environments in a 2:3:3 ratio.

(b) Possible structures: $CH_3CH_2CH_2COOH$, $CH_3CH(CH_3)COOH$, $CH_3CH_2COOCH_3$, $CH_3COOCH_2CH_3$, $HCOOCH_2CH_2CH_3$ and $HCOOCH(CH_3)_2$, although many of these do not fit the data in terms of the 2:3:3 ratio.

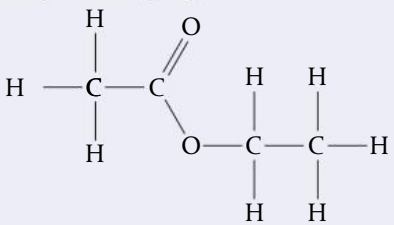
(c) The absence of a broad peak in the 2500–3000 cm^{-1} region indicates there is no O–H bond present and the compound is not a carboxylic acid.

The peaks at 1730 cm^{-1} and 1210 cm^{-1} are likely due to a C=O and a C–O bond respectively and indicate the compound is an ester.

(d)

Chemical shift / ppm	Integration	Type of proton	Splitting pattern	Structural information
1.0–1.5	3H	—CH_3	triplet	CH_3 next to CH_2
2.0–2.5	3H		singlet	CH_3 next to CO
3.8–4.1	2H		quartet	OCH_2 next to CH_3

The correct structure is $CH_3COOCH_2CH_3$



HL end

Guiding Question revisited

How does the classification of organic molecules help us to predict their properties?

In this chapter we have learnt that:

- Organic compounds can be grouped into classes based on their functional groups.
- The presence of different functional groups means that different classes of compounds have different physical and chemical properties.
- Homologous series exist for each class of compound and successive members of a series differ by a CH_2 unit.

- Applying IUPAC nomenclature to generate unique names for individual compounds allows for further classification of organic compounds.
- Structural isomers are compounds that have the same molecular formula but different connectivities. They have unique IUPAC names as well as different chemical and physical properties.
  - Chain isomers occur when C–C bonds are connected differently to form structures that are a straight chain or branched.
  - Positional isomers contain the same functional group but it is at different positions on the carbon chain.
  - Functional group isomers contain different functional groups.
  - Positional isomers of alcohols, halogenoalkanes and amines can be classified as primary, secondary or tertiary depending on the number of carbon atoms bonded to the functional group site.

HL

- Stereoisomers are compounds with the same connectivities but different spatial arrangements of atoms. This includes *cis–trans* isomers and optical isomers.
- Structures of organic compounds can be determined using analytical techniques:
  - Mass spectrometry and fragmentation patterns give information about the groups and branching present in a molecule.
  - Infrared spectroscopy gives information on the covalent bonds present in a molecule.
  - ^{1}H NMR spectroscopy gives information about the number of different proton chemical environments in a molecule, along with the functional groups that are present and the number of hydrogen atoms on adjacent carbons.
  - Results from more than one analytical technique may be required to conclusively determine the structure of an organic compound.

HL end

Practice questions

1. Which of the following compounds are structural isomers?

I. $CH_3CH_2COCH_3$ II. $CH_3CH_2CH_2CHO$ III. $CH_3CH(CH_3)CHO$

A I and III **B** I, II and III **C** I and II **D** II and III

2. Which of the following compounds is a secondary alcohol?

A $CH_3CH_2CH_2OH$ **B** $(CH_3)_2CHCH_2OH$

C $(CH_3)_2C(OH)CH_3$ **D** $CH_3CH_2CH(OH)CH_3$

3. Which molecule has a secondary nitrogen?

A CH_3NHCH_3 **B** $H_2NCH_2CH_2NH_2$

C $CH_3CH_2NH_2$ **D** $(CH_3)_3N$

4. Which of the following has the molecules ordered by decreasing volatility?

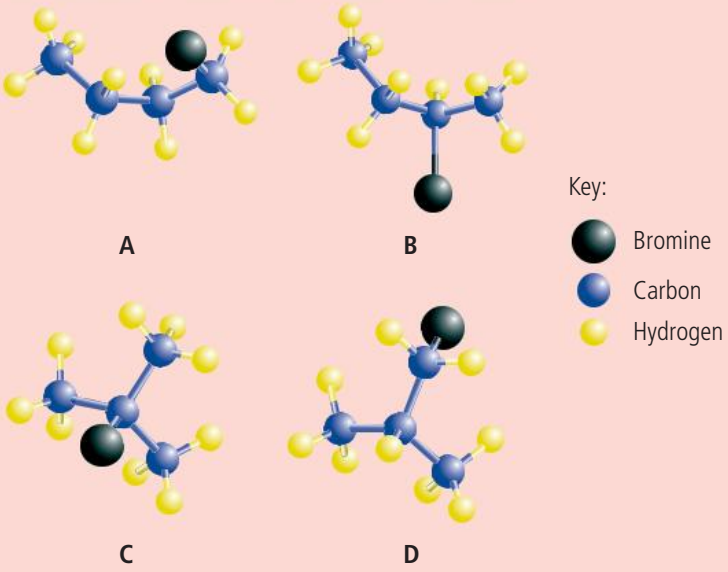
A butan-1-ol, butan-2-ol, 2-methylpropan-2-ol

B butanal, butan-1-ol, butanone

C 2-methylpropan-2-ol, butanone, butan-1-ol

D butanone, 2-methylpropan-2-ol, butan-1-ol

5. **(a)** Below are four structural isomers with molecular formula C_4H_9Br. State the name of each of the isomers A, B, C and D.



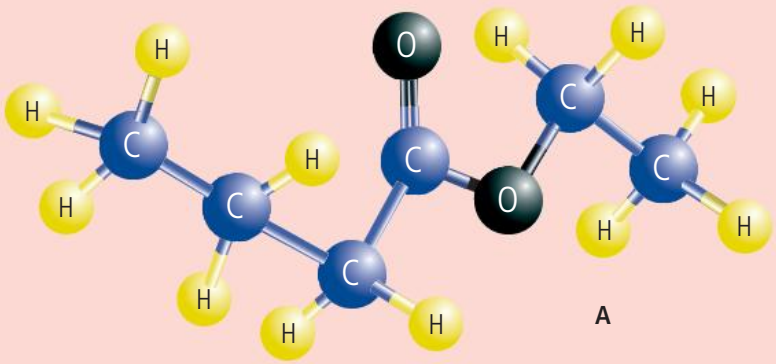
A B C D

(4)

(b) HL Identify the isomer of C_4H_9Br that can exist as stereoisomers. Outline how a polarimeter will distinguish between the isomers, and how their physical and chemical properties compare. (5)

(Total 9 marks)

6. For the organic compound A shown below:



A

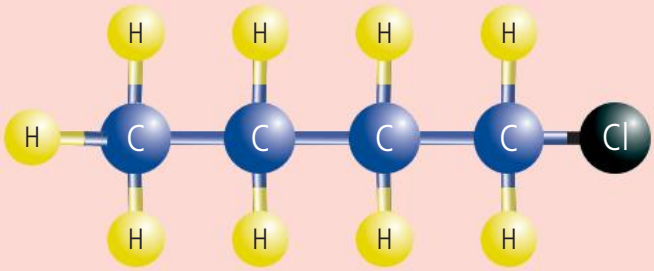
(a) Identify the class of compound it belongs to. (1)

(b) Determine the IUPAC name of the compound. (1)

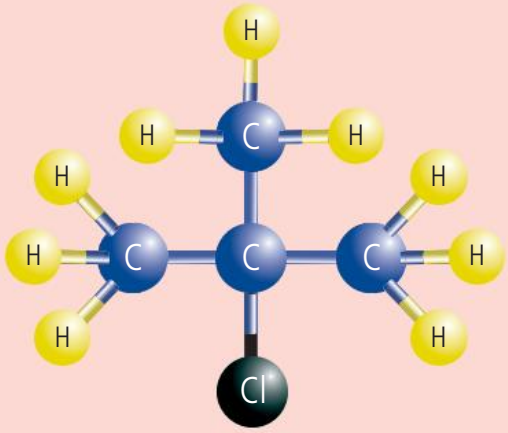
(c) Draw the structural formula of two isomers of A; one that belongs to the same class of compound, and one that belongs to a different class of compound. (2)

(Total 4 marks)

7. Two isomers, A and B, with the molecular formula C_4H_9Cl are shown below:



A



B

(a) Determine the IUPAC name for each isomer and state whether it is a primary, secondary or tertiary compound. (3)

(b) HL State the number of signals that would be observed in the ^1H NMR spectrum for each isomer. (1)

(c) HL A third isomer of C_4H_9Cl is a chiral compound. Draw the three-dimensional shapes of the two enantiomers of this isomer. (2)

(Total 6 marks)

8. Propanoic acid, ethyl methanoate and methyl ethanoate all have the same chemical formula, $C_3H_6O_2$.

(a) **(i)** What class of compounds do ethyl methanoate and methyl ethanoate belong to? (1)

(ii) What is the relationship between these three compounds? (1)

(iii) Draw the full structural formula for each compound. (3)

(b) HL Deduce the ^{1}H NMR spectra you would expect for each compound and complete the table below. The answers for ethyl methanoate are given as a guide.

Note that some of the boxes may be blank. (5)

Compound	Number of signals	Chemical shift range / ppm	Integrated area	Splitting pattern
ethyl methanoate	3	0.9–1.0	3	triplet
		3.7–4.8	2	quartet
		9.4–10.0	1	singlet
propanoic acid				
methyl ethanoate				

(Total 10 marks)

HL

9. Which of the following compounds can exhibit *cis–trans* isomerism?

I. 1,4-dimethylcyclohexane

II. 1,2-dichlorohexane

III. but-2-ene

A I and II only **B** I, II and III **C** I only **D** I and III

10. What is not true for optical isomers of the same compound?

A They have the same boiling point.

B They rotate polarized light in opposite directions.

C They have the same molecular formula.

D They have different volatilities.

11. How many chiral carbon atoms are present in one molecule of $CH_3CHClCH(CH_3)CHBrCH_3$?

A 0 **B** 1 **C** 2 **D** 3

12. Which of the following atmospheric gases is not IR active?

A N_2 **B** CO_2 **C** H_2O **D** NO

13. What can be determined about a molecule from its IR spectrum?

A The number of bonds in the molecule.

B The molar mass of the molecule.

C The types of bonds present in the molecule.

D The number of different chemical environments.

14. What can be determined from the splitting patterns in an ^{1}H NMR spectrum?

A The number of different chemical environments.

B The number of hydrogens on neighbouring atoms.

C The number of hydrogens making each signal.

D The number of carbon atoms in the molecule.

15. The ^{1}H NMR spectrum of a compound contains a single peak at 1.5 ppm. What can be deduced from this spectrum?

A There is only one hydrogen atom in the compound.

B The compound is an alcohol.

C The compound is a hydrocarbon.

D There is only one chemical environment in the compound.

16. A compound gives the following signals in its ^{1}H NMR spectrum.

Chemical shift/ppm	Integrated intensity	Splitting pattern
1.1	3	triplet
2.2	3	singlet
2.5	2	quartet

Which compound gives this spectrum?

A $CH_3CH_2COCH_3$ **B** $CH_3CH_2CH_2CHO$

C CH_3CH_2COOH **D** CH_3COOCH_3

17. What is the ratio of area under each signal in the ^{1}H NMR spectrum of 2,2-dimethylbutanal?

A 3 : 6 : 2 **B** 9 : 2 : 1 **C** 3 : 3 : 3 : 2 : 1 **D** 3 : 2 : 6 : 1

18. Which is correct for benzene, C_6H_6?

A It contains alternate single and double carbon–carbon bonds.

B Its ^{1}H NMR spectrum shows six signals.

C Its ^{1}H NMR spectrum shows one signal.

D It has three structural isomers.

19. Compounds A and B are alcohols with the molecular formula C_3H_8O. The following information was obtained from a mass spectrum of each alcohol.

A: peaks at $m/z = 29, 31, 60$ **B:** peaks at $m/z = 45, 60$

(a) Deduce the formula of the species responsible for the peak at $m/z = 60$. (1)

(b) Deduce the formula of the species with $m/z = 31$. (1)

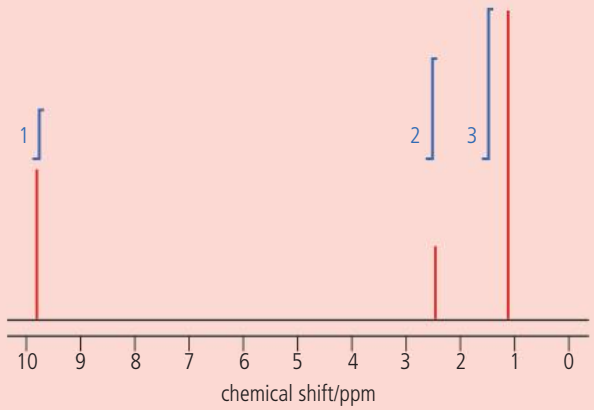
(c) Deduce the structure of each alcohol. (2)

(Total 4 marks)

20. Infrared (IR) spectroscopy is widely used as a technique in analytical chemistry. Explain what happens at a molecular level during the absorption of IR radiation by carbon dioxide, CO_2. (3)

(Total 3 marks)

21. A low resolution ^1H NMR spectrum does not show the splitting patterns for each signal but still provides other information. The low resolution ^1H NMR spectrum of compound X with molecular formula C_3H_6O is shown below.



(a) Deduce which of the following compounds is X and explain your answer.

A $CH_3–CO–CH_3$ **B** $CH_3–CH_2–CHO$ **C** $CH_2=CH–CH_2OH$

(2)

(b) Deduce which one of the peaks in the ^1H NMR spectrum of X would also occur in the spectrum of one of the other isomers, giving your reasoning. (2)

(c) The infrared and mass spectra for X were also recorded.

(i) Apart from absorptions due to C–C and C–H bonds, suggest one absorption, in wavenumbers, that would be present in the infrared spectrum of X. (1)

(ii) Apart from absorptions due to C–C and C–H bonds, suggest one absorption, in wavenumbers, absent in the infrared spectrum of X, but present in one of the other compounds shown in part **(a)**. (1)

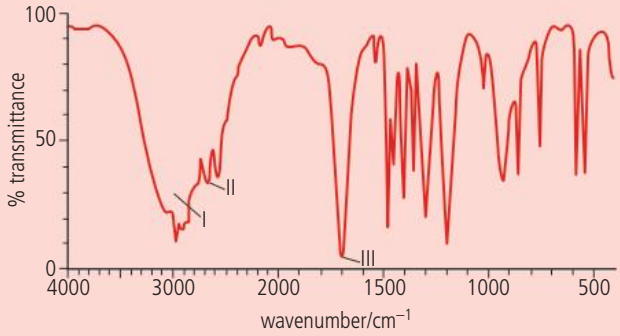
(d) Suggest the formulas and m/z values of two species that would be detected in the mass spectrum of X. (2)

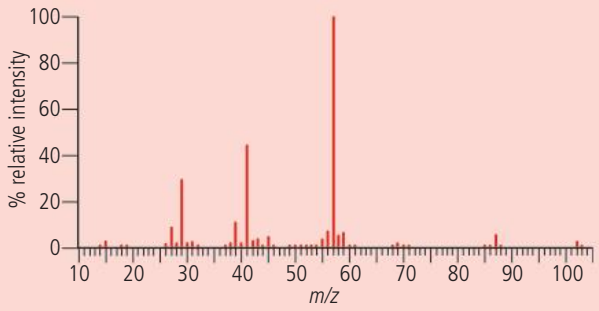
(Total 8 marks)

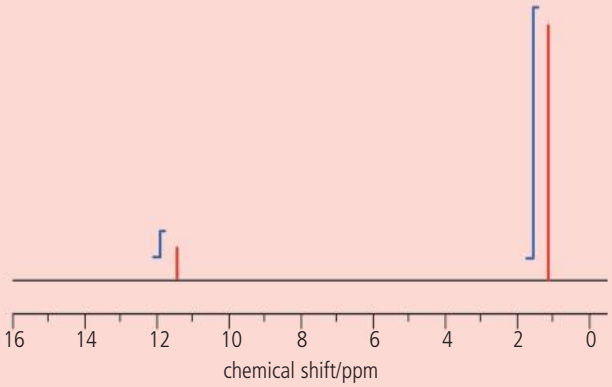
22. Infrared spectroscopy is commonly used as an analytical technique by inorganic, physical, and organic chemists.

(a) Explain why hydrogen bromide, HBr, is IR active whereas bromine, Br_2, is IR inactive. (1)

(b) The IR spectrum, mass spectrum, and ^1H NMR spectrum of an unknown compound, X, of molecular formula $C_5H_{10}O_2$, are as follows:







(i) In the IR spectrum, identify the bond responsible for each of the absorptions labelled I, II and III. (3)

(ii) In the mass spectrum, deduce which fragments the *m*/*z* values at 102, 57 and 45 correspond to. (3)

(iii) Identify the signal at 11.5 ppm in the ^1H NMR spectrum. (1)

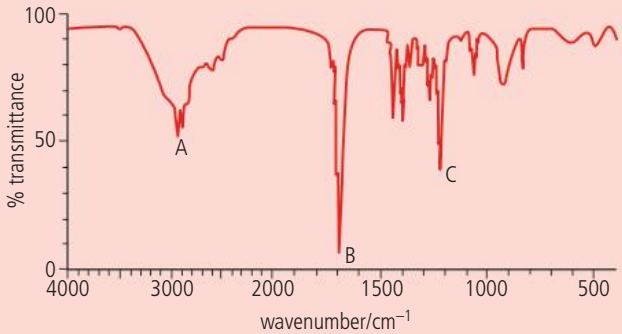
(iv) State what information can be obtained from the integration traces in the ^1H NMR spectrum about the hydrogen atoms responsible for the signal at 1.2 ppm. (1)

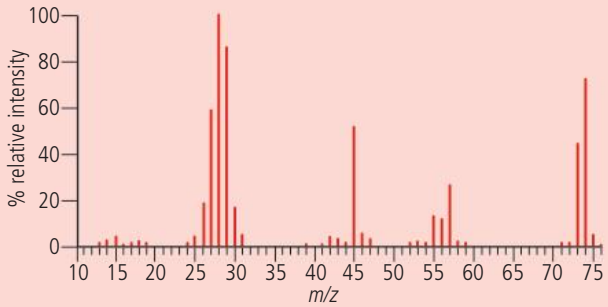
(v) Deduce the structure of X. (1)

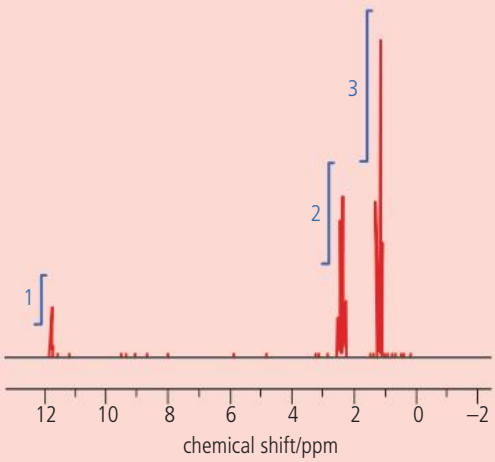
(vi) $CH_3COOCH_2CH_2CH_3$ is an isomer of X. Deduce two differences between the ^1H NMR spectrum of this isomer and that of X. (2)

(Total 12 marks)

23. The IR spectrum, mass spectrum, and ^1H NMR spectrum of an unknown compound, X, of molecular formula $C_3H_6O_2$ are as follows.







(a) Identify the bonds responsible for the peaks A, B and C in the IR spectrum of X. (2)

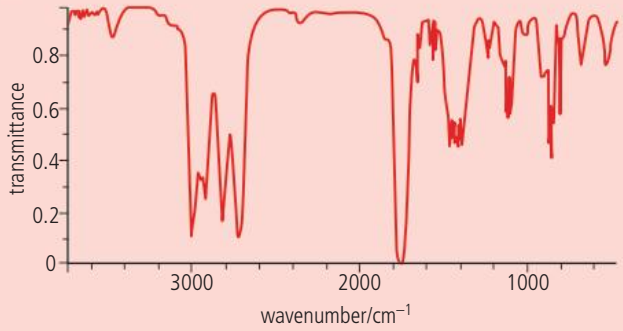
(b) In the mass spectrum of X, deduce which ions the *m*/*z* values at 74, 45, and 29 correspond to. (3)

(c) Identify the signal at 11.73 ppm in the ^1H NMR spectrum. (1)

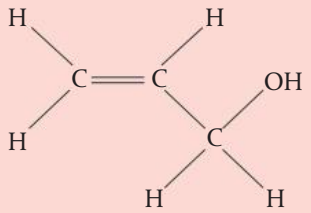
(d) Deduce the structure of X. (1)

(Total 7 marks)

24. The infrared spectrum of a substance, X, with empirical formula C_3H_6O, is given below.



(a) Explain why the structural formula of X cannot be:



(2)

(b) The ^{1}H NMR spectrum of X consists of three signals. Deduce the structural formula of X and the relative areas under each signal. (2)

(Total 4 marks)

25. Butan-1-ol, butan-2-ol, 2-methylpropan-1-ol and 2-methylpropan-2-ol are four structural isomers with the molecular formula $C_4H_{10}O$.

(a) Details of the ^{1}H NMR spectra of two of these alcohols are given below.

Spectrum 1

Two signals: One at 1.3 ppm with an integration trace of nine units and the other at 2.0 ppm with an integration trace of one unit.

Spectrum 2

Four signals: The first at 0.9 ppm with an integration trace of six units, the second at 1.7 ppm with an integration trace of one unit, the third at 2.1 ppm with an integration trace of one unit and the fourth at 3.4 ppm with an integration trace of two units.

Consider the proton environments present in each of the alcohol molecules when answering the following questions.

(i) Identify which alcohol gives spectrum 1 and explain your answer by stating which hydrogen atoms in the molecule are responsible for each of the two peaks. (3)

(ii) Deduce which alcohol gives spectrum 2. Explain which particular hydrogen atoms in the molecule are responsible for the peaks at 0.9 ppm and 3.4 ppm. (3)

(b) The mass spectrum of one of the alcohols shows peaks at m/z values of 74, 59 and 45.

(i) Deduce which two of the alcohols could produce this spectrum and identify the species responsible for the three peaks. (4)

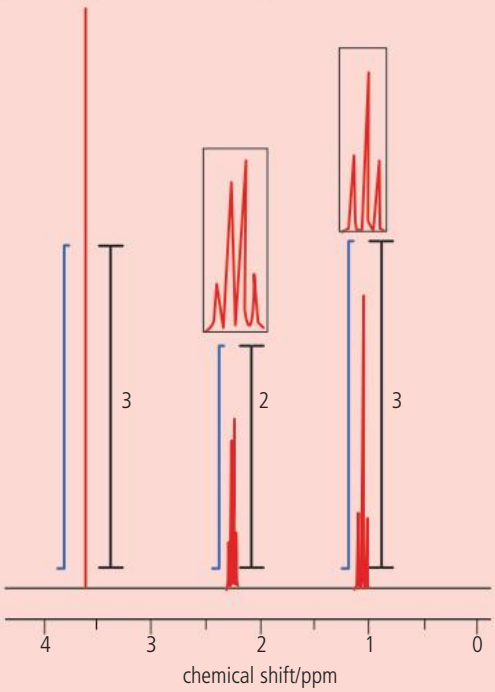
(ii) The spectrum also shows a significant peak at $m/z = 31$. Suggest which alcohol is responsible for this spectrum and deduce the species responsible for the peak at $m/z = 31$. (2)

(c) Explain why the infrared spectra of all four alcohols are very similar. (1)

(Total 13 marks)

26. A feature of some ^{1}H NMR spectra is the electron-withdrawing effect of electronegative atoms. These atoms cause nearby protons to produce peaks at higher chemical shift values, often in the range 2.5 to 4.5 ppm.

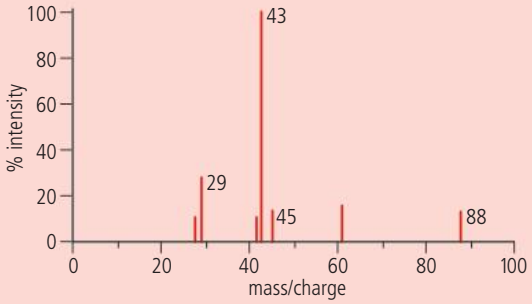
Consider the ^{1}H NMR spectrum of an unknown compound, D, which has a molecular formula $C_4H_8O_2$ and is known to have an absorption in its IR spectrum corresponding to a C=O absorption.



Use this information and the values in Section 21 of the data booklet to deduce the structure of D. (4)

(Total 4 marks)

27. The mass spectrum of an unknown compound, X, of empirical formula C_2H_4O is shown below.

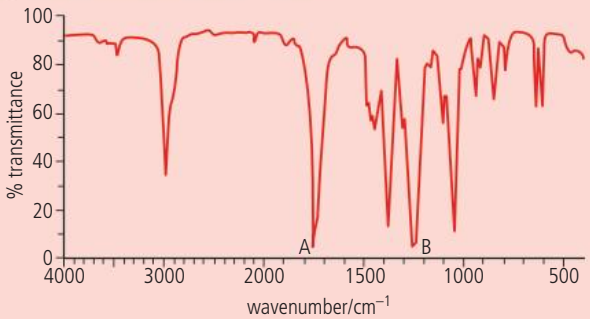


(a) **(i)** Determine the relative molecular mass of X from the mass spectrum and deduce the formula of the molecular ion. (2)

(ii) Identify a fragment which gives rise to the peak at $m/z = 29$. (1)

(iii) Comment on the absence of a peak at $m/z = 59$. (1)

(b) The IR spectrum of X is shown below.



(i) Use Section 20 of the data booklet to identify the bonds which correspond to absorptions A and B. (1)

(ii) Deduce the name of the functional group present in X. (1)

(c) Typical proton chemical shift values are given in Section 21 of the data booklet.

The ^{1}H NMR spectrum of X contains three signals. Details of two of these are shown in the table below.

Signal	Chemical shift / ppm	Relative peak area	Splitting pattern
first	2.0	3	singlet
second	4.1	2	quartet
third			

(i) Deduce a possible structure for X that is consistent with the mass, IR, and ^{1}H NMR spectra. (1)

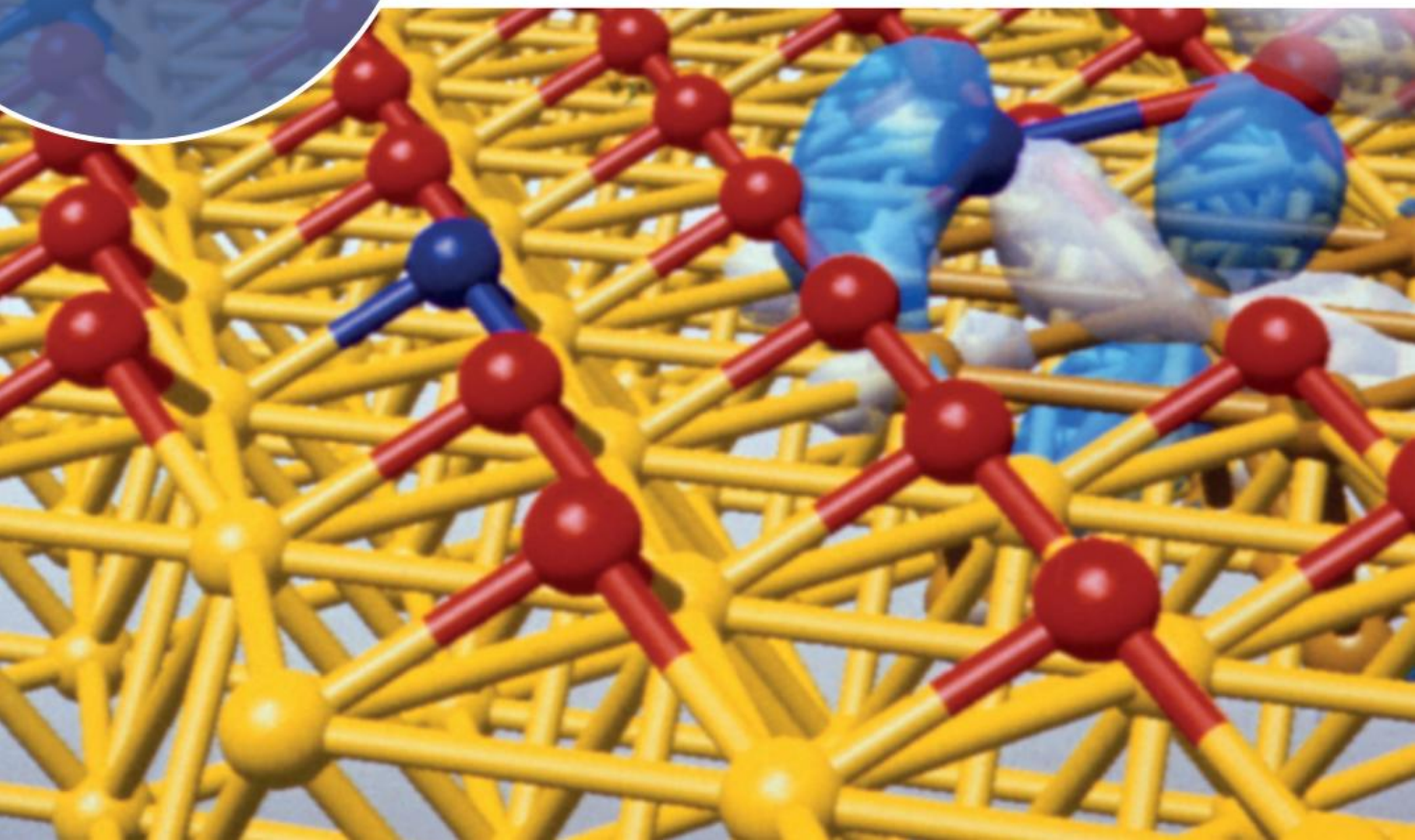
(ii) Complete the table above by suggesting the chemical shift of the third signal, and state its relative area and splitting pattern. (3)

(iii) Explain the splitting pattern of the signal at chemical shift 4.1 ppm. (2)

(Total 12 marks)

HL end

THEME Reactivity





Molecular graphic showing a catalytic converter in a vehicle exhaust system. The yellow framework is the catalyst, a lattice of copper atoms. The reactant gases NO and CO are shown adsorbed onto the copper surface. A chemical reaction occurs on the surface of the catalyst, converting these polluting gases into non-polluting products:

$$2NO(g) + 2CO(g) \rightarrow N_2(g) + 2CO_2(g)$$

Catalysts are widely used in research and industry to increase the rate of reactions.

Reactivity

Reactivity refers to the ways in which chemical reactions transform reactants into products. These reactions occur through bond-breaking and bond-making, and so they change structures into new forms. An understanding of what drives these reactions helps us to determine how they can be controlled and how we can influence the product.

In Reactivity 1 we explore the direction of energy transfer in reactions, starting with measurements of temperature change as an indication of heat transfer. The conservation of energy during reactions is an application of the First Law of Thermodynamics, and is illustrated through energy cycles. We consider the release of energy from different fuels to supply our daily energy needs within the context of their relative benefits and environmental impact. Through an investigation of the direction of change, we learn that reactions are spontaneous when they lead to products which have lower free energy than the reactants.

In Reactivity 2 we use experimental data to examine the factors that influence both the extent and the rate of reactions, while stoichiometric principles help us to assess the yield and the atom economy of reactions. The role of catalysts in increasing the efficiency of reactions is explained.

The focus of Reactivity 3 is the mechanisms of reactions and how reactions proceed at the molecular level. Mechanisms are classified on the basis of the transfer or sharing of subatomic particles between reactants. In this way, we can see how our understanding of reactivity is based on the application of our knowledge of structure.

Chemical reactivity is at the heart of chemical industries such as resource extraction, and processes which synthesize novel products such as pharmaceuticals and petrochemicals. These reactions supply many products for our modern world, but can also be responsible for unwanted side-products and harmful effects on the environment. Throughout this study, you are encouraged to consider how the application of Green Chemistry principles can ameliorate some of the negative side-effects of chemical reactivity.

Structure determines reactivity, which in turn transforms structure.

REACTIVITY

1 What drives chemical reactions?



The burning of a firework increases the disorder in the universe, as both energy and matter become dispersed. This is the natural direction of change.

The law of conservation of energy states that energy cannot be created or destroyed. It can, however, be transformed from one form into another, and all chemical reactions are accompanied by energy changes. These energy changes are vital. For example, our bodies' processes are dependent on the energy changes which occur during respiration, when glucose reacts with oxygen; and modern lifestyles are dependent on the transfer of energy that occurs when fuels burn. As we explore the source of these energy changes, we will deepen our understanding of why bonds are broken and formed during a chemical reaction, and why electron transfer can lead to the formation of stable ionic compounds. The questions of why things change will lead to the development of the concept of entropy. We will see that this concept allows us to give the same explanation for a variety of physical and chemical changes: the universe is becoming more disordered as matter and energy are dispersed. This provides us with a signpost for the direction of all change. The distinction between the quantity and quality of energy will lead to the development of the concept of free energy, a useful accounting tool for chemists to predict the feasibility of any hypothetical reaction.

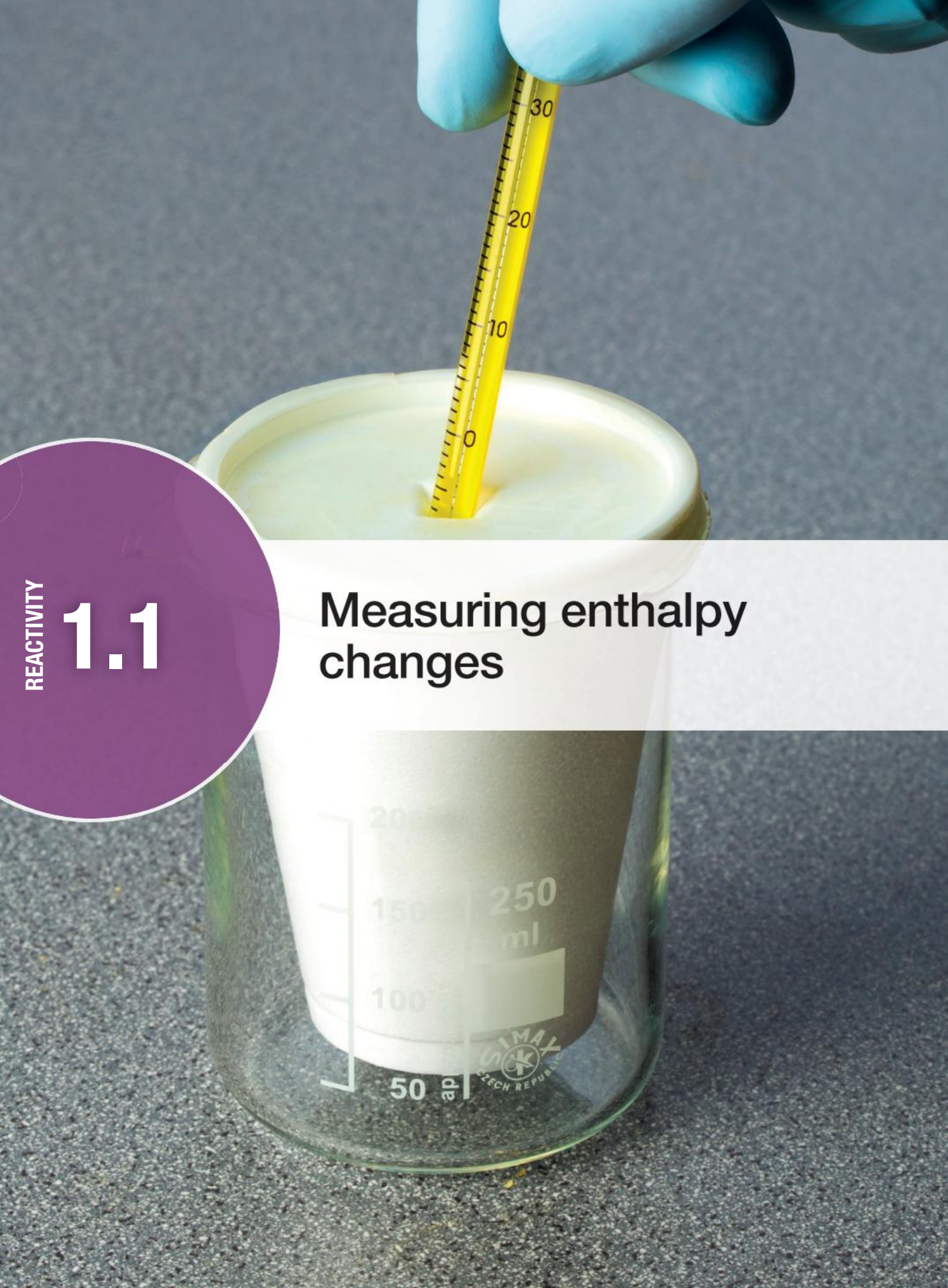
We will see how creative thinking, accurate calculations, and careful observations and measurement can work together to lead to a deeper understanding of the relationship between heat and chemical change.

TOK

The Nobel Prize winning physicist, Richard Feynman, on the scientific idea of energy:
'... the conservation of energy.... says that there is a certain quantity, which we call energy, that does not change in the manifold changes which nature undergoes. That is a most abstract idea, because it is a mathematical principle; it says that there is a numerical quantity, which does not change when something happens.'

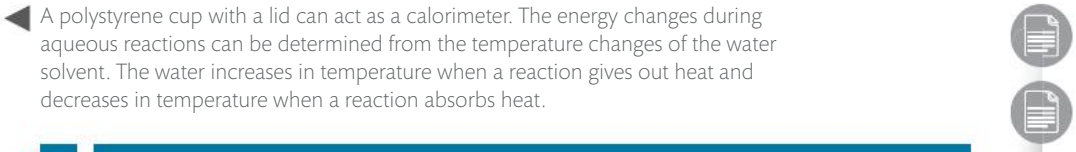
'It is important to realize that we have no knowledge of what energy is.'

Why are many of the laws in the natural sciences stated using the language of mathematics? Do you agree that we have no *knowledge* of what energy is?



REACTIVITY

1.1 Measuring enthalpy changes



A polystyrene cup with a lid can act as a calorimeter. The energy changes during aqueous reactions can be determined from the temperature changes of the water solvent. The water increases in temperature when a reaction gives out heat and decreases in temperature when a reaction absorbs heat.

Guiding Question

What can be deduced from the temperature change that accompanies chemical or physical change?

It is important to distinguish between heat and temperature. Heat is a method of energy transfer and temperature is a measure of the average kinetic energy of the constituent particles in an object. Heat transfers can, however, be determined from temperature changes. The heat needed to change the temperature of an object by 1 K is a property of the mass and composition of the object, known as the heat capacity, which can be experimentally determined. Generally, we determine the heat transfers during a chemical reaction by measuring the temperature changes of a known mass of water. For example, the heat from a flame during combustion reactions is transferred to the water in a metal calorimeter. Alternatively, reactions in aqueous solution are investigated in calorimeters made from an insulating material, and the heat is transferred between the reactants and the water solvent. The temperature of the water increases during an exothermic reaction, which releases heat as the reactants change to products with less potential energy. The temperature of the water decreases during the less common endothermic reactions as heat is transferred from the water to the products with more potential energy than the reactants.

Reactivity 1.1.1 – Chemical reactions involve heat transfers

Reactivity 1.1.1 – Chemical reactions involve a transfer of energy between the system and the surroundings, while total energy is conserved.	
Understand the difference between heat and temperature.	
	Structure 1.1 – What is the relationship between temperature and kinetic energy of particles?

Heat is a process of energy transfer

Energy is a measure of the ability to do **work**, that is, to move an object against an opposing force. Energy can be transferred in different ways including heat, light, sound and electricity, and stored in different forms of potential energy such as chemical potential energy. This chapter focuses on the heat transfers which accompany chemical reactions. Reactions that involve the transfer of electrical energy are explored in Reactivity 3.2.

Heat is a form of energy transfer that occurs as a result of a temperature difference. When heat is transferred to a system, the average kinetic energy of the molecules and temperature are increased and the kinetic energy is more dispersed among the particles. Heat is a process of energy transfer, whereas temperature, a measure of the *average* kinetic energy of the particles, is a property of the object or system.

More heat energy is needed to raise the temperature of water in a swimming pool by 1 K than is needed for the water in a kettle because there are more water molecules in the swimming pool.



The heat needed to boil a kettle will only lead to a very small increase in the temperature of a swimming pool.

Structure 1.1 – What is the relationship between temperature and kinetic energy of particles?

Work is another form of energy transfer and is a more ordered process than energy transfer by heat. For example, you do work on a beaker of water when you lift it from a table.

The joule is the unit of energy and work. You do 1 J of work when you exert a force of 1 N over a distance of 1 m. 1 J of energy is used every time the human heart beats.

System and surroundings

Chemical and physical changes take place in many different environments such as test tubes, polystyrene cups, industrial plants and living cells. It is useful in these cases to distinguish between the **system** – the area of interest, and the **surroundings** – in theory, everything else in the universe (Figure 1).

Energy is conserved in chemical reactions.



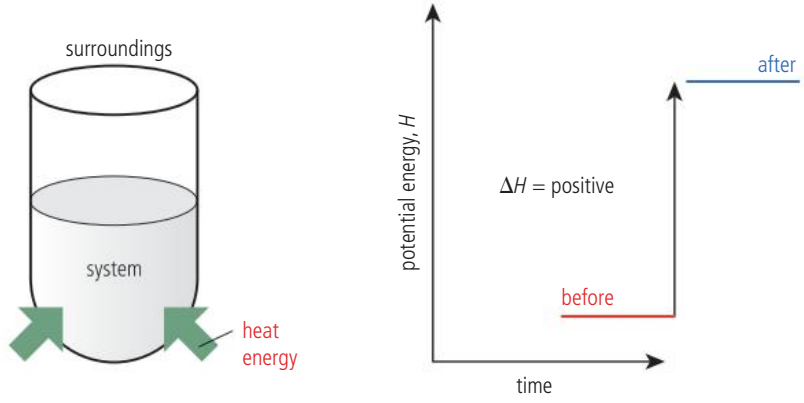
R1.1 Figure 1 The system is the sample or reaction vessel of interest. The surroundings are the rest of the universe.

- An open system can exchange matter and energy with its surroundings.
- A closed system allows the transfer of energy but not matter with its surroundings.
- An isolated system cannot exchange matter or energy with its surroundings.

Most chemical reactions take place in an **open system** in which energy and matter can be exchanged with the surroundings. For example, in an open system, gases and heat produced by a reaction in a test tube can be transferred to the surroundings. In a **closed system**, energy can be exchanged with the surroundings but matter cannot. Although energy can be exchanged between a closed system and the surroundings, the total energy cannot change during the process; any energy lost by the system is gained by the surroundings and vice versa. An **isolated system** cannot exchange matter or energy with the surroundings.

The chemical potential energy of a system is its enthalpy

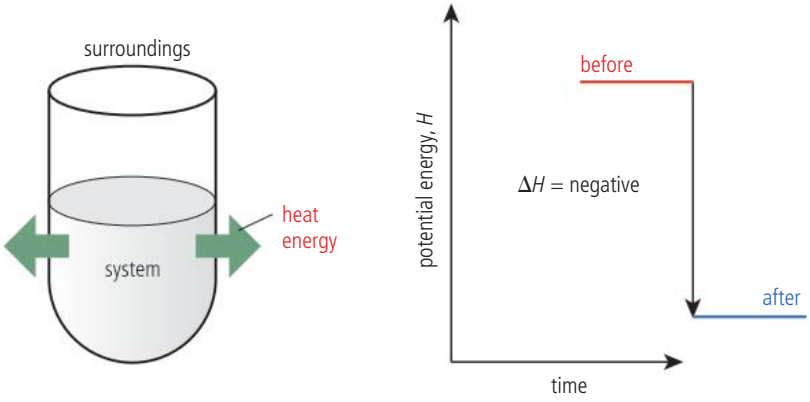
Although, according to the law of conservation of energy, the total energy of the system and surroundings cannot change during a process, heat can be transferred between a system and its surroundings. The chemical potential energy of a system is called its **enthalpy**, a name which comes from the Greek word for 'heat inside'. A system acts like a reservoir of chemical potential energy or enthalpy. When heat is added to a system from the surroundings, the enthalpy of the system increases and when a system gives out heat its enthalpy decreases. Changes in enthalpy are denoted by ΔH. ΔH is positive when heat is added to the system (Figure 2).



R1.1 Figure 2 When heat is added from the system to the surroundings, the enthalpy of the system increases and ΔH is positive.

Enthalpy (H) is a measure of the chemical potential energy stored in a system. The enthalpy changes as chemical bonds and intermolecular forces change during a reaction. This results in a heat transfer which can be observed.

When heat is released from the system to the surroundings, the chemical potential energy or enthalpy of the system decreases and ΔH is negative (Figure 3).



R1.1 Figure 3 When heat is given out from the system to the surroundings, the enthalpy or potential energy of the system decreases and ΔH is negative.

TOK

How important are technical terms such as enthalpy in different areas of knowledge? To what extent does the technical language we use help or hinder the acquisition of knowledge?

Exercise

Q1. A large iron cube at high temperature, T_H, is brought into contact with a small iron cube at lower temperature, T_C. Discuss the changes that occur, assuming that both objects are insulated from all other objects.

Q2. The temperature of a volume of water increases from 300 K to 310 K. State the temperature increase in °C.

Reactivity 1.1.2 – Endothermic and exothermic reactions

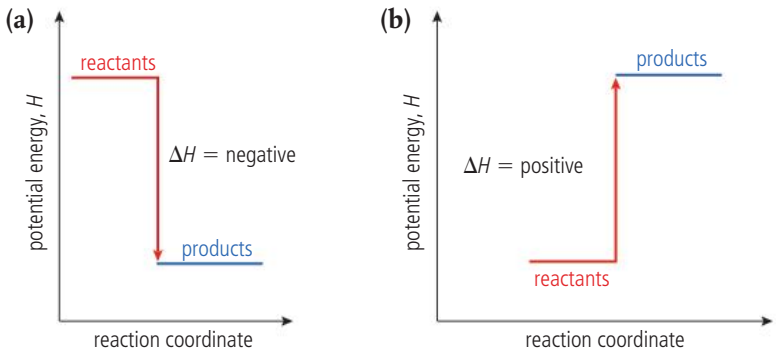
Reactivity 1.1.2 – Reactions are described as endothermic or exothermic, depending on the direction of energy transfer between the system and the surroundings.	
Understand the temperature change (decrease or increase) that accompanies endothermic and exothermic reactions, respectively.	
	Tool 1, Inquiry 2 – What observations would you expect to make during an endothermic and an exothermic reaction?

SKILLS

Observe endothermic and exothermic processes in action. Full details of how to carry out this experiment with a worksheet are available in the eBook.

Exothermic and endothermic reactions involve heat transfers between the system and the surroundings

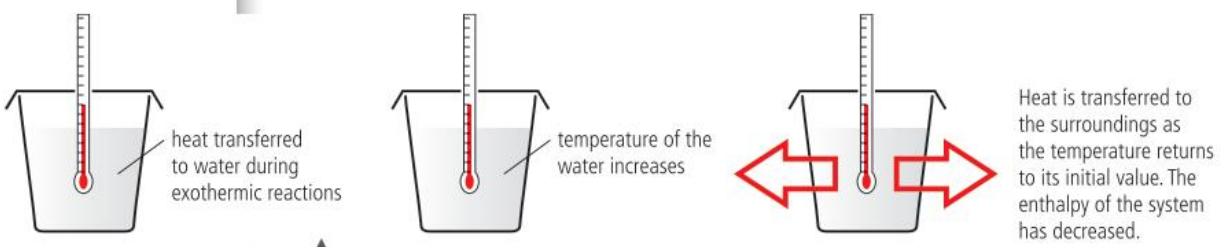
The enthalpy (H) of the system changes as the chemical and intermolecular forces change. Most chemical reactions, including most combustion and all neutralization reactions, are exothermic. They give out heat to the surroundings and $\Delta H_{reaction}$ is negative (Figure 4a). Some reactions are **endothermic** as they result in a heat transfer from the surroundings to the system. In this case, the products have more stored potential energy than the reactants and $\Delta H_{reaction}$ is positive (Figure 4b).



R1.1 Figure 4 **(a)** An exothermic reaction. The stored chemical energy, or enthalpy, of the products is less than the enthalpy of the reactants. **(b)** An endothermic reaction. The enthalpy of the products is greater than the enthalpy of the reactants. The change from reactants to products is represented on the horizontal axis and labelled as the reaction coordinate.

Temperature changes during reactions in solution

When a reaction occurs in aqueous solution, any enthalpy changes in the reaction are best observed by changes in the temperature of the water, which is acting as the solvent. In an exothermic reaction, the heat released by the chemical reaction is first transferred to the solvent. The temperature increases as the water molecules increase their average kinetic energy. Heat is eventually transferred from the water to the wider surroundings as the system returns to its initial temperature. The net result is transfer from the system to the surroundings, and the enthalpy of the system decreases (Figure 5).



R1.1 Figure 5 Temperature changes during an exothermic reaction.

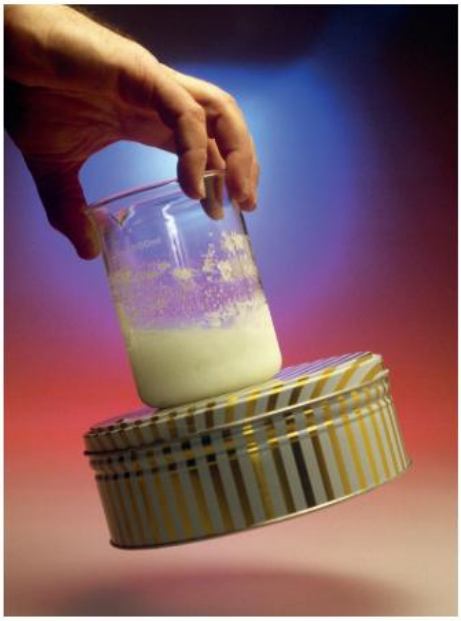


The oxidation of glycerin by potassium permanganate is an exothermic reaction.

Conversely, any heat needed for an endothermic reaction is transferred from the water, leading to a decrease in temperature of the aqueous solvent. The system returns to its initial temperature when heat is transferred to the water from the wider surroundings.

Nature of Science

Scientists share their knowledge using a precise language. In everyday language, heat and work are both nouns and verbs, whereas in science they are nouns which describe energy transfer processes. Heat is often said to 'flow' from high temperature to low temperature. This image originates from the incorrect view that heat was a liquid, *calorique*, which was included in Lavoisier's list of chemical elements. Heat is now more correctly characterized as a process of energy transfer.



An endothermic reaction. The reaction between ammonium thiocyanate and barium hydroxide absorbs so much heat from water placed between the flask and the metal container that the water freezes.

Tool 1, Inquiry 2 – What observations would you expect to make during an endothermic and an exothermic reaction?

Exercise

Q3. When a sample of $NH_4SCN(s)$ is mixed with $Ba(OH)_2.8H_2O(s)$ in a glass beaker, the mixture changes to a liquid and the temperature drops sufficiently to freeze the beaker to the table. Which statement is true about the reaction?

A The process is endothermic and ΔH is negative.
B The process is endothermic and ΔH is positive.
C The process is exothermic and ΔH is negative.
D The process is exothermic and ΔH is positive.

Q4. Which one of the following statements is true of all exothermic reactions?

A They produce gases.
B They give out heat.
C They occur quickly.
D They involve combustion.

Q5. Which is the best explanation of why the temperature of the liquid decreases when it evaporates?

A The number of liquid molecules is decreasing.
B The mean kinetic energy of the liquid molecules is decreasing.
C The pressure above the liquid surface is increasing.
D The rate of evaporation is increasing.

Q6. Two objects made of different masses of aluminium have the same temperature.

Which is the best description of the relative average kinetic energy and total energies of the aluminium atoms in the different objects?

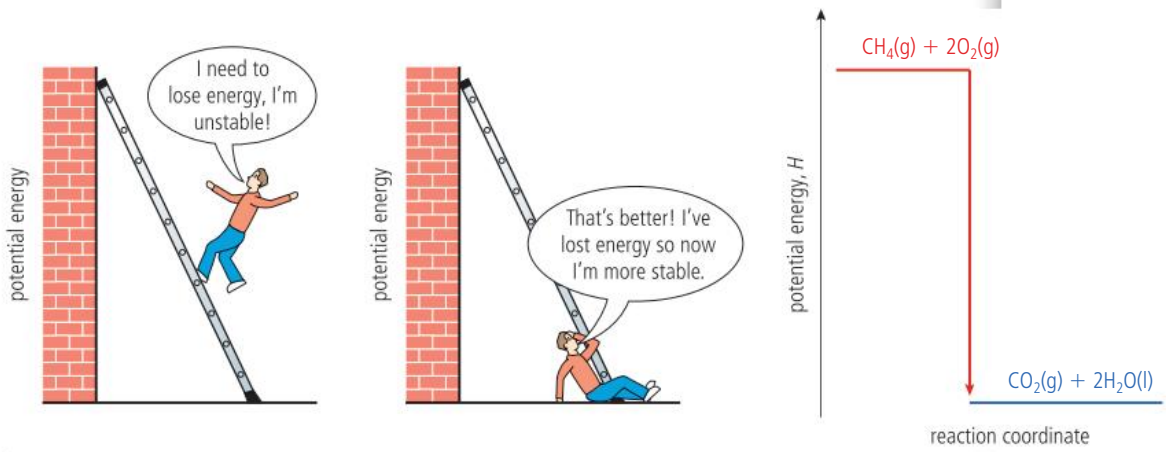
	Average kinetic energy of the atoms	Total energy of the atoms
A	greater in object of larger mass	same
B	less in object of larger mass	same
C	same	greater in object of larger mass
D	same	less in object of larger mass

Reactivity 1.1.3 – Energetic stability and the direction of change

Reactivity 1.1.3 – The relative stability of reactants and products determines whether reactions are endothermic or exothermic.	
Sketch and interpret potential energy profiles for endothermic and exothermic reactions.	
Axes for energy profiles should be labelled as reaction coordinate *x*, potential energy *y*.	Structure 2.2 – Most combustion reactions are exothermic; how does the bonding in N_2 explain the fact that its combustion is endothermic?

Enthalpy changes as the direction of a reaction

There is a natural direction for change. When we slip on a ladder, we go down, not up (Figure 6). The direction of change is in the direction of lower stored, or potential, energy. In a similar way, we expect methane to burn when we strike a match and form carbon dioxide and water. The chemicals are changing in a way which reduces their chemical potential energy or enthalpy.

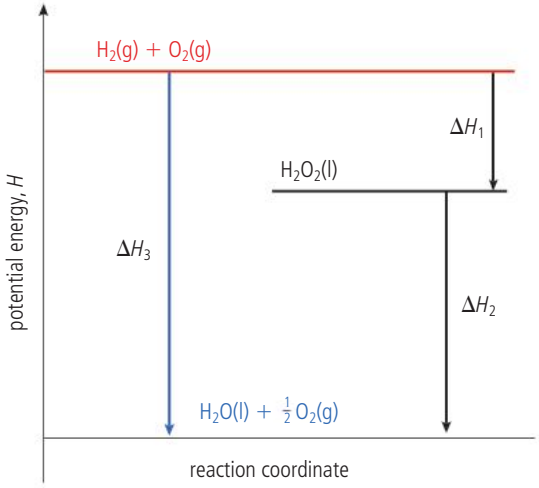


R1.1 Figure 6 An exothermic reaction can be compared to a person falling off a ladder. Both changes lead to a decrease in potential energy. The state of lower potential energy is more stable. The mixture of carbon dioxide and water is more stable than a mixture of methane and oxygen.

There are many examples of exothermic reactions, and we generally expect a reaction to occur if it leads to a reduction in the potential energy or enthalpy. In the same way that a ball is more stable on the ground than in mid-air, we can say that the products in an exothermic reaction are more stable than the reactants. Most combustion reactions, for example, are exothermic as the energy needed to break the bonds in the reactants is less than the energy produced as the bonds form in the products. The enthalpy changes that occur as bonds are broken and formed are discussed in more detail in Reactivity 1.2.

Structure 2.2 – Most combustion reactions are exothermic; how does the bonding in N_2 explain the fact that its combustion is endothermic?

It is important to realize that stability is a relative term. Hydrogen peroxide, for example, is stable with respect to its elements but unstable relative to its decomposition to water and oxygen (Figure 7).



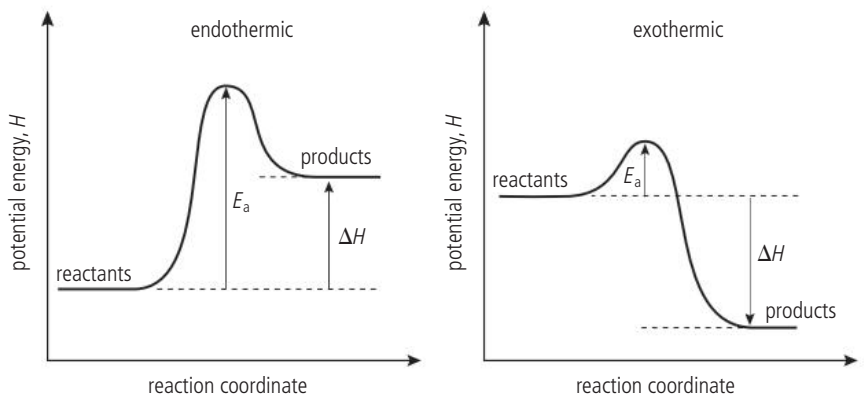
R1.1 Figure 7 Hydrogen peroxide is stable relative to hydrogen and oxygen but unstable relative to water. Note $\Delta H_3 = \Delta H_1 + \Delta H_2$ in agreement with Hess's law discussed in Reactivity 1.2.

The sign of Δ*H* is a guide for the likely direction of change but it is not a complete guide. We do not expect a person to fall up a ladder, and likewise reactions tend to proceed in the direction of lowering energy/increasing stability. But this is not always the case and some endothermic reactions do occur spontaneously. For example, the reaction below is extremely endothermic:

$$SOCl_2(l) + FeCl_3.6H_2O(s) \rightarrow FeCl_3(s) + 6SO_2(g) + 12HCl(g)$$

Endothermic reactions are less common and can only occur when there is an increase in the dispersal of the system, for example, owing to the production of sulfur dioxide and hydrogen chloride gas in the reaction above. This is explained more fully in Reactivity 1.4.

The other limitation of using Δ*H* values as a guide to change is that it does not indicate anything about the rate of reaction. Some reactions, which should take place on energetic grounds, do not occur at a noticeable rate in practice as the reactants need to be given some initial energy to react. The minimum kinetic energy to react is known as the **activation energy**, E_a. For example, a lighted match provides the necessary activation energy for the combustion of methane in oxygen. This energy is needed as some bonds in the reactants must be broken before new bonds in the products can form. Typical energy profiles are given in Figure 8.



R1.1 Figure 8 Energy profiles of an endothermic and exothermic reaction.

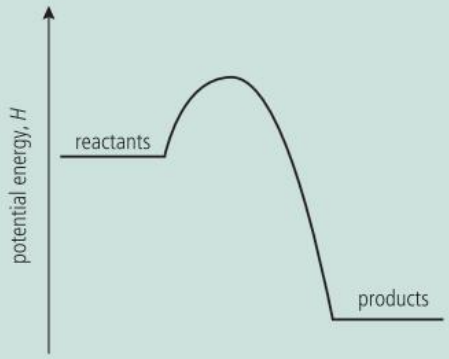
Activation energy is discussed in more detail in Reactivity 2.2.



Diamond is a naturally occurring form of carbon that has crystallized under great pressure. It is energetically unstable relative to graphite, but the reaction does not take place at an observable rate.

Exercise

Q7. Which statement is consistent with the potential energy profile shown?



A Heat is produced during the reaction and the products are more stable than the reactants.

B Heat is taken in during the reaction and the products are more stable than the reactants.

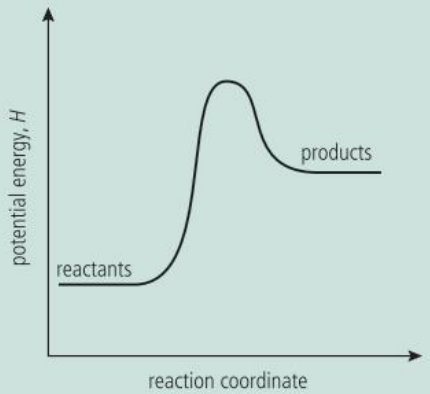
C Heat is produced during the reaction and the reactants are more stable than the products.

D Heat is taken in during the reaction and the reactants are more stable than the products.

Q8. Identify the endothermic reaction.

	Enthalpy	Direction of heat transfer
A	$H_{reactants} < H_{products}$	system → surroundings
B	$H_{reactants} < H_{products}$	surroundings → system
C	$H_{reactants} > H_{products}$	system → surroundings
D	$H_{reactants} > H_{products}$	surroundings → system

Q9. The potential energy profile of a reaction is shown.



What can be deduced about the nature of the reaction and the relative stability of the reactants and products?

	Nature of reaction	Most stable
A	endothermic	reactants
B	endothermic	products
C	exothermic	reactants
D	exothermic	products

Reactivity 1.1.4 – Measuring enthalpy changes

Reactivity 1.1.4 – The standard enthalpy change for a chemical reaction, $\Delta H^{\ominus}$, refers to the heat transferred at constant pressure under standard conditions and states. It can be determined from the change in temperature of a pure substance.

Apply the equations $Q = mc\Delta T$ and $\Delta H = -\frac{Q}{n}$ in the calculation of the enthalpy change of a reaction.

The units of $\Delta H^{\ominus}$ are kJ mol^{-1}. The equation $q = mc\Delta T$ and the value of c, the specific heat capacity of water, are given in the data booklet.	Tool 1, Inquiry 1, 2, 3 – How can the enthalpy change for combustion reactions, such as for alcohols or food, be investigated experimentally? Tool 1, Inquiry 3 – Why do calorimetry experiments typically measure a smaller change in temperature than is expected from theoretical values?

The standard conditions for enthalpy changes are as follows: a pressure of 100 kPa, concentrations of 1 mol dm^{-3} for all solutions, all the substances in their standard states.

The standard state of a substance is the pure form of the substance under standard conditions of 298 K (25 °C) and 1.00 × 10^5 Pa.

Standard enthalpy changes

The **standard enthalpy change**, $\Delta H^{\ominus}$, given in the literature, is measured under the following standard conditions:

- a pressure of 100 kPa
- concentration of 1 mol dm^{-3} for all solutions
- all substances in their standard states.

Temperature is not part of the definition of standard state, but 298 K is usually given as the specified temperature.

Thermochemical equations

The combustion of methane can be described by the thermochemical equation:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta H^{\ominus}_{reaction} = -890\,kJ\,mol^{-1}$$

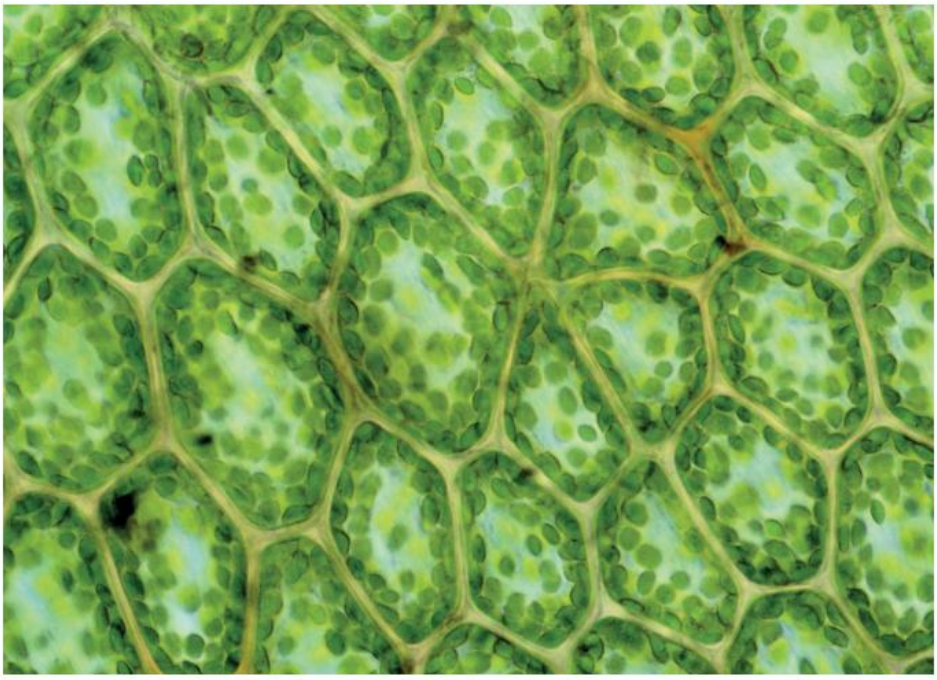
This is a shorthand way of expressing that *one mole* of methane gas reacts with *two moles* of oxygen gas to give *one mole* of gaseous carbon dioxide and *two moles* of liquid water and *releases* 890 kJ of heat energy.

It is important to give the state symbols in thermochemical equations because the enthalpy changes depend on the state of the reactants and the products.

The thermochemical equation for photosynthesis can be represented as:

$$6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6O_2(g) \qquad \Delta H^{\ominus}_{reaction} = +2802.5\,kJ\,mol^{-1}$$

which means that overall, 2802.5 kJ of energy is absorbed when one mole of glucose is formed under standard conditions from gaseous carbon dioxide and liquid water.



Light micrograph showing a section through a leaf. The green chloroplasts contain chlorophyll, which is responsible for the absorption of light during photosynthesis. Energy is needed for photosynthesis as the products have more potential energy than the reactants.

Enthalpy changes can be calculated from temperature changes

In Structure 1.1, we discuss the relationship between temperature and kinetic energy. The absolute temperature in K is a measure of the average kinetic energy E_k of particles. If the same amount of heat energy is added to two different objects made of the same material but with a different number of particles, the temperature change will not be the same because the average kinetic energy of the particles will not increase by the same amount. The object with the smaller number of particles will experience the larger temperature increase because the same energy is shared among a smaller collection of particles. As equal masses of different materials have different numbers of particles, the temperature change will also depend on the chemical nature of the material. In general, the increase in temperature (ΔT) when an object is heated depends on:

- the mass (m) of the object
- the heat added (q)
- the nature of the substance.

The **specific heat capacity** (c) gives the heat needed to increase the temperature of a unit mass of a substance by 1 K. The specific heat capacity (c) depends on the number of particles present in a unit mass sample, which in turn will depend on the mass of the individual particles.

heat added (q) = mass (m) × specific heat capacity (c) × temperature change (ΔT)

heat added (q) = $m \times c \times \Delta T$
q(J) = m(g) × c(J g^{-1} K^{-1}) × ΔT (K)
When the heat is absorbed by water, c = 4.18 J g^{-1} K^{-1}
This value is given in the data booklet.

A temperature rise of 1 K is the same as a temperature rise of 1 °C so there is no need to change the units of temperature when using the equation $q = m \times c \times \Delta T$.

The specific heat capacity (c) is the heat needed to increase the temperature of a unit mass of material by 1 K.

$$\text{specific heat capacity } (c) = \frac{\text{heat added } (q)}{\text{mass } (m) \times \text{temperature change } (\Delta T)}$$

Nature of Science

Enthalpy is a word rarely used in non-scientific contexts; it is an abstract entity with a precise mathematical definition. At this level we need not concern ourselves with absolute enthalpy values but only enthalpy changes which can be determined from temperature changes at constant pressure. The use of appropriate terminology is a key issue with scientific literacy and the public understanding of science, and scientists need to take this into account when communicating with the public.

TOK

Our shared knowledge is passed on from one generation to the next by language. The language we use today is often based on the shared knowledge of the past which can sometimes be based on outdated concepts. What do such phrases as 'keep the heat in and the cold out' tell us about previous concepts of heat and cold? How does the use of language hinder the pursuit of knowledge?

Worked example

How much heat is released when 10.0 g of copper with a specific heat capacity of 0.385 J g^{-1} °C^{-1} is cooled from 85.0 °C to 25.0 °C?

Solution

$q = m \times c \times \Delta T$

$= 10.0\,\text{g} \times 0.385\,\text{J g}^{-1}\,^{\circ}\text{C}^{-1} \times -60.0\,^{\circ}\text{C}$ (the value is negative because the Cu has lost heat)

$= -231\,\text{J}$

Challenge yourself

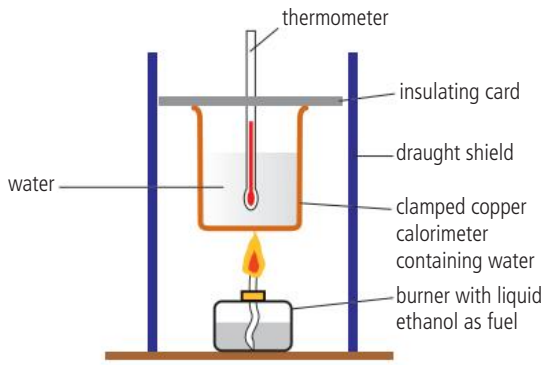
1. Explain the particularly high specific heat capacity of water.

SKILLS

Comparing the enthalpy of isopropanol and ethanol. Full details of how to carry out this experiment with a worksheet are available in the eBook.

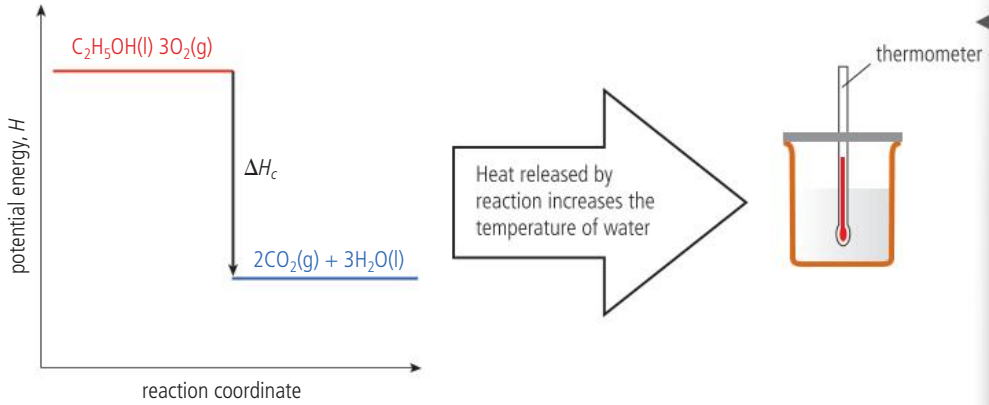
Measuring enthalpy changes of combustion

For liquids such as ethanol, the enthalpy change of combustion, ΔH_c, can be determined using the simple apparatus shown in Figure 9. The heat given out by the flame during combustion reactions is used to heat a known mass of water in a metal calorimeter. Copper is often used as it is a good conductor of heat. The heat absorbed by the water can be calculated from its temperature change and its mass. The heat absorbed by the calorimeter can also be calculated from its heat capacity.



R1.1 Figure 9 The heat produced by the combustion of the fuel is calculated from the temperature change of the water in the metal calorimeter. Copper is a good conductor of heat, so heat from the flame can be transferred to the water.

The temperature of the water increases due to the heat released by the combustion reaction (Figure 10). This heat is released as the ethanol and oxygen are converted to carbon dioxide and water. There is a decrease in enthalpy during the reaction.



R1.1 Figure 10 The enthalpy of the system decreases and the enthalpy of the water increases. The enthalpy change of the water can be calculated if it is assumed that all the heat from the reaction is transferred to the water.

Worked example

Calculate the enthalpy of combustion of ethanol from the following data. Assume all the heat from the reaction is absorbed by the water. Compare your value with the data booklet value and suggest reasons for any differences.

Mass of water in copper calorimeter / g	200.00
Temperature increase in water / °C	13.00
Mass of ethanol burnt / g	0.45

Solution

number of moles = mass (m) / molar mass (M)

number of moles of ethanol = $m(C_2H_5OH) / M(C_2H_5OH)$

$M(C_2H_5OH) = (12.01 \times 2) + (6 \times 1.01) + 16.00 = 46.08\,g\,mol^{-1}$

$\Delta H_{reaction} = -m(H_2O) \times c(H_2O) \times \Delta T(H_2O)$

Note the negative sign. The enthalpy change of the water is opposite to that in the reaction. ΔT is positive when the reaction is exothermic and ΔH is negative, and ΔT is negative when the reaction is endothermic and ΔH is positive.

$\Delta H_c = \Delta H_{reaction}$ (for one mole of ethanol)

$$= \frac{-m(H_2O) \times c(H_2O) \times \Delta T(H_2O)}{m(C_2H_5OH)/M(C_2H_5OH)}$$

$$= \frac{200\,g \times 4.18\,J\,g^{-1}\,°C^{-1} \times 13.00\,°C}{(0.45/46.08)\,g\,mol^{-1}}$$

$= -1\,112\,883\,J\,mol^{-1}$

$= -1100\,kJ\,mol^{-1}$

The precision of the final answer is limited by the precision of the mass of the ethanol.

It is important to state all assumptions when processing data such as all the heat released is absorbed by the water. The heat absorbed by the copper calorimeter can also be considered in more sophisticated calculations.

SKILLS

You can investigate the energy content of different foods and fuels.

Tool 1, Inquiry 1, 2, 3 – How can the enthalpy change for combustion reactions, such as for alcohols or food, be investigated experimentally?

It is important that you record qualitative as well as quantitative data when measuring enthalpy changes – for example, evidence of incomplete combustion in an enthalpy of combustion determination.

When asked to evaluate experiments and suggest improvements, avoid trivial answers such as incorrect measurement. Incomplete combustion, for example, can be reduced by burning the fuel in oxygen. Heat loss can be reduced by insulating the apparatus.

The data booklet value is $-1367\ kJ\ mol^{-1}$. The difference between the values can be accounted for by some of the following factors:

- Not all the heat produced by the combustion reaction is transferred to the water.
- Some heat is absorbed by the copper calorimeter, and some has passed to the surroundings.
- The combustion of the ethanol is incomplete owing to the limited oxygen available (rather than complete as is assumed by the literature value).
- The experiment was not performed under standard conditions.



▲ Some organic compounds burn with a sooty yellow flame. This is due to incomplete combustion.

Combustion reactions are generally exothermic, so ΔH_c values are generally negative.

Nature of Science

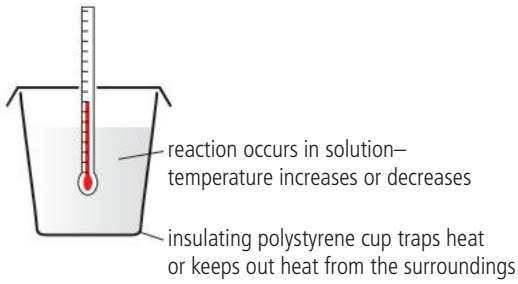
Quantitative measurements are more objective than qualitative observations and are amenable to mathematical analysis. All measurements are limited in precision and accuracy, however, and qualitative observations have a role in chemistry. The lower than expected exothermic value for an enthalpy of combustion of a fuel, for example, is often a result of incomplete combustion. The evidence for this comes from any black soot and residue observed during the experiment.



The combustion of fossil fuels such as coal produces carbon dioxide which is a greenhouse gas. It is important we are aware of how our lifestyle contributes to global warming. It is a global problem, but we need to act locally to solve it. The greenhouse effect is discussed in more detail in Reactivity 1.3.

Enthalpy changes of a reaction in solution

The enthalpy changes of a reaction in solution can be calculated by carrying out the reaction in an insulated system, for example, a polystyrene cup (Figure 11). The heat released or absorbed by the reaction can be measured from the temperature change in the water which is acting as a solvent. Note in this case the calorimeter is made from an insulator to maximize the amount of heat that is transferred between the reaction and the water in the system.

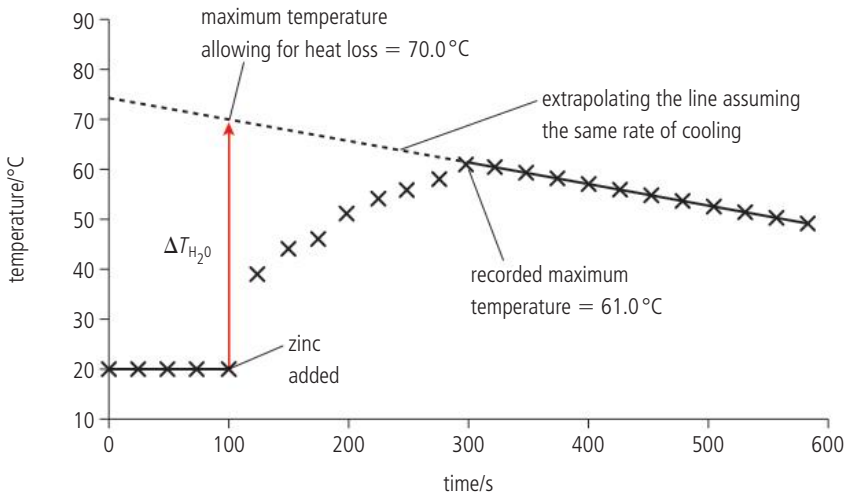


R1.1 Figure 11 A simple calorimeter. Polystyrene is a very good thermal insulator with a low heat capacity.

Coffee-cup calorimeter. Full details of how to carry out this experiment with a worksheet are available in the eBook.

In the previous calculation, we assumed that all the heat produced in the reaction is absorbed by the water. One of the largest sources of error in experiments conducted in a polystyrene cup is heat loss to the surroundings. Consider, for example, the exothermic reaction between zinc and aqueous copper sulfate (Figure 12):

$$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$$



R1.1 Figure 12 A known volume of copper sulfate solution is added to a calorimeter and its temperature measured every 25 s. Excess zinc powder is added after 100 s and the temperature starts to rise until a maximum after which it falls approximately linearly with time.

Heat is lost from the system as soon as the temperature rises above the temperature of the surroundings, in this case 20 °C, and so the maximum recorded temperature is lower than the true value obtained in a perfectly insulated system. We can make some allowance for heat loss by extrapolating the cooling section of the graph to the time when the reaction started (100 s). To proceed we can make the following assumptions:

1. no heat loss from the system
2. all the heat goes from the reaction to the water
3. the solution is dilute: $V(CuSO_4) = V(H_2O)$
4. water has a density of 1.00 g cm^{-3}.

$\Delta H_{(system)} = 0$ (Assumption 1)

$\Delta H_{(system)} = \Delta H_{(water)} + \Delta H_{reaction}$ (Assumption 2)

$\Delta H_{reaction} = -\Delta H_{(water)}$

For an exothermic reaction, $\Delta H_{reaction}$ is negative because heat has passed from the reaction into the water.

$$\Delta H_{(water)} = m_{(H_2O)} \times c_{(H_2O)} \times \Delta T_{(H_2O)}$$

The limiting reactant (see Reactivity 2.1) must be identified in order to determine the molar enthalpy change of the reaction.

$$\Delta H_{\text{reaction}} = \frac{-m(H_2O) \times c(H_2O) \times \Delta T(H_2O)}{\text{moles of limiting reactant}}$$

As the zinc was added in excess, the copper sulfate is the limiting reactant.

From Structure 1.4:

number of moles (n) = concentration (mol dm^{-3}) × volume (V dm^3)

There are 1000 cm^3 in 1 dm^3.

$$\text{volume } (V \text{ dm}^3) = \frac{\text{volume } (V \text{ cm}^3)}{1000 \text{ (cm}^3 \text{ dm}^{-3})}$$

$$\text{number of moles of } CuSO_4 (n(CuSO_4)) = \frac{[CuSO_4] \times V(CuSO_4)}{1000}$$

$$\Delta H_{\text{reaction}} = \frac{-m(H_2O) \times c(H_2O) \times \Delta T(H_2O)}{n(CuSO_4))} \text{ J mol}^{-1}$$

$$= \frac{-m(H_2O) \times c(H_2O) \times \Delta T(H_2O)}{([CuSO_4] \times V(CuSO_4))/1000} \text{ J mol}^{-1}$$

$$= \frac{-m(H_2O) \times c(H_2O) \times \Delta T(H_2O)}{([CuSO_4] \times V(CuSO_4))} \text{ kJ mol}^{-1}$$

$$= \frac{-m(H_2O) \times c(H_2O) \times \Delta T(H_2O)}{([CuSO_4] \times V(H_2O))} \text{ kJ mol}^{-1} \quad \text{from assumption 3}$$

$$\Delta H_{\text{reaction}} = \frac{-c(H_2O) \times \Delta T(H_2O)}{[CuSO_4]} \text{ kJ mol}^{-1} \quad \text{from assumption 4}$$

Worked example

Calculate the molar enthalpy change for the reaction between zinc and copper sulfate from the data in Figure 12. The copper sulfate has a concentration of 1.00 mol dm^{-3} and a volume of 100 cm^3.

Solution

From the equation we derived earlier:

$$\Delta H_{\text{reaction}} = \frac{-c(H_2O) \times \Delta T(H_2O)}{[CuSO_4]} \text{ kJ}$$

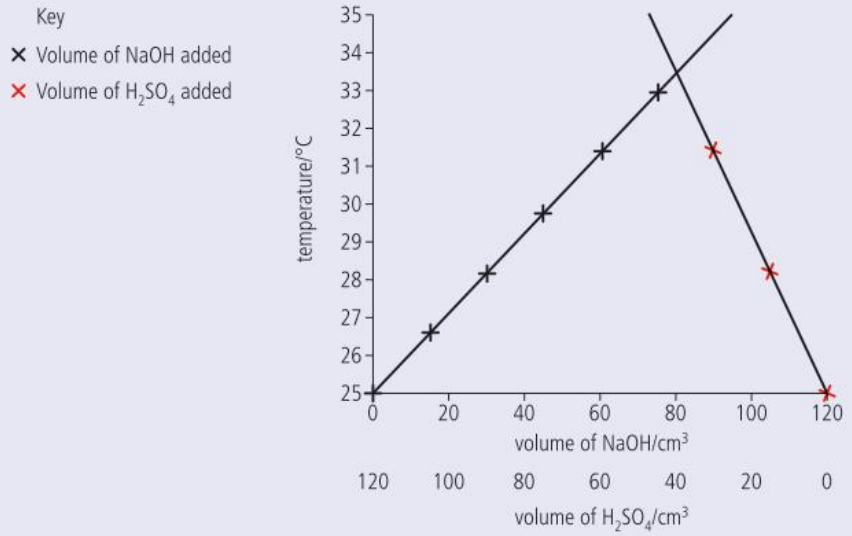
$$= \frac{-4.18 \times (70.0 - 20.0)}{1.00} \text{ kJ}$$

$$= -209 \text{ kJ mol}^{-1} \text{ (for 1 mole of 1 mol dm}^{-3} \text{ solution)}$$

Tool 1, Inquiry 3 – Why do calorimetry experiments typically measure a smaller change in temperature than is expected from theoretical values?

Worked example

The neutralization reaction between solutions of sodium hydroxide and sulfuric acid was studied by measuring the temperature changes when different volumes of the two solutions were mixed. The total volume was kept constant at 120.0 cm^3 and the concentrations of the two solutions were both 1.00 mol dm^{-3} (see figure below).



(a) Determine the volumes of the solutions which produce the largest increase in temperature.

(b) Calculate the heat produced by the reaction when the maximum temperature was produced.

(c) Calculate the heat produced for one mole of sodium hydroxide.

(d) The literature value for the enthalpy of neutralization is = −57.5 kJ mol^{-1}.

Calculate the percentage error value and suggest a reason for the discrepancy between the experimental and literature values.

Solution

(a) From the graph:
$V(NaOH) = 80.0\,cm^3$
$V(H_2SO_4) = 40.0\,cm^3$

(b) Assuming 120.0 cm^3 of the solution contains 120.0 g of water and all the heat produced by the neutralization reaction passes into the water:

$$\Delta H_{reaction} = -m(H_2O) \times c(H_2O) \times \Delta T(H_2O)\,J$$
$$= -120.0\,g \times 4.18\,J\,g^{-1}\,K^{-1} \times (33.5 - 25.0)\,K$$
$$= -4264\,J$$

A common error is to miss out or incorrectly state the units and to miss out the negative sign for ΔH.

(c) $\Delta H_{reaction} = \frac{-4264}{n(NaOH)}\,J\,mol^{-1}$

$= \frac{-4264}{1.00 \times 80.0/1000}\,J\,mol^{-1}$

$= \frac{-4264}{80.0}\,kJ\,mol^{-1}$

$= -53.3\,kJ\,mol^{-1}$

(d) % error $= \frac{-57.5 - -53.3}{-57.5} \times 100\% = 7\%$

The calculated value assumes:

- no heat loss from the system
- all heat is transferred to the water
- the solutions contain 120 g of water
- there are also uncertainties in the temperature, volume, and concentration measurements.

The literature value assumes standard conditions.

TOK

What criteria do we use in judging whether discrepancies between experimental and theoretical values are due to experimental limitations or theoretical assumptions? Being a risk taker is one attribute of the IB Learner Profile. When is a scientist justified in rejecting the generally accepted literature value in favour of their experimentally determined value?

Nature of Science

The accurate determination of enthalpy changes involves making careful observations and measurements, which inevitably have experimental uncertainties. The calculated enthalpy values are also dependent on the assumptions made. All these elements should be considered when reporting and evaluating experimental enthalpy values. Mathematics is a powerful tool in the sciences, but scientific systems are often too complex to treat rigorously. These underlying assumptions, which make a problem solvable, should not be ignored when evaluating quantitative data generated by a mathematical model.

Challenge yourself

SKILLS

The temperature of the Bunsen flame and the enthalpy of fusion can be investigated in the lab.

2. A piece of brass is held in the flame of a Bunsen burner for several minutes. The brass is then quickly transferred into an aluminium calorimeter which contains 200.00 g of water.

Determine the temperature of the Bunsen flame from the following data.

m(water) / ±0.01 g	200.00
m(brass) / ±0.01 g	212.10
m(aluminium calorimeter) / ±0.01 g	80.00
c(brass) / J g–1 K–1	0.400
c(Al) / J g–1 K–1	0.900
Initial temperature of water / ±0.1 °C	24.5
Final temperature of water / ±0.1 °C	77.5

Exercise

Q10. If 500 J of heat is added to 100.0 g samples of each of the substances below, which will have the largest temperature increase?

	Substance	Specific heat capacity / $J\,g^{-1}\,K^{-1}$
A	gold	0.129
B	silver	0.237
C	copper	0.385
D	water	4.18

Q11. Calculate the amount of heat needed to increase the temperature of a 5.0 g sample of copper from 27 °C to 29 °C. (Specific heat capacity of Cu is $0.385\,J\,g^{-1}\,°C^{-1}$)

A 0.770 J **B** 1.50 J **C** 3.00 J **D** 3.85 J

Q12. Consider the specific heat capacity of the following metals.

Metal	Specific heat capacity / $J\,g^{-1}\,K^{-1}$
Al	0.897
Be	1.82
Cd	0.231
Cr	0.449

1 kg samples of the metals at room temperature are heated by the same electrical heater for 10 minutes.

Identify the metal which has the highest final temperature.

A Al **B** Be **C** Cd **D** Cr

Q13. In an experiment to determine the enthalpy of combustion of an alcohol, the mass of a burner plus its contents, and the temperature of a known mass of water in a calorimeter are measured before and after the experiment. What are the expected results?

	Mass of burner and contents	Reading on thermometer
A	decreases	increases
B	decreases	stays the same
C	increases	increases
D	increases	stays the same

Q14. The experimental arrangement in Figure 9 is used to determine the enthalpy of combustion of an alcohol.

Which of the following would lead to an experimental result which is **less** exothermic than the literature value?

I. Heat loss from the sides of the copper calorimeter.

II. Evaporation of alcohol during the experiment.

III. The thermometer touches the bottom of the calorimeter.

A I and II only **B** I and III only **C** II and III only **D** I, II and III

Q15. A copper calorimeter was used to determine the enthalpy of combustion of butan-1-ol. The experimental value obtained was $-2100 \pm 200\,kJ\,mol^{-1}$, and the data booklet value is $-2676\,kJ\,mol^{-1}$.

Which of the following accounts for the difference between the two values?

I. random measurement errors

II. incomplete combustion

III. heat loss to the surroundings

A I and II only **B** I and III only **C** II and III only **D** I, II and III

Q16. The thermochemical equation for the combustion of propane is:

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l) \quad \Delta H^{\ominus} = -2219\,kJ\,mol^{-1}$

Identify the true statements.

I. If 1.00 g of propane is burnt completely, 2219 kJ of energy are produced.

II. The reactants have more potential energy than the products.

III. The reaction is exothermic.

A I and II only **B** I and III only **C** II and III only **D** I, II and III

Q17. An experiment is carried out to determine the enthalpy of combustion of methanol. A known mass of tap water is heated by burning a sample of methanol.

The following data were collected.

Mass of water m_{water}	Temperature change of the tap water ΔT
Initial mass of methanol $m_{initial}$	Final mass of methanol m_{final}

(a) Which formula can be used to calculate an experimental value for the enthalpy change of combustion of methanol?

A $m_{water} \times 4.18 \times \Delta T$ **B** $\dfrac{m_{water} \times 4.18 \times \Delta T \times 32.05}{(m_{initial} - m_{final})}$

C $(m_{initial} - m_{final}) \times 4.18 \times \Delta T$ **D** $\dfrac{m_{water} \times 4.18 \times \Delta T \times (m_{initial} - m_{final})}{32.05}$

(b) Identify the assumptions made in using the formula in part **(a)**.

I. The density of tap water is $1.0\,g\,cm^{-3}$.

II. All the energy from the combustion heats the beaker of water.

III. The specific heat capacity of the beaker is negligible.

A I and II only **B** I and III only

C II and III only **D** I, II and III

Q18. 20.0 cm^3 of 2.0 mol dm^{-3} HNO_3(aq) is mixed with 40 cm^3 of 1.0 mol dm^{-3} KOH(aq) at 25.0 °C. The temperature of the resulting solution increases by 9 °C.

Predict the temperature change when 5.0 cm^3 of 2.0 mol dm^{-3} HNO_3(aq) is mixed with 10.0 cm^3 of 1.0 mol dm^{-3} KOH(aq) at the same temperature.

A 4.5 °C **B** 9 °C **C** 18 °C **D** 27°C

Q19. The specific heat capacity of metallic mercury is 0.138 J g^{-1} $°C^{-1}$. What is the final temperature if 100.0 J of heat is added to a 100.0 g sample of mercury at 25.0 °C?

Q20. 1.10 g of glucose was completely burnt and the heat produced increased the temperature of the water in a copper calorimeter from 25.85 °C to 36.50 °C.

(a) Calculate the enthalpy of combustion of glucose from the data below.

Mass of water / g	200.00
Specific heat capacity of water / g–1 K–1	4.18
Mass of copper / g	120.00
Specific heat capacity of copper / g–1 K–1	0.385

(b) Draw an enthalpy level diagram to represent this reaction.

Q21. The heat released from the combustion of 0.0500 g of white phosphorus increases the temperature of 150.00 g of water from 25.0 °C to 31.5 °C. Calculate a value for the enthalpy change of combustion of phosphorus. Discuss possible sources of error in the experiment.

Q22. A student wanted to find the enthalpy of combustion of propan-1-ol and collected the following data.

Initial mass of burner and propan-1-ol / g	45.65
Final mass of burner and propan-1-ol / g	45.05
Mass of water heated / g	210
Initial temperature of water / °C	23.7
Final temperature of water / °C	41.5
Specific heat capacity of water / JK-1g-1	4.18

(a) Calculate the amount, in mol, of propan-1-ol burnt.

(b) Calculate the heat absorbed, in kJ, by the water.

(c) Determine the enthalpy change, in kJ mol^{-1}, for the combustion of one mole of propan-1-ol.

(d) Suggest why this value differs from the literature value of −2021 kJ mol^{-1}.

Guiding Question revisited

What can be deduced from the temperature change that accompanies chemical or physical change?

In this chapter we have seen that although energy is always conserved, many chemical reactions involve a transfer of energy between the system and the surroundings. We introduced the concept of enthalpy and saw that the enthalpy change of a reaction gives an indication of the relative stability of the reactants and products. These ideas can be summarized:

- A system is the reaction container and its contents. The surroundings include everything outside the system of interest. Exothermic reactions release heat energy to the surroundings, and endothermic reactions absorb heat energy from the surroundings.
- The heat transferred from the temperature change using a conversion factor known as the specific heat capacity. The specific heat capacity (c) of a pure material is the heat needed to change the temperature of a unit mass of the material by 1 K.

$$Q = mc\Delta T \text{ for a pure substance.}$$

- Generally, heat changes in the laboratory are determined by the temperature changes of a known mass of water. In experiments to determine the enthalpy of combustion, the water is heated in a copper calorimeter. In experiments to determine enthalpy changes in solution, the water is the solvent in an insulated calorimeter.
- The heat change transferred at constant pressure is known as the enthalpy change ΔH. ΔH is negative for exothermic reactions because they release heat, and positive for endothermic reactions which absorb heat.
- A thermochemical equation gives the equation for the reaction and the corresponding enthalpy change.

Practice questions

1. When equal masses of X and Y absorb the same amount of energy, their temperatures rise by 5 °C and 10 °C respectively. Which is correct?

A The specific heat capacity of X is twice that of Y.

B The specific heat capacity of X is half that of Y.

C The specific heat capacity of X is one fifth that of Y.

D The specific heat capacity of X is the same as Y.

2. A pure aluminium block with a mass of 10 g is heated so that its temperature increases from 20 °C to 50 °C. The specific heat capacity of aluminium is $8.99 \times 10^{-1}\,\text{J g}^{-1}\,\text{K}^{-1}$. Which expression gives the heat energy change in kJ?

A $10 \times 8.99 \times 10^{-1} \times 303$

B $10 \times 8.99 \times 10^{-1} \times 30$

C $\dfrac{10 \times 8.99 \times 10^{-1} \times 303}{1000}$

D $\dfrac{10 \times 8.99 \times 10^{-1} \times 30}{1000}$

3. Two 100 cm^3 aqueous solutions, one containing 0.010 mol NaOH and the other containing 0.010 mol HCl, are at the same temperature.

When the two solutions are mixed the temperature rises by y °C.

Assume the density of the final solution is 1.00 g cm^{-3}.

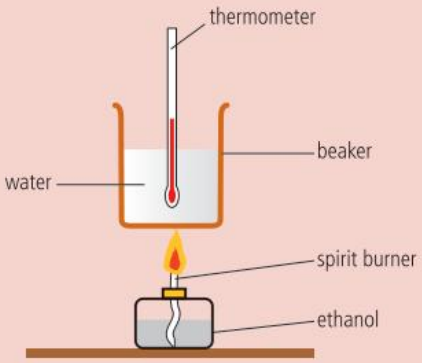
Specific heat capacity of water = 4.18 J g^{-1} K^{-1}

What is the enthalpy change of neutralization in kJ mol^{-1}?

A $\frac{200 \times 4.18 \times y}{1000 \times 0.020}$ **B** $\frac{200 \times 4.18 \times y}{1000 \times 0.010}$

C $\frac{100 \times 4.18 \times y}{1000 \times 0.010}$ **D** $\frac{200 \times 4.18 \times (y + 273)}{1000 \times 0.010}$

Questions 4 and 5 are about an experiment to measure the enthalpy of combustion, ΔH_c, of ethanol, using the apparatus and setup shown.



Maximum temperature of water: 30.0 °C
Initial temperature of water: 20.0 °C
Mass of water in beaker: 100.0 g
Loss in mass of ethanol: 0.230 g
M_r (ethanol): 46.08
Specific heat capacity of water: 4.18 J g^{-1} K^{-1}
$q = mc\Delta T$

4. What is the enthalpy of combustion, ΔH_c, of ethanol in kJ mol^{-1}?

A $-\frac{100.0 \times 4.18 \times (10.0 \times 273)}{\frac{0.230}{46.08} \times 1000}$ **B** $-\frac{0.0230 \times 4.18 \times 10.0}{\frac{100.0}{46.08} \times 1000}$

C $-\frac{100.0 \times 4.18 \times 10.0}{\frac{0.230}{46.08} \times 1000}$ **D** $-\frac{100.0 \times 4.18 \times 10.0}{\frac{0.230}{46.08}}$

5. Which quantity is likely to be the most inaccurate due to the sources of error in this experiment?

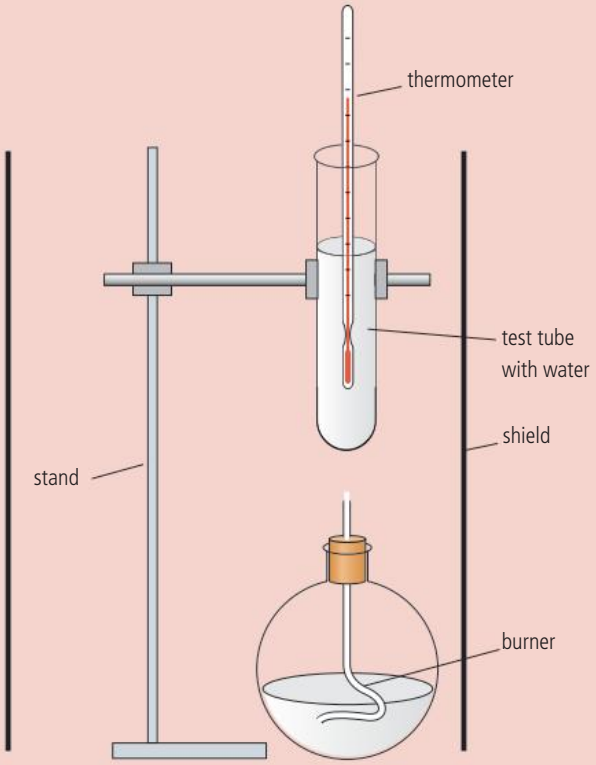
A mass of ethanol burnt **B** molecular mass of ethanol

C mass of water **D** temperature change

6. Methanol is made in large quantities because it is used in the production of polymers and in fuels. The enthalpy of combustion of methanol can be determined theoretically or experimentally.

$$CH_3OH(l) + 1\tfrac{1}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

(a) The enthalpy of combustion of methanol can be determined experimentally in a school laboratory. A burner containing methanol was weighed and used to heat water in a test tube, as illustrated below.



The following data was collected.

Initial mass of burner and methanol / g	80.557
Final mass of burner and methanol / g	80.034
Mass of water in test tube / g	20.000
Initial temperature of water / °C	21.5
Final temperature of water / °C	26.4

(i) Calculate the amount, in mol, of methanol burnt. (2)

(ii) Calculate the heat absorbed, in kJ, by the water. (3)

(iii) Determine the enthalpy change, in kJ mol^{-1}, for the combustion of 1 mole of methanol. (2)

(b) The data booklet value for the enthalpy of combustion of methanol is −726 kJ mol^{-1}. Suggest why this value differs from the value calculated in part **(a)**. (1)

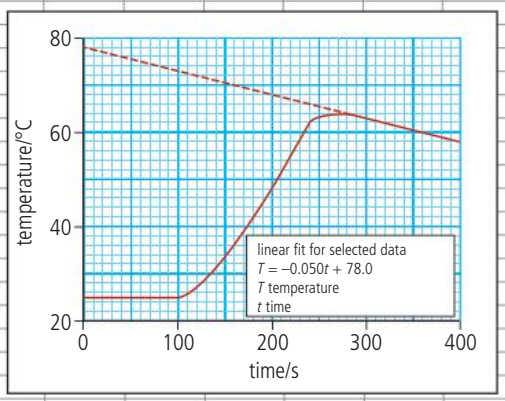
(Total 8 marks)

7. The data below is from an experiment to measure the enthalpy change for the reaction of aqueous copper(II) sulfate, $CuSO_4(aq)$, and zinc, Zn(s).

$$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$$

50.0 cm^3 of 1.00 mol dm^{-3} copper(II) sulfate solution was placed in a polystyrene cup and zinc powder was added after 100 s. The temperature–time data was taken from a data logging software program. The table shows the initial 19 readings.

	A	B	C	D	E	F	G	H
1	time/s	temperature/°C						
2	0.0	24.8						
3	1.0	24.8						
4	2.0	24.8						
5	3.0	24.8						
6	4.0	24.8						
7	5.0	24.8						
8	6.0	24.8						
9	7.0	24.8						
10	8.0	24.8						
11	9.0	24.8						
12	10.0	24.8						
13	11.0	24.8						
14	12.0	24.8						
15	13.0	24.8						
16	14.0	24.8						
17	15.0	24.8						
18	16.0	24.8						
19	17.0	24.8						
20	18.0	24.8						
21								
22								
23								
24								



A straight line has been drawn through some of the data points. The equation for this line is given by the data-logging software as

$$T = -0.050t + 78.0$$

where T is the temperature at time t.

(a) The heat produced by the reaction can be calculated from the temperature change, ΔT, using the expression below.

heat change = volume of $CuSO_4(aq)$ × specific heat capacity of H_2O × ΔT

Describe **two** assumptions made in using this expression to calculate heat changes. (2)

(b) **(i)** Use the data presented by the data-logging software to deduce the temperature change, ΔT, which would have occurred if the reaction had taken place instantaneously with no heat loss. (2)

(ii) State the assumption made in part **(b)(i)**. (1)

(iii) Calculate the heat, in kJ, produced during the reaction using the expression given in part **(a)**. (1)

(c) The colour of the solution changed from blue to colourless. Deduce the amount, in moles, of zinc which reacted in the polystyrene cup. (1)

(d) Calculate the enthalpy change, in kJ mol^{-1}, for this reaction. (1)

(Total 8 marks)

8. **(a)** Calculate the enthalpy of neutralization based on the following data.

Initial temperature of solutions / °C	24.5
Concentration of KOH(aq) / mol dm–3	0.950
Concentration of HCl(aq) / mol dm–3	1.050
Volume of HCl(aq) / cm3	50.00
Volume of KOH(aq) / cm3	50.00
Final temperature of mixture / °C	30.3

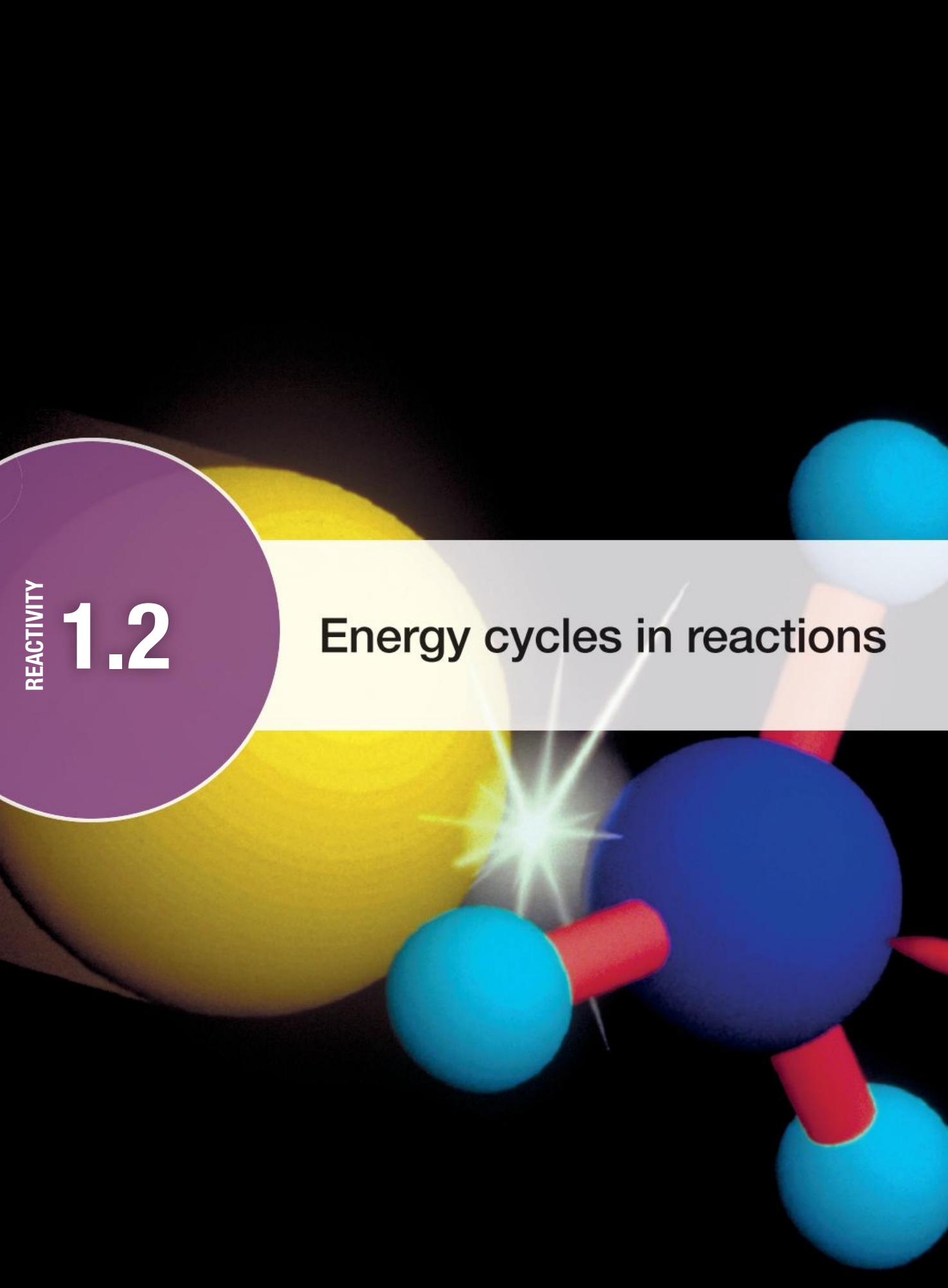
(4)

(b) State the assumptions you have made in your calculation. (1)

(Total 5 marks)

9. A student added 5.35 g of ammonium chloride to 100.00 cm^3 of water. The initial temperature of the water was 25.55 °C but it decreased to 21.79 °C. Calculate the enthalpy change that would occur when 1 mol of the solute is added to 1.000 dm^3 of water. (3)

(Total 3 marks)



REACTIVITY

1.2 Energy cycles in reactions

A chemical reaction involves the breaking and making of bonds. 300–500 kJ of heat are typically needed to break one mole of covalent bonds. This image shows a change in the bond between the atoms represented by the yellow (on the left) and the dark blue (in the centre).

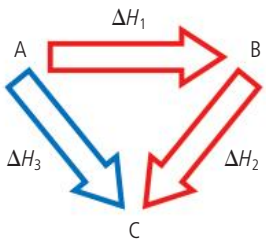
Guiding Question

How does application of the law of conservation of energy help us to predict energy changes during reactions?

Energy changes occur during chemical reactions as bonds are broken and new bonds are formed. Energy is needed to separate particles held together by chemical bonds, and energy is released when the same particles come together in a different arrangement with new bonds. The net enthalpy change is the difference between the two energy contributions of bond-breaking and making. The reaction is exothermic overall when bond formation releases more energy than is needed for bond-breaking.

The law of conservation of energy tells us that the total energy of the universe is constant and cannot be changed. The energy can be converted from one form to another, but no process can change its amount. This law imposes restrictions on energy changes when a chemical change can occur via different routes.

Consider the energy cycle below (Figure 1) in which A can be converted to C either directly or indirectly.



R1.2 Figure 1 An energy cycle.

Going around the cycle in a clockwise route from A → B → C → A, according to the law of conservation of energy the total energy change is zero:

$$\Delta H_1 + \Delta H_2 - \Delta H_3 = 0$$

Otherwise, the cycle could form the basis of a perpetual motion machine with energy being generated continually by going around the cycle in one direction.

The construction of the cycle allows us to calculate enthalpy changes to reactions indirectly. ΔH_3 can be calculated from ΔH_1 and ΔH_2:

$$\Delta H_1 + \Delta H_2 = \Delta H_3$$

We can then determine enthalpy changes of hypothetical reactions and make predictions about the relative stability of different compounds. The law of conservation of energy imposes restrictions but also adds order. Energy cycles are a key tool in understanding any chemical change.

Reactivity 1.2.1 – Bond enthalpy

Reactivity 1.2.1 – Bond-breaking absorbs and bond-forming releases energy. Calculate the enthalpy change of a reaction from the given average bond enthalpy data.	
Include an explanation of why bond enthalpy data are average values and may differ from those measured experimentally. Average bond enthalpy values are given in the data booklet.	Structure 2.2 – How would you expect bond enthalpy data to relate to bond length and polarity? Reactivity 3.4 – How does the strength of a carbon–halogen bond affect the rate of a nucleophilic substitution reaction?

Breaking bonds is an endothermic process

In Structure 2.2, we see that a covalent bond is due to the electrostatic attraction between a shared pair of electrons and the positive nuclei of the bonded atoms. Energy is needed to separate the atoms in a bond.

The **bond enthalpy** is the energy needed to break one mole of bonds in gaseous molecules under standard conditions.

The energy change, for example, during the formation of two moles of chlorine atoms from one mole of chlorine molecules can be represented in a thermochemical equation.

$$Cl_2(g) \rightarrow 2Cl(g) \qquad \Delta H^{\ominus} = +242\,kJ\,mol^{-1}$$

The enthalpy change is positive as it is an endothermic process.

The situation is complicated in molecules which contain more than two atoms. More energy is needed to break the first O–H bond in a water molecule than the second bond:

$$H_2O(g) \rightarrow H(g) + OH(g) \qquad \Delta H^{\ominus} = +502\,kJ\,mol^{-1}$$

$$OH(g) \rightarrow H(g) + O(g) \qquad \Delta H^{\ominus} = +427\,kJ\,mol^{-1}$$

Similarly, the energy needed to break the O–H bond in other molecules such as ethanol, C_2H_5OH, differs from either of these values. To compare bond enthalpies for bonds which occur in different environments, **average bond enthalpies** are tabulated.

The two previous equations can be combined:

$$H_2O(g) \rightarrow H(g) + H(g) + O(g) \qquad \Delta H^{\ominus} = (+502) + (+427)\,kJ\,mol^{-1}$$

As there are two O–H bonds,we can determine the average value (E(O–H)):

$$E(O{-}H) = \frac{+502 + 427}{2}\,kJ\,mol^{-1}$$

$$= \frac{929}{2} = 464.5\,kJ\,mol^{-1}$$

This value should be compared with the bond enthalpies given in the table on the next page, which are calculated for a larger range of molecules.

Bond	E(X–Y) / kJ mol^{-1}	Bond length / 10^{-12} m
H–H	+436	74
C–C	+346	154
C–H	+414	108
O–H	+463	97
C–O	+358	143
Cl–Cl	+242	199
C–Cl	+324	177
H–Cl	+431	128
F–F	+159	142
C–F	+492	138
H–F	+567	92
Br–Br	+193	228
H–Br	+366	141
I–I	+151	267
H–I	+298	160
O–O	+144	148
C=C	+614	134
O=O	+498	121
C=O	+804	122

The average bond enthalpy is the energy needed to break one mole of bonds in gaseous molecules under standard conditions averaged over similar compounds.

As expected, multiple bonds which involve more bonding electrons generally have higher bond enthalpies and shorter bond lengths than single bonds.

All bond enthalpies refer to reactions in the gaseous state, so any enthalpy changes resulting from the formation or breaking of **intermolecular** forces are not included.

Note that the definition of bond enthalpy indicates that all the species have to be in the gaseous state.

Bond enthalpy and polarity

You can improve your understanding by comparing the average bond enthalpy of the H–H and X–X bonds in the halogens and then comparing them to those in H–X.

X	Average of E(H–H) and E(X–X) / kJ mol^{-1}	E(H–X) / kJ mol^{-1}	$E(\text{H–X}) = \left(\frac{E(\text{H–H}) + E(\text{X–X})}{2}\right)$ / kJ mol^{-1}
Cl	$\frac{436 + 242}{2} = +339$	+431	92
Br	$\frac{436 + 193}{2} = +314.5$	+366	51.5
I	$\frac{436 + 151}{2} = +293.5$	+298	4.5

We can see that the difference in bond enthalpies between the hydrogen halide bonds and the average bonds in the corresponding elements, as shown in the fourth column, is greatest with chlorine and smallest with iodine. These differences can be related to the polarity of the molecule with the largest difference occurring with the more polar H–Cl bond. More generally we can say that the polar X–Y bond between two elements X and Y is stronger than the non-polar X–X and Y–Y bonds.

Electronegativities on the Pauling scale are calculated from bond enthalpy differences.

$$\chi_A - \chi_B = \sqrt{E(A-B)} - \left(\frac{E(A-A) + (B-B)}{2}\right)$$

The units of energy used are eV not kJ mol^{-1}. You are not required to know the details.

1 eV = 1.6 × 10^{-19} × 6.02 × 10^{23} J mol^{-1} = 96 kJ mol^{-1}

Challenge yourself

1. Fluorine shows some anomalous properties due to its small atomic radius.
   - **(a)** Comment on the bond enthalpy of F–F compared to the X–X bond in the other halogens.
   - **(b)** Compare the bond enthalpy of H–F with the average bond enthalpies of H_2 and F_2.

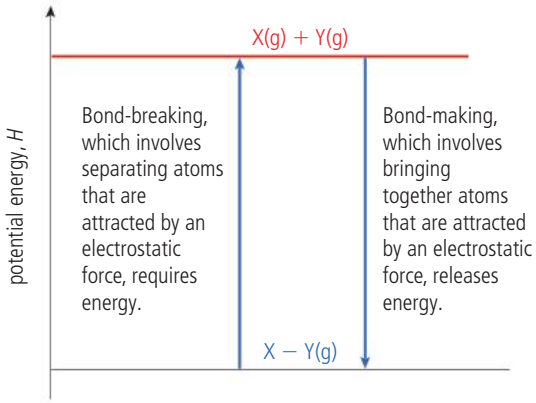
Structure 2.2 – How would you expect bond enthalpy data to relate to bond length and polarity?

Making bonds is an exothermic process

The same amount of energy is absorbed when a bond is broken as is given out when a bond is formed (Figure 2). For example:

$$H(g) + H(g) \rightarrow H_2(g) \qquad \Delta H^{\ominus} = -436\,kJ\,mol^{-1}$$

The negative enthalpy change shows that bond-making is an exothermic process.



R1.2 Figure 2 The energy changes that occur when bonds are broken and formed.

Endothermic processes involve the separation of particles which are held together by a force of attraction. Exothermic processes involve the bringing together of particles which are mutually attracted.

Worked example

Identify the endothermic process.

A $2Cl(g) \rightarrow Cl_2(g)$

B $Na(g) \rightarrow Na^+(g) + e^-$

C $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$

D $Na(g) \rightarrow Na(s)$

Solution

Only one of the processes involves the separation of particles:

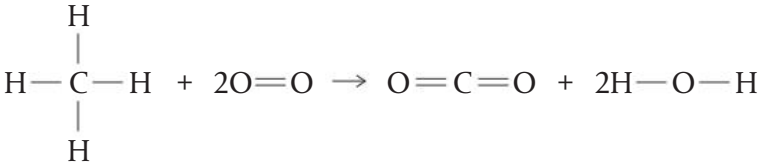
$$Na(g) \rightarrow Na^+(g) + e^-$$

A negatively charged electron e^- is separated from a positive ion $Na^+(g)$.

Answer = B

Energy changes in reactions

To understand the energy changes that occur in chemical reactions, consider, for example, the complete combustion of methane:



Energy is needed to break the C–H and O=O bonds in the reactants and is given out when the C=O and O–H bonds are formed. The reaction is exothermic overall as the bonds formed are stronger than those broken. Conversely, a reaction is endothermic when the bonds broken are stronger than the bonds formed.

Worked example

Use bond enthalpies to calculate the enthalpy of combustion of methane, the principal component of natural gas.

Solution

1. Write down the equation for the reaction showing all the bonds. (This has already been done above.)
2. Construct a table to show the bonds which are broken and formed during the reaction with the corresponding enthalpy changes.

Bonds broken	$\Delta H^{\ominus}$ / kJ mol^{-1} (endothermic)	Bonds formed	$\Delta H^{\ominus}$ / kJ mol^{-1} (exothermic)
4 C–H	4 (+414)	2 C=O	2 (–804)
2 O=O	2 (+498)	4 O–H	4 –463)
Total	**= +2652**		**= –3460**

$\Delta H^{\ominus} = +2652 - 3460\ \text{kJ mol}^{-1} = -808\ \text{kJ mol}^{-1}$

The value calculated from the bond enthalpies should be compared with the experimental value of –891 kJ mol^{-1} measured under standard conditions given in Section 14 of the data booklet. The values are significantly different because the standard state of water is liquid and the bond enthalpy calculation assumes that the reaction occurs in the gaseous state. The use of average bond enthalpies is an additional approximation.

Challenge yourself

2. Compare the value of the enthalpy of combustion of methane obtained in the worked example to that in Section 14 of the data booklet and estimate the strength of a hydrogen bond.

The worked example illustrates a general result:

$$\Delta H^{\ominus} = \Sigma E(\text{bonds broken}) - \Sigma E(\text{bonds formed})$$



$\Delta H^{\ominus} = \Sigma E(\text{bonds broken}) - \Sigma E(\text{bonds formed})$

Worked example

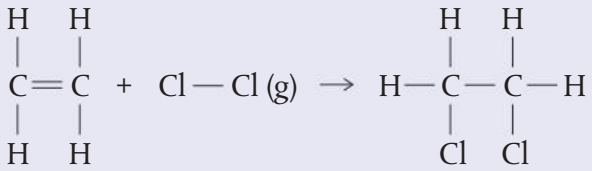
Use bond enthalpy data given earlier to calculate the enthalpy change of reaction between ethene and chorine:

$$C_2H_4(g) + Cl_2(g) \rightarrow CH_2ClCH_2Cl(g)$$

Solution

Follow the same strategy as the previous example.

Start with a balanced chemical equation showing all the bonds:



Identify the bonds broken and formed and the corresponding enthalpy changes.

Bonds broken	ΔH / kJ mol^{-1} (endothermic)	Bonds formed	ΔH / kJ mol^{-1} (exothermic)
Cl–Cl	+242	2 C–Cl	−2(324)
C=C	+614	C–C	−(346)
Total	= +242 +614 = +856		= −2(324) − (346) = −994

$$\Delta H^{\ominus} = \Sigma E(\text{bonds broken}) - \Sigma E(\text{bonds formed})$$
$$= +856 - 994 = -138\,\text{kJ mol}^{-1}$$

As discussed in Reactivity 1.1, some reactants need to be given an initial energy known as the activation energy before they will react. This energy is needed as some bonds in the reactants must break before new bonds in the products can form. The rate of some reactions can be explained by the relative bond enthalpy of the bonds broken. The relative strength of the carbon–halogen bond, for example, can be used to explain the relative reactivity of the halogenoalkanes discussed in Reactivity 3.4. The iodoalkanes are the most reactive as the C–I bond is relatively easy to break compared with the other carbon–halogen bonds.

Reactivity 3.4 – How does the strength of a carbon–halogen bond affect the rate of a nucleophilic substitution reaction?



The Earth is unique among the planets in having an atmosphere that is chemically active and rich in oxygen. Oxygen, O_2, and ozone, O_3, both play a key role in protecting life. The oxygen-to-oxygen bond in ozone is weaker than the double bond in O_2 and so is broken by long-wavelength ultraviolet radiation. The absorption of harmful ultraviolet (UV) radiation.in the ozone layer protects the Earth's surface.

Challenge yourself

3. The bond enthalpy in ozone is +363 kJ mol^{-1}.

(a) Compare this bond enthalpy with the oxygen–oxygen bond enthalpies tabulated earlier on page 455 and comment on its value.

(b) Explain why ozone (O_3) can be decomposed by ultraviolet radiation with a longer wavelength than that required to decompose oxygen (O_2).

Exercise

Q1. Which of the following processes are endothermic?

I. $H_2O(s) \rightarrow H_2O(g)$

II. $CO_2(g) \rightarrow CO_2(s)$

III. $O_2(g) \rightarrow 2O(g)$

A I and II only **B** I and III only **C** II and III only **D** I, II and III

Q2. Identify the equation that represents the bond enthalpy for the H–Cl bond.

A $HCl(g) \rightarrow H(g) + Cl(g)$

B $HCl(g) \rightarrow \frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g)$

C $HCl(g) \rightarrow H^+(g) + Cl^-(g)$

D $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$

Q3. Identify the bonds that are broken in the following process.

$$C_2H_6(g) \rightarrow 2C(g) + 6H(g)$$

Q4. Which of the following enthalpy changes corresponds to the bond enthalpy of the carbon–oxygen bond in carbon monoxide?

A $CO(g) \rightarrow C(s) + O(g)$

B $CO(g) \rightarrow C(g) + O(g)$

C $CO(g) \rightarrow C(s) + \frac{1}{2}O_2(g)$

D $CO(g) \rightarrow C(g) + \frac{1}{2}O_2(g)$

Q5. The hydrogenation of the alkene double bond in unsaturated oils is an important reaction in margarine production. Calculate the enthalpy change when one mole of C=C bonds is hydrogenated from the bond energy data tabulated earlier.

A −290 kJ mol^{-1} **B** −124 kJ mol^{-1}

C +124 kJ mol^{-1} **D** +290 kJ mol^{-1}



Weather balloon being inflated by a meteorologist. A measuring device attached below the balloon will measure ozone distribution to an altitude of 35–40 kilometres, allowing study of the ozone layer at 20–30 kilometres. Ozone at this level (formed by sunlight) absorbs the dangerous types of UV radiation in sunlight.

Q6. Use bond enthalpy data to calculate the enthalpy change of the reaction between methane and fluorine.

$$C_2H_4(g) + F_2(g) \rightarrow CH_2FCH_2F(g)$$

A $+557\,kJ\,mol^{-1}$ **B** $+65\,kJ\,mol^{-1}$

C $-65\,kJ\,mol^{-1}$ **D** $-557\,kJ\,mol^{-1}$

Q7. Use bond enthalpy data to calculate $\Delta H^{\ominus}$ for the reaction:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

Q8. Use the bond enthalpies given earlier to estimate the enthalpy of combustion of ethanol and comment on the reliability of your result.

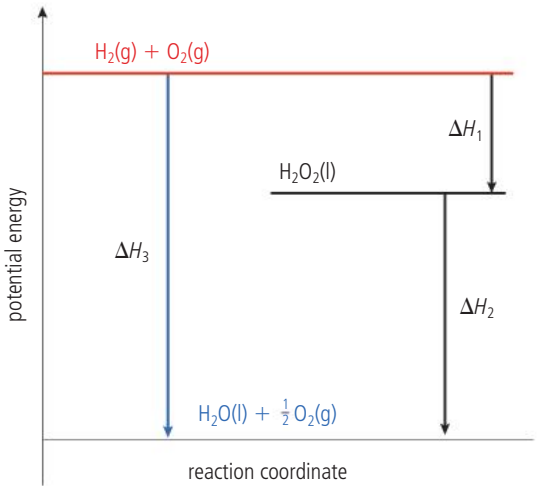
Reactivity 1.2.2 – Hess's law

Reactivity 1.2.2 – Hess's law states that the enthalpy change for a reaction is independent of the pathway between the initial and final states.

Apply Hess's law to calculate enthalpy changes in multistep reactions.

Hess's law is a consequence of the law of conservation of energy

Consider again the energy level diagram in R1.1 Figure 7 on page 431.



The thermochemical equations for the three reactions are:

$H_2(g) + O_2(g) \rightarrow H_2O_2(l)$ $\Delta H_1 = -188\,kJ\,mol^{-1}$

$H_2O_2(l) \rightarrow H_2O(l) + \frac{1}{2}O_2(g)$ $\Delta H_2 = -98\,kJ\,mol^{-1}$

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\Delta H_3 = -286\,kJ\,mol^{-1}$

We can see from the figure on the previous page that $\Delta H_1 + \Delta H_2 = \Delta H_3$ and can confirm this by adding the first two equations:

$$H_2(g) + O_2(g) + \cancel{H_2O_2(l)} \rightarrow \cancel{H_2O_2(l)} + H_2O(l) + \tfrac{1}{2}O_2(g) \qquad \Delta H_3 = -188 - 98\,\text{kJ mol}^{-1}$$

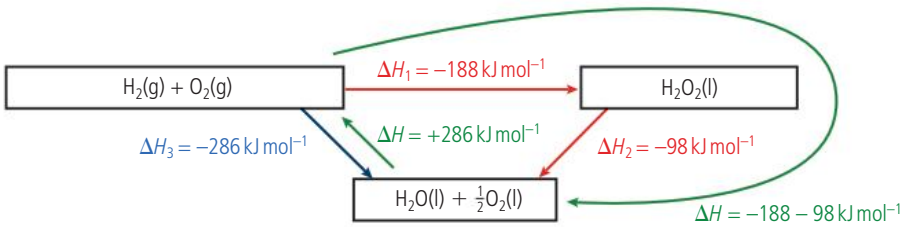
$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H_3 = -286\,\text{kJ mol}^{-1}$$

This shows that the overall enthalpy change that occurs when hydrogen and oxygen combine to form water is the same whether the chemical change occurs in one step (ΔH_3) or two steps ($\Delta H_1 + \Delta H_2$).

This result can be generalized and is known as **Hess's law**: the enthalpy change for any chemical reaction is independent of the route, provided the starting conditions and final conditions, and reactants and products, are the same.

Hess's law states that the enthalpy change for any chemical reaction is independent of the route, provided the starting conditions and final conditions, and reactants and products, are the same.

These reactions form an energy cycle. In the clockwise direction shown in Figure 3, the starting and end points are $H_2(g) + O_2(g)$ so there is no net chemical reaction or enthalpy change.



R1.2 Figure 3 There is no net chemical or enthalpy change as the start and end points are the same.

As per the law of conservation of energy, the enthalpy change in a complete cycle = 0.

$$0 = \Delta H_1 + \Delta H_2 - \Delta H_3$$

This leads to:

$$\Delta H_3 = \Delta H_1 + \Delta H_2$$

TOK

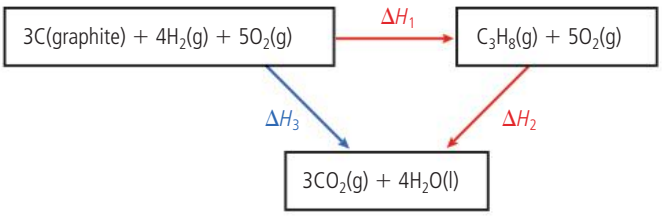
Hess's law is a natural consequence of the law of conservation of energy. If you know the law of conservation of energy, do you automatically know Hess's law?

Using Hess's law

Hess's law states that the enthalpy change for any chemical reaction is independent of the route, provided the starting and final conditions, and reactants and products, are the same. The importance of Hess's law is that it allows us to calculate the enthalpy changes of reactions that we cannot measure directly in the laboratory. For example, although the elements carbon and hydrogen do not combine directly to form propane, the enthalpy change for the reaction:

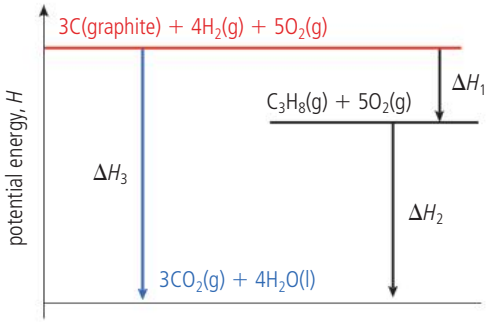
$$3C(\text{graphite}) + 4H_2(g) \rightarrow C_3H_8(g)$$

can be calculated from the enthalpy of combustion data of the elements and the compound (Figure 4).



R1.2 Figure 4 $\Delta H_1 + \Delta H_2 = \Delta H_3$, therefore $\Delta H_1 = \Delta H_3 - \Delta H_2$. Although ΔH_1 cannot be measured directly, it can be calculated from the enthalpies of combustion of carbon and hydrogen (ΔH_3) and propane (ΔH_2).

The steps in an enthalpy cycle may be hypothetical. The only requirement is that the individual chemical reactions in the cycle must balance. The relationship between the different reactions is clearly shown in an energy level diagram (Figure 5).



R1.2 Figure 5 Energy level diagram used to obtain the enthalpy of formation of propane indirectly.

Reversing the direction of a reaction reverses the sign of ΔH.

The general use of enthalpies of combustion in determining enthalpies of reaction is discussed in more detail in the next section.

Worked example

Calculate the standard enthalpy change, $\Delta H^{\ominus}$, for the formation of sulfur dioxide from the thermochemical equations (1) and (2).

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

$$S(s) + 1\tfrac{1}{2}O_2(g) \rightarrow SO_3(g) \qquad \Delta H^{\ominus} = -395\,kJ\,mol^{-1} \qquad (1)$$

$$SO_2(g) + \tfrac{1}{2}O_2(g) \rightarrow SO_3(g) \qquad \Delta H^{\ominus} = -98\,kJ\,mol^{-1} \qquad (2)$$

Solution

We can think of the reaction as a journey from S(s) to $SO_2(g)$. As the standard enthalpy change cannot be measured directly, we must go by an alternative route suggested by the equations given.

Reaction 1 starts from the required reactant:

$$S(s) + 1\tfrac{1}{2}O_2(g) \rightarrow SO_3(g) \qquad \Delta H^{\ominus} = -395\,kJ\,mol^{-1} \qquad (1)$$

Reaction 2 relates $SO_3(g)$ to $SO_2(g)$. To finish with the required product, we reverse the chemical change and the sign of enthalpy change:

$$SO_3(g) \rightarrow SO_2(g) + \tfrac{1}{2}O_2(g) \qquad \Delta H^{\ominus} = -(-98)\,kJ = +98\,kJ\,mol^{-1} \qquad (2)$$

SKILLS

The enthalpy change for the decomposition of metal carbonates can be determined in the school laboratory by reacting the metal carbonate and the metal oxide or hydrogen carbonate with dilute acids using Hess's law.

We can now combine these equations:

$S(s) + 1\frac{1}{2}O_2(g) + SO_3(g) \rightarrow SO_3(g) + SO_2(g) + \frac{1}{2}O_2(g)$ $\Delta H^{\ominus} = -395 + 98\,kJ\,mol^{-1}$

Simplifying:

$S(s) + 1\frac{1}{2}O_2(g) + \cancel{SO_3(g)} \rightarrow \cancel{SO_3(g)} + SO_2(g) + \cancel{\frac{1}{2}O_2(g)}$ $\Delta H^{\ominus} = -297\,kJ\,mol^{-1}$

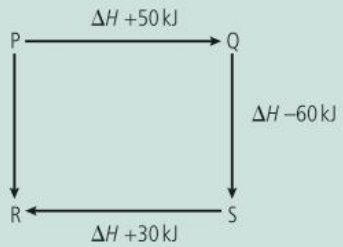
$S(s) + O_2(g) \rightarrow SO_2(g)$ $\Delta H^{\ominus} = -297\,kJ\,mol^{-1}$

Challenge yourself

4. Explain why it is difficult to determine the enthalpy change of thermal decomposition reactions directly.

Exercise

Q10. The diagram illustrates the enthalpy changes for a set of reactions.



Which of the following statements are correct?

I. $P \rightarrow S$ $\Delta H = -10\,kJ$

II. $R \rightarrow Q$ $\Delta H = +90\,kJ$

III. $P \rightarrow R$ $\Delta H = +20\,kJ$

A I and II only **B** I and III only

C II and III only **D** I, II and III

Q11. The thermochemical equations for three related reactions are shown.

$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ $\Delta H_1 = -283\,kJ\,mol^{-1}$

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ $\Delta H_2 = -572\,kJ\,mol^{-1}$

$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(l)$ $\Delta H_3 = ?$

What is the value of ΔH_3?

A $+289\,kJ\,mol^{-1}$ **B** $-3\,kJ\,mol^{-1}$

C $-289\,kJ\,mol^{-1}$ **D** $-855\,kJ\,mol^{-1}$



The heat produced when water is added to anhydrous copper(II) sulfate (white) is enough to produce steam and disturb the powder.

SKILLS

The heat produced when an anhydrous salt is converted to a hydrated salt can be determined by adding the anhydrous and hydrated salt to separate samples of water. Full details of how to carry out this experiment with a worksheet are available in the eBook.

Q12. Calculate the enthalpy change, $\Delta H^{\ominus}$, for the reaction:

$$C(graphite) + \tfrac{1}{2}O_2(g) \rightarrow CO(g)$$

from the information below:

$C(graphite) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^{\ominus} = -394\,kJ\,mol^{-1}$

$CO(g) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g)$ $\Delta H^{\ominus} = -283\,kJ\,mol^{-1}$

Q13. Calculate the enthalpy change, $\Delta H^{\ominus}$, for the reaction:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

from the information below:

$N_2(g) + O_2(g) \rightarrow 2NO(g)$ $\Delta H^{\ominus} = +180.5\,kJ\,mol^{-1}$

$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$ $\Delta H^{\ominus} = +66.4\,kJ\,mol^{-1}$

Q14. Calculate the enthalpy change for the dimerization of nitrogen dioxide:

$$2NO_2(g) \rightarrow N_2O_4(g)$$

from the following data:

$\tfrac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g)$ $\Delta H^{\ominus} = +33.2\,kJ\,mol^{-1}$

$N_2(g) + 2O_2(g) \rightarrow N_2O_4(g)$ $\Delta H^{\ominus} = +9.16\,kJ\,mol^{-1}$

HL

Reactivity 1.2.3 – Standard enthalpy changes of combustion and formation

Reactivity 1.2.3 – Standard enthalpy changes of combustion, $\Delta H_c^{\ominus}$, and formation, $\Delta H_f^{\ominus}$, data are used in thermodynamic calculations.	
Deduce equations and solutions to problems involving these terms.	
Enthalpy of combustion and formation data are given in the data booklet.	Structure 2.2 – Would you expect allotropes of an element, such as diamond and graphite, to have different $\Delta H_f^{\ominus}$ values?

Standard enthalpy change of combustion

The **standard enthalpy change of combustion ($\Delta H_c^{\ominus}$)** of a substance is the enthalpy change that occurs when one mole of the substance burns completely under standard conditions. As discussed in Reactivity 1.1, enthalpy changes of combustion of a substance can be determined experimentally by measuring the temperature changes of a known mass of water when heated by the combustion of the substance. Enthalpy changes can be used directly to compare the energy output of different fuels. These enthalpy changes can also be used as we saw on page 461–462 to calculate the enthalpy change of other reactions. This is explored further in the next section.

The standard enthalpy change of combustion ($\Delta H_c^{\ominus}$) of a substance is the enthalpy change that occurs when one mole of the substance burns completely under standard conditions of 298 K (25 °C) and 1.00×10^5 Pa.

Worked example

The enthalpy of combustion of hexane is given in Section 14 of the data booklet.

Give the thermochemical equation which corresponds to the standard enthalpy of combustion of hexane.

Solution

The equation refers to the combustion of one mole of hexane.

Balancing the carbon and the hydrogens:

$$C_6H_{14}(l) + _O_2(g) \rightarrow \mathbf{6}CO_2(g) + \mathbf{7}H_2O(l)$$

Balancing the oxygens: 19 Os on both sides.

$$C_6H_{14}(l) + 9\tfrac{1}{2}O_2(g) \rightarrow \mathbf{6}CO_2(g) + \mathbf{7}H_2O(l)$$

Standard enthalpy change of formation

The **standard enthalpy change of formation** ($\Delta H_f^{\ominus}$) of a substance is the enthalpy change that occurs when one mole of the substance is formed from its elements in their standard states. These standard measurements are taken at a specified temperature (usually 298 K) and a pressure of 1.00×10^5 Pa. The standard state of an element is its most stable form under these conditions.

The standard enthalpy change of formation of a substance is the enthalpy change that occurs when one mole of the substance is formed from its elements in their standard states at 1.00×10^5 Pa and at a specified temperature (usually 298 K). The standard state of an element is its most stable form at these conditions.

The measurements are important as they:

- give a measure of the stability of a substance relative to its elements
- can be used to calculate the enthalpy changes of all reactions, either hypothetical or real.

Worked example

Which of the following **does** have a standard enthalpy change of formation value of zero at 25 °C and 1.00×10^5 Pa?

A H(g) **B** Hg(s) **C** C(diamond) **D** Si(s)

Solution

The standard enthalpy change of formation of a substance is zero when it is an element in its standard state.

Considering each of the options in turn. The standard state of the elements:

hydrogen is $H_2(g)$, mercury is Hg(l), carbon is C(graphite), C(diamond) is a less stable allotrope, silicon is Si(s).

Answer = **D**

The standard enthalpy change of formation of an element in its most stable form is zero. There is no chemical change and so no enthalpy change when an element is formed from itself.

Structure 2.2 – Would you expect allotropes of an element, such as diamond and graphite, to have different $\Delta H_f^\ominus$ values?

Challenge yourself

5. Suggest, based on the discussion of bonding and structure in Structure 2.2, why graphite is more stable than diamond.

Worked example

The enthalpy change of formation of ethanol is given in Section 13 of the data booklet. Give the thermochemical equation which represents the standard enthalpy of formation of ethanol.

Solution

The value from the data booklet: $\Delta H_f^\ominus = -278\,\text{kJ mol}^{-1}$

Ethanol (C_2H_5OH) is made up of the elements carbon (C(graphite)), hydrogen ($H_2(g)$) and oxygen ($O_2(g)$).

$$__C(\text{graphite}) + __H_2(g) + __O_2(g) \rightarrow C_2H_5OH(l) \qquad \Delta H_f^\ominus = -278\,\text{kJ mol}^{-1}$$

Balancing the equation:

$$\mathbf{2}C(\text{graphite}) + \mathbf{3}H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow C_2H_5OH(l) \qquad \Delta H_f^\ominus = -278\,\text{kJ mol}^{-1}$$

Note that as the enthalpy change of formation refers to one mole of product, there are fractional coefficients in the balanced equation.

Exercise

Q15. Which of the following does **not** have a standard enthalpy change of formation value of zero at 25 °C and 1.00×10^5 Pa?

A $Cl_2(g)$ **B** $I_2(s)$ **C** $Br_2(g)$ **D** Na(s)

Q16. Which of the following **does** have an enthalpy change of formation of zero at 25 °C and 1.00×10^5 Pa?

A $O_3(g)$ **B** $S_8(s)$ **C** $C_{60}(s)$ **D** $I_2(aq)$

Q17. Identify the equation which corresponds to an enthalpy change of formation.

A $CuSO_4(aq) + Zn(s) \rightarrow ZnSO_4(aq) + Cu(s)$

B $Cu(s) + S(s) + 2O_2(g) \rightarrow CuSO_4(aq)$

C $5H_2O(l) + CuSO_4(s) \rightarrow CuSO_4.5H_2O(s)$

D $Cu(s) + S(s) + 2O_2(g) \rightarrow CuSO_4(s)$

Q18. The enthalpy changes of combustion of hydrogen and methane are given in Section 14 of the data booklet. Calculate the maximum amount of energy available from burning 1.00 g of each of the gases.

Q19. The standard enthalpy changes for the combustion of propane, $C_3H_8(g)$, and butane, $C_4H_{10}(g)$, are given in Section 14 of the data booklet.

(a) Give the equations for the complete combustion of propane and butane.

(b) Identify the fuel which releases the most energy when a 1.0 g sample is burnt.

Q20. **(a)** Write the thermochemical equation for the standard enthalpy of formation of propanone, $CH_3COCH_3(l)$.

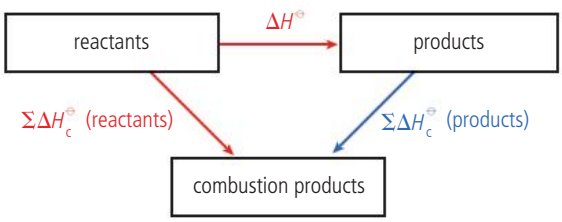
(b) State the conditions under which standard enthalpy changes are measured.

Reactivity 1.2.4 – Calculating enthalpy changes

Reactivity 1.2.4 – An application of Hess's law uses enthalpy of formation data or enthalpy of combustion data to calculate the enthalpy change of a reaction.	
Calculate enthalpy changes of a reaction using $\Delta H_f^\ominus$ data or $\Delta H_c^\ominus$ data: $\Delta H^\ominus = \Sigma\Delta H_f^\ominus(\text{products}) - \Sigma\Delta H_f^\ominus(\text{reactants})$ $\Delta H^\ominus = \Sigma\Delta H_c^\ominus(\text{reactants}) - \Sigma\Delta H_c^\ominus(\text{products})$	
The equations to determine the enthalpy change of a reaction using $\Delta H_f^\ominus$ data or $\Delta H_c^\ominus$ data are given in the data booklet.	

Calculating enthalpy changes from standard enthalpy changes of combustion

We saw earlier that the enthalpy change of formation of propane could be calculated from the enthalpy change of combustion data as both reactants and products form the same combustion products (Figure 4). This approach can be applied to all reactions. Consider the generalized energy cycle in Figure 6, which includes the combustion products of both reactants and products.



R1.2 Figure 6 Generalized energy cycle.

The chemical change from reactants to combustion products can either occur directly or indirectly. The total enthalpy change must be the same for both routes.

From Figure 6:

$$\Delta H^\ominus + \Sigma\Delta H_c^\ominus(\text{products}) = \Sigma\Delta H_c^\ominus(\text{reactants})$$

This gives the general expression for $\Delta H^\ominus$:

$$\Delta H^\ominus = \Sigma\Delta H_c^\ominus(\text{reactants}) - \Sigma\Delta H_c^\ominus(\text{products})$$

$\Delta H^\ominus = \Sigma\Delta H_c^\ominus$(reactants) – $\Sigma\Delta H_c^\ominus$(products)

Worked example

Use the data in Section 14 of the data booklet to calculate the enthalpy change of formation of glucose.

Solution

First, write down the equation which corresponds to the enthalpy change of formation of glucose and add the enthalpy changes of combustion for the reactants and products below.

$$6C(\text{graphite}) + 6H_2(g) + 3O_2(g) \rightarrow C_6H_{12}O_6(s)$$

$$\mathbf{6}(-394) \quad \mathbf{6}(-286) \quad \mathbf{3}(0) \quad -2803 \quad \Delta H_c^{\ominus}/\text{kJ mol}^{-1}$$

The energy produced when oxygen reacts is included in the enthalpy of combustion of the other reactants and products. This can be given an enthalpy of combustion of zero.

As the standard enthalpies of combustion are given per mole, they should be multiplied by the number of moles in the balanced equation as shown in bold above.

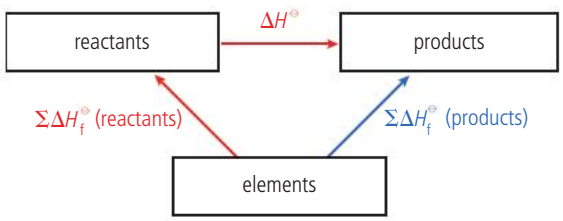
Write down the general expression for $\Delta H^{\ominus}$:

$$\Delta H^{\ominus} = \Sigma\Delta H_c^{\ominus}(\text{reactants}) - \Sigma\Delta H_c^{\ominus}(\text{products})$$

$$= 6(-394) + 6(-286)) - (-2803) = -1277\,\text{kJ mol}^{-1}$$

Calculating enthalpy changes from standard enthalpy changes of formation

Standard enthalpy changes of formation can also be used to calculate the standard enthalpy change of reactions. Consider the general energy cycle in Figure 7 which includes the formation of the reactants and products from their constituent elements.



R1.2 Figure 7 The chemical change of elements to products can either occur directly or indirectly. The total enthalpy change must be the same for both routes.

We have from Figure 7:

$$\Sigma\Delta H_f^{\ominus}(\text{reactants}) + \Delta H^{\ominus} = \Sigma\Delta H_f^{\ominus}(\text{products})$$

This gives the general expression for $\Delta H^{\ominus}$ of any reaction:

$$\Delta H^{\ominus} = \Sigma\Delta H_f^{\ominus}\text{products}) - \Sigma\Delta H_f^{\ominus}(\text{reactants})$$

$\Delta H^{\ominus} = \Sigma\Delta H_f^{\ominus}(\text{products}) - \Sigma\Delta H_f^{\ominus}(\text{reactants})$

Worked example

Calculate the enthalpy change of combustion of propane from the following standard enthalpy changes of formation data.

Compound	$\Delta H_f^\ominus$ / kJ mol^{-1}
$C_3H_8(g)$	−105
$CO_2(g)$	−394
$H_2O(l)$	−286

Solution

First, write down the equation with the corresponding enthalpies of formation underneath:

$$C_3H_8(g) + \mathbf{5}O_2(g) \rightarrow \mathbf{3}CO_2(g) + \mathbf{4}H_2O(g)$$
$$-105 \qquad 0 \qquad \mathbf{3}(-394) \quad \mathbf{4}(-286) \qquad \Delta H_f^\ominus \text{ / kJ mol}^{-1}$$

As the standard enthalpies of formation are given per mole, they should be multiplied by the number of moles in the balanced equation, shown in bold above.

Write down the general expression for $\Delta H^\ominus$:

$$\Delta H^\ominus = \Delta H_f^\ominus(\text{products}) - \Delta H_f^\ominus(\text{reactants})$$

and express $\Delta H^\ominus$ in terms of the data given:

$$\Delta H^\ominus = 3(-394) + 4(-286) - (-105) = -2221 \text{ kJ mol}^{-1}$$

Do not confuse the different methods of calculating enthalpy changes.
A common error when using enthalpies of formation is reversal of the sign.
The correct expression is: $\Delta H^\ominus = \Delta H_f^\ominus(\text{products}) - \Delta H_f^\ominus(\text{reactants})$
This should be contrasted with the expression using bond enthalpies:

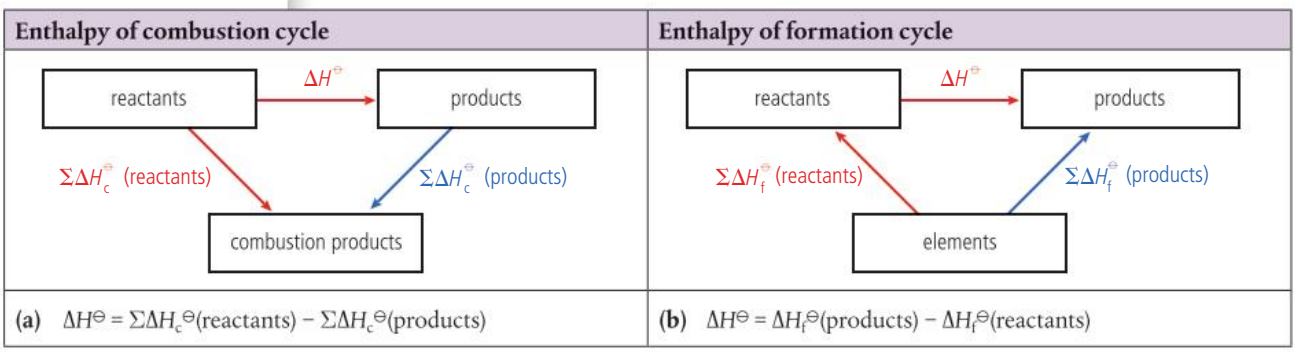
$$\Delta H = \Sigma E(\text{bonds broken}) - \Sigma E(\text{bonds formed})$$

Nature of Science

The transfer of heat drives a country's industrial development and an individual's life. It is a concept that has enlightened our understanding of why things change in the natural world. This scientific understanding and the harnessing of heat energy has helped make the modern world. The conservation of energy, on which Hess's law is based, developed as a result of practical considerations about the use and effect of heat and work. Hess's law is important on both a practical and theoretical level as it allows us to predict the energy changes of possible and impossible reactions. The study of energetics shows how scientific theories evolve and generally accommodate other theories, creating a consistent understanding across a range of phenomena and disciplines.

Standard enthalpy changes of combustion and formation: a comparison

It is instructive to compare the energy cycles derived from the two enthalpy changes shown in Figure 8. The different forms of the expression for $\Delta H^{\ominus}$ are due to the reversal of the arrows from or to the reactants and products in the respective energy cycles.



R1.2 Figure 8 Note that the diagonal arrows are pointing away from the reactant and products in **(a)** and towards the reactants and products in **(b)**. The corresponding expressions for $\Delta H^{\ominus}$ reflect this.

You should construct the appropriate energy cycles from the definitions of the corresponding enthalpy change and deduce the expressions for $\Delta H^{\ominus}$ from the cycle.

Exercise

Q21. An alkane can be 'cracked' to produce an alkane with a shorter carbon chain, and an alkene.

Determine the enthalpy change of the reaction from the enthalpy of combustion data.

$$C_{10}H_{22}(l) \rightarrow C_8H_{18}(l) + C_2H_4(g)$$

Compound	$\Delta H_c^{\ominus}$ / kJ mol^{-1}
$C_{10}H_{22}(l)$	−6778
$C_8H_{18}(l)$	−5470
$C_2H_4(g)$	−1411

A −10 837 kJ mol^{-1} **B** −103 kJ mol^{-1}

C +103 kJ mol^{-1} **D** +13 659 kJ mol^{-1}

Q22. Identify the best expression for the enthalpy of combustion of hexane.

Compound	$\Delta H_f^{\ominus}$ / kJ mol^{-1}
$C_6H_{14}(l)$	x
$CO_2(g)$	y
$H_2O(g)$	z

A $6y + 6z + x$ **B** $6y + 7z - x$

C $12y + 14z - 2x$ **D** $12y + 14z + 2x$

Q23. Hydrogen peroxide slowly decomposes into water and oxygen.

$$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$$

Calculate the enthalpy change of this reaction from the data table.

	$\Delta H_f^\ominus$ / kJ mol^{-1}
$H_2O_2(l)$	−188
$H_2O(l)$	−286

A +98 kJ mol^{-1} **B** −98 kJ mol^{-1}

C +196 kJ mol^{-1} **D** −196 kJ mol^{-1}

Q24. Enthalpy changes of combustion data are tabulated in Section 14 of the data booklet.

(a) State the chemical equation for the formation of benzene.

(b) Use enthalpy changes of combustion data to calculate the enthalpy of formation of benzene.

(c) Compare your answer for part **(b)** to the value given in Section 13 of the data booklet and comment on any differences.

Q25. Use the enthalpy change of combustion data in Section 14 of the data booklet to calculate $\Delta H^\ominus$ (in kJ mol^{-1}) for the reaction:

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

Q26. Use the data in the table below to calculate $\Delta H^\ominus$ (in kJ mol^{-1}) for the reaction:

$$Fe_3O_4(s) + 2C(\text{graphite}) \rightarrow 3Fe(s) + 2CO_2(g)$$

	$\Delta H_f^\ominus$ / kJ mol^{-1}
$Fe_3O_4(s)$	−1118
$CO_2(g)$	−394

Q27. Calculate the enthalpy change for the hypothetical reduction of magnesium oxide by carbon, according to the equation below from the data given in the table below. Comment on the feasibility of using carbon as a reducing agent.

$$2MgO(s) + C(\text{graphite}) \rightarrow CO_2(g) + 2Mg(s)$$

	$\Delta H_f^\ominus$ / kJ mol^{-1}
$CO_2(g)$	−394
$MgO(s)$	−602

Reactivity 1.2.5 – Born–Haber cycles

Reactivity 1.2.5 – A Born–Haber cycle is an application of Hess's law, used to show energy changes in the formation of an ionic compound.	
Interpret and determine values from a Born–Haber cycle for compounds composed of univalent and divalent ions.	
The cycle includes ionization energies, enthalpy of atomization (using sublimation and/or bond enthalpies), electron affinities, lattice enthalpy, enthalpy of formation. The construction of a complete Born–Haber cycle will not be assessed.	Structure 2.1 – What are the factors that influence the strength of lattice enthalpy in an ionic compound?

First ionization energies and electron affinities

In Structure 2.1 the formation of ionic compounds such as sodium chloride is discussed. Metal atoms lose electrons and non-metal atoms gain electrons. The **first ionization energy** ($\Delta H_i^\ominus$) corresponds to the energy needed to form the positive ion from a gaseous atom:

The first ionization energy $\Delta H_i^\ominus$ is the minimum energy required to remove one mole of electrons from one mole of gaseous atoms.

$$Na(g) \rightarrow Na^+(g) + e^-(g) \qquad \Delta H_i^\ominus = +496\,kJ\,mol^{-1}$$

It is an endothermic process as it involves pulling an electron away from the attractive electrostatic force due to the positively charged nucleus.

The first **electron affinity** ($\Delta H_e^\ominus$) is the enthalpy change when one mole of gaseous atoms attracts one mole of electrons. For chlorine:

The first electron affinity ($\Delta H_e^\ominus$) is the enthalpy change when one mole of gaseous electrons is added to one mole of gaseous atoms.

$$Cl(g) + e^-(g) \rightarrow Cl^-(g) \qquad \Delta H_e^\ominus = -349\,kJ\,mol^{-1}$$

As the electron is attracted to the positively charged nucleus of the Cl atom, the process is exothermic.

Values for both energy terms are tabulated in Section 9 of the data booklet.

Lattice enthalpies

Adding the two equations for ionization energy and electron affinity:

$$Na(g) + Cl(g) \rightarrow Na^+(g) + Cl^-(g) \qquad \Delta H^\ominus = -349 + 496 = +147\,kJ\,mol^{-1}$$

We can now see that the electron transfer process is endothermic overall and so energetically unfavourable, despite leading to the formation of ions with stable noble gas electron configurations. To understand the formation of ionic compounds, we need to look deeper. The oppositely charged gaseous ions come together to form an **ionic lattice**; this is a very exothermic process as there is strong attraction between the oppositely charged ions.

$$Na^+(g) + Cl^-(g) \rightarrow NaCl(s) \qquad \Delta H^\ominus = -790\,kJ\,mol^{-1}$$

It is this step that explains the readiness of sodium and chlorine to form an ionic compound.

The **lattice enthalpy** $\Delta H_{lat}^{\ominus}$ expresses this enthalpy change in terms of the reverse endothermic process. The lattice enthalpy relates to the formation of gaseous ions from one mole of a solid crystal breaking into gaseous ions. For sodium chloride:

$$NaCl(s) \rightarrow Na^+(g) + Cl^-(g) \qquad \Delta H_{lat}^{\ominus} = +790\,kJ\,mol^{-1}$$

The lattice enthalpy ($\Delta H_{lat}^{\ominus}$) is the enthalpy change that occurs when one mole of a solid ionic compound is separated into gaseous ions under standard conditions.

Experimental lattice enthalpies and the Born–Haber cycle

Experimental lattice energies cannot be determined directly. An energy cycle based on Hess's law, known as the **Born–Haber cycle**, is used. The formation of an ionic compound from its elements is supposed to take place in a number of steps including the formation of the solid lattice from its constituent gaseous ions. From Hess's law, the enthalpy change for the overall formation of the solid must be equal to the sum of the enthalpy changes accompanying the individual steps.

Note that the data booklet expresses lattice enthalpy as an endothermic process of ion separation. It can also be represented as the reverse exothermic process in some sources.

Consider, for example, the formation of sodium chloride:

$$Na(s) + \tfrac{1}{2}Cl_2(g) \rightarrow NaCl(s) \qquad \Delta H_f^{\ominus}(NaCl) = -411\,kJ\,mol^{-1}$$

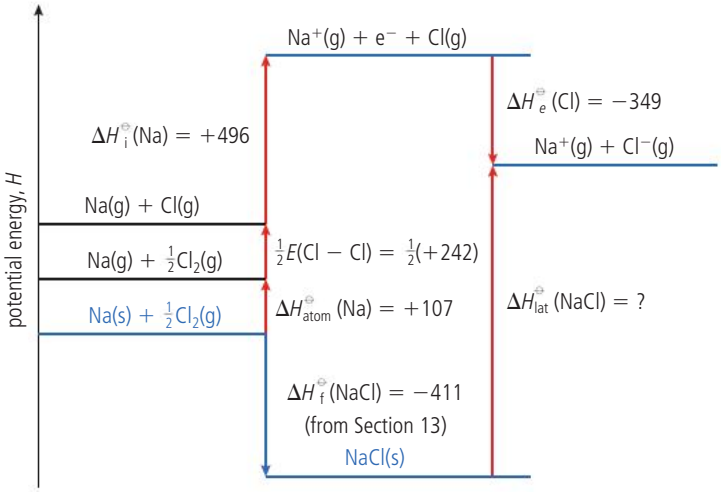
This can be considered to take place in several steps as shown in the table below.

Step	$\Delta H^{\ominus}$ / kJ mol^{-1}
Sodium is atomized to form one mole of gaseous ions: $Na(s) \rightarrow Na(g)$ The corresponding enthalpy change is known as the enthalpy change of atomization.	$\Delta H_{atom}^{\ominus}(Na) = +107$
One mole of chlorine atoms is formed as $\frac{1}{2}$ mole of Cl–Cl bonds break: $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$ E = bond enthalpy (page 454) This is also known as the enthalpy of atomization of chlorine.	$\frac{1}{2}E(Cl{-}Cl) = \frac{1}{2}(+242)$
One electron is removed from the outer shell of the gaseous sodium atom: $Na(g) \rightarrow Na^+(g) + e^-$ First ionization energy of sodium.	$\Delta H_i^{\ominus}(Na) = +496$
One electron is added to the outer energy level of the gaseous chlorine atom: $Cl(g) + e^- \rightarrow Cl^-(g)$ Electron affinity of chlorine.	$\Delta H_e^{\ominus}(Cl) = -349$
The gaseous ions come together to form one mole of solid sodium chloride: $Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$ Lattice enthalpy of sodium chloride.	$-\Delta H_{lat}^{\ominus} = ???$

It is good practice to explicitly state the + value for the enthalpy change of an endothermic reaction.

The enthalpy change of atomization ($\Delta H_{atom}^{\ominus}$) is the enthalpy change that occurs when one mole of gaseous atoms is formed from the element in its standard state.

These changes are best illustrated using an energy level diagram (Figure 9).



R1.2 Figure 9 Born–Haber cycle for sodium chloride. The enthalpy change of formation of sodium chloride, shown in blue, can be equated to a combination of the enthalpy changes associated with the changes shown in red.

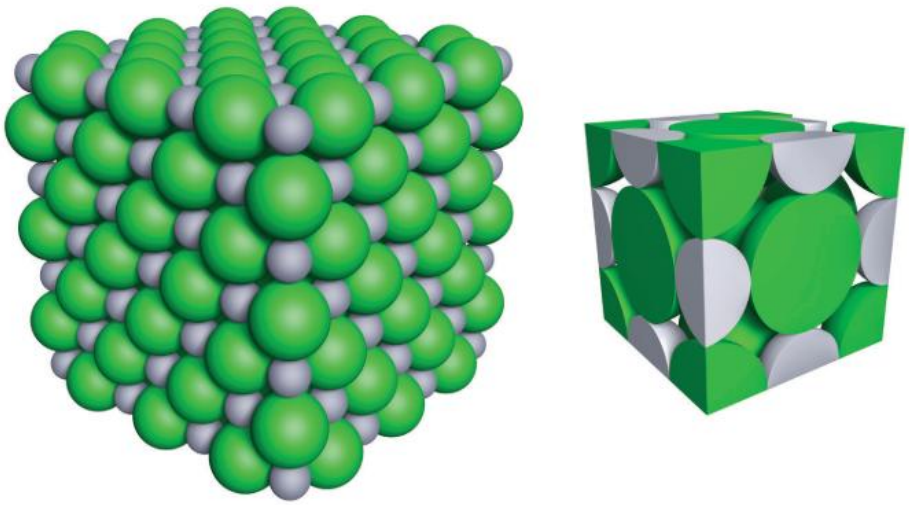
$$\Delta H_f^\ominus(\text{NaCl}) = \Delta H_{atom}^\ominus(\text{Na}) + \Delta H_i^\ominus(\text{Na}) + \tfrac{1}{2}E(\text{Cl–Cl}) + \Delta H_e^\ominus(\text{Cl}) - \Delta H_{lat}^\ominus(\text{NaCl})$$

This allows an equation for the lattice enthalpy to be expressed in terms of experimentally verifiable quantities:

$$\Delta H_{lat}^\ominus(\text{NaCl}) = \Delta H_{atom}^\ominus(\text{Na}) + \Delta H_i^\ominus(\text{Na}) + \tfrac{1}{2}E(\text{Cl–Cl}) + \Delta H_e^\ominus(\text{Cl}) - \Delta H_f^\ominus(\text{NaCl})$$

$$\Delta H_{lat}^\ominus(\text{NaCl}) = +107 + 496 + \tfrac{1}{2}(+242) - 349 - (-411)\ \text{kJ mol}^{-1}$$
$$= +786\ \text{kJ mol}^{-1}$$

Lattice structure of sodium chloride. The strength of an ionic bond and the reason for its existence is the energy that is released as the oppositely charged ions form an ionic lattice. The energy changes that occur when an ionic compound is formed can be related in a Born–Haber cycle.



Nature of Science

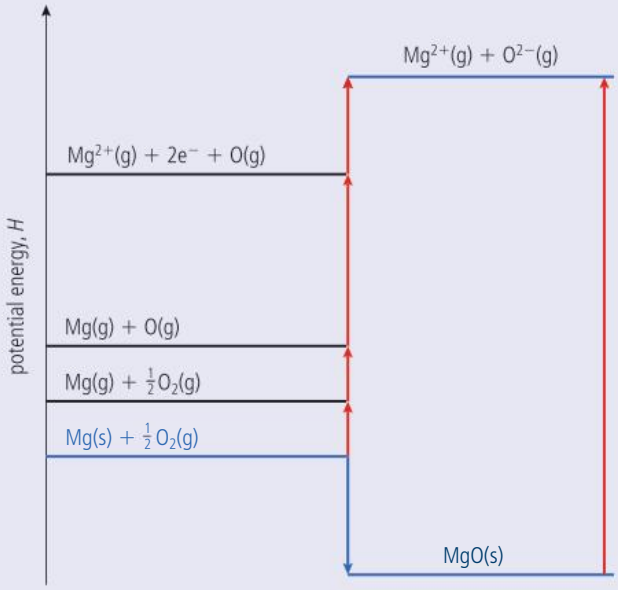
The energy changes that occur when an ionic crystal forms can be accurately predicted by the ionic model which considers all the electrostatic interactions that occur. As the interactions decrease with distance, an infinite number of interactions can be summed mathematically and calculated. Such models give us insight into the underlying chemical principles.

Worked example

(a) Write an equation which corresponds to the lattice enthalpy of magnesium oxide, MgO.

(b) Write equations which correspond to the first and second electron affinities of oxygen and comment on the relative values of the first and second electron affinities given in Section 9 of the data booklet.

(c) Use the following data and further information from Sections 9 and 12 of the data booklet to complete the Born–Haber cycle for magnesium oxide.



(d) Calculate the lattice energy of magnesium oxide.

Additional data:

- enthalpy change of atomization for Mg(s) = +148 kJ mol^{-1}
- second ionization energy of magnesium = +1451 kJ mol^{-1}
- enthalpy change of formation of MgO(s) = −602 kJ mol^{-1}

Solution

(a) $MgO(s) \rightarrow Mg^{2+}(g) + O^{2-}(g)$

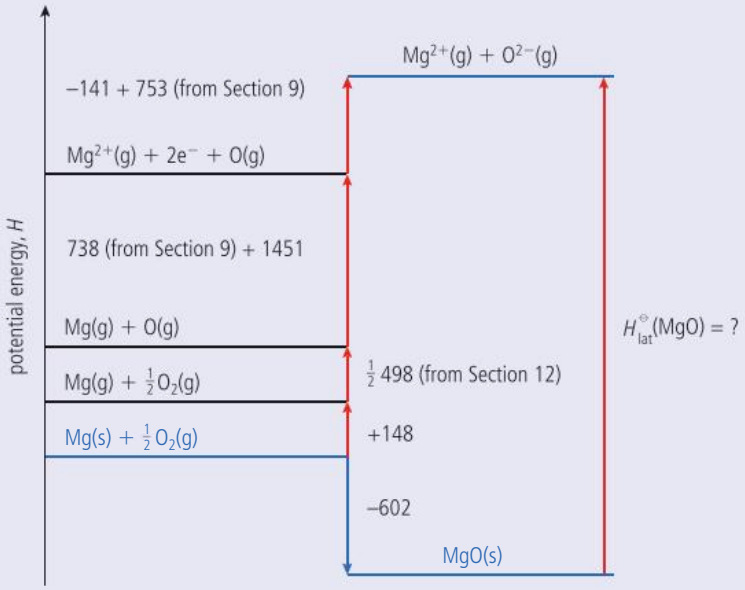
(b) $O(g) + e^-(g) \rightarrow O^-(g)$

The first electron affinity corresponds to the attraction of an electron into the outer energy level of an oxygen atom. This is an exothermic process.

$O^-(g) + e^-(g) \rightarrow O^{2-}(g)$

The second electron affinity corresponds to a negatively charged oxide ion accepting an additional electron into its outer energy level despite the mutual repulsion between the negatively charged species. This is an endothermic process.

(c) Note that the enthalpy change of atomization for oxygen = half the bond energy for O_2.



(d) From the diagram we have:

$$\Delta H_{lat}^{\ominus}(MgO) = +602 + 148 + \tfrac{1}{2}(498) + (738 + 1451) + (753 - 141)\,kJ\,mol^{-1}$$

$$\Delta H_{lat}^{\ominus}(MgO) = +3800\,kJ\,mol^{-1}$$

In Structure 2.1 we see that theoretical lattice enthalpies can be determined from the ionic model. The lattice enthalpy is:

- proportional to the product of the charges on the positive and negative ions
- inversely proportional to the sum of the ionic radii of the positive and negative ions.

Structure 2.1 – What are the factors that influence the strength of lattice enthalpy in an ionic compound?

The lattice enthalpy is greater for ions with a larger charge density as they have a small radius and are highly charged.

Exercise

Q28. Identify the process that has an enthalpy change of different sign to the others.

A $Cl(g) + e^- \rightarrow Cl^-(g)$ **B** $K(g) \rightarrow K^+(g) + e^-$

C $KCl(g) \rightarrow K^+(g) + Cl^-(g)$ **D** $Cl_2(g) \rightarrow 2Cl(g)$

Q29. Which equation represents the electron affinity of potassium?

A $K(g) \rightarrow K^+(g) + e^-$ **B** $K(g) \rightarrow K^-(g) + e^-$

C $K(g) + e^- \rightarrow K^-(g)$ **D** $K^+(g) + e^- \rightarrow K(g)$

Q30. Identify the process which corresponds to the standard enthalpy change of atomization of bromine.

A $Br_2(g) \rightarrow 2Br(g)$ **B** $Br_2(l) \rightarrow 2Br(g)$

C $\frac{1}{2}Br_2(g) \rightarrow Br(g)$ **D** $\frac{1}{2}Br_2(l) \rightarrow Br(g)$

Q31. Identify the compound which has the greatest lattice energy.

A sodium chloride **B** potassium chloride

C magnesium bromide **D** calcium bromide

Q32. Which one of the following compounds would be expected to have the highest lattice enthalpy?

A K_2S **B** CaO **C** CaS **D** KCl

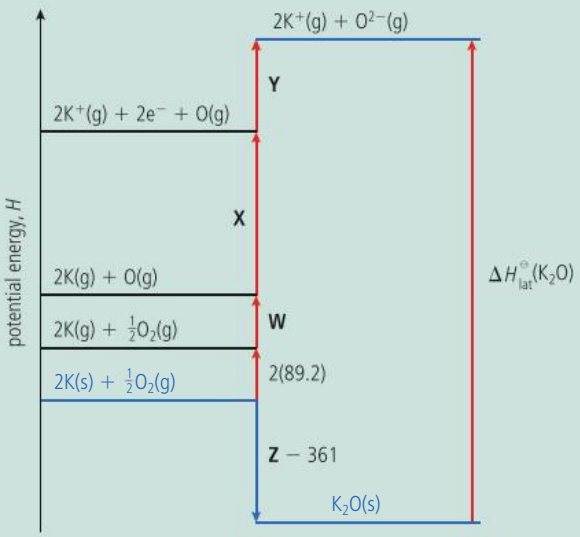
Q33. The experimental and theoretical lattice enthalpies of four compounds are compared.

Identify the compound that has the smallest difference between experimental and theoretical lattice enthalpies.

A CaO **B** CaS **C** MgO **D** MgS

Q34. **(a)** Write an equation to represent the lattice energy of potassium oxide, K_2O.

(b) The Born–Haber cycle shown below may be used to calculate the lattice energy of potassium oxide.



Identify the enthalpy changes labelled by the letters **W**, **X**, **Y** and **Z**.

(c) Use the energy cycle, and further information from Sections 9 and 12 of the data booklet to calculate an experimental value for the lattice energy of potassium oxide.

Q35. Theoretical lattice enthalpies can be calculated based on the ionic model. The values for the sodium halides are tabulated below.

Halide	$\Delta H_{lat}^{\ominus}$/ kJ mol^{-1}
NaF	+912
NaCl	+770
NaBr	+735
NaI	+687

(a) Explain the trend in lattice enthalpies of sodium halides.

(b) Compare these theoretical values with the experimental values listed in Section 16 of the data booklet.

Q36. The theoretical lattice enthalpies, based on the ionic model, of sodium chloride and magnesium oxide are shown below.

Compound	$\Delta H_{lat}^{\ominus}$/ kJ mol^{-1}
NaCl	770
MgO	3795

Explain why magnesium oxide has the higher lattice enthalpy compared with sodium chloride.

Q37. The experimental and theoretical lattice energies of three metal bromides are compared below.

Metal bromide	$\Delta H_{lat}^{\ominus}$/ kJ mol^{-1} (Born–Haber cycle)	$\Delta H_{ltt}^{\ominus}$/ kJ mol^{-1} (ionic model)
M_ABr	742	735
M_BBr	656	653
M_CBr	803	799

(a) Use the ionic model to identify the ion with the smallest ionic radius.

(b) Explain why the experimental lattice enthalpies are always larger than the theoretical values.

(c) Calculate the percentage difference between experimental and theoretical values for each of the metal bromides M_ABr, M_BBr and M_CBr.

(d) Identify the metal with the lowest electronegativity.

HL end

Guiding Question revisited

How does the application of the law of conservation of energy help us to predict energy changes during reactions?

In this chapter we introduced the concept of energy cycles and saw how they can be used to relate the enthalpy changes of related reactions. You can construct energy cycles for covalent compounds with the making and breaking of covalent bonds.

HL You can construct energy cycles for ionic compounds which involve the transfer of electrons from the metal to the non-metal and the formation of an ionic lattice.

Energy cycles can be used to predict the enthalpy changes of real or hypothetical reactions and so offer insight into underlying principles of chemical change. These ideas can be summarized as follows:

- Hess's law states that the total enthalpy change for a reaction is independent of the route taken. It is a special case of the law of conservation of energy.
- Energy cycles allow for the calculation of values corresponding to certain enthalpy changes which cannot be determined directly.
- The average bond enthalpy is the energy required to break one mole of the same type of bonds in the gaseous state averaged over a variety of similar compounds.
- Bond-breaking absorbs energy and is endothermic. Bond-making releases energy and is exothermic.
- Enthalpy of reactions calculated from bond enthalpies do not include intermolecular interaction and so are only accurate for reactions in the gaseous state.

HL

- The standard enthalpy change of combustion ($\Delta H_c^\ominus$) is the enthalpy change for the complete combustion of one mole of a substance in its standard state in excess oxygen under standard conditions. Most combustion reactions are exothermic.
- The standard enthalpy change of formation ($\Delta H_f^\ominus$) is the enthalpy change when one mole of the substance is formed from its elements in their standard states under standard conditions.
- The enthalpy of formation of any element in its stable state is zero as there is no enthalpy change when an element is formed from itself.
- ΔH calculated from $\Delta H_c^\ominus$ or $\Delta H_f^\ominus$ is more accurate than values based on bond enthalpies which apply only to the gaseous state and are average values.
- A Born–Haber cycle is a special case of Hess's law for the formation of ionic compounds. It allows the lattice enthalpy to be calculated from other enthalpy changes.
- Lattice enthalpy values from the Born–Haber cycle are experimental values, as they are based on other experimental data.
- The first electron affinity is the enthalpy change when one mole of gaseous atoms attracts one mole of electrons: $X(g) + e^-(g) \rightarrow X^-(g)$ $\Delta H_e^\ominus$
- The lattice enthalpy is the enthalpy change that occurs when one mole of a solid ionic compound is separated into gaseous ions under standard conditions. For example, for alkali metal halides: $MX(s) \rightarrow M^+(g) + X^-(g)$ $\Delta H_{lat}^\ominus$
- The lattice enthalpy depends on the attraction between the ions:
  - an increase in the ionic radius of the ions decreases $\Delta H_{lat}^\ominus$
  - an increase in ionic charge increases $\Delta H_{lat}^\ominus$.

HL end

Practice questions

1. Consider the following reactions.

$Cu_2O(s) + \frac{1}{2}O_2(g) \rightarrow 2CuO(s)$ $\Delta H^\ominus = -144\,kJ$

$Cu_2O(s) \rightarrow Cu(s) + CuO(s)$ $\Delta H^\ominus = +11\,kJ$

What is the value of $\Delta H^\ominus$, in kJ, for this reaction?

$$Cu(s) + \frac{1}{2}O_2(g) \rightarrow CuO(s)$$

A −144 + 11 **B** +144 − 11 **C** −144 − 11 **D** +144 + 11

2. Which equation best represents the bond enthalpy of HCl?

A $HCl(g) \rightarrow H^+(g) + Cl^-(g)$ **B** $HCl(g) \rightarrow H(g) + Cl(g)$

C $HCl(g) \rightarrow \frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g)$ **D** $2HCl(g) \rightarrow H_2(g) + Cl_2(g)$

3. Consider the equations below.

$CH_4(g) + O_2(g) \rightarrow HCHO(l) + H_2O(l)$ $\Delta H^\ominus = x$

$HCHO(l) + \frac{1}{2}O_2(g) \rightarrow HCOOH(l)$ $\Delta H^\ominus = y$

$2HCOOH(l) + \frac{1}{2}O_2(g) \rightarrow (COOH)_2(s) + H_2O(l)$ $\Delta H^\ominus = z$

What is the enthalpy change of the reaction below?

$$2CH_4(g) + 3\frac{1}{2}O_2(g) \rightarrow (COOH)_2(s) + 3H_2O(l)$$

A $x + y + z$ **B** $2x + y + z$ **C** $2x + 2y + z$ **D** $2x + 2y + 2z$

4. Which process has an enthalpy change that corresponds to the bond enthalpy for the O−H bond?

A $H_2O(l) \rightarrow H_2(g) + \frac{1}{2}O_2(g)$ **B** $\frac{1}{2}H_2O(l) \rightarrow \frac{1}{2}H_2(g) + O(g)$

C $\frac{1}{2}H_2O(g) \rightarrow H(g) + O(g)$ **D** $\frac{1}{2}H_2O(g) \rightarrow H(g) + \frac{1}{2}O(g)$

5. What is the energy, in kJ, released when 1.0 mol of carbon monoxide is burned according to the following equation?

$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$ $\Delta H^\ominus = -564\,kJ$

A 141 **B** 282 **C** 564 **D** 1128

6. Which enthalpy changes **cannot** be calculated accurately using only bond enthalpy data?

I. $C_2H_6(g) + \frac{7}{2}O_2(g) \rightarrow 3H_2O(l) + 2CO_2(g)$

II. $C_2H_4(g) + Br_2(l) \rightarrow CH_2ClCH_2Cl(l)$

III. $2H_2(g) + O_2(g) \rightarrow H_2O(g)$

A I and II only **B** I and III only **C** II and III only **D** I, II and III

7. Hydrazine is a valuable rocket fuel. The equation for the reaction between hydrazine and oxygen is given below.

$$N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2H_2O(l)$$

Use the bond enthalpy values from Section 12 of the data booklet to determine the enthalpy change for this reaction. (3)

(Total 3 marks)

8. HL Which ionic compound has the greatest lattice enthalpy?

A MgO **B** CaO **C** NaF **D** KF

9. HL Which step(s) is/are endothermic in the Born–Haber cycle for the formation of LiCl?

A $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$ and $Li(s) \rightarrow Li(g)$

B $Cl(g) + e^- \rightarrow Cl^-(g)$ and $Li(g) \rightarrow Li^+(g) + e^-$

C $Li^+(g) + Cl^-(g) \rightarrow LiCl(s)$

D $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$ and $Cl(g) + e^- \rightarrow Cl^-(g)$

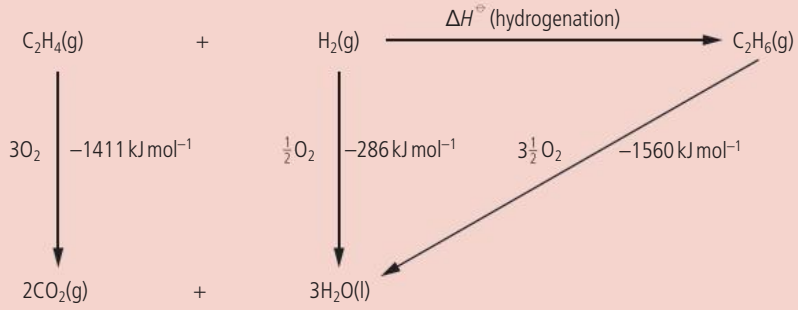
10. Two students were asked to use information from the data booklet to calculate a value for the enthalpy of hydrogenation of ethene to form ethane.

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

John used the average bond enthalpies from Section 12. Marit used the values of enthalpies of combustion from Section 14.

(a) Calculate the value for the enthalpy of hydrogenation of ethene obtained using the average bond enthalpies given in Section 12. (2)

(b) Marit arranged the values she found in Section 14 into an energy cycle.



Calculate the value for the enthalpy of hydrogenation of ethene from the energy cycle. (1)

(c) Suggest **one** reason why John's answer is slightly less accurate than Marit's answer. (1)

(d) John then decided to determine the enthalpy of hydrogenation of cyclohexene to produce cyclohexane.

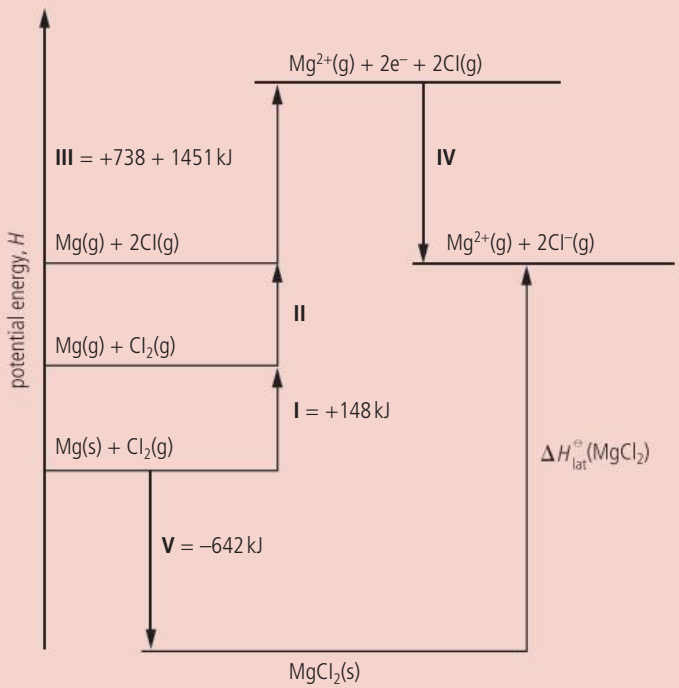
$$C_6H_{10}(l) + H_2(g) \rightarrow C_6H_{12}(l)$$

(i) Use the average bond enthalpies to deduce a value for the enthalpy of hydrogenation of cyclohexene. (1)

(ii) The percentage difference between these two methods (average bond enthalpies and enthalpies of combustion) is greater for cyclohexene than it was for ethene. John's hypothesis was that it would be the same. Determine why the use of average bond enthalpies is less accurate for the cyclohexene equation shown on the previous page, than it was for ethene. Deduce what extra information is needed to provide a more accurate answer. (2)

(Total 7 marks)

11. HL The lattice enthalpy of magnesium chloride can be calculated from the Born–Haber cycle shown below.



(a) Identify the enthalpy changes labelled **I** and **V** in the cycle. (2)

(b) Use the ionization energies given in the cycle above and further data from the data booklet to calculate a value for the lattice enthalpy of magnesium chloride. (4)

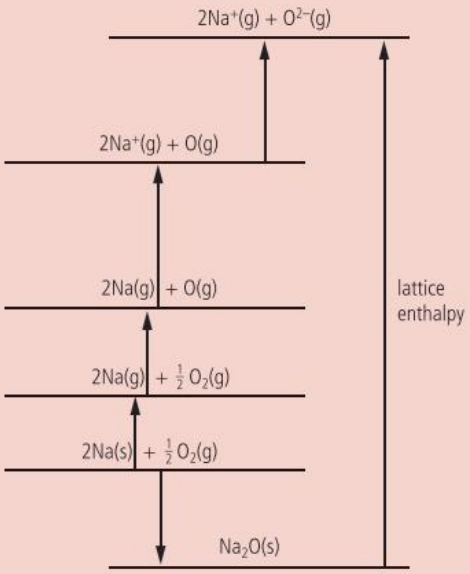
(c) The theoretically calculated value for the lattice enthalpy of magnesium chloride is +2326 kJ.

Explain the difference between the theoretically calculated value and the experimental value. (2)

(d) The experimental lattice enthalpy of magnesium oxide is given in Section 16 of the data booklet. Explain why magnesium oxide has a higher lattice enthalpy than magnesium chloride. (2)

(Total 10 marks)

12. HL The Born–Haber cycle for sodium oxide is shown (not to scale).



(a) Calculate values for the following changes using Section 9 of the data booklet.

$\Delta H_{atomisation}(Na) = 107\,kJ\,mol^{-1}$

$\Delta H_{atomisation}(O) = 249\,kJ\,mol^{-1}$

$\frac{1}{2}O_2(g) \rightarrow O^{2-}(g)$

$Na(s) \rightarrow Na^+(g)$ (2)

(b) The standard enthalpy of formation of sodium oxide is $-414\,kJ\,mol^{-1}$. Determine the lattice enthalpy of sodium oxide, in $kJ\,mol^{-1}$ using your answers to part **(a)**.

(If you did not get answers to **(a)**, use $+850\,kJ\,mol^{-1}$ and $+600\,kJ\,mol^{-1}$ respectively, but these are not the correct answers.) (2)

(c) Justify why K_2O has a lower lattice enthalpy (absolute value) than Na_2O. (1)

(d) Sodium peroxide is used in diving apparatus to produce oxygen from carbon dioxide.

$$2Na_2O_2(s) + 2CO_2(g) \rightarrow 2Na_2CO_3(s) + O_2(g)$$

Determine the enthalpy change, ΔH, in kJ, for this reaction using data from the table below and Section 13 of the data booklet. (3)

	ΔH_f / kJmol^{-1}
$Na_2O_2(s)$	−510.9
$Na_2CO_3(s)$	−1130.7

(e) Outline why bond enthalpy values are not valid in calculations such as that in part **(d)**. (1)

(Total 9 marks)

REACTIVITY

1.3 Energy from fuels





Oil refinery at dusk. Oil currently provides the world's economy with the most energy. It is, however, a limited resource which has a serious negative impact on our environment. We need to find alternative sources of energy.

Guiding Question

What are the challenges of using chemical energy to address our energy needs?

We are completely dependent on our energy resources. Our ability to harness energy has allowed us to transform our world and give us control of what we do and when and where we do it. The burning of fuels to provide heat is probably one of the oldest human technologies and still accounts for most of our primary energy. All this energy can be traced back to the formation of the Earth and the solar system. We are currently particularly dependent on the use of fossil fuels, which are a chemical store of solar energy from millions of years ago. Carbon dioxide (CO_2), released during the complete combustion of fossil fuels, is a greenhouse gas and a major cause of global warming. Incomplete combustion has resulted in more local pollutants: carbon monoxide and soot particulates. We need to find and use alternative high-quality energy sources, and the Sun again offers many options. Life itself is driven by the chemical changes of photosynthesis, which has always been the ultimate source of our food but can also be used to provide biofuels. Whatever energy source we use in the future it will need to be more sustainable and more environmentally friendly than those we currently use. It is difficult to predict the future, but it is clear our use of energy will have to change. Hydrogen is a possible alternative to fossil fuels, and fuel cells offer another source of electrical energy without the need for combustion.

TOK

The choice of energy source is controversial and complex. How can we navigate issues that involve questions and claims from different areas of knowledge?



View of New York City from the International Space Station (ISS). This image highlights our ability to harness energy supplies to allow us to control our environment.

Reactivity 1.3.1 – Combustion reactions

Reactivity 1.3.1 – Reactive metals, non-metals and organic compounds undergo combustion reactions when heated in oxygen.	
Deduce equations for reactions of combustion, including hydrocarbons and alcohols.	
	Reactivity 2.2 – Why is high activation energy often considered to be a useful property of a fuel? Reactivity 3.2 – Which species are the oxidizing and reducing agents in a combustion reaction?

Many substances undergo combustion reactions when heated in oxygen

It was originally thought that fire was an element, but we now know it is a process of chemical transformation and change. Many substances such as metals, non-metals and organic compounds undergo combustion reactions when heated in oxygen.

Nature of Science

Early ideas to explain chemical change in combustion and rusting included the 'phlogiston' theory. This proposed the existence of a fire-like element that was released during these processes. The theory seemed to explain some of the observations of its time, although these were purely qualitative. It could not explain later quantitative data showing that substances actually gain rather than lose mass during burning. In 1783, Lavoisier's work on oxygen confirmed that combustion and rusting involve combination with oxygen from the air, so overturning the phlogiston theory. This is a good example of how the evolution of scientific ideas, such as how chemical change occurs, is based on the need for theories that can be tested by experiment. Where results are not compatible with the theory, a new theory must be put forward, which must then be subject to the same rigour of experimental test.

TOK

Chemistry was a late developer as a physical science. Newton was working on the laws of physics more than a century before the work of the French chemist Antoine Lavoisier (1743–94) brought chemistry into the modern age. Chemical reactions involve changes in smell, colour and texture and these are difficult to quantify. Lavoisier appreciated the importance of attaching numbers to properties and recognized the need for precise measurement. His use of the balance allowed changes in mass to be used to analyse chemical reactions. A quantitative approach helped chemistry develop beyond the pseudoscience of alchemy. What differentiates the scientific from the non-scientific or 'pseudo-scientific'?

Combustion of metals and non-metals

Combustion is a reaction in which an element or compound burns in oxygen. The s block metals form ionic oxides which are basic and p block non-metals generally form covalent oxides which are acidic. As discussed in Structure 3.1, some non-metals can show a range of oxidation states and form different oxides when they undergo combustion.

Magnesium, for example, forms magnesium oxide and sulfur forms sulfur dioxide:

$$Mg(s) + \tfrac{1}{2}O_2(g) \rightarrow MgO(s)$$

$$S(s) + O_2(g) \rightarrow SO_2(g)$$



(a) Magnesium burns with an intensely brilliant white flame, leaving a residue of magnesium oxide. The metal is sometimes used in flares and flashbulbs.



(b) Sulfur burns with a blue flame in oxygen and the reaction produces the toxic gas sulfur dioxide.



Magnesium also reacts with nitrogen when it burns in the air. As discussed in Reactivity 3.2, this is also an oxidation reaction as the magnesium loses two electrons.

Elemental phosphorus exists as two allotropes: white phosphorus and red phosphorus. White phosphorus reacts when exposed to air to produce two oxides: $P_4O_{10}(s)$ and $P_4O_6(s)$.

Worked example

White phosphorus is an allotrope of phosphorus and exists as $P_4(s)$. Write an equation for the reaction of white phosphorus (P_4) with oxygen gas to form phosphorus(V) oxide.

Solution

Start with the unbalanced equation showing the reactants including $O_2(g)$ and products.

$$P_4(s) + \mathbf{5}O_2(g) \rightarrow P_4O_{10}(s)$$

Balance the Os on the left-hand side as shown in bold.

Most combustion reactions are exothermic, but nitrogen combines with oxygen only at high temperatures in an endothermic reaction to produce nitrogen monoxide.

TOK

A number of sources claim that combustion reactions are exothermic, but the reaction

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

is endothermic. Does this falsify the claim or is it 'an exception to a rule'?

Is the rule still useful or does it need to be reconsidered? What is the difference between such rules and scientific laws?

As discussed in Reactivity 3.2, these combustion reactions involve electron transfers to oxygen. Oxygen is an oxidizing agent in these cases because it accepts electrons. The metal or non-metal element is the reducing agent because it loses electrons.



The rusting of iron is also an oxidation reaction but not a combustion reaction. There is no flame involved.

Reactivity 3.2 – Which species are the oxidizing and reducing agents in a combustion reaction?

Combustion of organic compounds breaks the carbon chain

Many hydrocarbons and alcohols are used as fuels because their combustion reactions release energy at a reasonable rate to be useful. Although the compounds are energetically unstable relative to their combustion products, they are kinetically stable. They do not spontaneously combust because the reaction has a sufficiently high activation energy. The high activation energy also allows the fuels to be safely transported and stored. Activation energy is discussed in more detail in Reactivity 2.2.



Spontaneous combustion. The oxidation of glycerin by potassium manganate(VII) is very exothermic and after a few seconds the released heat causes the glycerin to ignite and burst into flame.

Reactivity 2.2 – Why is high activation energy often considered to be a useful property of a fuel?

The complete combustion of organic compounds breaks the carbon chain and results in the production of carbon dioxide and water and the release of a lot of heat energy.

For example, propane burns in the presence of excess oxygen to produce carbon dioxide and water:

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$$

This is known as complete combustion because the products are fully oxidized.

When the oxygen supply is limited, *incomplete* combustion occurs, as discussed in the next section.

Similarly, the alcohols with the general formula $C_nH_{2n+1}OH$ can be burnt to produce similar products:

$$C_2H_5OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

As discussed in Reactivity 3.2, the carbon atom attached to the OH group can be selectively oxidized by oxidizing agents such as potassium dichromate(VI).

Worked example

Write equations for the complete combustion of pentane.

Solution

Start with the unbalanced equation showing the reactants including $O_2(g)$ and products.

$$C_5H_{12}(g) + _O_2(g) \rightarrow \mathbf{5}CO_2(g) + \mathbf{6}H_2O(l)$$

Balance the Cs and the Hs on the right-hand side as shown in **bold** above.

Balance the Os on the left-hand side as shown in bold below:

$$C_5H_{12}(g) + \mathbf{8}O_2(g) \rightarrow 5CO_2(g) + 6H_2O(l)$$

Worked example

Write the equation for the complete combustion of ethanol.

Solution

Following the same strategy:

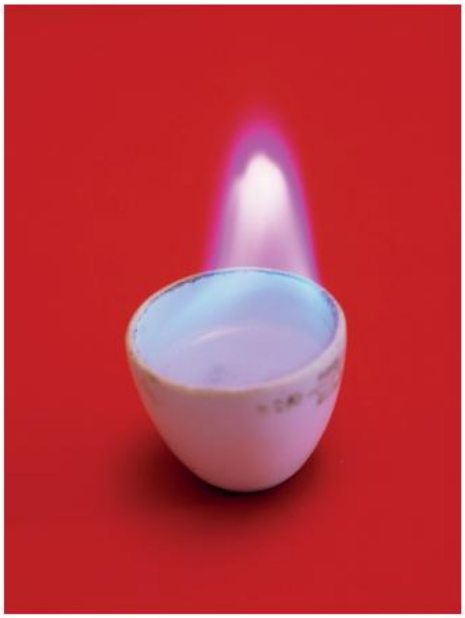
$$C_2H_5OH(l) + _O_2(g) \rightarrow \mathbf{2}CO_2(g) + \mathbf{3}H_2O(l)$$

Balance the Os on the left-hand side as shown but do not forget that the alcohol has an O atom:

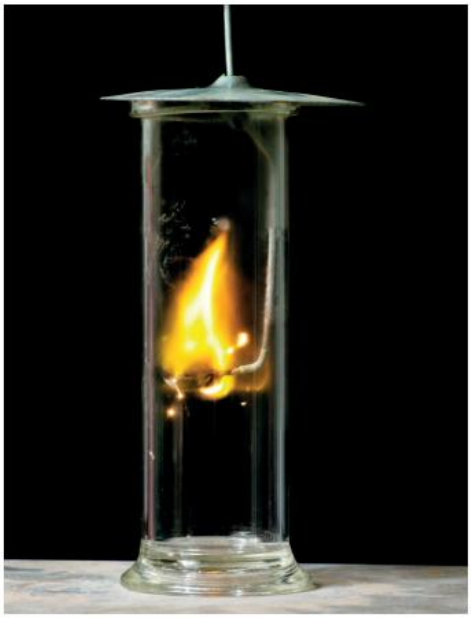
$$C_2H_5OH(l) + \mathbf{3}O_2(g) \rightarrow \mathbf{2}CO_2(g) + \mathbf{3}H_2O(l)$$

The combustion of organic compounds that contain elements other than carbon, hydrogen and oxygen produces a range of other products. Compounds containing nitrogen for example can release nitrogen gas or different nitrogen oxides. Combustion analysis can be used to determine the empirical formula of a compound as discussed in Structure 1.4.

i The combustion of organic molecules involves the formation and reaction of many radicals. The colour of a flame is due to the presence of carbon radicals which eventually all break up to form carbon dioxide.



(a) Ethanol burns with a relatively clean (not too sooty) flame, having a relatively short chain of carbon atoms for each molecule.



(b) Glucose is a carbohydrate which burns to produce carbon dioxide and water vapour, leaving behind carbon. The process releases a large amount of energy. Metabolism releases an equivalent amount of energy to burning, but in a slower, more controlled, and less direct way.

Challenge yourself

1. A compound containing carbon, hydrogen and nitrogen was analysed by combustion. 0.20 g of the compound produced 0.456 g of carbon dioxide and 0.248 g of water. Identify the empirical formula of the compound.

Exercise

Q1. Identify the element in the third period which reacts with the least amount of oxygen when 1.0 mol of the element undergoes complete combustion.

A aluminium **B** magnesium **C** sodium **D** sulfur

Q2. 1 mol of an organic compound X was found to require 2.5 mol of molecular oxygen for complete combustion. Which of the following could be X?

I. C_2H_2 II. CH_3CHO III. C_2H_5OH

A I and II only **B** I and III only **C** II and III only **D** I, II and III

Q3. Hydrazine, N_2H_4, is used as a rocket fuel. It reacts according to the thermochemical equation:

$$N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2H_2O(l) \qquad \Delta H^{\ominus} = -623\,kJ\,mol^{-1}$$

Hydrazine does not, however, burn spontaneously in oxygen. What is the best explanation for this?

A Hydrazine is a liquid. **B** The N≡N triple bond is too strong.

C The activation energy is too high. **D** The reaction is endothermic.

Q4. What mass of carbon dioxide is produced when 2.9 g of butane undergoes complete combustion?

Q5. The complete combustion of 0.60 g of a liquid compound, X, produces 0.88 g of carbon dioxide gas and 0.36 g of water vapour. What is the empirical formula of X?

Q6. Deduce the general equation for complete combustion of a hydrocarbon C_xH_y.

Reactivity 1.3.2 – Incomplete combustion of organic compounds

Reactivity 1.3.2 – Incomplete combustion of organic compounds, especially hydrocarbons, leads to the production of carbon monoxide and carbon. Deduce equations for the incomplete combustion of hydrocarbons and alcohols.	
	Inquiry 2 – What might be observed when a fuel such as methane is burnt in a limited supply of oxygen? Reactivity 2.1 – How does limiting the supply of oxygen in combustion affect the products and increase health risks?

Incomplete combustion of organic compounds produces carbon monoxide and carbon

Carbon dioxide and water are produced in complete combustion when there is a plentiful supply of air, but carbon monoxide or carbon in the form of soot are produced during incomplete combustion. This happens if the supply of air is limited or when the compound has a high percentage of carbon content.



(a) A Bunsen burner burns methane. The flame is controlled with a vent that changes the fuel : air mixture. Complete combustion produces a hot, blue flame. Incomplete combustion produces a yellow flame.



(b) Combustion of hydrocarbons with a benzene ring produces a sooty yellow flame due to their high percentage of carbon content.

Limiting the amount of oxygen limits the extent to which the carbon in organic compounds can be oxidized. Soot is produced when there is a very limited amount of oxygen available.

For example, the incomplete combustion of propane produces soot, C(s), or carbon monoxide.

$$2C_3H_8(g) + 7O_2(g) \rightarrow 6CO(g) + 8H_2O(g)$$

$$C_3H_8(g) + 2O_2(g) \rightarrow 3C(g) + 4H_2O(g)$$

Compounds with higher carbon content generally undergo more incomplete combustion and produce more soot when the oxygen supply is limited. This can be used to distinguish different organic compounds.

Worked example

How could samples of cyclohexane (C_6H_{12}), cyclohexene (C_6H_{10}) and methylbenzene ($CH_3C_6H_5$) be distinguished by observing their combustion?

Solution

Calculate the percentage carbon composition by mass in each of the three compounds.

	C_6H_{12}	C_6H_{10}	$CH_3C_6H_5$
M / g mol–1	84	82	92
% of C	86	88	91

Methylbenzene will produce the sootiest flame and cyclohexane the least sooty flame.

HL Worked example

Use data from Section 13 in the data booklet to compare the heat produced during the complete and incomplete combustion of hexane. Assume carbon monoxide is the product of incomplete combustion.

Solution

Complete combustion:

$$C_6H_{14}(g) + 9\tfrac{1}{2}O_2(g) \rightarrow 6CO_2(g) + 7H_2O(l)$$

$$-199 \qquad 9\tfrac{1}{2}(0) \qquad 6(-394) \qquad 7(-286) \qquad \Delta H_f^\ominus / \text{kJ mol}^{-1}$$

$\Delta H^\ominus = 6(-394) + 7(-286) - (-199) = -4167 \text{ kJ mol}^{-1}$

Incomplete combustion:

$$C_6H_{14}(g) + 6\tfrac{1}{2}O_2(g) \rightarrow 6CO(g) + 7H_2O(l)$$

$$-199 \qquad 6\tfrac{1}{2}(0) \qquad 6(-111) \qquad 7(-286) \qquad \Delta H_f^\ominus / \text{kJ mol}^{-1}$$

$\Delta H^\ominus = 6(-111) + 7(-286) - (-199) = -2469 \text{ kJ mol}^{-1}$

As the worked example illustrates, incomplete combustion releases less heat than complete combustion. This is why the enthalpy of formation of carbon dioxide is more exothermic than that of carbon monoxide or soot.

Worked example

Give the balanced equation for the formation of carbon monoxide (CO) in the internal combustion engine caused by the incomplete combustion of octane, $C_8H_{18}(l)$.

Solution

First write the unbalanced equation with $H_2O(g)$, produced at the temperature of the engine, and CO(g) as products.

$$C_8H_{18}(l) + _O_2(g) \rightarrow \mathbf{8}CO(g) + \mathbf{9}H_2O(g)$$

Balance the carbon atoms and hydrogen atoms from left to right as shown in bold above.

Then balance the oxygen atoms (from right to left) as shown in bold below.

$$C_8H_{18}(l) + \mathbf{8\tfrac{1}{2}}O_2(g) \rightarrow 8CO(g) + 9H_2O(g)$$

Multiply ×2 if an equation with only integers is needed:

$$2C_8H_{18}(l) + 17O_2(g) \rightarrow 16CO(g) + 18H_2O(g)$$

As mentioned in Structure 3.1, catalytic converters are used in cars to fully oxidize carbon monoxide to carbon dioxide:

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

and to convert unburnt and partially burnt fuel hydrocarbons to carbon dioxide and water.

Three-way catalytic converters also reduce nitrogen oxides to nitrogen and oxygen.

$$2CO(g) + 2NO(g) \rightarrow 2CO_2(g) + N_2(g)$$

Carbon monoxide (CO) is toxic to humans because it affects oxygen uptake in the blood. It is absorbed by the lungs and binds to haemoglobin (Hb) in red blood cells more effectively than oxygen.

Hb + CO ⇌ COHb
haemoglobin carboxyhaemoglobin

This prevents oxygen from being transported around the body. It can cause dizziness at low concentrations and can be fatal at high levels. As it is a colourless, odourless gas, it can rise to dangerous levels without being detected.

Carbon or soot produced from the incomplete combustion of hydrocarbons and coal in power stations is an example of a particulate. Particulates are solid particles of carbon or dust, or liquid droplets suspended in the air. They generally have a diameter in the range 0.001–10 μm, which is just large enough to be seen. They enter the body during breathing and can affect the respiratory system and cause lung diseases such as emphysema, bronchitis and cancer. Although they are sometimes inert solids, they are dangerous pollutants because they can act as catalysts in the production of secondary pollutants and increase the harmful effects of gaseous pollutants.

SKILLS

The combustion of an organic liquid can be observed by placing a few drops of the liquid on a watch glass.

Inquiry 2 – What might be observed when a fuel such as methane is burnt in a limited supply of oxygen?



This household device is designed to detect excessive levels of carbon monoxide (CO) which can be produced by malfunctioning gas boilers or fires. After six hours of exposure, 35 ppm of CO produces headaches and dizziness. Within hours, 800 ppm of CO causes unconsciousness, with higher levels causing death.

Parts per million (ppm) is a measure of concentration often used for pollutants present at low but dangerous levels.

Reactivity 2.1 – How does limiting the supply of oxygen in combustion affect the products and increase health risks?

Challenge yourself

2. Explain how nitrogen oxides are formed in an internal combustion engine and suggest an effect of these pollutants.

Exercise

Q7. Deduce the general equation for the incomplete combustion of a hydrocarbon C_xH_y which produces carbon monoxide.

Q8. Deduce the equation for the incomplete combustion of hexane which produces equal amounts of carbon dioxide and carbon monoxide.

Q9. **(a)** State the equation for the complete combustion of octane.

(b) Calculate the mass of oxygen which reacts with 1.00 g of octane during complete combustion.

(c) Assume that 20% by mass of the air is made up of oxygen. Calculate the mass of air which reacts with 1.00 g of octane.

(d) Explain why carbon monoxide is a dangerous pollutant.

(e) State one method of controlling carbon monoxide emissions from automobile engines.

Reactivity 1.3.3 – Fossil fuels

Reactivity 1.3.3 – Fossil fuels include coal, crude oil and natural gas, which have different advantages and disadvantages.	
Evaluate the amount of carbon dioxide added to the atmosphere when different fuels burn. Understand the link between carbon dioxide levels and the greenhouse effect.	
The tendency for incomplete combustion and energy released per unit mass should be covered.	Structure 3.2 – Why do larger hydrocarbons have a greater tendency to undergo incomplete combustion? HL Structure 3.2 – Why is carbon dioxide described as a greenhouse gas? Nature of Science, Reactivity 3.2 – What are some of the environmental, economic, ethical and social implications of burning fossil fuels?

An ideal fuel releases significant amounts of energy at a reasonable rate and produces minimal pollution

An energy source needs to be cheap, plentiful, and readily accessible, and provide high-quality energy at a reasonable rate – not too fast or too slow. It should do all this in a way that has minimal effect on the environment. We all use a great range of energy sources. Some of these, such as wood, are ancient technologies, while others, such as nuclear power and solar cells, are very recent. Most of our energy derives from the Sun, which drives the climate and photosynthesis. Humans harness this energy indirectly by burning fossil fuels. Oil is the fossil fuel that currently provides the world's

economy with the most energy, but this will change. Its use has had a very negative impact on our environment.

Fossil fuels are non-renewable and wood is a renewable source

Fossil fuels are non-renewable and non-sustainable energy sources as it takes millions of years for fossil fuels to form. They are used at a rate faster than they can be replaced and our finite resources will run out. Wood, by contrast, is a renewable source as trees can be grown to replace those chopped down to provide wood as fuel. Biofuels are discussed in more detail in the next section.

The properties of four fuels are summarized in the table below. The energy density of a fuel is the energy produced per unit volume, and the specific energy is the energy produced per unit mass.

The liquid fuels have significantly greater energy densities than the gases.

Formula	Energy released per unit mass / kJ g^{-1}	Energy released per unit / kJ cm^{-3}
$H_2(g)$	142	0.0129
$CH_4(g)$	55.5	0.0401
$C_8H_{18}(l)$	47.9	33.7
$CH_3OH(l)$	22.7	18.0

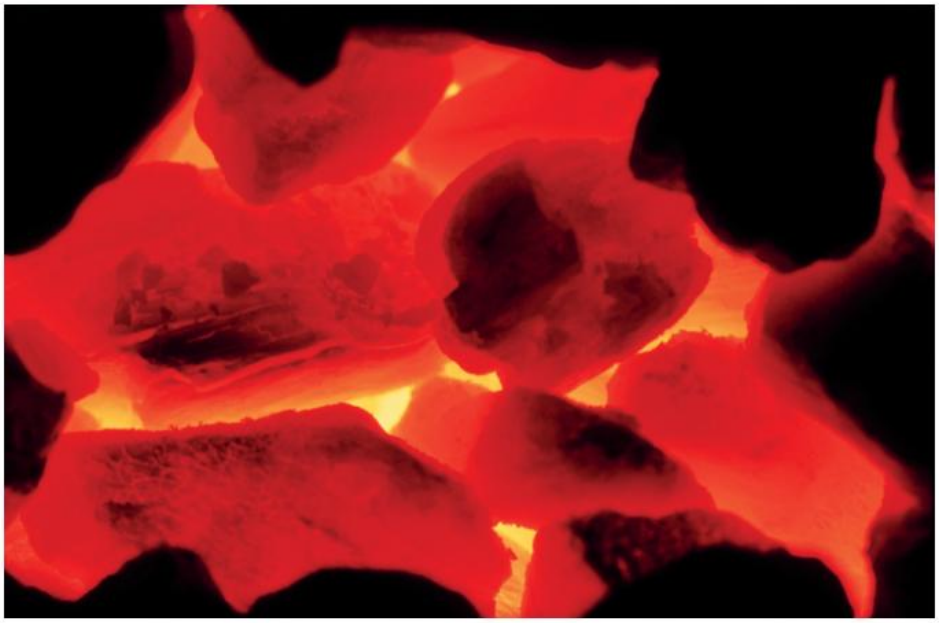
One advantage of using gasoline or petrol, which has octane as a main component, in car engines is its high energy density. Methane is preferred to hydrogen in pipelines for the same reason. When the mass of the fuel is important, for example in rockets, hydrogen is a better choice with its high specific energy. Hydrogen is the only fuel here which does not produce the greenhouse gas carbon dioxide.

Fossil fuels were formed by the reduction of biological compounds

The fossil fuels have been described as 'sunshine in the solid, liquid and gaseous form', as their energy comes from sunlight which was trapped by green plants millions of years ago. Fossil fuels are produced by the slow and partial decomposition of plant and animal matter that is trapped in the absence of air. Oxygen is lost from the biological molecules at a faster rate than other elements (carbon, hydrogen, nitrogen and sulfur). This results in reduced biological compounds which are generally hydrocarbons.

Coal is the most abundant fossil fuel

Coal is a combustible sedimentary rock formed from the remains of plant life which have been subject to geological heat and pressure. This action changed plant material in stages to increase the percentage of the carbon content. Anthracite, for example, is formed under conditions of very high heat and pressure and is almost pure carbon, but coal generally contains between 80% and 90% carbon by mass. Coal occurs in many areas, though the majority of the world's supplies are in the northern hemisphere. It is by far the most plentiful of the Earth's fossil fuels.



Burning anthracite. Anthracite has a fixed carbon content of 92–98%. It burns with a short blue flame and no noticeable smoke.

Nature of Science

Coal fueled much of the Industrial Revolution, which led to important advances in both science and technology. The development of steam power was crucial to a country's economy, but to understand the link between heat and work scientists had to unravel the nature of energy – its quality and its quantity and the underlying molecular basis for the laws governing the transfer of heat into work. Whatever the field, whether it is pure science or engineering technology, there is boundless scope for creative and imaginative thinking.

Crude oil is a valuable fuel and chemical feedstock

Crude oil is one of the most important raw materials in the world today. It is a complex mixture of straight-chain and branched-chain saturated alkanes, cycloalkanes and aromatic compounds, and, in smaller quantities, compounds of nitrogen, oxygen and sulfur. It supplies us with the fuels we need for transport and electricity generation and is an important chemical feedstock for the production of important organic compounds such as polymers, pharmaceuticals, dyes and solvents.

Crude oil was formed over millions of years from the remains of marine animals and plants, which were trapped under layers of rock. Under these conditions of high temperature and high pressure, organic matter decays in the presence of bacteria and the absence of oxygen. As it is a limited resource chemists will need to consider other sources of carbon, both as a fuel and as a chemical feedstock.

The Organization of the Petroleum Exporting Countries (OPEC) is an intergovernmental organization set up to stabilize oil markets in order to secure an efficient, economic, and regular supply of petroleum. There are political implications in being dependent on imported oil and gas. Price fluctuations have a significant effect on national economies; supplies and energy resources are therefore an important bartering tool in political disputes.

Oil and gas are easier to extract than coal since they are fluids and can be pumped up from underground reserves. It is possible to extract oil from beneath the sea. There are risks and benefits in using oil as a source of energy or as a source of carbon to make new products.

A petrol pump supplies energy to a car at a rate of about 34 MW (34 MJ s^{-1}).

Petrol is a highly concentrated and convenient energy source for use in transport. It could be argued, however, that burning hydrocarbons, with their resulting environmental side-effects such as smog and global warming, is a misuse of this valuable resource. When the great Russian chemist Dmitri Mendeleev (Structure 3.1) visited the oils fields of Azerbaijan at the end of the 19th century, he is said to have likened the burning of oil as a fuel to 'firing up a kitchen stove with banknotes'.

Natural gas is mainly methane

Methane is the primary constituent of natural gas, which also contains nitrogen and sulfur compounds (hydrogen sulfide) as impurities. Natural gas was formed millions of years ago by the action of heat, pressure, and perhaps bacteria on buried organic matter. The gas is trapped in geological formations capped by impermeable rock. It is also formed from the decomposition of crude oil and coal deposits. It can occur almost entirely on its own, dissolved under pressure in oil, or in a layer above the oil in a reservoir. Natural gas can also be found associated with coal when it is a major hazard as it forms an explosive mixture with air.

Natural gas is the cleanest of the fossil fuels to burn due to its low percentage carbon content. Impurities can easily be removed, and the combustion of natural gas produces minimal amounts of carbon monoxide, hydrocarbons, and particulates. Where it is available as mains gas, it flows through pipes to wherever it is needed, so little energy is needed to transport the gas from the ground to the consumer. Setting up such a distribution network, however, involves a massive capital investment, and in some countries liquefied gas (butane or propane) is used instead for domestic heating and cooking when no network is available.

Constructing international pipelines has financial costs and political risks.



▲ Natural gas pipelines.

The past and future of fossil fuels

The choice of fossil fuel used by different countries depends on historical, geological and technological factors. Different societies have different priorities in their energy choices.

As civilization has advanced, the carbon content of fuel has decreased. Coal was the first fossil fuel to be used. It is the most abundant and easiest to obtain and most similar in properties to charcoal, which was generally used as a fuel by primitive cultures. Coal has mainly been replaced by gasoline and natural gas as the fuel of choice as they have higher specific energies and energy densities and are easier to transport. The two fluids, gas and oil, are also cleaner burning and produce less carbon dioxide per unit energy.

The advantages and disadvantages of the three fossil fuels are summarized below.

	Coal	Petroleum	Natural gas
Advantages	Cheap and plentiful throughout the world. Longest lifespan compared to other fossil fuels. Can be converted into synthetic liquid fuels and gases. Safer than nuclear power. Ash produced can be used in making roads.	Easily transported in pipelines or by tankers. Convenient fuel for use in cars as volatile and burns easily. High enthalpy density. Sulfur impurities can be easily removed.	Higher specific energy. Clean; produces fewer pollutants per unit energy. Easily transported in pipelines and pressurized containers. Does not contribute to acid rain.
Disadvantages	Contributes to global warming due to CO_2. Contributes to acid rain, SO_2. Produces particulates (electrostatic preceptors can remove most of these). Difficult to transport. Waste can lead to visual and chemical pollution. Mining is dangerous.	Limited lifespan and uneven world distribution. Contributes to acid rain and global warming. Transport can lead to pollution. Carbon monoxide is a local pollutant produced by incomplete combustion of gasoline in internal combustion engines. Photochemical smog is produced as a secondary pollutant due to reactions of the primary pollutants (nitrogen oxides and hydrocarbons) released from internal combustion engines.	Limited supplies. Contributes to global warming. Risk of explosion due to leaks.

All fossil fuels are non-renewable and produce the greenhouse gas carbon dioxide.

One measure of the impact our activities have on the environment is given by our **carbon footprint**. The carbon footprint is a measurement of all the greenhouse gases we individually produce. It has units of mass of carbon dioxide equivalent and depends on the amount of greenhouse gases we produce in our day-to-day activities through the use of fossil fuels – such as heating, transport and electricity. 'Carbon footprint' has become a widely used term in the public debate on our responsibilities in the fight against global climate change.

Nature of Science

There is some limited consensus on how to quantify a carbon footprint. Some issues are:

- Should the carbon footprint include just carbon dioxide (CO_2) emissions or include other greenhouse gas emissions such as methane as well?
- Should it be restricted to carbon-based gases or can it include substances that do not have carbon in their molecules such as dinitrogen monoxide, which is another greenhouse gas?
- Should it include other gases such as carbon monoxide (CO), which is a toxic primary pollutant that can be oxidized to carbon dioxide in the atmosphere?

Scientific terms which have an impact on the public must be clearly communicated.

Challenge yourself

3. On a typical winter's day, 1.33×10^6 kJ of energy is needed in a home.

The specific energy densities and approximate empirical formulae of wood and coal and the efficiency of the heating systems are tabulated below.

Fuel	Formula of fuel	Specific energy / kJ g^{-1}	Efficiency of heating / %
Coal	CH	31	65
Wood	$C_5H_9O_4$	22	70

(a) Calculate the percentage mass of carbon in the two fuels.

(b) Determine the carbon footprint from using the two forms of heating in terms of the mass of carbon dioxide produced by the two fuels.

(c) Suggest a reason why the carbon footprint calculation for wood does not give a full account of its impact on the environment.

Combustion of the alkanes in detail

Here we look at the combustion of the alkanes in a little more detail.

Carbon content and incomplete combustion in the alkanes

As discussed earlier, the incomplete combustion of a hydrocarbon results in the incomplete combustion of the carbon in the compound with the production of carbon monoxide and carbon. The higher the carbon content of the compound, the greater the tendency for incomplete combustion. Consider the carbon content of the alkanes.

Alkane	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_7H_{16}	C_8H_{18}
% Carbon content	74.8	79.9	81.7	82.6	83.2	83.6	83.9	84.1
Mass of CO2 /g when 1 g of fuel is burnt	2.74	2.93	2.99	3.03	3.05	3.06	3.07	3.08
Energy released per unit mass / kJ g–1	61.1	51.9	50.3	49.5	48.6	48.3	0.0	47.9

Structure 3.2 – Why do larger hydrocarbons have a greater tendency to undergo incomplete combustion?

The increase in percentage carbon content down the homologous series suggests that incomplete combustion increases with the length of the carbon chain.

This supports the claim that natural gas, which is mostly methane, is the cleanest of the fossil fuels to burn, and coal, which has a very high carbon content, is the dirtiest.

Carbon content and carbon dioxide production during complete combustion

The amount of carbon dioxide gas produced by a fuel is another important factor when considering the use of different fuels. Complete combustion of a hydrocarbon produces carbon dioxide and water, and the mass of carbon dioxide produced per unit mass of fuel increases with the percentage carbon content as shown in the previous table.

This also supports the claim that natural gas is the cleanest of the fossil fuels to burn and coal is the dirtiest.

Worked example

Calculate the mass of carbon dioxide produced when 1.00 g of pentane undergoes complete combustion.

Solution

$$\underset{1\text{ mol}}{C_5H_{12}(l)} + 8O_2(g) \rightarrow \underset{5\text{ mol}}{5CO_2(g)} + 6H_2O(l)$$

$$n(CO_2(g)) = 5n(C_5H_{12}(l))$$

$$= 5 \times \frac{1.00}{(12.01 \times 5) + (1.01 \times 12)} = 5 \times \frac{1.00}{72.17}$$

$$\text{mass}(CO_2(g)) = 5 \times \frac{44.01}{72.17} = 3.05\,\text{g}$$

HL Structure 3.2 – Why is carbon dioxide described as a greenhouse gas?

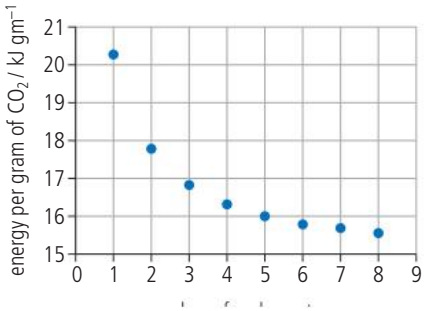
The mass of carbon dioxide produced for the other alkanes is calculated in the same way.

Carbon content and specific energy in the alkanes

We saw earlier that hydrogen has higher specific energy than methane. Comparing the specific energy of the alkanes we see that the higher the percentage carbon content (and the lower the percentage hydrogen), the lower the specific energy.

SKILLS Comparing the enthalpy of pentane and hexane. Full details of how to carry out this experiment with a worksheet are available in the eBook.

The energy obtained per gram of CO_2 produced during complete combustion (Figure 1) is another important consideration when choosing fuels.



R1.3 Figure 1 A graph showing how the energy obtained per gram of CO_2 produced varies with the length of the carbon chain in the alkanes.

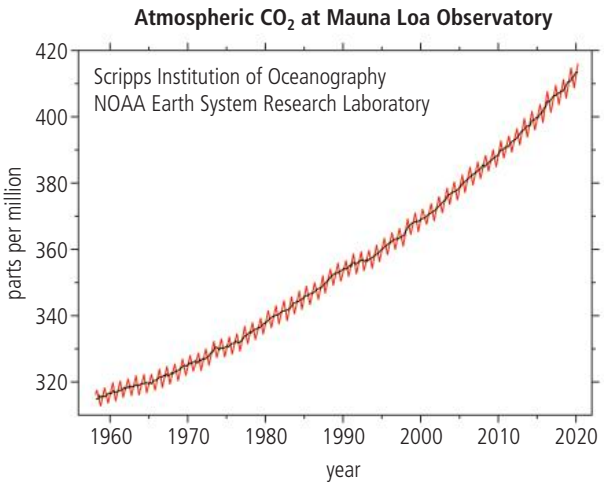
The graph shows that natural gas (which is mainly CH_4) produces the most energy per gram of CO_2 added to the atmosphere. The higher alkanes found in petroleum and carbon in coal produce less energy for the same level of carbon dioxide pollution.

Fossil fuels and the greenhouse effect

The level of carbon dioxide produced from burning fossil fuels has been increasing steadily over the last 200 years.

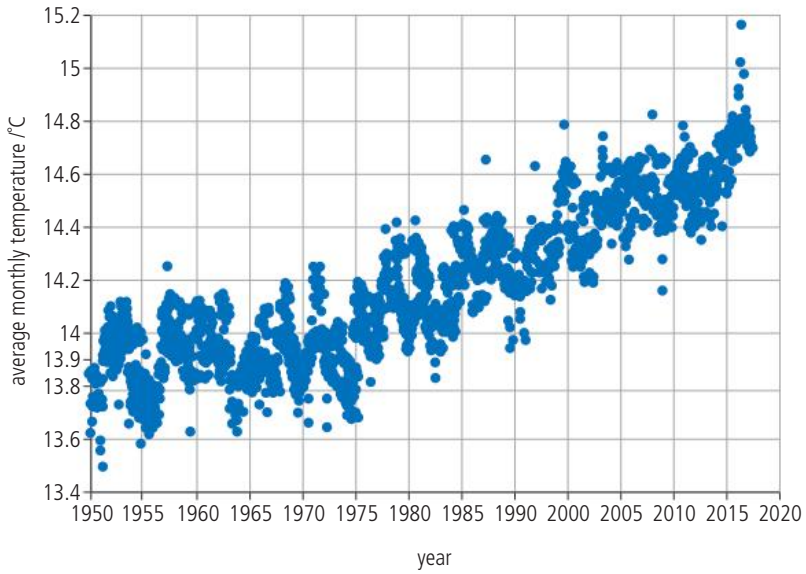
Carbon dioxide levels and the greenhouse effect

Levels of carbon dioxide have been measured at Mauna Loa in Hawaii since the International Geophysical Year in 1957 (Figure 2).



R1.3 Figure 2 Graph showing the rising concentration of atmospheric CO_2 between 1958–2021 measured 4170 m up on Mauna Loa, Hawaii. The graph shows the steady rise of CO_2 levels in the atmosphere each year due to increasing fossil fuel consumption. The regular fluctuations reflect seasonal plant growth in the spring and decay in the autumn in the northern hemisphere each year.

We can compare the increase in levels of carbon dioxide to changes in average global temperatures during the same period (Figure 3). It is estimated that carbon dioxide contributes about 50% to global warming.



R1.3 Figure 3 Global average temperatures from 1950 to 2016.

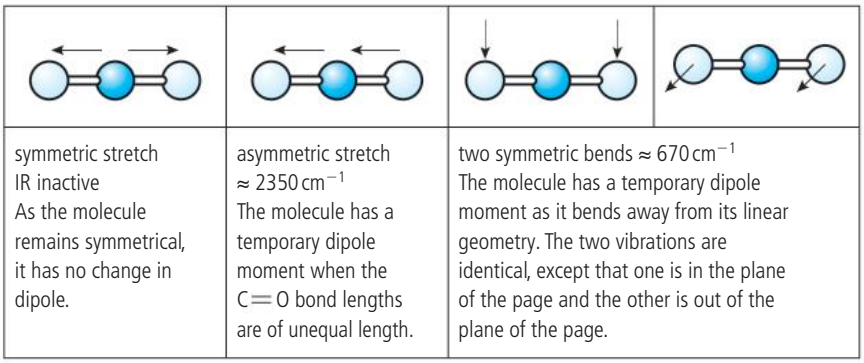


The Mauna Loa Observatory monitors all atmospheric constituents that may contribute to climatic change, such as greenhouse gases and aerosols.

Nature of Science

Data are not enough to prove the causal link between CO_2 concentration and temperature. Both changes could be due to changes in a third variable. The ideas of correlation and cause are very important in science. A correlation is a statistical link or association between one variable and another. To establish a causal relationship, scientists need to have a plausible mechanism linking the factors. This has been proposed in the case of the greenhouse effect. Ideally, however, the relationship between the variables needs to be experimentally investigated with all other possible key variables being controlled. This is often impossible; levels of carbon dioxide cannot be added to the environment in such a controlled way, and so we need to rely on computer models.

Greenhouse gases allow shortwave radiation from the Sun to pass through the atmosphere but absorb the longer wave infrared radiation re-radiated from the Earth's surface. As discussed in Structure 3.2, carbon dioxide is a greenhouse gas as its molecules increase their vibrational energy by absorbing infrared radiation. Three of the vibrational modes of the carbon dioxide molecule are IR active – the dipole changes as it vibrates (Figure 4). The molecules then re-radiate this energy back to the Earth's surface, contributing to global warming.



R1.3 Figure 4 Three of the vibrational modes of the carbon dioxide molecule are IR active. The symmetric stretch produces no change in dipole and so is IR inactive.

Challenge yourself

4. (a) Suggest why the first measurements of CO_2 levels were taken at Mauna Loa in Hawaii and at the South Pole.

(b) Explain the annual fluctuations in CO_2 levels at Mauna Loa.

(c) Identify two different means by which CO_2 can be removed from the atmosphere naturally and give balanced equations for both of these.

(d) Suggest how the depletion of tropical forests can lead to an increase in CO_2 levels.

The impact of increasing amounts of greenhouse gases on the climate

There is little doubt that, since the 19th century, the amount of carbon dioxide and other anthropogenic (resulting from the impact of humans on nature) greenhouse gases in the atmosphere have increased dramatically and that the average temperature of the world has also increased, even if rather erratically. It has been suggested that

levels of carbon dioxide will double in about 100 years. Allowing for the effect of all the gases, the temperature of the Earth could rise by 2 °C within 50 years. These temperature changes could have a drastic effect on the climate, for example:

- changes in agriculture such as crop yields
- changes in biodistribution due to desertification and loss of cold-water fish habitats
- rising sea levels because of thermal expansion and the melting of polar ice caps and glaciers.



Retreating glacier in Iceland most probably caused by global warming.

TOK

Some people question the reality of climate change and question the motives of scientists who have 'exaggerated' the problem. How do we assess the evidence collected and the models used to predict the impact of human activities? What effect does a highly sensitive political context have on objectivity? Can politicians exploit the ambiguity of conclusions coming from the scientific community for their own ends?

Nature of Science, Reactivity 3.2 – What are some of the environmental, economic, ethical and social implications of burning fossil fuels?

Exercise

Q10. Consider the following specific energies of different fuels.

Fuel	Specific energy / kJ g^{-1}	Carbon content by mass / %
Coal	32	94
Oil	42	83
Natural gas	55	75
Wood	15	70
Hydrogen	142	0

(a) Suggest an explanation for the trend in specific energies between coal, oil, natural gas and hydrogen.

(b) The choice of fuel also depends on other factors besides specific energies. One of these is the amount of carbon dioxide produced. Explain why this is an important factor to consider.

(c) Calculate the carbon dioxide production for 1000 kJ of energy from each source and identify the best and worst fuel on this basis.

Q11. An analytical chemist determines the percentage composition by mass of a sample of coal.

C	H	O	N	S
84.96	5.08	7.55	0.73	1.68

(a) Determine the empirical formula of the coal.

(b) Explain how the combustion of the coal could produce acid rain. Give equations to illustrate how the elements in the coal can produce acidic gases.

Q12. The coal burnt in a 500 MW (500×10^3 kJ s^{-1}) power station has a specific energy of 33.0 kJ g^{-1}.

(a) Determine the mass of coal burnt each second when the power station is operating at full capacity, assuming an efficiency of 38%.

(b) The empirical formula of the coal can be approximated as CH. Calculate the mass of carbon dioxide produced each second.

Q13. State three reasons for not relying on carbon-containing fuels in the future.

Q14. Crude oil currently provides a greater percentage of the world's energy than any other energy source.

(a) State three reasons for its wide use as an energy source.

(b) Describe briefly how crude oil is formed in nature.

Q15. State three reasons why, worldwide, gas is preferred to oil as a fuel in power stations.

Reactivity 1.3.4 – Biofuels

Reactivity 1.3.4 – Biofuels are produced from the biological fixation of carbon over a short period of time through photosynthesis.	
Understand the difference between renewable and non-renewable energy sources.	
Consider the advantages and disadvantages of biofuels.	
The reactants and products of photosynthesis should be known.	

Photosynthesis converts light energy into chemical energy

Energy from the Sun fuels the sequence of redox reactions that is photosynthesis. **Chlorophyll**, the green pigment in green plants, absorbs solar energy which is then used to convert carbon dioxide and water into glucose. The reactions can be summarized by the equation:

$$6CO_2(l) + 6H_2O(l) \rightarrow C_6H_{12}O_6(s) + 6O_2(g)$$

The products of photosynthesis can be used for food, as a primary fuel such as wood, or converted to other fuels such as ethanol. **Biofuels,** produced from the biological fixation of carbon over a short period of time, are a renewable and sustainable energy source. Photosynthesis is not very efficient, however, so relatively little of the available solar energy is trapped.

Challenge yourself

5. One part of the Earth's surface receives 1.25×10^6 J of solar energy. Green plants such as algae absorb 1.25×10^4 J of this energy.

(a) Determine the percentage of the Sun's energy absorbed by green plants.

(b) Suggest two reasons why the remainder of the Sun's energy is not absorbed by green plants.

Wood is mainly cellulose, a polymer made up of glucose molecules. Comparing coal with wood is very useful as the latter has not been subject to the same geological conditions.

Worked example

Coal and wood are used domestically to provide heating.

	Percentage composition				Specific energy / kJ g^{-1}
	C	H	O	N	
Wood	50	6	43	1	10–18
Bituminous coal	88	5	5–15	1	30
Anthracite	95	2–3	2–3	Trace	31

(a) Describe the relationship between the oxygen content of a fuel and its specific energy.

(b) Describe how the compositions of the fuels change as they are exposed to high pressure.

(c) State two advantages of coal use over wood.

(d) State one advantage of the use of wood.

(e) Discuss some of the disadvantages of the use of coal.

(f) What harmful pollutants are produced when wood is burnt in an enclosed space?

Solution

(a) The lower the oxygen content the greater its specific energy.

(b) Oxygen (and water vapour) are lost as the pressure increases.

(c) Coal is the most abundant fossil fuel and has a high specific energy.

(d) Wood is a renewable and sustainable fuel.

(e) Difficult and expensive to mine and transport; produces sulfur oxides, which lead to acid rain, particulates (soot) and carbon dioxide, a greenhouse gas which leads to global warming; mining has an environmental impact.

(f) Particulates (soot), hydrocarbons and carbon monoxide are produced due to incomplete combustion.



▲ Wood-burning stove. Wood has a lower specific energy than fossil fuels due to its relatively high oxygen content.

Ethanol can be used as a biofuel

Ethanol is a liquid biofuel, which can be used in internal combustion engines. It can be made from biomass by fermenting plants high in starches and sugars.

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$

This process can be carried out at approximately 37 °C in the absence of oxygen by yeast, which provides an enzyme which catalyses the reaction.

Worked example

(a) State the equation for the complete combustion of ethanol.

(b) The enthalpy of combustion of ethanol is −1367 kJ mol^{-1}. Calculate the specific energy of ethanol in kJ g^{-1}.

(c) Compare this value with the corresponding value for octane and explain the difference.

Solution

(a) $C_2H_5OH(l) + 3O_2(g) \rightarrow 3H_2O(l) + 2CO_2(g)$

(b) heat produced by one mole of ethanol (46.08 g) = 1367 kJ

heat produced by 1.00 g = $\frac{-1367}{46.08}$ kJ g^{-1} = 29.67 kJ g^{-1}

(c) heat produced by one mole of octane (114.26 g) = 5470 kJ

heat produced by 1.00 g = $\frac{-5470}{114.26}$ kJ g^{-1} = 47.87 kJ g^{-1}

Less heat is produced per unit mass with ethanol because it is already partially oxidized.

Gasohol is a mixture of 10% ethanol and 90% unleaded gasoline. Ethanol can be produced from several types of plant material and gasohol can generally be substituted for gasoline with only minor changes in fuel consumption and performance. The advantages of using ethanol include:

- it is renewable
- it produces lower emissions of carbon monoxide and nitrogen oxides
- it decreases a country's dependence on oil.

One disadvantage is that ethanol absorbs water as it can form hydrogen bonds with the water molecules in the atmosphere. This leads to the ethanol separating from the hydrocarbon components in the fuel. It can also cause corrosion.

Methanol can also be used; it is produced by heating wood in the presence of steam and limited amounts of oxygen.



Test flight to study the effects of the use of biofuels. A 50–50 blend of JP-8 Jet fuel and a renewable alternative fuel produced from Camelina plant oil was used. This NASA study concluded that the use of biofuels reduced the amount of pollution.

Challenge yourself

6. A possible incomplete equation for the conversion of wood into hydrogen, carbon monoxide, and carbon dioxide is:

$$2C_{16}H_{23}O_{11} + 19H_2O + O_2 \rightarrow xH_2 + yCO + zCO_2$$

(a) Identify the oxidation number of all the elements in the equation.
(b) Identify the elements which are oxidized and reduced in the reaction.
(c) Deduce the value of *x* by balancing the hydrogen atoms.
(d) Determine the values of *y* and *z* by balancing the changes of oxidation numbers and the number of carbon atoms.
(e) Deduce how many methanol molecules can be produced from one wood molecule.

Methane can be made from the bacterial breakdown of plant material in the absence of oxygen. The process can be controlled to produce a clean burning biogas such as natural gas.

Carbohydrates, for example, produce a mixture which is about 50% methane:

$$C_6H_{12}O_6(s) \rightarrow 3CO_2(g) + 3CH_4(g)$$

Fats with a lower oxygen content produce 72% methane:

$$2C_{15}H_{31}COOH + 14H_2O \rightarrow 9CO_2 + 23CH_4$$

The advantages and disadvantages of using biofuels

Advantages	Disadvantages
Cheap and readily available. If crops/trees are replanted, they can be a renewable and sustainable source. Less polluting than fossil fuels.	Uses land which could be used for other purposes, such as growing food. High cost of harvesting and transportation in large volumes. Takes nutrients from soil/uses large amounts of fertilizers. Lower specific energy than fossil fuels.

Exercise

Q16. **(a)** Scientists have described solar energy as the ultimate energy source. Identify energy sources which derive from photosynthesis.

(b) Discuss the advantages and disadvantages of the use of biomass as a fuel.

Q17. **(a)** State the chemical equation for the photosynthesis of glucose.

(b) Identify the molecule needed by plants to photosynthesize.

(c) Glucose can be converted to ethanol, which can be used as a fuel. State the name and equation of the process and describe the conditions needed.

Q18. **(a)** When biomass decomposes in the absence of oxygen, biogas is formed. Name the main gas present in biogas.

(b) When wood is burnt in an enclosed space, the combustion produces harmful pollutants. Identify the pollutants.

(c) Suggest why biomass is likely to become more important in the future as a fuel.

Reactivity 1.3.5 – Fuel cells

Reactivity 1.3.5 – A fuel cell can be used to convert chemical energy from a fuel directly to electrical energy.	
Deduce half-equations for the electrode reactions in a fuel cell.	
Hydrogen and methanol should be covered as fuels for fuel cells. The use of proton exchange membranes will not be assessed.	Reactivity 3.2 – What are the main differences between a fuel cell and a primary (voltaic) cell?

The hydrogen fuel cell

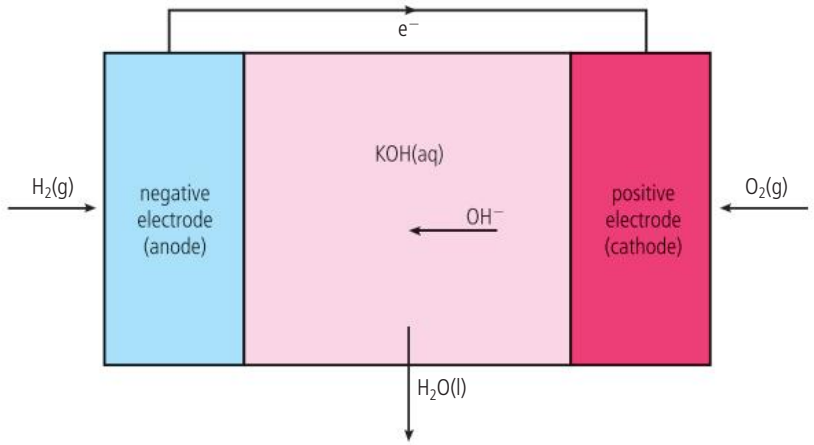
As we have seen, hydrogen is a possible alternative fuel to fossil fuels as it does not produce carbon dioxide. One mole of hydrogen can release 286 kJ of heat energy when it combines directly with oxygen:

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H^{\ominus} = -286\,kJ\,mol^{-1}$$

As this is a redox reaction that involves the transfer of electrons from hydrogen to oxygen, it can be used to produce an electric current directly if the reactants are physically separated. This is the basis of a **fuel cell**, where the reactants are continuously supplied to different electrodes. The hydrogen–oxygen fuel cell operates with either an acidic or alkaline electrolyte.

The hydrogen–oxygen fuel cell with an alkaline electrolyte

The most commonly used hydrogen–oxygen fuel cell has an alkaline electrolyte (Figure 5).



R1.3 Figure 5 The hydrogen–oxygen fuel cell with an alkaline electrolyte.

The balanced equation can be deduced from changes in oxidation states as discussed in Reactivity 3.2.

Worked example

Deduce the two half-reactions that occur at the anode and the cathode in the hydrogen–oxygen fuel cell with aqueous sodium hydroxide as the electrolyte.

Solution

$H_2(g)$ is oxidized at the anode. Start with a simplified equation and the oxidation state of the hydrogen in the reactant and product showing the oxidation states in blue as in Structure 3.2 and Reactivity 3.2.

$$H_2(g) + _ \rightarrow H_2O(l) + _$$
$$2(0) \qquad 2(+1) \qquad \text{oxidation state}$$

2 electrons are produced as both Hs are oxidized: $0 \rightarrow +1$

$$H_2(g) + \rightarrow H_2O(l) + 2e^-$$

As the conditions are alkaline, add $2OH^-$ on the left to balance the negative charges.

Balance the Hs and Os by adding another H_2O on the right-hand side.

$$H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$$

$O_2(g)$ is reduced at the cathode. Start with a simplified equation and the oxidation state of the oxygen in the reactant and product.

$$O_2(g) + _ \rightarrow 2H_2O(l) + _$$
$$2(0) \qquad 2(-2) \qquad \text{oxidation state}$$

4 electrons are needed as both Os are reduced: $0 \rightarrow -2$

$$O_2(g) + 4e^- \rightarrow 2H_2O(l) + _$$

As the conditions are alkaline, add $4OH^-$ on the right to balance the negative charges.

Balance the Hs and Os by adding another $4H_2O$ on the left-hand side and simplify.

$$O_2(g) + 4e^- + 4H_2O \rightarrow 2H_2O(l) + 4OH^-$$
$$O_2(g) + 4e^- + 2H_2O \rightarrow 4OH^-(aq)$$

Preparing a simple fuel cell: electrolysis of water. Full details of how to carry out this experiment with a worksheet are available in the eBook.

SKILLS

The overall reaction is the sum of the oxidation and reduction half-reactions:

$$2H_2(g) + \cancel{4OH^-(aq)} + 2H_2O(l) + O_2(g) + \cancel{4e^-} \rightarrow 4H_2O(l) + \cancel{4e^-} + \cancel{4OH^-(aq)}$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

The fuel cell will function as long as hydrogen and oxygen are supplied. The electrodes are often made of porous carbon with added transition metals such as nickel. The potassium hydroxide provides the hydroxide ions that are transferred across the cell.

The equations for the hydrogen fuel cell under acid conditions are discussed in Reactivity 3.2.

One of the problems with the hydrogen fuel cell is that hydrogen gas is almost never found as the element in nature and needs to be extracted from other sources. Hydrocarbons, including fossil fuels and biomass (waste organic matter), for example, can be processed to break down into hydrogen and carbon dioxide. The alternative is to electrolyze water, but this of course needs electricity and then only becomes a way of storing energy at times of low demand.

For the whole process to be environmentally clean, the hydrogen should be generated using renewable resources such as wind power.

Challenge yourself

7. Explain the increased efficiency of a hydrogen–oxygen fuel cell which produces steam compared with a cell that produces water.

Methanol is oxidized using catalysts in the methanol fuel cell

Methanol is an alternative fuel used in fuel cells. Methanol is a stable liquid at normal environmental conditions, has a high energy density, and is easy to transport. In the direct methanol fuel cell (DMFC), the fuel is oxidized under acidic conditions on a catalyst surface to form carbon dioxide. The H^+ ions formed are transported across a proton exchange membrane from the anode to the cathode where they react with oxygen to produce water, and electrons are transported through an external circuit from the anode to the cathode. Water is consumed at the anode and is produced at the cathode.

Worked example

Deduce the two half-reactions that occur at the anode and the cathode in the methanol–oxygen fuel cell with an acidic electrolyte.

Solution

$CH_3OH(g)$ is oxidized to carbon dioxide at the anode. Start with a simplified equation and the oxidation state of the carbon in the reactant and product.

$$CH_3OH(g) + _ \rightarrow CO_2(g) + _$$
$$(-2) \qquad (+4) \qquad \text{oxidation state}$$

6 electrons are produced as C is oxidized: −2 → +4

$$CH_3OH(g) + _ \rightarrow CO_2(g) + 6e^-$$

As the conditions are acidic, add $6H^+$ on the right to balance the charges.

Balance the Hs and Os by adding another H_2O on the left-hand side.

$$CH_3OH(g) + H_2O(l) \rightarrow CO_2(g) + 6e^- + 6H^+$$

As in the hydrogen fuel cell, $O_2(g)$ is reduced at the cathode.

$$O_2(g) + 4e^- \rightarrow 2H_2O(l)$$

As the conditions are acidic, add $4H^+$ on the left-hand side to balance the charges.

$$O_2(g) + 4e^- + 4H^+ \rightarrow 2H_2O(l)$$

The overall equation for the methanol fuel cell can be obtained by balancing the number of electrons in the two half-reactions:

$$CH_3OH(g) + H_2O(l) \rightarrow CO_2(g) + 6e^- + 6H^+(aq)$$

$$\tfrac{3}{2}O_2(g) + 6e^- + 6H^+(aq) \rightarrow 3H_2O(l)$$

$$CH_3OH(g) + \tfrac{3}{2}O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

Microbial fuel cells (MFC) may one day offer a cheap and renewable source of energy. They can be used to harness the energy produced from the microbial oxidation of a huge range of organic substances. Bacteria are very small organisms which oxidize many organic compounds into CO_2 and H_2O with the production of energy. Some of this energy is needed by the organisms to grow and maintain their metabolism, but the rest can be harvested and used to generate electricity. Microbial fuel cells offer many potential advantages over hydrogen fuel cells. For example, hydrogen fuel cells require a very pure source of a highly explosive gas that is difficult to store and distribute. Furthermore, hydrogen is generally derived mainly from fossil fuels rather than renewable sources. In contrast, the energy sources for microbial fuel cells are renewable organics, including some that are, literally, 'dirt cheap'. The details of the microbial fuel cell will not be assessed in this course.



Researcher holding a two-chambered microbial fuel cell filled with a solution of organic acids. Microbial fuel cells may one day offer a cheap and renewable source of energy.

The main difference between a fuel cell and a primary (voltaic) cell is that fuel cells do not run out. The fuel is supplied continuously to the cell as it is oxidized. The chemicals are contained within a primary cell and so it stops working when the redox reaction which generates the current is complete.



Reactivity 3.2 – What are the main differences between a fuel cell and a primary (voltaic) cell?

The advantages and disadvantages of different cells are summarized in Reactivity 3.2.

Exercise

Q19. One type of fuel cell uses hydrogen as the fuel under acid conditions with a proton exchange membrane. The overall equation for the process is:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

(a) State the two half-equations for the reactions involving each reactant.

(b) Hydrogen is a more expensive source of chemical energy than gasoline. Explain why fuel cells are considered to be more economical than gasoline engines.



Guiding Question revisited

What are the challenges of using chemical energy to address our energy needs?

In this chapter we have explored how potential energy released during combustion as heat can address our energy needs. We have also explored how it can generate electrical energy directly.

- Combustion is a reaction in which an element or compound burns in oxygen.
- Fossil fuels originate from living organisms that died millions of years ago. They include coal, crude oil or petroleum, and natural gas.
- Coal is a black rock that is mainly carbon.
- Natural gas is mainly methane, and is the cleanest of the fossil fuels.
- Crude oil (petroleum) is a black liquid mixture of mainly hydrocarbons.
- The different hydrocarbons in crude oil can be separated by fractional distillation. Longer chain molecules have stronger intermolecular dispersion forces and higher boiling points.
- Petrol (gasoline) is separated from crude oil by fractional distillation and is a mixture of hydrocarbons with between five and twelve carbon atoms.
- Complete combustion of hydrocarbons breaks the carbon chain and produces carbon dioxide and water. Carbon monoxide and carbon in the form of soot are formed during incomplete combustion.
- Carbon dioxide is a greenhouse gas as it absorbs infrared radiation. Its large-scale production due to the combustion of fossil fuels has led to global warming.
- Carbon monoxide is a poisonous gas that binds to haemoglobin. This limits the ability of the blood to transport oxygen around the body.
- Most of our energy comes from the Sun. Photosynthesis is an endothermic reaction that stores solar energy as chemical energy.

- Plants can be grown specifically for use as fuels. Burning biomass can also involve burning paper or other waste organic matter.
- Fuel cells generate electricity directly by reacting a fuel such as hydrogen or methanol with oxygen in an electrochemical cell.
- Fuels are evaluated according to several criteria including energy density, specific energy or the environmental and economic impact of their use.

Practice questions

1. It is now widely accepted that the increased production of carbon dioxide is leading to global warming.

(a) Describe how carbon dioxide acts as a greenhouse gas. (2)

(b) Outline why oxygen and nitrogen, which are more abundant in the air, are not greenhouse gases. (1)

(c) Identify two pollutants, other than carbon dioxide, that are produced in the combustion engines of cars and outline their polluting effect. (2)

(Total 5 marks)

2. **(a)** Most of the world's energy comes from fossil fuels. State two reasons for this. (2)

(b) The 'specific energy' is the energy produced per unit mass. Identify a fuel which has a higher specific energy than fossil fuels. (1)

(Total 3 marks)

3. **(a)** Determine the percentage of carbon by mass in the fuels, coal (CH), petrol (C_8H_{18}) and natural gas (CH_4). (3)

(b) Suggest two reasons why coal has been replaced by petrol and natural gas in many countries. (2)

(c) One fuel that has been proposed as a replacement for carbon-containing substances is hydrogen. State two advantages of using hydrogen as a fuel. (2)

(Total 7 marks)

4. The enthalpies of combustion of propane and butane are given in Section 14 of the data booklet.

(a) Calculate the heat produced by the combustion of 1 g of C_3H_8 and C_4H_{10} in kJ g^{-1}. (2)

(b) Use the ideal gas equation to calculate the density of the two gases at STP and hence calculate the heat produced when 1 cm^3 of the two gases are burnt. (3)

(Total 5 marks)

5. **(a)** State the name of the process by which green plants capture the Sun's energy and convert carbon dioxide and water into glucose. (1)

(b) State the overall equation for the full redox reaction. (1)

(c) Glucose can be converted into ethanol, which can be used in fuel cells. Identify this process by name and write the equation for the chemical reaction. (2)

(Total 4 marks)

6. **(a)** Use Section 14 of the data booklet to calculate the specific energy (the energy produced when 1 g of fuel is burnt in excess oxygen) of methane and methanol. (2)

(b) Deduce the average oxidation number of carbon in the two compounds. (1)

(c) Suggest a possible relationship between the oxidation number and specific energy. (1)

(d) Calculate the specific energy of glucose and discuss the validity of your hypothesis in part **(c)**. (3)

(Total 7 marks)

7. Fuel cells may be twice as efficient as the internal combustion engine. Although fuel cells are not yet in widespread use, NASA has used a basic hydrogen–oxygen fuel cell as the energy source for space vehicles.

Deduce the half-equations occurring at each electrode in the hydrogen–oxygen fuel cell in an alkaline medium. (2)

(Total 2 marks)

8. **(a)** One method of comparing fuels is by considering their specific energies.

Calculate the specific energy of octane, C_8H_{18}, in kJ kg^{-1} using Sections 7 and 14 of the data booklet. (2)

(b) A typical wood has a specific energy of 17×10^3 kJ kg^{-1}. Comment on the usefulness of octane and wood for powering a moving vehicle, using your answer to part **(a)**.

If you did not work out an answer for part **(a)**, use 45×10^3 kJ kg^{-1}, but this is not the correct answer. (1)

(Total 3 marks)

9. **(a)** Determine the specific energy (heat produced when 1 g is burnt) and energy density (heat produced from 1 cm^3) of petrol (gasoline), using data from Sections 7 and 14 of the data booklet. Assume petrol is pure octane, C_8H_{18}. Octane: molar mass = 114.26 g mol^{-1}; density = 0.703 g cm^{-3}. (2)

(b) Outline why the energy available from an engine will be less than these theoretical values. (1)

(Total 3 marks)

10. **(a)** Identify the major constituent of natural gas and write a balanced chemical equation for its combustion. (2)

(b) Compare natural gas with other fossil fuels as a source of air pollution for a given amount of energy and account for any differences. (3)

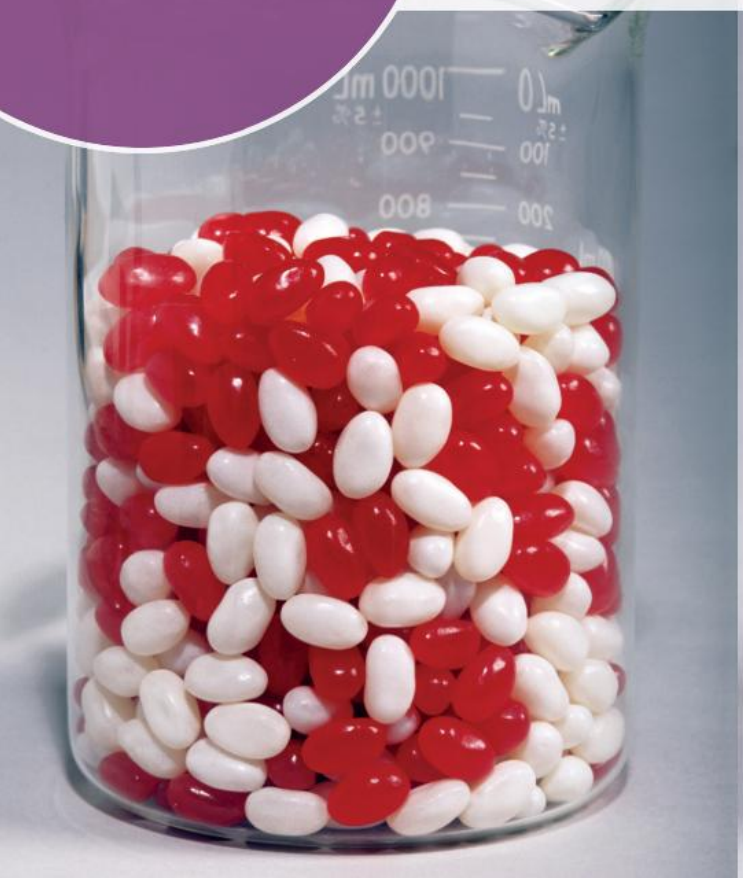
(c) Compare the relative supplies of natural gas and other fossil fuels. (1)

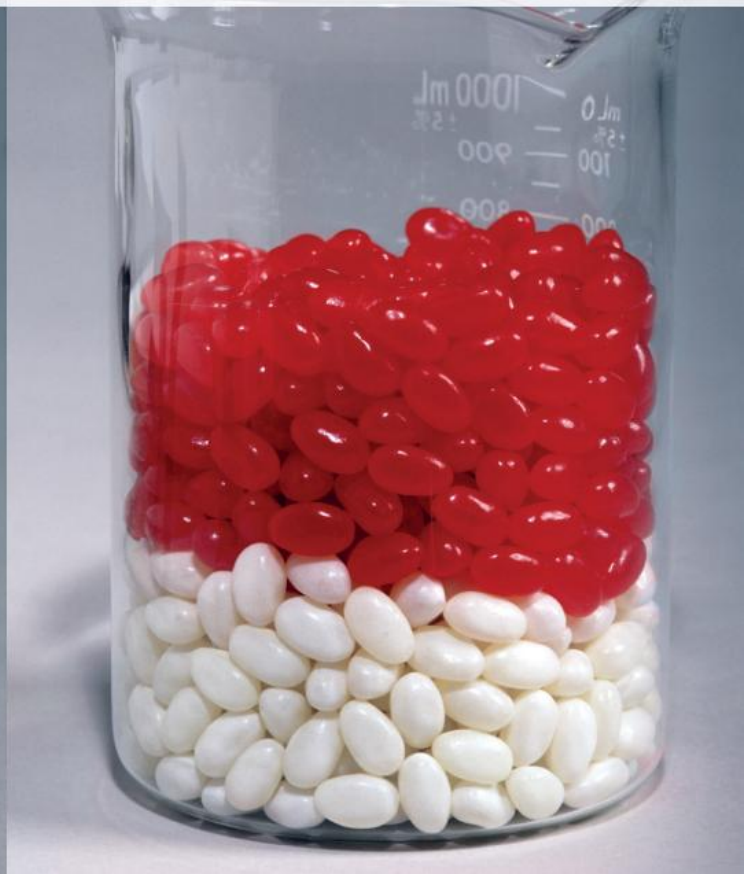
(Total 6 marks)

REACTIVITY

1.4 Entropy and spontaneity (HL)







(Top) Energy tends to be transferred from a cup with a high temperature to the surroundings at a lower temperature. This can be expressed more precisely when the degree of dispersal of matter and energy of a system is quantified by its **entropy** (*S*). Entropy is a measure of the amount of dispersal of matter or energy in a system. **(Bottom)** If the beaker on the left is stirred, an arrangement similar to the beaker on the right is produced. The arrangement on the right has higher entropy because the red and white jelly beans are now dispersed throughout the beaker.

HL

Guiding Question

What determines the direction of chemical change?

Bubbles rise and escape from a carbonated drink, and warm cups of coffee become cold. These examples illustrate a general principle known as the second law of thermodynamics: matter and energy tend to disperse and become more dispersed. Carbon dioxide tends to diffuse from the drink into the surroundings, and the energy tends to be transferred from a cup with a high temperature to the surroundings at a lower temperature. These everyday experiences can be expressed more precisely when the degree of dispersal of matter and energy of a system is quantified by its **entropy** (S). The direction of natural or spontaneous change is from low dispersal or entropy to high entropy. This principle also provides us with a signpost for chemical change. Chemical reactions will occur if the total *entropy of the universe increases*. We see in Reactivity 1.1 that exothermic reactions are more common than endothermic reactions. We will see that these reactions increase the total entropy of the universe as heat is dispersed into the surroundings. We will learn that as heat can be transferred in the reverse direction in endothermic reactions, there is high-level dispersal generated within the system by the heat transfer.



Perfume molecules disperse into the surroundings. Both changes lead to an increase in the entropy of the universe and illustrate the second law of thermodynamics.

Nature of Science

Scientists have called the second law of thermodynamics the most fundamental law in all of science and some, including Albert Einstein, have argued that it is one of the few laws that will never be overthrown. It is important, however, to understand that it is a statement of experience which cannot be proved. It is not impossible for a disordered arrangement to spontaneously change into a more ordered arrangement, but it is statistically unlikely. The term 'law' is sometimes used for statements that allow predictions to be made about natural phenomena without explaining them. Does the second law fit this description? Can the second law ever be falsified?

Reactivity 1.4.1 – Entropy

Reactivity 1.4.1 – Entropy, *S*, is a measure of the dispersal or distribution of matter and/or energy in a system. The more ways the energy can be distributed, the higher the entropy. Under the same conditions, the entropy of a gas is greater than that of a liquid, which in turn is greater than that of a solid.	
Predict whether a physical or chemical change will result in an increase or decrease in entropy of a system.	
Calculate standard entropy changes, $\Delta S^{\ominus}$, from standard entropy values, $S^{\ominus}$.	
Standard entropy values are given in the data booklet.	Structure 1.1 – Why is the entropy of a perfect crystal at 0 K predicted to be zero?

Entropy is a measure of the dispersal or distribution of matter

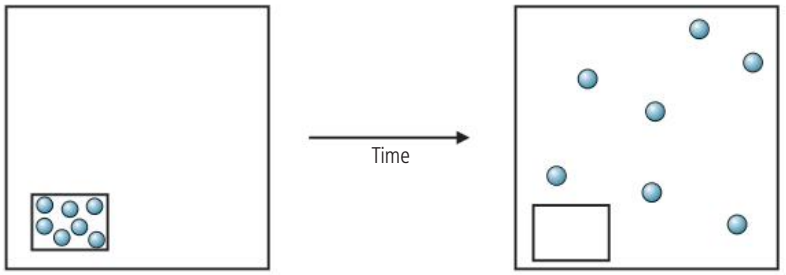
If a bottle of a carbonated drink is left open, we expect it to find it 'flat' after a couple of days. The carbon dioxide escapes from solution and diffuses (spreads out) into the wider surroundings. We do not expect all the carbon dioxide to return to the bottle at a later date. In a similar way, a hot cup of coffee will cool down and transfer heat to the surroundings. The heat will not return to the cup. Both these examples illustrate a general principle: energy and matter tend to disperse and the universe becomes more disordered. These are both examples of **spontaneous change**; they occur naturally without the need to do work. We can reverse the natural tendency of change but only at the expense of doing work. Similarly, sodium and chlorine have a natural tendency to react together to form sodium chloride. We can reverse this process and split sodium chloride into its constituents, but only at the expense of using valuable electrical energy, as discussed in Reactivity 3.2.

Spontaneous changes occur without the need to do work. A spontaneous reaction occurs without adding energy (beyond that required to overcome the activation energy barrier).

Entropy, *S*, is a measure of the dispersal or distribution of matter and/or energy in a system. Ordered states with a small energy distribution are said to have low entropy; disordered states with a high energy distribution have high entropy. As time moves forward, matter and energy become more dispersed, and the total entropy of the universe increases.

Entropy, *S*, is a measure of the dispersal or distribution of matter and/or energy in a system.

This is an expression of the second law of thermodynamics, which is one of the most important laws in science (Figure 1).



All gas particles are concentrated in a small volume. This is an ordered state with low entropy.

The gas particles are dispersed throughout the room. This is a disordered state with high entropy.

R1.4 Figure 1 Particles naturally adopt a more dispersed state with higher entropy. A mixed-up system allows the energy to be more dispersed than a system in which different particles are separated. This illustrates the second law of thermodynamics: spontaneous processes always occur with an increase in the entropy of the universe.



(a) Some potassium manganate(VII) crystals were placed at the centre of a water-filled Petri dish.
(b) Some hours later the crystals have diffused throughout the water:

$$KMnO_4(s) \rightarrow K^+(aq) + MnO_4^-(aq)$$

The aqueous ions have higher entropy than the solid. Entropy increases with time as the potassium manganate(VII) becomes more dispersed.

The power of the second law of thermodynamics is that it offers an explanation for all change. For example, a hot cup of coffee naturally cools when left for essentially the same reason that a gas disperses – the energy disperses so as to lead to the situation with the widest energy distribution. This change results in an increase in the entropy of the universe.

Predicting entropy changes

As the solid state is the most ordered state with the least dispersal of matter and the gaseous state is the most dispersed, we can predict that the entropy of a system increases as solid changes to liquid and as liquid changes to gas. Similarly, doubling the number of particles present in a sample also increases the opportunity for matter and energy to be more dispersed and for its entropy to increase. More precisely, it can be shown that doubling the amount of a substance doubles the entropy. Similar considerations allow us to predict the entropy changes of the system (ΔS) during any physical or chemical change. Some examples are tabulated below.

Change	ΔS
solid → liquid	increase (+)
solid → gas	increase (+)
liquid → gas	increase (+)
liquid → solid	decrease (−)
gas → solid	decrease (−)
gas → liquid	decrease (−)

When predicting entropy changes, the change due to a change in the number of particles in the gaseous state is usually greater than any other possible factor.

Worked example

Predict the entropy change ΔS for the following changes.

(a) $Br_2(l) \rightarrow Br_2(g)$

(b) $2Cu(s) + O_2(g) \rightarrow 2CuO(s)$

(c) $Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$

(d) $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

(e) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

(f) $Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$

Solution

(a) One mole of liquid is changing into one mole of gas. There is an increase in dispersal of matter and an increase in entropy. ΔS is positive.

(b) There is a decrease in the number of moles of gas during the reaction. This leads to a reduction in the dispersal of matter in the products. ΔS is negative.

(c) There are two moles of aqueous ions on the left-hand side and one mole of solid on the right-hand side. There is a decrease in dispersal and there will be a decrease in entropy. ΔS is negative.

(d) There are two moles of gas in the reactants and in the products. There is no significant change in dispersal. The entropy change will be close to zero. $\Delta S \approx 0$.

(e) There are three moles of gas in the reactants and one mole of gas in the products. There is a decrease in the dispersal of matter and so there will be a decrease in entropy. ΔS is negative.

(f) One mole of solid and one mole of aqueous ions are changed into one mole of solid and one mole of aqueous ions. The entropy change will be close to zero. $\Delta S \approx 0$.

TOK

Entropy is a technical term which has a precise meaning. How important are such technical terms in different areas of knowledge?

When explaining changes in entropy, you must refer to changes in state and the number of moles. The change in number of moles of gas is often the key factor.

Absolute entropy

The absolute entropy of different substances can be calculated. As entropy depends on the temperature and pressure, tabulated entropy values refer to standard conditions and are represented as $S^\ominus$. Some values are shown in the table below.

Substance	Formula	$S^\ominus$ / $JK^{-1}mol^{-1}$
hydrogen	$H_2(g)$	+131
oxygen	$O_2(g)$	+205
nitrogen	$N_2(g)$	+191
graphite	C(graphite)	+5.7
methane	$CH_4(g)$	+186
ammonia	$NH_3(g)$	+193
water	$H_2O(l)$	+70.0
steam	$H_2O(g)$	+188.8
ethane	$C_2H_6(g)$	+230
ethene	$C_2H_4(g)$	+220
ethanol	$C_2H_5OH(l)$	+161

Section 13 of the data booklet has a list of values for organic compounds. The units are explained on page 525.

A perfectly ordered solid at absolute zero has zero entropy. All other states, which are more dispersed, have positive entropy values. Entropy increases with temperature as energy becomes more dispersed.

As expected, the entropy values increase in the order: solid, liquid, gas. It should be noted that all entropy values are positive. A perfectly ordered solid at absolute zero has an entropy of zero. All other states, which are more dispersed, have positive entropy values.

Structure 1.1 – Why is the entropy of a perfect crystal at 0 K predicted to be zero?

Calculating entropy changes

The entropy change of the system during a reaction can be calculated from the differences between the total entropy of the products and the total entropy of the reactants.

$$\Delta S^{\ominus} = \Sigma S^{\ominus}(\text{products}) - \Sigma S^{\ominus}(\text{reactants})$$

The strategy and potential pitfalls of solving problems related to entropy change are similar to those discussed when calculating enthalpy changes, but note that entropy values are absolute values which are always positive.

Worked example

Calculate the entropy change for the hydrogenation of ethene:

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

using the entropy values given in Section 13 of the data booklet and the table on the previous page.

Solution

When asked to calculate an entropy change, it is always a good idea to start by predicting the sign of $\Delta S^{\ominus}$.

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

Two moles of gas are converted to one mole of gas: therefore there will be a decrease in the dispersal of matter and a decrease in entropy. So $\Delta S^{\ominus}$ will be negative.

Write down the equation with the corresponding entropy values below it:

$$\begin{array}{cccc} C_2H_4(g) & + & H_2(g) & \rightarrow & C_2H_6(g) \\ 220 & & 131 & & 230 \quad S^{\ominus}/\,J\,K^{-1}\,mol^{-1} \end{array}$$

$$\Delta S^{\ominus} = \Sigma S^{\ominus}(\text{products}) - \Sigma S^{\ominus}(\text{reactants})$$
$$= 230 - (220 + 131) = -121\,J\,K^{-1}\,mol^{-1}$$

Exercise

Q1. Identify the process expected to have a value of ΔS closest to zero.

A $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$ **B** $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

C $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ **D** $H_2O(l) \rightarrow H_2O(g)$

Q2. Identify the processes which have an associated increase in entropy.

I. $Br_2(g) \rightarrow Br_2(l)$

II. $Br_2(g) \rightarrow 2Br(g)$

III. $KBr(s) \rightarrow K^+(aq) + Br^-(aq)$

A I and II **B** I and III **C** II and III **D** I, II and III

Q3. Which is the best description of the entropy and enthalpy changes accompanying the sublimation of iodine?

$$I_2(s) \rightarrow I_2(g)$$

A ΔS +, ΔH +, reaction is endothermic

B ΔS +, ΔH −, reaction is exothermic

C ΔS −, ΔH +, reaction is endothermic

D ΔS −, ΔH −, reaction is exothermic

Q4. Identify the reaction which has the largest increase in entropy.

A $AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$

B $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

C $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

D $Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$

Q5. Predict the entropy change ΔS for the following reactions.

(a) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

(b) $3Fe(s) + 4H_2O(g) \rightarrow Fe_3O_4(s) + 4H_2(g)$

(c) $Ba(OH)_2{\cdot}8H_2O(s) + 2NH_4SCN(s) \rightarrow Ba(SCN)_2(aq) + 2NH_3(aq) + 10H_2O(l)$

Q6. Sketch a graph to show how the entropy of a solid changes as the temperature increases.

Q7. Calculate the entropy change ΔS for the Haber process, shown below, using tabulated standard molar entropies at 25 °C.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

Q8. Calculate the standard entropy change associated with the formation of methane from its elements.

Q9. Calculate the standard entropy change associated with the combustion of one molecule of hydrogen.

Reactivity 1.4.2 – Gibbs energy

Reactivity 1.4.2 – Change in Gibbs energy, Δ*G*, relates the energy that can be obtained from a chemical reaction to the change in enthalpy, Δ*H*, change in entropy, Δ*S*, and absolute temperature, *T*. Apply the equation $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ to calculate unknown values of these terms.	
Thermodynamic data values are given in the data booklet. Note the units: ΔH kJ mol^{-1}; ΔS J K^{-1} mol^{-1}; ΔG kJ mol^{-1}.	

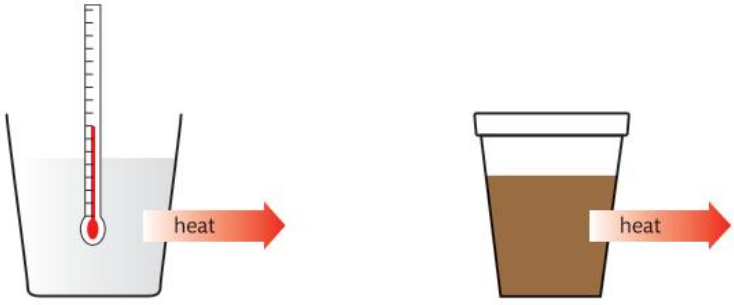
Entropy changes of the surroundings

This discussion of the direction of change based on entropy changes is incomplete. In Reactivity 1.1 we suggest that enthalpy changes could be used as an indicator of the direction of change, but this left endothermic reactions unexplained. Similarly, we have also discussed the need for the entropy to increase during spontaneous changes, but we have seen that many reactions occur with a decrease of entropy. This section resolves these issues.

So far, our discussion of entropy has focused on the entropy of the substances present in the system. To consider the total entropy change of a reaction, we must also consider the accompanying entropy change in the surroundings. Consider the reaction between zinc and copper sulfate, discussed in Reactivity 1.1.

$$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq) \qquad \Delta H^\ominus = -217\,\text{kJ mol}^{-1},\ \Delta S^\ominus \approx 0$$

How does this reaction increase the total entropy of the universe? The key to answering this question is that heat is transferred to the surroundings, leading to a general dispersal of energy into the surrounding universe. The reaction can be compared to the cooling of a hot cup of coffee discussed earlier. Both result in an increase in total entropy as heat is dispersed (Figure 2).



The entropy of the surroundings increases as the heat given out by the reaction increases the dispersal of the surroundings.

The entropy of the surroundings increases as the heat given out by the hot coffee increases the dispersal of the surroundings.

R1.4 Figure 2 Both an exothermic reaction and a cooling coffee cup increase the entropy of the universe.

The change of the entropy of the surroundings, ΔS(surroundings), can be calculated from the enthalpy change in the system, ΔH(system), and the absolute temperature, T.

The change in entropy of the surroundings is $\frac{-\Delta H(\text{system})}{T}$

We have seen that exothermic reactions, with a negative value for ΔH(system), result in an increase in the entropy of the surroundings. This explains the inclusion of the negative sign when relating ΔH(system) to ΔS(surroundings).

$$\Delta S(\text{surroundings}) \propto -\Delta H(\text{system})$$

We are now in a position to understand why exothermic reactions are generally more common than endothermic reactions. The key is not the decrease in energy of the system but the associated increase in entropy of the surroundings.

The impact of a transfer of heat to the surroundings on its entropy will depend on the current state of dispersal. If the surroundings have a high temperature, the addition of a little extra heat will make little difference to the dispersal, but if the surroundings are cold, the same amount of heat causes a more dramatic change in entropy. This explains the inclusion of absolute temperature, T, in the denominator in the expression:

$$\Delta S(\text{surroundings}) \propto -\frac{1}{T}$$

The impact of an addition of heat depends on the present state of dispersal, as indicated by the absolute temperature.





A busy street is a 'hot' and disordered environment; a quiet library is a 'cold' and ordered environment. Which do you think would cause more disruption: sneezing in a busy street or in a quiet library?

An expression consistent with the above discussion is:

$$\Delta S(\text{surroundings}) = \frac{-\Delta H(\text{system})}{T} \qquad (T \text{ must be measured in K})$$

For the zinc/copper sulfate displacement reaction discussed, at $T = 25\,^{\circ}\text{C} = 298\,\text{K}$:

$$\Delta S(\text{surroundings}) = \frac{-217}{298}\,\text{kJ K}^{-1}\,\text{mol}^{-1} = +0.729\,\text{kJ K}^{-1}\,\text{mol}^{-1} = 729\,\text{J mol}^{-1}$$

We can now see the origins of the units used for entropy in the values tabulated earlier. Entropies are generally expressed in the units $J\,K^{-1}\,mol^{-1}$. These units are consistent with its characterization as a distribution of available energy.

If a system were at absolute zero (0 K), an additional small amount of heat energy would lead to an infinite increase in entropy. Such a state is impossible. Absolute zero can never be achieved.

Calculating total entropy changes and understanding endothermic reactions

The second law of thermodynamics tells us that for a spontaneous change:

$$\Delta S(\text{total}) = \Delta S(\text{system}) + \Delta S(\text{surroundings}) > 0$$

Substitute for ΔS(surroundings) from the expression developed earlier:

$$\Delta S(\text{total}) = \Delta S(\text{system}) - \frac{\Delta H(\text{system})}{T} > 0$$

This equation allows us to understand how endothermic reactions can occur. Endothermic reactions occur if the change in the entropy of the system can compensate for the negative entropy change of the surroundings produced as the heat is transferred from the surroundings to the system. For example, the strongly endothermic reaction

$$Ba(OH)_2{\cdot}8H_2O(s) + 2NH_4SCN(s) \rightarrow Ba(SCN)_2(aq) + 2NH_3(aq) + 10H_2O(l)$$

is possible because there is a very large increase in dispersal of matter and entropy of the system. Three moles of solid are converted to ten moles of liquid and three moles of compounds in aqueous solution.

This emphasizes a general point. We must consider the universe (i.e. both the system and the surroundings) when applying the second law of thermodynamics. Order may increase in local areas but only at the expense of greater disorder elsewhere in the universe. For chemical reactions, neither ΔH(system) nor ΔS(system) alone can reliably be used to predict the feasibility of a reaction.



Such local manifestations of order as the development of life, and the construction of beautiful buildings, are only possible at the expense of greater disorder generated elsewhere in the universe.

Photosynthesis is a remarkable reaction. There is a decrease in entropy of the system as the particles adopt more ordered structures and the reaction is endothermic as the system absorbs energy:

$$6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(s) + 6H_2O(l)$$

This, however, does not break the second law of thermodynamics as the increase in entropy of the Sun during the fusion reaction that provides the necessary light energy more than compensates for the local decrease in entropy in a green leaf. A ray of light connects the entropy changes in the leaf and those at the Sun.

Gibbs energy is a useful accounting tool

We have seen that for chemical reactions, neither ΔH(system) nor ΔS(system) alone can reliably be used to predict the feasibility of a reaction. The ultimate criterion for the feasibility of a reaction is:

$$\Delta S(\text{total}) = \Delta S(\text{system}) - \frac{\Delta H(\text{system})}{T} > 0$$

This expression can be tidied up. Multiplying by T (as it is always positive):

$$T\Delta S(\text{total}) = T\Delta S(\text{system}) - \Delta H(\text{system}) > 0$$

Multiplying by −1 and reversing the inequality:

$$-T\Delta S(\text{total}) = -T\Delta S(\text{system}) + \Delta H(\text{system}) < 0$$

This combination of entropy and enthalpy of a system gives a new function known as the **Gibbs energy** (ΔG(system)):

$$\Delta G(\text{system}) = \Delta H(\text{system}) - T\Delta S(\text{system}) = -T\Delta S(\text{total}) < 0$$

That is, ΔG(system) must be negative for a spontaneous process.

ΔG(system) = ΔH(system) – $T\Delta S$(system)
ΔG(system) must be negative for a spontaneous process.

ΔG(system) gives a measure of the quality of the energy available

Whereas ΔH(system) is a measure of the *quantity* of heat change during a chemical reaction, ΔG(system) gives a measure of the *quality* of the energy available. It is a measure of the energy which is free to do useful work rather than just leave a system as heat. Spontaneous reactions have negative Gibbs energy changes because they can do useful work. Josiah Willard Gibbs (1839–1903) was the first person to develop this concept.

For example, one mole of hydrogen releases 286 kJ of heat energy when it combines directly with oxygen:

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H^{\ominus} = -286\,\text{kJ mol}^{-1}$$

We saw earlier in **Question 9** that the standard entropy change associated with this reaction is $-164\,\text{J K}^{-1}\text{mol}^{-1}$.

These results can be combined to give the total entropy change for the reaction:

$$\Delta S(\text{total}) = \Delta S(\text{system}) - \frac{\Delta H(\text{system})}{T} > 0$$

$$= -164 + \frac{286 \times 10^3}{298} = -164 + 960 = 796\,\text{J K}^{-1}\,\text{mol}^{-1}$$

We see from this that it is not essential for all the heat to be transferred to the surroundings to produce the necessary increase in the total entropy. Enough energy must be transferred to the surroundings to compensate for the entropy decrease in the system, but the remaining energy is available to do useful work.

$$\text{necessary energy transferred to the surroundings} = 164 \times 298\,\text{J mol}^{-1}$$
$$= 48\,872\,\text{J mol}^{-1} = 48.9\,\text{kJ mol}^{-1}$$

$$\text{energy available to do work} = 286 - 48.9 = 237\,\text{kJ mol}^{-1}$$

This is the amount of energy that can be converted to electrical energy when hydrogen and oxygen react in a fuel cell (see Reactivity 3.2).

More generally:

$$\text{necessary energy transferred to the surroundings} = -\Delta S(\text{system}) \times T$$

$$\text{energy available to do work} = -\Delta H(\text{system}) + \Delta S(\text{system}) \times T$$
$$= -\Delta G(\text{system})$$

In Reactivity 3.2 we will see that for redox reactions ΔG is related to the cell potential.

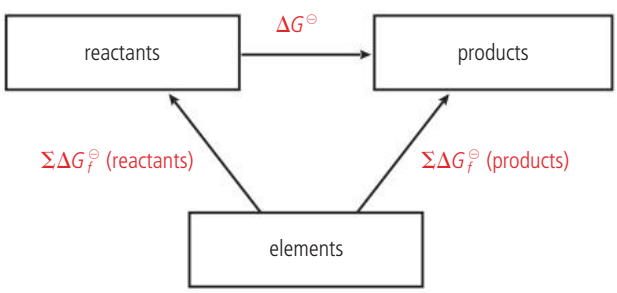
Calculating ΔG values

There are two routes to calculating changes in Gibbs energy during a reaction. $\Delta G^\ominus$ (at 298 K) can be calculated from tabulated values of $\Delta G_f^\ominus$ in the same way enthalpy changes are calculated. ΔG values are, however, very sensitive to changes in temperature, and ΔG values calculated using this method are not applicable when the temperature is changed. Changes in Gibbs energy at other temperatures can be obtained by applying the equation:

$$\Delta G(\text{system}) = \Delta H(\text{system}) - T\Delta S(\text{system})$$

Calculating ΔG from $\Delta G_f^\ominus$

$\Delta G^\ominus$ for reactions at 298 K can be calculated from $\Delta G_f^\ominus$ values in the same way $\Delta H^\ominus$ can be calculated from $\Delta H_f^\ominus$ values (Figure 3).



R1.4 Figure 3 A Gibbs energy cycle.

Worked example

Calculate $\Delta G^{\ominus}$ for the reaction:

$$2Al(s) + Fe_2O_3(s) \rightarrow 2Fe(s) + Al_2O_3(s)$$

from the following data.

Compound	$\Delta G_f^{\ominus}$ / kJ mol^{-1}
$Fe_2O_3(s)$	−742
$A_{l2}O_3(s)$	−1582

Comment on the significance of the value obtained.

Solution

First, write the chemical equation with the values below it:

$$\begin{array}{llll} 2Al(s) + Fe_2O_3(s) & \rightarrow & 2Fe(s) + Al_2O_3(s) & \\ 2 \times 0 \quad -742 & & 2 \times 0 \quad -1582 & \Delta G_f^{\ominus} \text{ / kJ mol}^{-1} \end{array}$$

Note: $\Delta G_f^{\ominus}$ (element) is zero by definition just as it is for $\Delta H_f^{\ominus}$ (element).

$$\Delta G^{\ominus} = \Sigma \Delta G_f^{\ominus}(\text{products}) - \Sigma \Delta G_f^{\ominus}(\text{reactants})$$
$$= -1582 - (-742)\ \text{kJ mol}^{-1}$$
$$= -840\ \text{kJ mol}^{-1}$$

The reaction is spontaneous under standard conditions.

Using $\Delta S^{\ominus}$ and $\Delta H^{\ominus}$ values to calculate ΔG at all temperatures

As the standard values of $\Delta G_f^{\ominus}$ refer to standard conditions, they can only be used to calculate $\Delta G^{\ominus}$ at 298 K. ΔG can be calculated at other temperatures using the equation:

$$\Delta G = \Delta H - T\Delta S$$

As ΔH and ΔS are effectively constant, $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ can be used in the equation:

$$\Delta G = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

Worked example

Calculate $\Delta G^{\ominus}$ at 298 K for the thermal decomposition of calcium carbonate from the following data.

Compound	$\Delta H_f^{\ominus}$ / kJ mol^{-1}	$S^{\ominus}$ / J K^{-1} mol^{-1}
$CaCO_3(s)$	−1207	+92.9
$CaO(s)$	−635	+39.7
$CO_2(g)$	−394	+214

Solution

First calculate $\Delta H^{\ominus}$.

Write the chemical equation with the $\Delta H_f^{\ominus}$ values in the appropriate places.

$$\begin{array}{llll} CaCO_3(s) & \rightarrow & CaO(s) + & CO_2(g) \\ -1207 & & -635 \quad -394 & \Delta H_f^{\ominus} / \text{kJ mol}^{-1} \end{array}$$

Using the equation

$$\Delta H^{\ominus} = \Sigma \Delta H_f^{\ominus}(\text{products}) - \Sigma \Delta H_f^{\ominus}(\text{reactants})$$
$$= (-635 + -394) - (-1207)\ \text{kJ mol}^{-1}$$
$$= +178\ \text{kJ mol}^{-1}$$

Now calculate the standard entropy change of reaction. As always, predict whether the value is positive or negative.

One mole of solid is converted to one mole of solid and one mole of gas. There is an increase in dispersal of matter and an increase in entropy. $\Delta S^{\ominus}$ is positive.

Now do the calculation:

$$\begin{array}{llll} CaCO_3(s) & \rightarrow & CaO(s) + & CO_2(g) \\ +92.9 & & +39.7 \quad +214 & S^{\ominus} / \text{J K}^{-1}\text{ mol}^{-1} \end{array}$$

Using the equation:

$$\Delta S^{\ominus} = \Sigma S^{\ominus}(\text{products}) - \Sigma S^{\ominus}(\text{reactants})$$
$$= (39.7 + 214) - (+92.9)\ \text{J K}^{-1}\ \text{mol}^{-1}$$
$$= +160.8\ \text{J K}^{-1}\text{ mol}^{-1}$$
$$= +161\ \text{J K}^{-1}\text{ mol}^{-1}$$

Now calculate the change in Gibbs energy of the reaction.

$$\Delta G = \Delta H^{\ominus} - T\Delta S^{\ominus}$$
$$= +178 - (298 \times 160.8 \times 10^{-3})\ \text{kJ mol}^{-1}$$
$$= +130\ \text{kJ mol}^{-1}$$

Note that as the temperature is 298 K, this value agrees with that calculated in the previous exercise using Gibbs energy of formation data.

Exercise

Q10. The equation for the complete combustion of methane is shown below.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

Which is the best description of the enthalpy and entropy changes for the process?

	$\Delta H^\ominus$	$\Delta S^\ominus$
A	+	+
B	+	−
C	−	+
D	−	−

Q11. Ammonium chloride dissolves in water spontaneously in an endothermic process. Identify the best explanation for these observations.

A Endothermic processes are energetically favourable.

B The bonds in solid NH_4Cl are very weak.

C The entropy change of the system drives the process.

D The entropy change of the surroundings drives the process.

Q12. The enthalpy and entropy changes for the reaction

$$A(s) + B(aq) \rightarrow C(aq) + D(g)$$

are $\Delta H^\ominus = 100\,kJ\,mol^{-1}$ and $\Delta S^\ominus = 100\,J\,K^{-1}\,mol^{-1}$

What does this tell you about the reaction?

A The reaction is not spontaneous at any temperature.

B The reaction is spontaneous at all temperatures.

C The reaction is spontaneous at all temperatures below 1000 °C.

D The reaction is spontaneous at all temperatures above 1000 K.

Q13. Calculate $\Delta G^\ominus$ for the thermal decomposition of calcium carbonate:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

from the following data, and comment on the significance of the value obtained.

Compound	$\Delta G_f^\ominus$ / kJ mol^{-1}
$CaCO_3(s)$	−1129
$CaO(s)$	−604
$CO_2(g)$	−394

Q14. Consider the reaction between aqueous copper sulfate and zinc.

$$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$$

$$\Delta H^\ominus = -217\,kJ\,mol^{-1};\ \Delta G^\ominus = -212\,kJ\,mol^{-1}$$

(a) Calculate the entropy change of the reaction at 298 K and comment on the value.

(b) Deduce how much electrical energy can be obtained from this reaction.

Reactivity 1.4.3 – ΔG and spontaneity

Reactivity 1.4.3 – At constant pressure, a change is spontaneous if the change in Gibbs energy, ΔG, is negative. Interpret the sign of ΔG calculated from thermodynamic data. Determine the temperature at which a reaction becomes spontaneous.	
ΔG takes into account the direct entropy change resulting from the transformation of the chemicals and the indirect entropy change of the surroundings resulting from the transfer of heat energy.	Reactivity 3.2 – How can electrochemical data also be used to predict the spontaneity of a reaction?

Using ΔG(system) to predict the feasibility of a change

In the previous section we defined the function ΔG(system) and saw that ΔG(system) must be negative for a spontaneous process.

$$\Delta G(\text{system}) = \Delta H(\text{system}) - T\Delta S(\text{system}) = -T\Delta S(\text{total}) < 0$$

You should note that ΔG is related to the total entropy change and this result is just a reformulation of the second law of thermodynamics. ΔG takes into account the direct entropy change resulting from the transformation of the chemicals in the system and the indirect entropy change of the surroundings resulting from the transfer of heat energy. We can use the expression for ΔG(system) to predict how a system changes as the temperature is changed.

As T is always positive, the above expression can be rearranged to give:

$$\Delta H(\text{system}) < T\Delta S(\text{system})$$

- At low temperatures when $T\Delta S(\text{system}) \approx 0$ this condition is met for all exothermic reactions as $\Delta H(\text{system}) < 0$.

We can think of the temperature, T, as a 'tap' which adjusts the significance of the term ΔS(system) in determining the spontaneity of the reaction.

- Endothermic reactions, which have a positive value of ΔS(system) can be spontaneous at higher temperatures when $T\Delta S(\text{system}) > \Delta H(\text{system})$.

The temperature $T_{\text{spontaneous}}$ at which an endothermic reaction becomes spontaneous can be determined from the equation:

$$T_{\text{spontaneous}}\,\Delta S(\text{system}) = \Delta H(\text{system})$$

which can be rearranged to give:

$$T_{\text{spontaneous}} = \frac{\Delta H(\text{system})}{\Delta S(\text{system})}$$

Worked example

(a) Give an equation for the boiling of water.

(b) Predict a sign for the enthalpy change and the entropy change for this process.

(c) Predict a value for the sign of ΔG at low and high temperatures.

(d) Suggest why water boils at 100 °C.

(e) Use the entropy values in the table on page 520 to calculate the entropy change for this process.

(f) Use the data below to calculate the enthalpy change for the process.

	$\Delta H_f^\ominus$ / kJ mol^{-1}
$H_2O(l)$	−286
$H_2O(g)$	−242

(g) Deduce the boiling point of water from your calculations. Describe any assumptions you have made.

Solution

(a) $H_2O(l) \rightarrow H_2O(g)$

(b) As there is an increase in moles of gas, ΔS(system) is positive. The process involves the breaking of intermolecular (hydrogen) bonds so ΔH(system) is positive.

(c) At low temperature: ΔG(system) ≈ ΔH(system) and so is positive.
At high temperature: ΔG(system) ≈ $-T\Delta S$(system) and so is negative.

(d) The change only occurs at higher temperatures where ΔG is negative.

$$\Delta G = 0 \text{ at } 100\,^\circ\text{C}$$

(e) $H_2O(l) \rightarrow H_2O(g)$

+70.0 +188.8 S / J K^{-1} mol^{-1}

$$\Delta S^\ominus = \Sigma S^\ominus(\text{products}) - \Sigma S^\ominus(\text{reactants})$$
$$= +188.8 - (70) = +118.8\,\text{J K}^{-1}\,\text{mol}^{-1}$$

(f) $$\Delta H^\ominus = \Sigma \Delta H_f^\ominus(\text{products}) - \Sigma \Delta H_f^\ominus(\text{reactants})$$
$$= -242 - (-286) = +44\,\text{kJ mol}^{-1}$$

(g) At the boiling point: ΔG(system) = ΔH(system) − $T\Delta S$(system) = 0

$$T_{\text{spontaneous}} = \frac{\Delta H(\text{system})}{\Delta S(\text{system})}$$

$$T_{\text{spontaneous}} = \frac{44\,\text{kJ mol}^{-1}}{118.8 \times 10^{-3}\,\text{kJ K}^{-1}\,\text{mol}^{-1}} = 370\,\text{K}$$

It is assumed that ΔH(system) and ΔS(system) do not change with temperature.

Do not forget to use consistent units for $\Delta H^\ominus$ and $\Delta S^\ominus$ when calculating ΔG. Temperatures in all Gibbs energy calculations must be in kelvin. The units of energy, J or kJ, should also be consistent.

Values of ΔG can only give information about the feasibility of a reaction. They give no information about the rate of the reaction. Some spontaneous reactions need to be heated to occur. The reactants need energy to overcome the activation energy barrier. This is discussed further in Reactivity 2.2.

The effect of ΔH, ΔS, and T on the spontaneity of the reaction

The effect of temperature on different reactions is summarized in the table below.

$\Delta H^\ominus$	$\Delta S^\ominus$	T	ΔG	Spontaneity
positive (endothermic)	positive (more disordered products)	low	positive $\approx \Delta H^\ominus$	not spontaneous
positive (endothermic)	positive (more disordered products)	high	negative $\approx -T\Delta S^\ominus$	spontaneous
positive (endothermic)	negative (more ordered products)	low	positive $\approx \Delta H^\ominus$	not spontaneous
positive (endothermic)	negative (more ordered products)	high	positive $\approx -T\Delta S^\ominus$	not spontaneous
negative (exothermic)	positive (more disordered products)	low	negative $\approx \Delta H^\ominus$	spontaneous
negative (exothermic)	positive (more disordered products)	high	negative $\approx -T\Delta S^\ominus$	spontaneous
negative (exothermic)	negative (more ordered products)	low	negative $\approx \Delta H^\ominus$	spontaneous
negative (exothermic)	negative (more ordered products)	high	positive $\approx -T\Delta S^\ominus$	not spontaneous

We will explore in Reactivity 3.2 how cell potentials can also be used to predict whether a reaction is spontaneous. This is because the ΔG value of a reaction and the cell potential are both measures of the useful electrical energy that can be obtained from a reaction.

Work through all the different sets of conditions to make sure that you agree with the results of this table. Do not attempt to memorize it!

Reactivity 3.2 – How can electrochemical data also be used to predict the spontaneity of a reaction?

Exercise

Q15. Which property of an element has a value of zero in its standard state?

I. $\Sigma\Delta H_f^\ominus$ II. $S^\ominus$ III. $\Sigma\Delta G_f^\ominus$

A I and II **B** I and III **C** II and III **D** I, II and III

Q16. Identify the combination of ΔH and ΔS which results in a reaction being spontaneous at low temperatures but non-spontaneous at higher temperatures.

A $\Delta S-$ and $\Delta H-$ **B** $\Delta S+$ and $\Delta H-$

C $\Delta S-$ and $\Delta H+$ **D** $\Delta S+$ and $\Delta H+$

Q17. Identify the combination of ΔH and ΔS which leads to a reaction that is **not** spontaneous at low temperatures but becomes spontaneous at higher temperatures.

A $\Delta H-$ and $\Delta S-$ **B** $\Delta H-$ and $\Delta S+$

C $\Delta H+$ and $\Delta S-$ **D** $\Delta H+$ and $\Delta S+$

Q18. The ΔH and ΔS values for the combustion of hydrogen are both negative. Which is the correct description of this reaction at different temperatures?

	Low temperature	High temperature
A	not spontaneous	not spontaneous
B	spontaneous	not spontaneous
C	spontaneous	spontaneous
D	not spontaneous	spontaneous

Q19. Magnesium carbonate, $MgCO_3$, is a white solid that occurs in nature as the mineral magnesite.

Magnesite decomposes to the oxide at temperatures above 540 °C.

$$MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$$

Identify the correct description of this reaction at 800 °C.

	ΔG	ΔH	ΔS
A	+	+	+
B	+	−	−
C	−	+	+
D	−	+	−

Q20. Calculate ΔG at 2000 K for the thermal decomposition of calcium carbonate from the data given in the worked example.

Q21. The standard enthalpy change for the formation of ethanol, $C_2H_5OH(l)$, and its molar entropy are given in Section 13 of the data booklet.

(a) Write an equation for the formation of ethanol.

(b) Calculate the entropy change for this process. The entropies of its constituent elements are:

$C(graphite) = 5.7\ J\ K^{-1}\ mol^{-1}$

$H_2(g) = 130.6\ J\ K^{-1}\ mol^{-1}$

$O_2(g) = 102.5\ J\ K^{-1}\ mol^{-1}$

(c) Calculate the standard Gibbs energy change of formation of ethanol at 500 K.

(d) Deduce whether the reaction is spontaneous at 500 K, and give a reason.

(e) Predict the effect, if any, of an increase in temperature on the spontaneity of this reaction.

Q22. **(a)** Use data from Section 13 of the data booklet and additional data ($\Delta H_f^{\ominus}(H_2O(s)) = -292\ kJ\ mol^{-1}$) to calculate the enthalpy change that occurs when ice melts.

(b) The entropy change when ice melts is $22.0\ J\ K^{-1}\ mol^{-1}$. Deduce a value for the melting point of ice.

Reactivity 1.4.4 – ΔG and equilibrium

Reactivity 1.4.4 – As a reaction approaches equilibrium, ΔG becomes less negative and finally reaches zero.	
Perform calculations using the equation $\Delta G = \Delta G^{\ominus} + RT\ln Q$ and its application to a system at equilibrium $\Delta G^{\ominus} = -RT\ln K$.	
The equations are given in the data booklet.	Reactivity 2.3 – What is the likely composition of an equilibrium mixture when $\Delta G^{\ominus}$ is positive?

Gibbs energy and equilibrium

So far, we have considered reactions in which it is assumed that all the reactants are converted into products.

The equilibrium mixture when $\Delta G^{\ominus} = 0$

Consider the following hypothetical reaction in which an ideal gas reactant is converted into an ideal gas product.

$$\text{reactant(g)} \rightarrow \text{product(g)}$$

For this idealized reaction there are no bonds broken or formed during the reaction, so $\Delta H = 0$.

There is no change in entropy as 1 mol of gas is converted to 1 mol of gas, so $\Delta S = 0$.

From this we can deduce that $\Delta G = 0$.

We have seen that spontaneous change can only occur if $\Delta G < 0$, so what happens in this case?

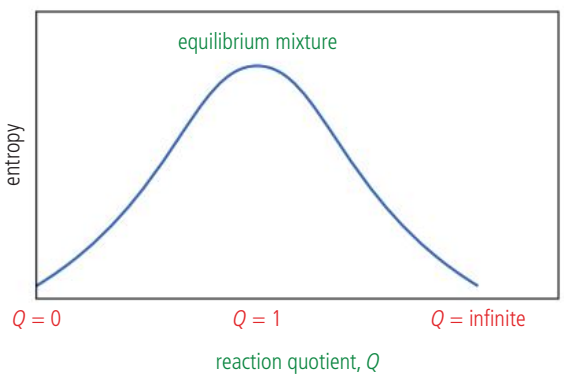
Challenge yourself

1. Consider the enthalpy and entropy changes for the same reaction in the reverse direction:

$$\text{product(g)} \rightarrow \text{reactant(g)} \qquad \Delta G^{\ominus} = 0$$

What does this suggest about the direction of change?

The key is that a mixture of reactant and product has higher entropy than pure samples of reactant or product. The total entropy reaches a maximum when we have equal amounts of reactant and product (Figure 4).



R1.4 Figure 4 The total entropy of a reaction mixture for the reaction involving two hypothetical ideal gases as the reaction progresses. Starting with either pure reactants or pure products, the total entropy increases as the reaction moves towards equilibrium. The equilibrium mixture consists of equal amounts of products and reactants.

Challenge yourself

2. Explain the shape of the graph in Figure 4.

The extent of the reaction can be characterized by the ratio of products to reactants called the **reaction quotient, *Q*.** In this simple example**:**

$$Q = \frac{[\text{products}]}{[\text{reactants}]}$$

The position of equilibrium corresponds to a maximum value of entropy.

At the beginning of the reaction, $Q = 0$ and if the reaction goes to completeness Q = infinite. We see that in this case the reaction quotient increases as the reaction moves to equilibrium.

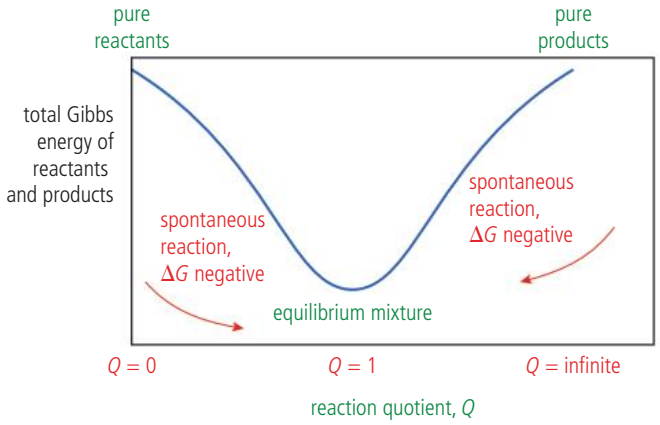
The reaction quotient (Q) measures the relative amounts of products and reactants present during a reaction at a particular point in time. Q is the equilibrium expression with non-equilibrium concentrations.

$$\text{equilibrium value of } Q_{eqm} = \frac{[\text{products}]_{eqm}}{[\text{reactants}]_{eqm}} = 1$$

The reaction quotient is discussed in more detail in Reactivity 2.3 on page 646.

In this hypothetical example the system reaches a minimum of Gibbs energy at equilibrium (Figure 5).

$$\Delta G(\text{system}) = -T\Delta S(\text{total}) < 0$$



R1.4 Figure 5 The total Gibbs energy of a reaction mixture as the reaction progresses. Starting with either pure reactants or pure products, the Gibbs energy decreases as the reaction moves towards equilibrium. As the change in Gibbs energy for the complete reaction, $\Delta G^{\ominus}$, is 0 the equilibrium mixture consists of an equimolar mixture of products and reactants, $K = 1$.

As discussed in more detail in Reactivity 2.3, the value of the reaction quotient at equilibrium is called the equilibrium constant, K.

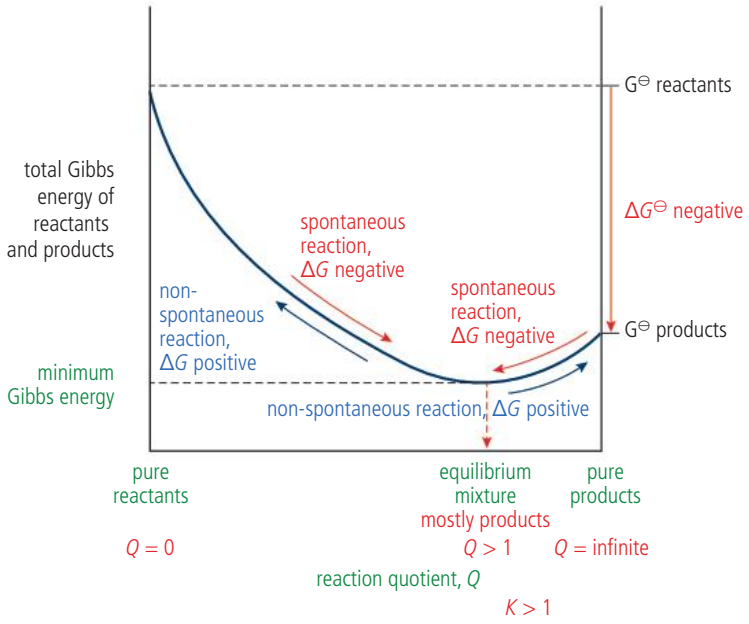
$$K = \frac{[\text{products}]_{eqm}}{[\text{reactants}]_{eqm}} = 1 \text{ when } \Delta G^{\ominus}_{\text{reaction}} = 0$$

The equilibrium mixture when $\Delta G^{\ominus}$ is negative

Now we consider what happens to the total Gibbs energy during a reaction when $\Delta G^{\ominus}$ is negative.

- At the start of the reaction, the total Gibbs energy of the reactants is greater than that of the products so the reaction proceeds in the forward direction and Q increases.
- As the reaction continues converting reactants to products, the Gibbs energy of the system decreases until it reaches equilibrium. Q equals the equilibrium constant K.
- Once equilibrium is reached, all possible changes would lead to an increase in Gibbs energy and a decrease in the total entropy of the universe and do not happen.
- The position of equilibrium corresponds to a mixture with more products than reactants.

Figure 6 shows how the Gibbs energy changes with the composition of the mixture. As the Gibbs energy decreases in both directions, the reaction must go through a composition which corresponds to the minimum value of Gibbs energy. This is the equilibrium state where the net reaction stops. The relative amounts of reactants and products at equilibrium, the *composition* of this equilibrium mixture, is determined by the difference in Gibbs energy between the reactants and products.

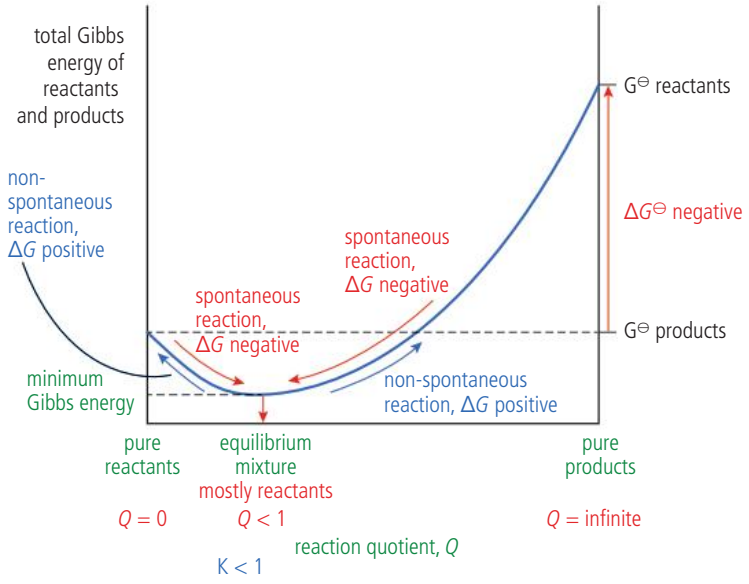


R1.4 Figure 6 The Gibbs energy of the pure reactants is greater than the Gibbs energy of the pure products. $\Delta G^\ominus$ is negative. As the forward reaction progresses, the Gibbs energy decreases and reaches a minimum at equilibrium. The equilibrium mixture consists largely of products, $K > 1$.

$$K = \frac{[\text{products}]_{\text{eqm}}}{[\text{reactants}]_{\text{eqm}}} > 1 \text{ when } \Delta G^\ominus < 0$$

The equilibrium mixture when $\Delta G^\ominus$ is positive

Similar arguments can be used to explain why the equilibrium mixture contains more reactants than products when $\Delta G^\ominus$ is positive (Figure 7).



R1.4 Figure 7 The Gibbs energy of reaction when the pure reactants have less Gibbs energy than the pure products. $\Delta G^\ominus$ is positive. As the forward reaction progresses, the Gibbs energy decreases. The equilibrium mixture consists largely of reactants. $K < 1$.

Equilibrium occurs when a reaction mixture has the minimum value of Gibbs energy.

Challenge yourself

3. For the reaction A → B, $K = \frac{[\text{products}]}{[\text{reactants}]} = \frac{[B]}{[A]}$

Find a mathematical function of K which gives values of $\Delta G^{\ominus}$ consistent with the previous discussion.

The equilibrium constant K is related to $\Delta G^{\ominus}$

We have identified two terms which relate to the position of equilibrium:

- K, the equilibrium constant
- $\Delta G^{\ominus}$, the change in Gibbs energy.

The relationship between these terms is outlined in the table below.

$\Delta G^{\ominus}$	Equilibrium mixture	K
negative	mainly products	$K > 1$
positive	mainly reactants	$K < 1$
0	appreciable amounts of both reactants and products	$K = 1$

More formally we can see that the relationship is summarized by the equation:

$$\Delta G^{\ominus} = -RT \ln K$$

This equation is given in Section 1 of the data booklet. $\Delta G^{\ominus}$ is the standard Gibbs energy change of the reaction; R is the gas constant ($8.31\,\text{J K}^{-1}\,\text{mol}^{-1}$), T is the absolute temperature in kelvin, and $\ln K$ is the natural logarithm of the equilibrium constant, K. Note the constant RT has the same units as $\Delta G^{\ominus}$, as expected.

The equation can be used to calculate the equilibrium constant from the standard Gibbs energy change of a reaction and vice versa. This can be useful in situations where the equilibrium constant is difficult to measure directly, for example, because a reaction may be too slow to reach equilibrium, or where the amounts of some of the components are too small to measure.

The equilibrium constant for a reaction is determined by the sign and value of its Gibbs energy change, $\Delta G^{\ominus}$, through the equation $\Delta G^{\ominus} = -RT \ln K$.

As we see in Reactivity 2.3 the reaction quotient, Q, and equilibrium constant, K, both take into account the stoichiometry of the reaction. For a more general reaction:

$aA + bB \rightleftharpoons cC + dD$

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Worked example

The esterification reaction that produces ethyl ethanoate has a Gibbs energy change $\Delta G^{\ominus} = -4.38\,\text{kJ mol}^{-1}$.

$$CH_3COOH(aq) + C_2H_5OH(aq) \rightleftharpoons CH_3COOC_2H_5(aq) + H_2O(aq)$$

Calculate the value of the equilibrium constant of this reaction at 298 K.

Solution

$$\Delta G^{\ominus} = -RT \ln K$$

$$\therefore \quad -4.38 \times 1000\,\text{J mol}^{-1} = -(8.31\,\text{J K}^{-1}\,\text{mol}^{-1}) \times (298\,\text{K}) \times \ln K$$

$$\ln K = \frac{4380\,\text{J mol}^{-1}}{2478\,\text{J mol}^{-1}} = 1.77$$

$$\therefore \quad K = e^{1.77} = 5.8$$

Reactivity 2.3 – What is the likely composition of an equilibrium mixture when $\Delta G^{\ominus}$ is positive?

The table below summarizes the relationship between $\Delta G^\ominus$ and the extent of reaction.

$\Delta G^\ominus$	Extent of reaction
$\Delta G^\ominus > +30\,\text{kJ mol}^{-1}$	Spontaneous change impossible: no reaction. $K \approx 0$
$0\,\text{kJ mol}^{-1} < \Delta G^\ominus < +30\,\text{kJ mol}^{-1}$	Partial reaction producing equilibrium mixture. $K < 1$
$\Delta G^\ominus = 0\,\text{kJ mol}^{-1}$	Partial reaction producing equilibrium mixture. $K = 1$
$0\,\text{kJ mol}^{-1} > \Delta G^\ominus > +30\,\text{kJ mol}^{-1}$	Partial reaction producing equilibrium mixture. $K > 1$
$\Delta G^\ominus < -30\,\text{kJ mol}^{-1}$	Complete reaction. $K >> 1$

The reaction quotient and Gibbs energy changes

Exercise

Q23. Which of the following correctly describes the entropy and Gibbs energy of a system at equilibrium?

	Entropy, S	Gibbs energy, G
A	maximum value	maximum value
B	minimum value	maximum value
C	maximum value	minimum value
D	minimum value	minimum value

Q24. What signs of $\Delta H^\ominus$ and $\Delta S^\ominus$ result in a complete reaction at all temperatures?

	$\Delta H^\ominus$	$\Delta S^\ominus$
A	−	−
B	+	−
C	−	+
D	+	+

Q25. Which conditions correspond to a system at equilibrium?

I. The entropy of the system is at a maximum.

II. The Gibbs energy of the system is at a minimum.

III. $\Delta G^\ominus = 0$

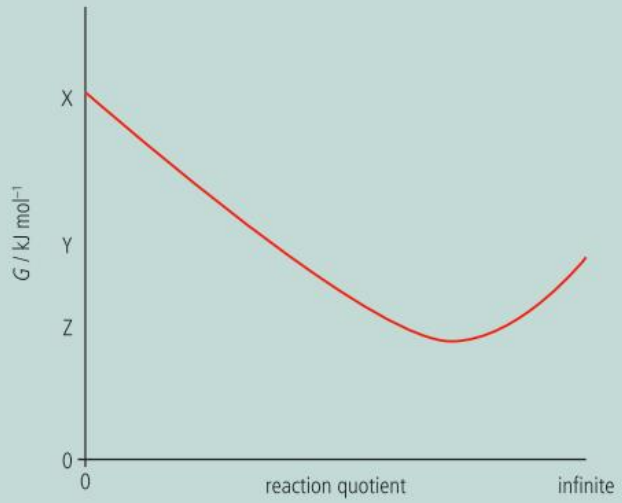
A I and II only **B** I and III only **C** II and III only **D** I, II and III

Q26. Which values correspond to a reaction that can be reversed by changing the temperature?

	$\Delta H^\ominus$	$\Delta S^\ominus$
I.	−	−
II.	+	−
III.	+	+

A I and II only **B** I and III only **C** II and III only **D** I, II and III

Q27. The graph shows how the Gibbs energy of a mixture of reactants and products changes with the reaction quotient.



Identify the Gibbs energy at equilibrium and $\Delta G^{\ominus}$ from the graph.

	G at equilibrium	$\Delta G^{\ominus}$
A	X – Z	X – Y
B	Y – Z	Y – X
C	Z	X – Y
D	Z	Y – X

Q28. What is the sign of $\Delta G^{\ominus}$ for a reaction when:

(a) $K = 1$ **(b)** $K > 1$ **(c)** $K < 1$

Q29. Use the equation $\Delta G = \Delta G^{\ominus} + RT\ln Q$ to show the reaction quotient at equilibrium equals the equilibrium constant.

Q30. Propene reacts with hydrogen in the presence of a nickel catalyst to form propane.

$$C_3H_6(g) + H_2(g) \rightarrow C_3H_8(g)$$

$\Delta H^{\ominus} = -123\,\text{kJ mol}^{-1}$; $\Delta S^{\ominus} = -128\,\text{J K}^{-1}\,\text{mol}^{-1}$

Estimate the temperature range in which a mixture of all three gases will be present.

Q31. Iodine reacts with hydrogen to form hydrogen iodide in the gaseous state.

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

The equilibrium constant at 500 K is 160.

Determine ΔG for the reaction at this temperature.

Q32. **(a)** What is the value of $\Delta G^{\ominus}$ for a reaction in which $K = 1$?

(b) Nitrogen oxide, NO, is oxidized in the air to NO_2.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

At 298 K, the value of K for this reaction is 1.7×10^{12}. Calculate the value of $\Delta G^{\ominus}$ for the reaction.

Guiding Question revisited

What determines the direction of chemical change?

In this chapter we introduced the concept of entropy, S, which is a measure of the dispersal or distribution of matter and/or energy. We have seen that entropy determines the direction of reactions. Reactions can occur spontaneously if the entropy of the universe increases. These ideas can be summarized as follows:

- Changes are spontaneous if they correspond to an increase in total entropy of the systems and the surroundings.
- The changes in entropy of the surroundings are related to the enthalpy change of the system and the temperature. When heat is transferred to the surroundings during exothermic reactions, the entropy of the surroundings increases.
- Endothermic reactions are less common but can be spontaneous if the increase in the entropy of the system is sufficient to offset the decrease in entropy of the surroundings that occurs when heat is transferred from the surroundings to the system.
- The total entropy change can be expressed in terms of the Gibbs energy of a system. The direction of spontaneous change is the direction of decreasing Gibbs energy. A reaction is spontaneous if the standard Gibbs energy change is negative.
- $-\Delta G$ is the useful energy that can be obtained from a chemical reaction.
- The direction of some reactions can be changed by altering the temperature: $\Delta G(\text{system}) = \Delta H(\text{system}) - T\Delta S(\text{system})$
- The standard Gibbs energy change at 298 K can be calculated from the standard free energies of formation. The Gibbs energy change at other temperatures can be calculated from enthalpy and entropy changes.
- The standard Gibbs energy depends on the composition of the reaction system.
- A system is at equilibrium when $\Delta G = 0$. As a reaction approaches equilibrium, the reaction quotient approaches the equilibrium constant.
- Equilibrium constants and standard Gibbs energy changes are related by the equation:

$$\Delta G^{\ominus} = -RT \ln K$$

Practice questions

1. Which reaction has the greatest increase in entropy?

A $SO_2(g) + 2H_2S(g) \rightarrow 2H_2O(l) + 3S(s)$

B $CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$

C $CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + C_2H_2(g)$

D $N_2(g) + O_2(g) \rightarrow 2NO(g)$

2. Which change will **not** increase the entropy of a system?

A increasing the temperature

B changing the state from liquid to gas

C mixing different types of particles

D a reaction where four moles of gaseous reactants changes to two moles of gaseous products

3. What is the standard Gibbs energy change, $\Delta G^\ominus$ in kJ, for the following reaction?

$$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$$

Compound	$\Delta G_f^\ominus$ / kJ mol^{-1}
$C_2H_5OH(l)$	−175
$CO_2(g)$	−394
$H_2O(g)$	−229
$O_2(g)$	0

A −1650 **B** −1300 **C** −448 **D** +1300

4. What is the standard entropy change, $\Delta S^\ominus$, for the following reaction?

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

	CO(g)	$O_2(g)$	$CO_2(g)$
$S^\ominus$ / J K^{-1} mol^{-1}	198	205	214

A −189 **B** −173 **C** +173 **D** +189

5. A reaction has a standard enthalpy change, $\Delta H^\ominus$, of +10.00 kJ mol^{-1} at 298 K. The standard entropy change, $\Delta S^\ominus$, for the same reaction is +10.00 J K^{-1} mol^{-1}. What is the value of $\Delta G^\ominus$ for the reaction in kJ mol^{-1}?

A +9.75 **B** +7.02 **C** −240 **D** −2970

6. What are the signs for the entropy changes associated with this reaction?

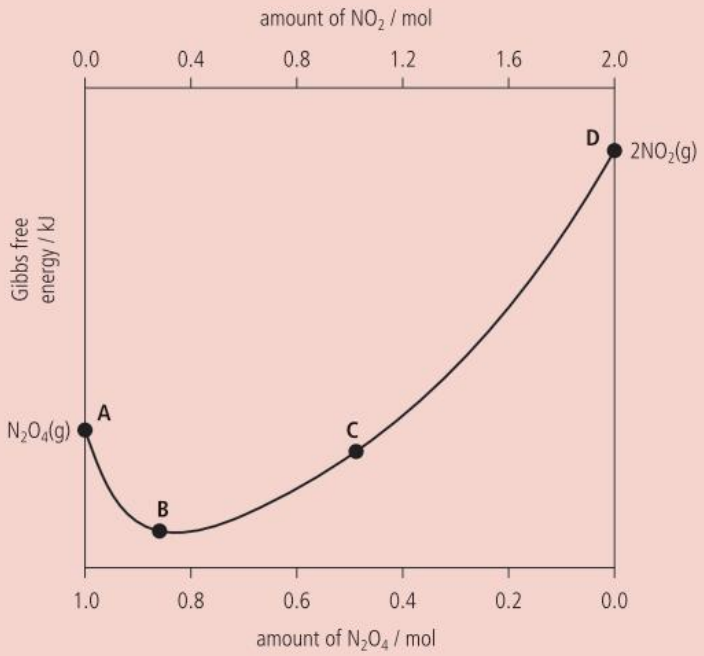
$$H_2O(g) \rightarrow H_2O(l)$$

	$\Delta S_{surroundings}$	ΔS_{system}
A	+	−
B	+	+
C	−	−
D	−	+

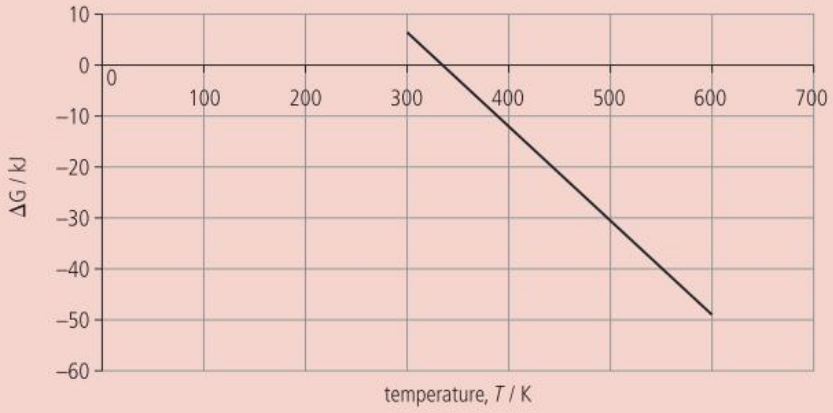
7. The graph shows the Gibbs energy of a mixture of $N_2O_4(g)$ and $NO_2(g)$ in different proportions.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Which point on the graph shows the system at equilibrium?



8. The graph shows values of ΔG for a reaction at different temperatures.



Which statement is correct?

A The standard entropy change of the reaction is negative.

B The standard enthalpy change of the reaction is positive.

C At higher temperatures, the reaction becomes less spontaneous.

D The standard enthalpy change of the reaction is negative.

9. An equilibrium exists between PCl_3 and PCl_5.

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

(a) Calculate the standard enthalpy change ($\Delta H^{\ominus}$) for the forward reaction in kJ mol^{-1}.

$\Delta H_f^{\ominus}$ $PCl_3(g) = -306.4$ kJ mol^{-1}

$\Delta H_f^{\ominus}$ $PCl_5(g) = -398.9$ kJ mol^{-1} (1)

(b) Calculate the entropy change, ΔS, in J K^{-1} mol^{-1}, for this reaction. (1)

Substance	Entropy J K^{-1} mol^{-1}
$PCl_3(g)$	311.7
$PCl_5(g)$	364.5
$Cl_2(g)$	223.0

(c) Calculate the Gibbs energy change (ΔG), in kJ mol^{-1}, for this reaction at 25°C. Use your answers to parts **(a)** and **(b)** and Section 1 of the data booklet.

If you did not obtain an answer in parts **(a)** or **(b)** use −87.6 kJ mol^{-1} and −150.5 J K^{-1} mol^{-1} respectively, but these are not the correct answers. (2)

(d) Determine the equilibrium constant, K, for this reaction at 25 °C, referring to Section 1 of the data booklet.

If you did not obtain an answer in part **(c)**, use $\Delta G = -43.5$ kJ mol^{-1}, but this is not the correct answer. (2)

(Total 6 marks)

10. Calcium carbonate is heated to produce calcium oxide, CaO.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

Thermodynamic data for the decomposition of calcium carbonate is given in the table.

Substance	$\Delta H_f^{\ominus}$ / kJ mol^{-1}	$S^{\ominus}$ / J K^{-1} mol^{-1}
$CaCO_3(s)$	−1207	93
$CaO(s)$	−635	40
$CO_2(g)$	−393.5	214

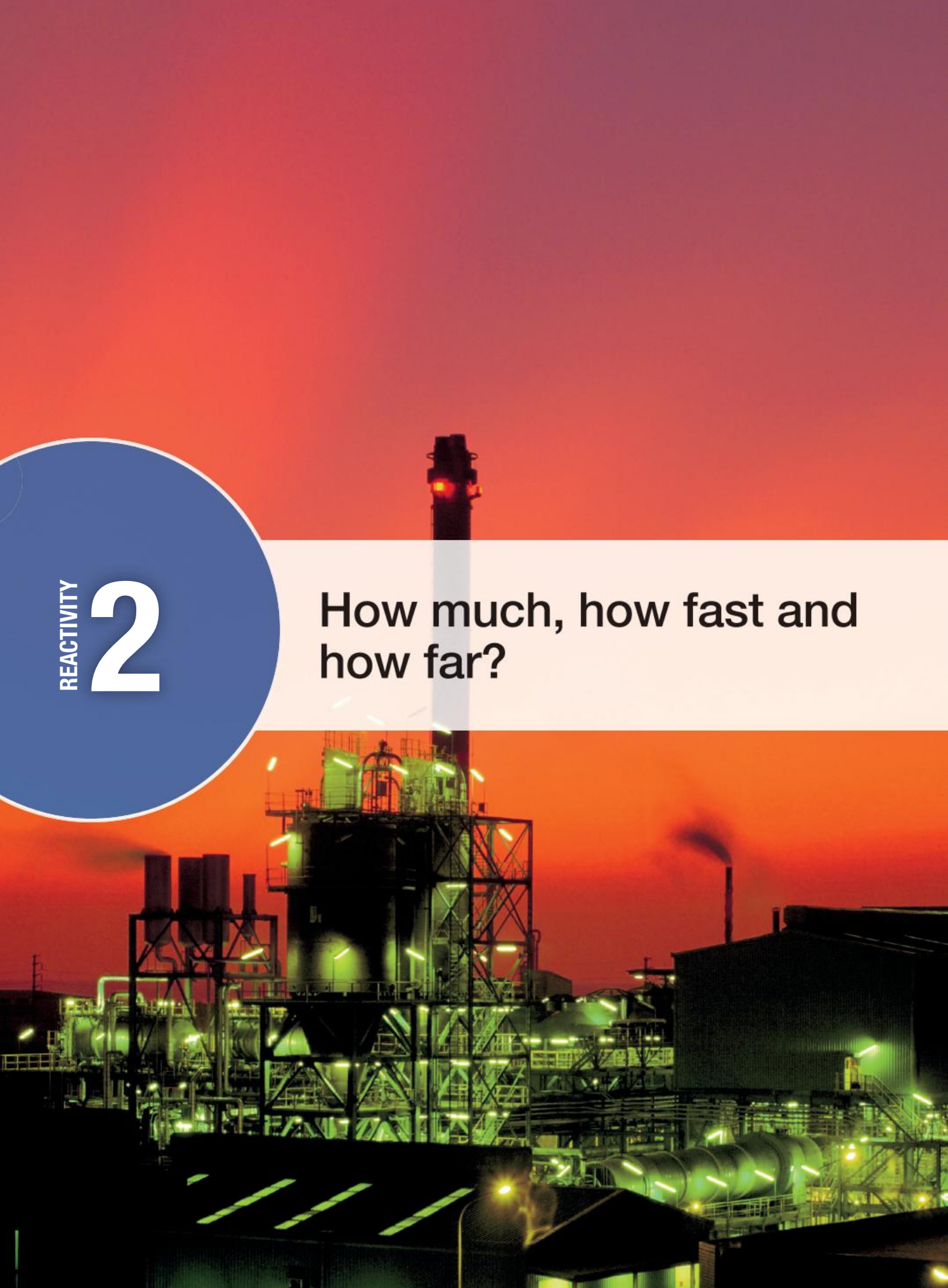
(a) Calculate the enthalpy change of reaction, ΔH, in kJ mol^{-1}, for the decomposition of calcium carbonate. (2)

(b) Calculate the change in entropy, ΔS, in J K^{-1} mol^{-1}, for the decomposition of calcium carbonate. (1)

(c) Determine the temperature, in K, at which the decomposition of calcium carbonate becomes spontaneous, using your answers to parts **(a)** and **(b)** and Section 1 of the data booklet.

If you did not obtain an answer in parts **(a)** or **(b)**, use $\Delta H = 190\,\text{kJ mol}^{-1}$ and $\Delta S = 180\,\text{J K}^{-1}\,\text{mol}^{-1}$, but these are not the correct answers. (2)

(Total 5 marks)



REACTIVITY

2 How much, how fast and how far?



A Taiwanese petrochemical plant. This plant is used for the production of ethene (C_2H_4) via a process called cracking. Larger organic molecules found in natural gas and the naptha component of crude oil are split into smaller molecules for use in a number of chemical processes such as polymerisation to make plastics. Ethene is one of the most widely manufactured organic compounds with about 200 million tonnes produced anually.

Between 1800 and the mid 2020s, the global population grew from 1 billion to over 8 billion. To support this growth, large-scale production of chemicals has been required to meet the demand for essential feedstock in industries such as agriculture, construction, oil and gas, and pharmaceuticals. For example, each year, 250 million tonnes of sulfuric acid is produced world-wide for use in the production of fertilizers, steel processing, petroleum refining, and as a solvent in many industrial processes. In order to effectively support this demand, chemists must understand the nature of chemical change so that they are able to quantify the amounts of chemicals involved and maximize the rate of and yield in their production.

Reactivity 2.1 explores the reacting ratios in chemical reactions, a study known as stoichiometry, and how these ratios can be used to determine the quantities of reactants and products. In Reactivity 2.2, we consider a range of techniques for measuring the rate of a chemical process and the theory behind the factors that affect it, including the role of catalysts, The application of this knowledge greatly enhances the efficiency with which we can carry out chemical reactions.

HL Further mathematical relationships identified in experimental data will provide us with an insight into possible mechanisms by which reactions take place and the determination of quantities such as the rate constant and activation energy.

In Reactivity 2.3, we investigate the reversible nature of chemical processes and determine how we are able to increase the yield of desired products by manipulating reaction conditions. Again, the use of mathematical approaches will play a key role in our ability to quantify the composition of reaction mixtures and analyse chemical change.

Central to this chapter are the principles of Green Chemistry. Maximizing atom economy, rate and yield whilst minimizing waste and energy consumption are key tenets of this framework, and allow us to make more sustainable decisions in relation to the design of chemical processes.

SKILLS

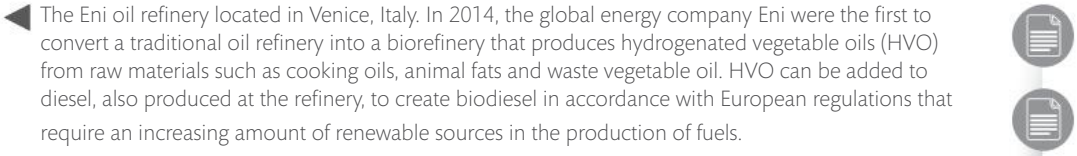
Much of the content in Reactivity 2 uses the mathematical tools given in the Skills in the study of chemistry chapter. There are also links to related lab work using these tools in each chapter.



REACTIVITY

2.1 How much? The amount of chemical change





The Eni oil refinery located in Venice, Italy. In 2014, the global energy company Eni were the first to convert a traditional oil refinery into a biorefinery that produces hydrogenated vegetable oils (HVO) from raw materials such as cooking oils, animal fats and waste vegetable oil. HVO can be added to diesel, also produced at the refinery, to create biodiesel in accordance with European regulations that require an increasing amount of renewable sources in the production of fuels.

Nature of Science

The negative impacts of large-scale chemical industries such as fuel production place a responsibility on scientists to continually strive for greater efficiency and sustainability in the processes and products we use. This approach is described by the principles of Green Chemistry that identify ways to reduce or eliminate the use and generation of hazardous substances.

Guiding Question

How are chemical equations used to calculate reacting ratios?

We can trace the birth of chemistry as a true science back to the first successful attempts to quantify (or measure) chemical change. At the heart of this endeavour is the relationship between the amount of reactants and products in a chemical equation. This is known as **stoichiometry**.

The term stoichiometry is derived from two Greek words – *stoicheion* for element and *metron* for measure. Stoichiometry describes the **reacting ratios** during chemical reactions. As we know that matter is conserved during chemical change, stoichiometry is a form of book-keeping at the atomic level. It enables chemists to determine what amounts of substances they should react together and enables them to predict how much product they will obtain. The application of stoichiometry closes the gap between what is happening on the atomic scale and what can be measured.

In many ways, you can consider this chapter as a toolkit for the mathematical content in much of the course. It covers the universal language of chemistry, **chemical equations**, and their application to predict the masses, volumes and concentrations of reactants and products involved, as well as tools for quantifying the efficiency of these processes.

Reactivity 2.1.1 – Chemical equations

Reactivity 2.1.1 – Chemical equations show the ratio of reactants and products in a reaction.	
Deduce chemical equations when reactants and products are specified.	
Include the use of state symbols in chemical equations.	Reactivity 3.2 – When is it useful to use half-equations?



Antoine-Laurent Lavoisier, French chemist (1743–1794).

Chemical equations summarize chemical change

Antoine-Laurent Lavoisier (1743–1794) is often called the 'father of chemistry'. Among his many accomplishments, he established an understanding of combustion as a process involving combination with oxygen from the air, and recognized that matter retains its mass through chemical change, leading to the law of conservation of mass. He also compiled the first extensive list of elements in his book *Elements of Chemistry* (1789). In short, he changed chemistry from a qualitative to a quantitative science. But, as an unpopular tax collector in France during the French Revolution and Terror, he was tried for treason and guillotined in 1794. One and a half years after his death he was exonerated, and his early demise was recognized as a major loss to France.

The formation of compounds from elements is an example of **chemical change** and can be represented by a chemical equation. A chemical equation is a representation, using chemical symbols, of the simplest ratio of atoms, as elements or in compounds, undergoing chemical change. The left-hand side of the equation shows the **reactants** and the right-hand side shows the **products**.

For example:

copper + chlorine → copper(II) chloride

$Cu + Cl_2 \rightarrow CuCl_2$

As atoms are neither created nor destroyed during a chemical reaction, *the total number of atoms of each element must be the same on both sides of the equation*. This is known as **balancing the equation**, and uses numbers called **stoichiometric coefficients** to denote the number of units of each term in the equation. A correctly balanced equation indicates the ratio of reactants and products in the reaction.

A chemical equation shows:

reactants —(direction of change)→ products

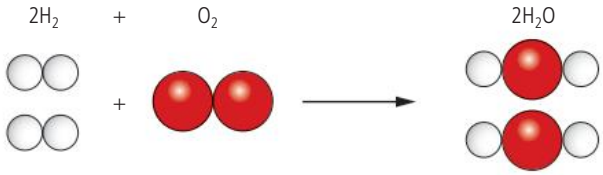
For example:

hydrogen + oxygen → water

$2H_2 + O_2 \rightarrow 2H_2O$

coefficients

We now have an identical number of each atom on both sides of the chemical equation.



When hydrogen and oxygen react to form water, the atoms are rearranged, but the number of atoms of each element remains the same.

	total on left side	total on right side
hydrogen	4	4
oxygen	2	2

Note that when the coefficient is 1, this does not need to be explicitly stated.

TOK

Chemical equations are the universal language of chemistry. What other languages are universal, and to what extent do they help or hinder the pursuit of knowledge?



A satellite image of the Fukushima Daiichi Nuclear Power Plant following three hydrogen explosions in the wake of the 2011 Tōhoku earthquake and tsunami. After the earthquake disrupted the electricity grid in the area, the emergency generators were then flooded by the tsunami preventing the cooling of the reactor. Without a functioning cooling system, the extremely high temperatures around the fuel rods caused the breakdown of steam inside the reactor to form hydrogen gas which formed an explosive mixture with atmospheric oxygen.

Chemical equations are used to show all types of reactions in chemistry, including reactions of decomposition, combustion, neutralization, and so on. Examples of these are given below and you will come across very many more during this course. Learning to write equations is an important skill in chemistry, which develops quickly with practice.

Worked example

Write an equation for the decomposition reaction of sodium hydrogencarbonate ($NaHCO_3$) into sodium carbonate (Na_2CO_3), water (H_2O), and carbon dioxide (CO_2) on heating.

Solution

First write the information from the question in the form of an equation, and then check the number of atoms of each element on both sides of the equation.

$$NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

	total on left side	total on right side
sodium	1	2
hydrogen	1	2
carbon	1	2
oxygen	3	6

In order to balance this, we introduce a coefficient, 2, on the left.

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

Finally check that the equation is now balanced for all elements.

	total on left side	total on right side
sodium	2	2
hydrogen	2	2
carbon	2	2
oxygen	6	6

Note that **state symbols** are commonly included in chemical equations as an additional layer of detail to indicate the physical state of a substance: solid (s), liquid (l), gas (g) or an aqueous solution (aq).

An equation, by definition, has to be *balanced*, so do not expect this to be specified in a question. After you have written an equation, *always* check the numbers of atoms of each element on both sides to ensure the equation is correctly balanced.

When a question refers to 'heating' a reactant or to 'thermal decomposition', this does not mean the addition of oxygen, only that heat is the source of energy for the reaction. If the question refers to 'burning' or 'combustion', this indicates that oxygen is a reactant.

Reactivity 3.2 – When is it useful to use half-equations?

We can also present some chemical equations as two half-equations. In this case, each half-equation identifies elements that have lost and gained electrons during a chemical reaction. These processes are called oxidation and reduction respectively. Species that have not been involved in electron transfer are ignored. This is discussed in more detail in Reactivity 3.2.

The four state symbols are as follows:

Physical state	State symbol
solid	(s)
liquid	(l)
gas	(g)
aqueous	(aq)

Nature of Science

Early ideas to explain chemical change in combustion and rusting included the 'phlogiston' theory. This proposed the existence of a fire-like element that was released during these processes. The theory seemed to explain some of the observations of its time, although these were purely qualitative. It could not explain later quantitative data showing that substances actually gain rather than lose mass during burning. In 1783, Lavoisier's work on oxygen confirmed that combustion and rusting involve combination with oxygen from the air, so overturning the phlogiston theory. This is a good example of how the evolution of scientific ideas, such as how chemical change occurs, is based on the need for theories that can be tested by experiment. Where results are not compatible with the theory, a new theory must be put forward, which must then be subject to the same rigour of experimental test.

When balancing an equation, change the stoichiometric coefficient but never change the subscript in a chemical formula.

Exercise

Q1. Write balanced chemical equations, including state symbols, for the following reactions:

(a) The decomposition of copper(II) carbonate powder ($CuCO_3$) into copper(II) oxide powder (CuO) and carbon dioxide gas (CO_2).

(b) The combustion of a magnesium strip (Mg) in oxygen gas (O_2) to form magnesium oxide powder (MgO).

(c) The neutralization of sulfuric acid solution (H_2SO_4) with sodium hydroxide solution (NaOH) to form aqueous sodium sulfate (Na_2SO_4) and water (H_2O).

(d) The synthesis of ammonia gas (NH_3) from nitrogen gas (N_2) and hydrogen gas (H_2).

(e) The combustion of methane gas (CH_4) to produce gaseous carbon dioxide (CO_2) and water vapour (H_2O).

Q2. Write balanced chemical equations for the following reactions:

(a) $K + H_2O \rightarrow KOH + H_2$

(b) $C_2H_5OH + O_2 \rightarrow CO_2 + H_2O$

(c) $Cl_2 + KI \rightarrow KCl + I_2$

(d) $CrO_3 \rightarrow Cr_2O_3 + O_2$

(e) $Fe_2O_3 + C \rightarrow CO + Fe$

Q3. Use the same processes to balance the following more difficult examples:

(a) $C_4H_{10} + O_2 \rightarrow CO_2 + H_2O$

(b) $NH_3 + O_2 \rightarrow NO + H_2O$

(c) $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO + H_2O$

(d) $H_2O_2 + N_2H_4 \rightarrow N_2 + H_2O + O_2$

(e) $C_2H_7N + O_2 \rightarrow CO_2 + H_2O + N_2$

When balancing equations, start with the most complex species, and leave terms that involve a single element to last.

Reactivity 2.1.2 – Using mole ratios in equations

Reactivity 2.1.2 – The mole ratio of an equation can be used to determine:
- **the masses and/or volumes of reactants and products**
- **the concentrations of reactants and products for reactions occurring in solution.**

Calculate reacting masses and/or volumes and concentrations of reactants and products.

Avogadro's law and definitions of molar concentration are covered in Structure 1.4. The values for A_r given in the data booklet to two decimal places should be used in calculations.	Structure 1.5 – How does the molar volume of a gas vary with changes in temperature and pressure? Nature of Science, Structure 1.4 – In what ways does Avogadro's law help us to describe, but not explain, the behaviour of gases?

The mole ratio of an equation can be used to determine the masses of reactants and products

As we have seen in the previous section, a chemical equation is simply an expression of reactants combining in fixed ratios to form products. The most convenient way to express this ratio is as moles, as that gives us a means of relating the number of particles that react to the mass that we can measure. So, for example, when methane, CH_4, burns in air, we can conclude the following, all from the balanced chemical equation:

	$CH_4(g)$	+	$2O_2(g)$	→	$CO_2(g)$	+	$2H_2O(g)$
Reacting ratio by mole:	1 mole		2 moles		1 mole		2 moles
Reacting ratio by mass:	16.05 g		64.00 g		44.01 g		36.04 g
	80.05 g reactant				80.05 g product		

(The figures for total mass of reactant and product are just a check, as we know something would be wrong if they did not equate.)

This simple interpretation of equations, going directly from coefficients to molar ratios, opens the door to a wide range of calculations involving reacting masses.

The term **carbon footprint** refers to the mass of carbon dioxide and other greenhouse gases, such as methane, that an individual emits in a one-year period. It is often expressed as the carbon dioxide equivalent, or CO_2e, to represent the total climate change impact of all the greenhouse gases caused by an item or activity. It includes emissions from fuels used in transport, services such as heating, production and consumption of food, and the direct and indirect emissions from manufactured goods and construction. It is extremely difficult to measure all sources accurately, but the fundamental concept uses the type of calculation shown here. The carbon footprint is a measure of an individual's consumption of resources, and suggests the link between this and the enhanced greenhouse effect.

Remember to convert between mass and moles using

$n = \frac{m}{M}$ or $m = nM$

It is common for students to waste time solving questions like this by doing the mole to gram conversions for all the species represented in the equation. You can save yourself a lot of trouble by focusing only on the terms indicated in the question, as shown in this example.

Worked example

Calculate the mass of carbon dioxide produced from the complete combustion of 1.00 g of methane.

Solution

Write the balanced equation and deduce the mole ratio as above. Then pick out from the question the terms that we need to analyse, here they are marked in red; these are the species where we need to convert moles to grams.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

Reacting ratio by mole:	1 mole	1 mole
Reacting ratio by mass / g:	16.05	44.01
For 1.00 g methane:	1.00	x

Now solve the ratio, shown here using cross-multiplication, to determine the value of x.

$$\frac{g CH_4}{g CO_2} = \frac{16.05}{44.01} = \frac{1.00}{x}$$

$$x = \frac{1.00 \times 44.01}{16.05} = 2.74\,g\ CO_2$$

When using A_r values given in the data booklet to calculate M, make sure to use the two decimal places provided.

All questions on reacting ratios involve a variation of this approach:

- write the balanced equation
- work out the mole ratio for the species identified in the question
- work out the reacting ratio by mass for these species, using $m = nM$
- insert the data from the question and solve the ratio.

In exam questions, it is appropriate to state the final calculated value to a similar number of significant figures as those stated in the data provided.

Worked example

Iodine chloride, ICl, can be made by the following reaction:

$$2I_2 + KIO_3 + 6HCl \rightarrow 5ICl + KCl + 3H_2O$$

Calculate the mass of iodine, I_2, needed to prepare 28.60 g of ICl by this reaction.

Solution

The relevant terms from the question are I_2 and ICl, so these are our focus.

$$2I_2 + KIO_3 + 6HCl \rightarrow 5ICl + KCl + 3H_2O$$

reacting ratio by mole:	2 moles	5 moles
reacting ratio by mass:	$2 \times (126.90 \times 2)$	$5 \times (126.90 + 35.45)$
	$= 507.60\,g$	$= 811.75\,g$
For 28.60 g ICl:	x	28.60 g

$$\frac{g I_2}{g ICl} = \frac{507.60}{811.75} = \frac{x}{28.60}$$

$$x = \frac{507.60 \times 28.60}{811.75}\,g\ I_2 = 17.88\,g\ I_2$$

The mole ratio of an equation can be used to determine the volumes of gaseous reactants and products

All the examples above use mass as a way to measure the amount, the number of moles. But in the laboratory, we often work with gases, where *volume* is a more convenient measure. As explained in Structure 1.4, gas volume is determined only by the number of particles and by the temperature and pressure. This understanding is known as Avogadro's law, which states that:

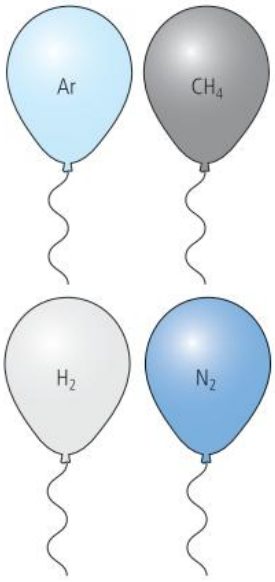
Equal volumes of all gases measured under the same conditions of temperature and pressure contain equal numbers of molecules.

Alternatively, it can be stated that equal numbers of molecules of all gases, when measured at the same temperature and pressure, occupy equal volumes.

Using V for volume and n for number of moles:

$$V \propto n$$

This relationship enables us to relate gas volume (of any gas) to the number of moles, and so to reacting ratios in equations.



At the same conditions of temperature and pressure, each balloon contains the same number of molecules of gas.

Avogadro's law states that equal volumes of all gases at the same conditions of temperature and pressure contain equal numbers of molecules: $V \propto n$

Nature of Science

Avogadro's hypothesis was not widely accepted initially. Experiments led him to suggest that equal volumes of all gases at the same temperature and pressure contain the same number of molecules, but data to confirm this was somewhat lacking. In addition, his ideas conflicted with Dalton's atomic theory, which suggested that particles in gases could be only single atoms, not molecules as Avogadro proposed. It took the logical argument of Cannizzaro, nearly 50 years later, to show that Avogadro's hypothesis could be explained, and moreover used as a means to determine molecular weight. Following this, the relationship between gas volume and number of molecules became widely accepted and known as Avogadro's law. History has shown that the acceptance of scientific ideas by the scientific community is sometimes influenced by the time and manner of their presentation, as well as by their power to explain existing ideas.

The descriptive nature of Avogadro's law allows us to accurately predict the behaviour of gases in mathematical terms but does not offer an explanation as to why they behave in this manner. To do so, we must consider the underlying model of ideal gases, which identifies characteristics of particles in the gaseous state.

Nature of Science, Structure 1.4 – In what ways does Avogadro's law help us to describe, but not explain, the behaviour of gases?

Worked example

10 cm^3 of nitrogen is reacted with excess hydrogen in the reaction:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

What volume of ammonia would you expect to be produced? (Assume all volumes are measured at the same temperature and pressure.)

Solution

'Excess' hydrogen indicates that there is enough to react with *all* of the nitrogen.

First identify the mole ratios in the equation:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$
$$1 \text{ mole} \quad \text{excess} \quad 2 \text{ moles}$$

As the ratio of moles is equivalent to the ratio of reacting volumes, we can deduce:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$
$$10\,cm^3 \qquad 20\,cm^3$$

Therefore, we expect 20 cm^3 of ammonia to be produced. (Although it is not asked for in this question, we could also deduce that 30 cm^3 of H_2 would be expected to react.)

Note that in reality, this is a reversible reaction so we would be unlikely to collect 20 cm^3 ammonia experimentally. More detail can be found on reversible reactions in Reactivity 2.3.

Worked example

When 10 cm^3 of a gaseous hydrocarbon (a compound containing only carbon and hydrogen) is burnt in excess oxygen, the products consist of 30 cm^3 of carbon dioxide and 30 cm^3 of water vapour, measured under the same conditions of temperature and pressure. Determine the molecular formula of the hydrocarbon.

Solution

'Excess' oxygen indicates that the combustion reaction is complete. Therefore *all* of the hydrocarbon would react to form *only* CO_2 and H_2O.

	C_xH_y + O_2 →	CO_2 +	H_2O
volumes:	10 cm^3 excess	30 cm^3	30 cm^3
ratio of volumes / mole:	1	3	3

$\therefore$ 1 molecule hydrocarbon → 3 molecules CO_2 + 3 molecules H_2O

3 C atoms 6 H atoms

The molecular formula is C_3H_6.

All gases under the same conditions have the same molar volume

On the basis of Avogadro's law, the volume occupied by one mole of any gas, known as the **molar volume** (V_m), must be the same for *all* gases when measured under the same conditions of temperature and pressure.

At standard temperature and pressure (STP), one mole of a gas has a volume of $2.27 \times 10^{-2}\,m^3\,mol^{-1}$ (= $22.7\,dm^3\,mol^{-1}$). The conditions at STP are a temperature of 0 °C (273 K) and a pressure of 100 kPa. The value of the molar volume and the conditions for STP are given in Section 2 of the data booklet.

It is important to note that when temperature and pressure deviate from STP, the molar volume will also change. An increase in temperature will increase the molar volume whereas an increase in pressure will lead to a decrease in molar volume. These effects are described by the combined gas law seen in Structure 1.5.

The molar volume can be used to calculate the amount of gas in a similar way to the use of molar mass earlier in this chapter. Here though, the calculations are easier, as all gases have the same molar volume.

$$\text{number of moles of gas } (n) = \frac{\text{volume } (V)}{\text{molar volume } (V_m)}$$

Worked example

Calculate the volume occupied by 0.0200 g He at standard temperature and pressure.

Solution

First convert the mass of He to moles.

$$n = \frac{m}{M} = \frac{0.0200}{4.00} = 0.00500\,\text{mol} = 0.00500\,\text{mol} = 5.00 \times 10^{-3}\,\text{mol}$$

volume = number of moles of gas × molar volume

$= (5.00 \times 10^{-3}\,\text{mol}) \times 22.7\,dm^3\,mol^{-1} = 0.114\,dm^3$

Worked example

What volume of oxygen at standard temperature and pressure would be needed to completely burn 1.00 mole of butane, C_4H_{10}?

Solution

As always, start with the balanced equation and pick out the terms from the question.

$$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(g)$$

mole / volume ratio: 1 : 6.5

So 1.00 mol butane will react completely with 6.50 mol O_2.

6.50 moles of gas at STP have volume = 6.50 mol × $22.7\,dm^3\,mol^{-1}$ = $148\,dm^3$

Structure 1.5 – How does the molar volume of a gas vary with changes in temperature and pressure?

Note that standard temperature and pressure (STP) is not the same as the 'standard state', which is used in thermodynamic data and is explained in Reactivity 1.1.

STP refers to a temperature of 273 K and a pressure of 100 kPa.

The SI unit of pressure is Pa ($N\,m^{-2}$), but the bar (10^5 Pa) is now widely used as it is conveniently close to 1 atmosphere. Different countries continue to use a variety of units for pressure, including millimetres of mercury (mm Hg), torr (Torr), pounds per square inch (psi), and atmosphere (atm). The SI unit of volume is m^3, although litre (l or L) is widely used to represent $1\,dm^3$.

Nature of Science

Committee on Data for Science and Technology (CODATA) is an interdisciplinary scientific committee of the International Council of Science. It was established in 1966 to promote the worldwide compilation and sharing of reliable numerical data, such as the molar volume of a gas. What might be some of the responsibilities held by bodies such as CODATA?

Challenge yourself

1. The combustion of both ammonia, NH_3, and hydrazine, N_2H_4, in oxygen gives nitrogen and water only. When a mixture of ammonia and hydrazine is burnt in pure oxygen, the volumetric N_2:H_2O ratio in the product gas is 0.40. Calculate the % by mass of ammonia in the original mixture. What assumptions are being made here?

A note about units of volume

The litre (l or L) is widely used in place of dm^3, and millilitre (ml or mL) in place of cm^3. You will not be penalized for the use of these terms in an examination, but they will not be used in examination questions, so it is essential that you know the correct use of m^3, dm^3, and cm^3.

The metric unit m^3 is widely used in industrial and engineering calculations, but is too large to be convenient for many volume measurements in the laboratory. Instead, dm^3 and cm^3 are commonly used, so it is important to be able to interconvert these.

$$cm^3 \underset{\text{multiply by 1000}}{\overset{\text{divide by 1000}}{\rightleftharpoons}} dm^3 \underset{\text{multiply by 1000}}{\overset{\text{divide by 1000}}{\rightleftharpoons}} m^3$$

Nature of Science

Early ideas on gas behaviour were suggested from the postulates of the kinetic theory, but could not advance without scientific evidence. This was provided by experimental work, mainly that of Boyle and Mariotte, Charles, and Gay-Lussac who contributed quantitative data based on testable predictions of how gases would respond to changes in temperature, volume and pressure. In a fairly classic example of scientific process, the data supported the theory, and the theory explained the data. As a result, there was wide acceptance of what became known as 'the gas laws' by the 18th century.

The mole ratio of an equation can be used to determine the concentrations of reactants and products in solutions

A standard solution is a solution of accurately known concentration.

Suppose we have an unlabelled bottle of hydrochloric acid, HCl, and want to know its concentration. We can find out the concentration by reacting the acid with a standard solution of an alkali such as sodium hydroxide, NaOH, and determining the exact volumes that react together. From the stoichiometry of the reaction, when we know the volumes of both solutions and the concentration of one of them, we can use the mole ratio to calculate the unknown concentration as follows.

	$HCl(aq)$	+	$NaOH(aq)$	$\rightarrow$	$NaCl(aq) + H_2O(l)$
mole ratio:	1	:	1		
volume:	known		known (by titration)		
conc.:	unknown = x		known (standard solution)		

- moles NaOH can be calculated as follows:
  $n(NaOH) = c(NaOH) \times V(NaOH)$
- use the mole ratio in the equation:
  $n(NaOH) = n(HCl)$
- $\therefore$ concentration of HCl, x, can be calculated from:
  $n(HCl) = x \times V(HCl)$

This is an example of a process called **volumetric analysis**. Most commonly, a technique called **titration** is used to determine the reacting volumes precisely.

A **pipette** is used to measure a known volume of one of the solutions into a **conical flask**. The other solution is put into a **burette**, a calibrated glass tube that can deliver precise volumes into the conical flask by opening the tap at the bottom. The point at which the two solutions have reacted completely, the **equivalence point**, is usually determined by an indicator that is added to the solution in the conical flask. The indicator changes colour at its **end point**. Specific indicators are chosen for different titrations to change colour at the equivalence point. This is explained more fully in Reactivity 3.1.

Titration usually involves multiple trials to obtain a more accurate result of the volume required to reach the equivalence point; this volume is known as the **titre**. A good titration result gives readings which are consistent with each other relative to the precision of the burette used. Most commonly, this means within 0.05 cm^3 of each other. Remember, the uncertainty in the measurement of analogue instruments is half the smallest division, usually ± 0.05 cm^3 in a burette. Titration is widely used in acid–base chemistry and also in redox chemistry (discussed in Reactivity 3.2). Its applications include industrial chemical processing, chemical research, quality control checks in the food and pharmaceutical industries, and aspects of environmental monitoring.

When recording volume measurements from a burette, it is important to remember that the total volume of solution added, the titre, is calculated using an initial and final measurement. Therefore, the absolute uncertainty is 0.05 cm^3 + 0.05 cm^3 = ± 0.10 cm^3.

Worked example

25.00 cm^3 of 0.100 mol dm^{-3} sodium hydrogencarbonate, $NaHCO_3$, solution were titrated with dilute sulfuric acid, H_2SO_4.

$$2NaHCO_3(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l) + 2CO_2(g)$$

15.20 cm^3 of the acid were needed to neutralize the solution. Calculate the concentration of the acid.

The amount of solute (mol) = concentration (mol dm^{-3}) × volume (dm^3) or $n = cV$



Acid–base titration. The burette tap controls the flow of a standard solution of sodium hydroxide into the conical flask which contains hydrochloric acid solution of unknown concentration and a few drops of phenolphthalein indicator. The equivalence point occurs when the exact volumes of the two solutions have reacted completely. This is indicated by a colour change from colourless to pink.

Burettes generally read to ± 0.05 cm^3, so be sure to record your results to this precision. Readings such as 0, 12.0, or 3.5 are not acceptable but should be recorded as 0.00, 12.00, and 3.50 respectively.

Solution

We can calculate the amount of $NaHCO_3$ as we are given both the volume and the concentration.

$$n = cV$$

$$n(NaHCO_3) = 0.100\,\text{mol dm}^{-3} \times \frac{25.00}{1000}\,\text{dm}^3 = 2.50 \times 10^{-3}\,\text{mol}$$

Look at the mole ratio in the equation:

$$2n(NaHCO_3) = n(H_2SO_4)$$

$$\therefore n(H_2SO_4) = 0.5 \times (2.50 \times 10^{-3}\,\text{mol}) = 1.25 \times 10^{-3}\,\text{mol}$$

$$\therefore c = \frac{n}{V} = \frac{1.25 \times 10^{-3}\,\text{mol}}{15.20/1000\,\text{dm}^3} = 0.0822\,\text{mol dm}^{-3}$$

$$\therefore [H_2SO_4] = 0.0822\,\text{mol dm}^{-3}$$

Here is a summary of the steps in volumetric analysis calculations:

- If it is not already given, write a balanced equation for the reaction.
- Look for the reactant whose volume and concentration are given and calculate its number of moles from $n = cV$.
- Use this answer and the mole ratio in the equation to determine the number of moles of the other reactant.
- Use the number of moles and volume of the second reactant to calculate its concentration from $c = \frac{n}{V}$.

Back titration

As the name implies, a **back titration** is done in reverse by returning to the end point after it is passed. Back titration is used when the end point is hard to identify or when one of the reactants is impure. A known excess of one of the reactants is added to the reaction mixture, and the unreacted excess is then determined by titration against a standard solution. By subtracting the amount of unreacted reactant from the original amount used, the reacting amount can be determined.

Worked example

An antacid tablet with a mass of 0.300 g and containing $NaHCO_3$ was added to 25.00 cm^3 of 0.125 mol dm^{-3} hydrochloric acid. After the reaction was complete, the excess hydrochloric acid required 3.50 cm^3 of 0.200 mol dm^{-3} NaOH to reach the equivalence point in a titration. Calculate the percentage of $NaHCO_3$ in the tablet.

Solution

original reaction: $NaHCO_3(s) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l) + CO_2(g)$

mole ratio: 1 : 1

First calculate the total amount of HCl added, which is a known excess.

$$n(\text{HCl total}) = \frac{25.00}{1000}\,\text{dm}^3 \times 0.125\,\text{mol dm}^{-3} = 0.00313\,\text{mol HCl total}$$

titration reaction: $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

mole ratio: 1 : 1

$$n(NaOH) = 0.00350\,dm^3 \times 0.200\,mol\,dm^{-3} = 0.000700\,mol$$

$n(NaOH) = n(HCl\ unreacted) = 0.000700\,mol\ HCl\ unreacted$

$\therefore n(HCl\ reacted) = 0.00313 - 0.000700 = 0.00243\,mol$

$\therefore$ from the mole ratio in the first equation $n(NaHCO_3) = n(HCl) = 0.00243\,mol$

$M(NaHCO_3) = 22.99 + 1.01 + 12.01 + (16.00 \times 3) = 84.01\,g\,mol^{-1}$

$m = nM = 0.00243\,mol \times 84.01\,g\,mol^{-1} = 0.204\,g$

$$\text{percentage by mass in tablet} = \frac{0.204}{0.300} \times 100 = 68.0\%$$

Note that there are several assumptions made in this calculation. These include the fact that all the $NaHCO_3$ did react with the acid, and that the only component of the tablet that reacted with HCl was $NaHCO_3$. You may like to think about how you could test the validity of these assumptions in the laboratory.

Exercise

Q4. Iron ore can be reduced to iron by the following reaction:

$$Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe + 3H_2O(l)$$

(a) How many moles of Fe can be made from 1.25 moles of Fe_2O_3?

(b) How many moles of H_2 are needed to make 3.75 moles of Fe?

(c) If the reaction yields 12.50 moles of H_2O, what mass of Fe_2O_3 was used up?

Q5. Lighters commonly use butane, C_4H_{10}, as the fuel.

(a) Formulate the equation for the combustion of butane.

(b) Determine the mass of butane that burnt when 2.46 g of water were produced.

Q6. The fuel used in booster rockets for the Space Shuttle is a mixture of aluminium and ammonium perchlorate. The reaction equation is as follows:

$$3Al(s) + 3NH_4ClO_4(s) \rightarrow Al_2O_3(s) + AlCl_3(s) + 3NO(g) + 6H_2O(g)$$

Calculate the mass of NH_4ClO_4 that should be added to this fuel mixture to react completely with every kilogram of Al.

Q7. Limestone is mostly calcium carbonate, $CaCO_3$, but it also contains other minerals. When heated, the $CaCO_3$ decomposes into CaO and CO_2. A sample of 1.605 g of limestone was heated and gave off 0.657 g of CO_2.

(a) Formulate the equation for the thermal decomposition of calcium carbonate.

(b) Determine the percentage mass of $CaCO_3$ in the limestone.

(c) State the assumptions you are making in this calculation.

Q8. How many moles are present in each of the following at STP?

(a) 54.5 dm^3 CH_4

(b) 250.0 cm^3 CO

(c) 1.0 m^3 O_2

Q9. What is the volume of each of the following gases at STP?

(a) 44.00 g N_2

(b) 0.25 mol NH_3

Q10. Pure oxygen gas was first prepared by heating mercury(II) oxide, HgO.

$$2HgO(s) \rightarrow 2Hg(l) + O_2(g)$$

What volume of oxygen, at STP, is released by heating 12.45 g of HgO?

Q11. At STP, which sample contains more molecules, 3.14 dm^3 of bromine, Br_2, or 11.07 g of chlorine, Cl_2?

Q12. Calcium reacts with water to produce hydrogen.

$$Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + H_2(g)$$

Calculate the volume of hydrogen gas produced, at STP, when 0.200 g of calcium reacts completely with water.

Q13. Dinitrogen oxide, N_2O, is a greenhouse gas produced from the decomposition of artificial nitrate fertilizers. Calculate the volume of N_2O produced from 1.0 g of ammonium nitrate when it reacts, at STP, according to the equation:

$$NH_4NO_3(s) \rightarrow N_2O(g) + 2H_2O(l)$$

Q14. In a titration, a 15.00 cm^3 sample of H_2SO_4 required 36.42 cm^3 of 0.147 mol dm^{-3} NaOH solution for complete neutralization. What was the concentration of the H_2SO_4?

Q15. Gastric juice contains hydrochloric acid, HCl. A 5.00 cm^3 sample of gastric juice required 11.00 cm^3 of 0.0100 mol dm^{-3} KOH for neutralization in a titration. What was the concentration of HCl in this fluid? If we assume a density of 1.00 g cm^{-3} for the fluid, what was the percentage by mass of HCl?

Q16. Sodium sulfate, Na_2SO_4, reacts in aqueous solution with lead nitrate, $Pb(NO_3)_2$, as follows:

$$Na_2SO_4(aq) + Pb(NO_3)_2(aq) \rightarrow PbSO_4(s) + 2NaNO_3(aq)$$

In an experiment, 35.30 cm^3 of a solution of sodium sulfate reacted exactly with 32.50 cm^3 of a solution of lead nitrate. The precipitated lead sulfate was dried and found to have a mass of 1.13 g. Determine the concentrations of the original solutions of lead nitrate and sodium sulfate. State what assumptions are made.

Reactivity 2.1.3 – The limiting reactant and theoretical yield

Reactivity 2.1.3 – The limiting reactant determines the theoretical yield.	
Identify the limiting and excess reactants from given data.	
Distinguish between the theoretical yield and the experimental yield.	Tool 1, Inquiry 1, 2, 3 – What errors may cause the experimental yield to be (i) higher and (ii) lower than the theoretical yield?

The theoretical yield is determined by the limiting reactant

Imagine that you are following a recipe to make 12 cookies. It calls for you to mix two eggs with four cups of flour. The problem is that you only have one egg. You will quickly realize that this means you can use only two cups of flour and end up with only six cookies. We could say that the number of eggs *limited* the amount of product.

In many chemical reactions, the relative amounts of reactants available to react together will similarly affect the amount of product. The reactant that determines the quantity of product is known as the **limiting reactant**. Other reactants will not be fully used, and are said to be in **excess**. Identifying the limiting reactant is therefore a crucial step before we can calculate the expected quantity of product. The **theoretical yield**, which is usually expressed in grams or moles, refers to the maximum amount of product obtainable, assuming 100% of the limiting reactant is converted to product.

The concept of limiting reactant is often useful in the design of experiments and synthetic processes. By deliberately making one reactant available in a greater amount than that determined by its mole ratio in the balanced equation, it ensures that the other reactant is limiting and so will be fully used up. For example, in order to remove lead ions in lead (II) nitrate, $Pb(NO_3)_2$, from a contaminated water supply, sodium carbonate, Na_2CO_3, is added to precipitate lead carbonate, as shown in the equation:

$$\underset{\text{limiting}}{Pb(NO_3)_2(aq)} + \underset{\text{excess}}{Na_2CO_3(aq)} \rightarrow PbCO_3(s) + 2NaNO_3(aq)$$

By using excess Na_2CO_3, this ensures that *all* the lead ions react and so are removed from the water supply.



A medical worker taking a blood sample. Blood samples can be used to test for lead exposure. During the Flint water crisis in the US state of Michigan in 2014, after Flint switched its water supply to save money during a financial state of emergency, tens of thousands of people were exposed to elevated levels of lead ions in their drinking water. In addition to other methods, salts such as Na_2CO_3 can be added in excess to contaminated water to precipitate and then remove heavy metal ions such as Pb^{2+} and Pb^{4+}.

Note that identification of the limiting reactant depends on the *mole ratios* in the balanced chemical equation for the reaction. This means that if reactant quantities are given in grams, they must first be converted to moles.

The limiting reactant determines the amount of product that can form. The theoretical yield is the quantity of product that can form from the complete conversion of the limiting reactant.

Worked example

Nitrogen gas (N_2) can be prepared according to this reaction:

$$2NH_3(g) + 3CuO(s) \rightarrow N_2(g) + 3Cu(s) + 3H_2O(g)$$

If 18.1 g NH_3 are reacted with 90.4 g CuO, determine the mass of N_2 that can be formed.

Solution

First we must determine the limiting reactant. We convert the mass of reactants to moles, and then compare the mole ratio in the balanced equation with the mole ratio of reactants given.

$$n(NH_3) = \frac{18.1}{14.01 + (3 \times 1.01)} = 1.06 \text{ mol } NH_3$$

$$n(CuO) = \frac{90.4}{63.55 + 16.00} = 1.14 \text{ mol CuO}$$

mole ratio from equation: $\frac{NH_3}{CuO} = \frac{2}{3} = 0.67$

mole ratio from given masses: $\frac{NH_3}{CuO} = \frac{1.06}{1.14} = 1.14$

As the ratio NH_3:CuO of the given masses is *larger* than the required ratio in the equation, it means NH_3 is in excess and CuO is the limiting reactant.

This means that the amount of N_2 that can form will be determined by the amount of CuO. This is now similar to the earlier questions, where we write out the equation and focus on the terms identified in the question.

$$2NH_3(g) + 3CuO(s) \rightarrow N_2(g) + 3Cu(s) + 3H_2O(g)$$

reacting ratio by mole: 3 moles 1 mole

for 1.14 moles CuO: 1.14 x

mole ratio: $\frac{CuO}{N_2} = \frac{3}{1} = \frac{1.14}{x}$

$x = \frac{1.14 \times 1}{3} = 0.380 \text{ mol } N_2$

$\therefore$ mass $N_2 = 0.380 \times M(N_2) = 0.380 \times 28.02 = 10.7 \text{ g } N_2$

There are alternative approaches to determining the limiting reactant, such as calculating which given amount of reactant would yield the smallest amount of product. But in essence, all questions on limiting reactant and theoretical yield involve comparing the mole ratio of given quantities of reactants with the coefficients in the equation. This is a summary of the steps:

- write the balanced equation and focus on the mole ratio of reactants
- convert the given mass of reactants to moles
- compare the given mole ratios with the ratio of coefficients in the equation
- identify the limiting reactant from the above ratios
- calculate the moles of product from the given moles of *limiting* reactant.

Sometimes it is useful to measure how much excess reactant will remain when all the limiting reactant has been used up and the reaction stops. One example of this is a technique called back titration, seen in the previous section, which analyses excess acid or alkali after a reaction is complete, and so indirectly measures the amount of a limiting reactant. A simple example of how to calculate the excess is shown below, using an example of burning CH_4 when 1 mole of CH_4 and 1 mole of O_2 are supplied.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

reacting mole ratio in equation:	1	2		
reactant mole ratio given:	1	1		
$\Rightarrow O_2$ is the limiting reactant				
mole ratio at the end of reaction:	0.5	0	0.5	1

As the 1 mole of O_2 has been identified at the limiting reactant, only 0.5 moles of CH_4 will react, leaving 0.5 moles of CH_4 unreacted at the end of the reaction.

Tool 1, Inquiry 1, 2, 3 – What errors may cause the experimental yield to be (i) higher and (ii) lower than the theoretical yield?

Exercise

Q17. 0.40 moles of magnesium are mixed with 0.20 moles of hydrochloric acid.

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

Which is correct?

	Limiting reactant	Theoretical yield of H_2 (mol)
A	HCl	0.20
B	Mg	0.40
C	HCl	0.10
D	Mg	0.20

Q18. 0.30 moles of hydrochloric acid are mixed with 0.30 moles of calcium carbonate.

$$2HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + H_2O(g) + CO_2(g)$$

Which is correct?

	Limiting reactant	Theoretical yield of CO_2 (mol)
A	HCl	0.30
B	HCl	0.15
C	$CaCO_3$	0.15
D	$CaCO_3$	0.30

Q19. 5 cm^3 of nitrogen are reacted with 20 cm^3 of hydrogen in the reaction:

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

Assuming that all volumes are measured at the same temperature and pressure:

(a) What volume of ammonia would you expect to be produced?

(b) What volume of H_2 would remain unreacted?

Q20. Methanol, CH_3OH, is a useful fuel that can be made as follows:

$$CO(g) + 2H_2(g) \rightarrow CH_3OH(l)$$

A reaction mixture used 12.0 g of H_2 and 74.5 g of CO.

(a) Determine the theoretical yield of CH_3OH.

(b) Calculate the amount of the excess reactant that remains unchanged at the end of the reaction.

Q21. The dry-cleaning solvent 1,2-dichloroethane, $C_2H_4Cl_2$, is prepared by the following reaction:

$$C_2H_4(g) + Cl_2(g) \rightarrow C_2H_4Cl_2(l)$$

Determine the mass of product that can be formed from 15.4 g of C_2H_4 and 3.74 g of Cl_2.

Reactivity 2.1.4 – Percentage yield

Reactivity 2.1.4 – The percentage yield is calculated from the ratio of experimental yield to theoretical yield.

Solve problems involving reacting quantities, limiting and excess reactants, theoretical, experimental and percentage yields.



A separating funnel being used to extract iodine from an aqueous solution containing other impurities (the upper layer). As iodine is more soluble in dichloromethane (the lower layer), I_2 molecules will migrate into it upon gentle shaking of the separating funnel, causing a pink solution. However, some I_2 may remain in the aqueous layer so the experimental yield will be less than the theoretical value.

The percentage yield can be calculated from the experimental and theoretical yields

So far in this chapter, worked examples have focused on chemical reactions occurring with no loss, impurities present, wastage, or incomplete reaction. In reality, all of these happen to different extents in most chemical reactions, and so the theoretical yield is usually different from the actual or **experimental yield**. Below are some sources of error that may cause the experimental yield to be lower or higher than the theoretical yield.

Factors that may cause the experimental yield to be *lower* than the theoretical yield	Factors that may cause the experimental yield to be *higher* than the theoretical yield
Side reactions occurring.	Impurities in a product.
The decomposition of reactants and/or products.	When a product has not been fully dried.
Loss of product during purification.	
Reversible chemical reactions preventing process completion. (See Reactivity 2.3 for more detail.)	
An incomplete reaction (this could impact the experimental yield in both directions depending on the type of reaction used).	

When we compare the experimental yield with the theoretical yield, we get a measure of the efficiency of the conversion of reactants to products. This is usually expressed as the **percentage yield**, defined as follows:

$$\text{percentage yield} = \frac{\text{experimental yield}}{\text{theoretical yield}} \times 100$$

In your own experiments, you may often be required to calculate the percentage yield of product in evaluating the results. In industry, this is a very important calculation used to determine the efficiency of a process, such as the synthesis of a drug in the pharmaceutical industry. Many aspects of Green Chemistry focus on ways to increase the yield of product by reducing wastage.



Industrial plants such as this oil refinery in Bangkok, Thailand, need to be able to track the efficiency of the chemical reactions taking place. Measuring the yield of product is an essential part of this.

Worked example

The synthesis of N_2 from NH_3 and CuO has a theoretical yield of 10.65 g N_2 from the starting amounts of reactants. Under the same conditions, an experiment produced 8.35 g N_2. Determine the percentage yield of the experiment.

Solution

$$\text{percentage yield} = \frac{\text{experimental yield}}{\text{theoretical yield}} \times 100$$

$$\therefore \text{percentage yield} = \frac{8.35}{10.65} \times 100 = 78.4\,\%$$

Exercise

Q22. Calcium carbonate, $CaCO_3$, is able to remove sulfur dioxide, SO_2, from waste gases by a reaction in which the two substances react in a 1:1 stoichiometric ratio to form equimolar amounts of $CaSO_3$ and CO_2. When 255 g of $CaCO_3$ reacted with 135 g of SO_2, 198 g of $CaSO_3$ were formed. Determine the percentage yield of $CaSO_3$.

Q23. Pentyl ethanoate, $CH_3COOC_5H_{11}$, which smells like bananas, is produced from the esterification reaction:

$$CH_3COOH(aq) + C_5H_{11}OH(aq) \rightarrow CH_3COOC_5H_{11}(aq) + H_2O(l)$$

A reaction uses 3.58 g of CH_3COOH and 4.75 g of $C_5H_{11}OH$ and has a yield of 45%. Determine the mass of ester that forms.

Q24. A student has to make a 100 g sample of chlorobenzene, C_6H_5Cl, from the following reaction:

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$$

Determine the minimum quantity of benzene, C_6H_6, that can be used to achieve this with a yield of 65%.

SKILLS

Synthesis and purification of Aspirin. Full details of how to carry out this experiment with a worksheet are available in the eBook.

Reactivity 2.1.5 – Atom economy

Reactivity 2.1.5 – The atom economy is a measure of efficiency in Green Chemistry. Calculate the atom economy from the stoichiometry of a reaction.	
Include discussion of the inverse relationship between atom economy and wastage in industrial processes. The equation for calculation of the atom economy is given in the data booklet.	Structure 2.4, Reactivity 2.2 – The atom economy and the percentage yield both give important information about the 'efficiency' of a chemical process. What other factors should be considered in this assessment?

The atom economy is a measure of efficiency in Green Chemistry

Green Chemistry is the sustainable design of chemical products and chemical processes. It aims to minimize the use and generation of chemical substances that are hazardous to human health and the environment. Traditionally, the efficiency of a reaction has been measured by calculating the percentage yield (the proportion of the desired product obtained compared to the theoretical maximum), but this is only a limited measure as it gives no indication of the quantity of waste produced. A synthetic route should maximize the **atom economy** by incorporating as many of the atoms of the reactants as possible into the desired product.

The atom economy of a reaction can be calculated from the equation provided in Section 1 of the data booklet:

$$\%\ \text{atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100$$

Efficient processes have high atom economies and are important for sustainable development, as they use fewer natural resources and create less waste. Addition polymerization reactions, for example, have an atom economy of 100% as all the reacting atoms end up in the polymer and there are no side products. Many real-world processes, for example, in drug synthesis, use a deliberate excess of reactants to increase the yield but have low atom economies.

The second principle of Green Chemistry states that synthesis design should aim to maximize atom economy in a chemical process

Worked example

Nickel can be produced by heating nickel oxide and carbon in the following reaction:

$$NiO(s) + C(s) \rightarrow Ni(s) + CO(g)$$

Calculate the atom economy for the production of nickel. Give your answer to 3 significant figures.

Solution

Molar mass of desired product = 58.69

Molar mass of all reactants = (58.69 + 16.00) + 12.01 = 86.70

$$\%\ \text{atom economy} = \frac{58.69}{86.70} \times 100 = 67.7\%$$

Challenge yourself

2. Percentage yield and atom economy are different concepts, but both can be used to assess aspects of the overall efficiency of a chemical process. See if you can find a reaction that has a high percentage yield under certain conditions, but a low atom economy.

In addition to atom economy and percentage yield, there are a number of other factors that can be used to gauge the efficiency of a chemical process. We might, for example, consider the rate at which a chemical reaction takes place (explored in Reactivity 2.2) or the quantities of reagents, such as solvents and catalysts, which are not consumed in the reaction. In industry, it is also important to evaluate energy usage and the economic efficiency of a process.

Structure 2.4, Reactivity 2.2 – The atom economy and the percentage yield both give important information about the 'efficiency' of a chemical process. What other factors should be considered in this assessment?

Exercise

Q25. Copper(II) sulfate, $CuSO_4$, can be produced by reacting copper(II) carbonate and sulfuric acid according to the following equation:

$$CuCO_3 + H_2SO_4 \rightarrow CuSO_4 + H_2O + CO_2$$

Calculate the atom economy for the reaction. Give your answer to 3 significant figures.

Q26. Chloroethene, C_2H_3Cl, is the monomer used in the manufacture of polyvinyl chloride. It can be produced from 1,2-dichloroethane, $C_2H_4Cl_2$, by the following reaction.

$$C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl$$

Calculate the atom economy for the reaction. Give your answer to 3 significant figures.

Q27. Identify which of these methods of producing hydrochloric acid, HCl, has the highest atom economy.

Method 1: $2NaCl(s) + H_2SO_4(l) \rightarrow 2HCl(g) + Na_2SO_4(s)$

Method 2: $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

Challenge yourself

3. The fertilizer triammonium phosphate is made from 'phosphate rock' by:

1. reacting the phosphate rock with sulfuric acid, H_2SO_4, to produce phosphoric acid, H_3PO_4
2. reacting the phosphoric acid with ammonia, NH_3, to give tri-ammonium phosphate, $(NH_3)_3PO_4$

If the phosphate rock contains 90% by mass $Ca_3(PO_4)_2$ from which the overall yield of triammonium phosphate is 95%, calculate the mass of phosphate rock required to make 1000 tonnes of triammonium phosphate.

4. Sulfuric acid, H_2SO_4, is produced from sulfur in a three-step process:

1. $S(s) + O_2(g) \rightarrow SO_2(g)$
2. $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$
3. $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$

Assuming 100% conversion and yield for each step, what is the minimum mass of sulfur needed to produce 980 tonnes of H_2SO_4?

5. The concentration of hydrogen peroxide, H_2O_2, in excess aqueous sulfuric acid, H_2SO_4, can be determined by redox titration using potassium permanganate, $KMnO_4$ as follows:

$2KMnO_4(aq) + 5H_2O_2(l) + 3H_2SO_4 \rightarrow 2MnSO_4(aq) + K_2SO_4(aq) + 8H_2O(l) + 5O_2(g)$

A 10.00 cm^3 sample of H_2O_2 solution requires 18.00 cm^3 of a 0.0500 mol dm^{-3} solution of $KMnO_4$ to reach the equivalence point in a titration. Calculate the concentration of H_2O_2 in the solution.

6. Mixtures of sodium carbonate, Na_2CO_3, and sodium hydrogencarbonate, $NaHCO_3$, in aqueous solution are determined by titration with hydrochloric acid, HCl, in a two-step procedure.

1. Titrate to the phenolphthalein end point:

$$Na_2CO_3(s) + HCl(aq) \rightarrow NaHCO_3(aq) + NaCl(aq)$$

2. Continue titration to the methyl orange end point:

$$NaHCO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l) + CO_2(g)$$

For an X cm^3 sample of a sodium carbonate/sodium hydrogencarbonate mixture titrated with Y mol dm^{-3} HCl, the respective end points are Step 1 = P cm^3 HCl and Step 2 = Q cm^3 HCl. Derive relationships between X, Y, P, and Q to obtain the concentrations of sodium carbonate and sodium hydrogencarbonate in the original mixture.

7. A sealed vessel with fixed total internal volume of 2 m^3 contains 0.740 kg pentane, C_5H_{12}, and oxygen only. The pentane is ignited and undergoes 100% conversion to carbon dioxide and water. Subsequently the temperature and pressure in the vessel are respectively 740 K and 400 kPa. Calculate the initial amount and mass of oxygen in the vessel.

Guiding Question revisited

How are chemical equations used to calculate reacting ratios?

In this chapter we have used chemical equations to:

- Deduce the mole ratio of reactants and products from their coefficients in the balanced equation.

- Determine masses, volumes and concentrations of reactants and products involved in chemical reactions.
  - When dealing with masses, mole ratios can be converted to a reacting ratio by mass using $m = nM$.
  - For gases, Avogadro's law can be applied to mole ratios to determine a reacting ratio by volume. At STP, we can also convert between moles and volume using $n = \frac{V}{V_m}$ where V_m is the molar volume of a gas (provided in the data booklet).
  - The volumetric analysis of solutions, often carried out using a titration, requires the use of $n = cV$ to calculate the number of moles of one reactant before using the mole ratio to determine the number of moles of the other reactant and then its concentration.
- Identify the reactant that will be used up first in a reaction, the limiting reactant, by comparing the mole ratio from the balanced equation to the mole ratio in the quantities being reacted. The reactant not fully used is said to be in excess. As the limiting reactant determines the amount of product being formed, we can use it to calculate the expected amount of product, known as the theoretical yield.
- Quantify the efficiency of a chemical process using percentage yield and atom economy.
  - Percentage yield is calculated from the ratio of experimental yield to theoretical yield using the formula:

$$\text{percentage yield} = \frac{\text{experimental yield}}{\text{theoretical yield}} \times 100$$

  - Atom economy takes into account the amount of waste produced in a reaction by comparing the molar mass of the target product to the molar mass of the reactants used. This formula can be found in the data booklet:

$$\%\ \text{atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass or all reactants}} \times 100$$

Practice questions

1. How many oxygen atoms are in the formula of hydrated copper sulfate, $CuSO_4.5H_2O$?

A 2 **B** 4 **C** 5 **D** 9

2. What is the sum of the coefficients when the following equation is balanced using whole numbers?

$$__\ Fe_2O_3(s) + __\ CO(g) \rightarrow __\ Fe(s) + __\ CO_2(g)$$

A 5 **B** 6 **C** 8 **D** 9

3. In which mixture is NaOH the limiting reactant?

A 0.10 mol NaOH + 0.05 mol H_2SO_4

B 0.05 mol NaOH + 0.05 mol H_2SO_4

C 0.20 mol NaOH + 0.05 mol HNO_3

D 0.20 mol NaOH + 0.10 mol HNO_3

4. Which volume, in cm^3, of 0.40 mol dm^{-3} NaOH(aq) is required to neutralize 0.050 mol of $H_2S(g)$?

$$H_2S(g) + 2NaOH(aq) \rightarrow Na_2S(aq) + 2H_2O(l)$$

A 0.25 **B** 0.50 **C** 250 **D** 500

5. What is the maximum volume, in dm^3, of $CO_2(g)$ produced when 1.00 g of $CaCO_3(s)$ reacts with 20.0 cm^3 of 2.00 mol dm^{-3} HCl(aq)?

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

Molar volume of gas = 22.7 dm^3 mol^{-1}; $M(CaCO_3)$ = 100.00

A $\frac{1}{2} \times \frac{20.0 \times 2.0}{1000} \times 22.7$ **B** $\frac{20.0 \times 2.0}{1000} \times 22.7$

C $\frac{1.0}{100.00} \times 22.7$ **D** $\frac{1.0}{100.00} \times 2 \times 22.7$

6. Which of the following is correct when 40 cm^3 hydrogen is reacted with 10 cm^3 oxygen?

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

	Limiting reactant	Volume of $H_2O(g)$ produced (cm^3)
A	H_2	40
B	H_2	80
C	O_2	10
D	O_2	20

7. What mass, in g, of hydrogen is formed when 3 moles of aluminium react with excess hydrochloric acid according to the following equation?

$$2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$$

A 3.0 **B** 4.5 **C** 6.0 **D** 9.0

8. What is the percentage yield when 7 g ethene produces 6 g of ethanol?

$$C_2H_4(g) + H_2O(g) \rightarrow C_2H_5OH(g)$$

M_r(ethene) = 28 and M_r(ethanol) = 46

A $\frac{6 \times 7 \times 100}{28 \times 46}$ **B** $\frac{6 \times 46 \times 100}{7 \times 28}$ **C** $\frac{6 \times 28}{7 \times 46 \times 100}$ **D** $\frac{6 \times 28 \times 100}{7 \times 46}$

9. What is the sum of all coefficients when the following equation is balanced using the smallest possible whole numbers?

$$__ C_2H_2 + __ O_2 \rightarrow __ CO_2 + __ H_2O$$

A 5 **B** 7 **C** 11 **D** 13

10. Chloroethene, C_2H_3Cl, reacts with oxygen according to the equation below:

$$2C_2H_3Cl(g) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(g) + 2HCl(g)$$

What is the amount, in mol, of H_2O produced when 10.0 mol of C_2H_3Cl and 10.0 mol of O_2 are mixed together, and the above reaction goes to completion?

A 4.00 **B** 8.00 **C** 10.0 **D** 20.0

11. Airbags are an important safety feature in vehicles. Sodium azide, a toxic compound, undergoes the following decomposition reaction under certain conditions to produce nitrogen gas which fills the airbag.

$$2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$$

(a) Calculate the mass of sodium azide, NaN_3, required to produce 80.0 dm^3 of nitrogen gas at STP. (3)

(b) Calculate the mass of sodium produced in this reaction. (2)

(Total 5 marks)

12. Nitrogen monoxide may be removed from industrial emissions via a reaction with ammonia as shown by the equation below:

$$4NH_3(g) + 6NO(g) \rightarrow 5N_2(g) + 6H_2O(l)$$

30.0 dm^3 of ammonia reacts with 30.0 dm^3 of nitrogen monoxide at 100 °C. Identify which gas is in excess and by how much, and calculate the volume of nitrogen produced. (2)

(Total 2 marks)

13. The percentage by mass of calcium carbonate in eggshell was determined by adding excess hydrochloric acid to ensure that all the calcium carbonate had reacted. The excess acid left was then titrated with aqueous sodium hydroxide.

(a) A student added 27.20 cm^3 of 0.200 mol dm^{-3} HCl to 0.188 g of eggshell. Calculate the amount, in mol, of HCl added. (1)

(b) The excess acid requires 23.80 cm^3 of 0.100 mol dm^{-3} NaOH for neutralization. Calculate the amount, in mol, of acid that is in excess. (1)

(c) Determine the amount, in mol, of HCl that reacted with the calcium carbonate in the eggshell. (1)

(d) State the equation for the reaction of HCl with the calcium carbonate in the eggshell. (2)

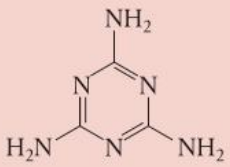
(e) Determine the amount, in mol, of calcium carbonate in the sample of the eggshell. (2)

(f) Calculate the mass **and** the percentage by mass of calcium carbonate in the eggshell sample. (3)

(g) Deduce **one** assumption made in arriving at the percentage of calcium carbonate in the eggshell sample. (1)

(Total 11 marks)

14. Melamine has the following structure:



(a) It can be produced from urea, $(NH_2)_2CO$, in the following reaction:

$$6(NH_2)_2CO \rightarrow C_3H_6N_6 + 6NH_3 + 3CO_2$$

Calculate the atom economy for the reaction. Give your answer to 3 significant figures. (2)

(b) Calculate the theoretical yield of melanine in grams produced when 14.0 g of urea is broken down. (2)

(c) Use your answer from part **(b)** to calculate the % yield of the reaction if 4.12 g melanine was produced experimentally. (1)

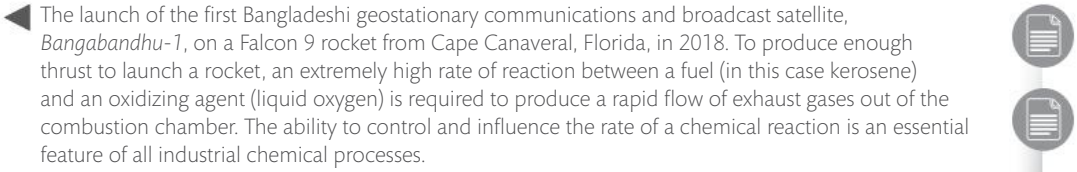
If you did not get an answer to part (b), use a theoretical yield of 5.00 g melanine.

(Total 5 marks)



REACTIVITY

2.2 How fast? The rate of chemical change



The launch of the first Bangladeshi geostationary communications and broadcast satellite, *Bangabandhu-1*, on a Falcon 9 rocket from Cape Canaveral, Florida, in 2018. To produce enough thrust to launch a rocket, an extremely high rate of reaction between a fuel (in this case kerosene) and an oxidizing agent (liquid oxygen) is required to produce a rapid flow of exhaust gases out of the combustion chamber. The ability to control and influence the rate of a chemical reaction is an essential feature of all industrial chemical processes.

Guiding Question

How can the rate of a reaction be controlled?

The **rate**, or kinetics, of a chemical reaction refers to the speed at which reactants are converted into products during a chemical process. We will all have some familiarity with this concept in everyday life. Imagine, for example, you are cooking in the kitchen. As you drop an egg into hot oil in the pan, it immediately changes to a white solid; meanwhile, a container of milk that was left out of the refrigerator is slowly turning sour. We observe a similarly wide variation in the rate of reactions that we study in the laboratory, and these data can be very useful.

Studies of rates of reaction are of prime importance in industry because they give information on how quickly products form and on the conditions that give the most efficient and economic yield. They can also be useful in situations where we want to slow reactions down – for example, the reactions that cause the destruction of ozone in the stratosphere, or the reactions where pollutants in the air combine to produce smog. At other times, it is important to know for how long a certain reaction will continue – for example, the radioactive effect from radioactive waste.

This chapter begins with a study of reaction rates and a consideration of how these are measured in different cases. Through the explanation of **collision theory**, we will come to understand why different factors affect the rate of reactions. These factors will include pressure, concentration, surface area, temperature and presence of a catalyst.

HL Knowledge of rates of reaction also gives insights into how reactions happen at the molecular level by suggesting a sequence of bond breaking and bond making, known as a **reaction mechanism**.

Reactivity 2.2.1 – Rate of reaction

Reactivity 2.2.1 – The rate of reaction is expressed as the change in concentration of a particular reactant or product per unit time.	
Determine rates of reaction.	
Calculation of reaction rates from tangents of graphs of concentration, volume or mass against time should be covered.	Tool 1, 3, Inquiry 2 – Concentration changes in reactions are not usually measured directly. What methods are used to provide data to determine the rate of reactions? Tool 1 – What experiments measuring reaction rates might use time as (i) a dependent variable or (ii) an independent variable?

Rate of reaction is defined as the rate of change in concentration

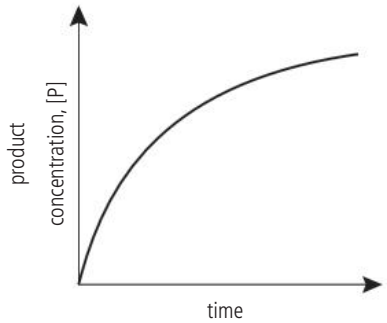
When we are interested in how quickly something happens, the factor that we usually measure is **time**. For example, in a sports race, the competitors are judged by the time it takes them to reach the finishing line. However, if we want to compare their performance in different races over different distances, we would need to express this as a rate – in other words, how they performed ***per unit time***.

Rate takes the reciprocal value of time, so is expressed *per unit time* or, in SI units, *per second* (symbol = s^{-1}).

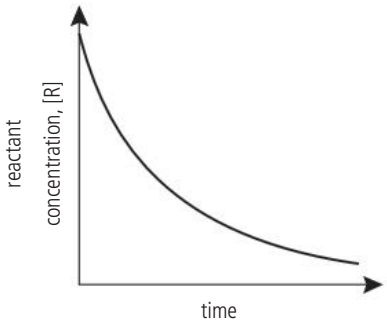
$$\text{rate} = \frac{1}{\text{time}} = \frac{1}{\text{s}} = \text{s}^{-1}$$

Note that because time and rate are reciprocal values, as one decreases, the other increases. So in the example above, the racer with the *shortest time* wins the race, because they had the *fastest rate*.

In the study of chemical reactions, we use the concept of **rate of reaction** to describe how quickly a reaction happens. As the reaction proceeds, reactants are converted into products, and so the concentration of reactants decreases as the concentration of products increases. The graphs in Figures 1 and 2 show sketches of typical data from reactions.



R2.2 Figure 1 Concentration of product against time.



R2.2 Figure 2 Concentration of reactant against time.

The rate of a reaction depends on how quickly the concentration of either reactant or product changes with respect to time. It can be defined as follows:

$$\text{rate of reaction} = \frac{\text{increase in product concentration}}{\text{time taken}} \text{ or } \frac{\text{decrease in reactant concentration}}{\text{time taken}}$$

Using Δ to represent 'change in', [R] for concentration of reactant, and [P] for concentration of product, we can express this as:

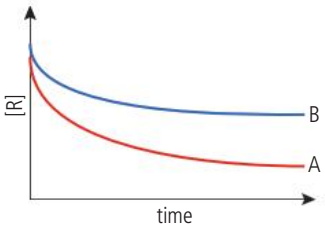
$$\text{rate of reaction} = \frac{\Delta[\text{P}]}{\Delta t} \text{ or } -\frac{\Delta[\text{R}]}{\Delta t}$$

The rate of a chemical reaction is the increase in concentration of products, or the decrease in concentration of reactants, per unit time.

It is worth noting that, by convention, rate should be expressed as a positive value. For this reason, a negative sign has been placed in front of the reactant expression which would otherwise produce a negative value due to [R] decreasing over time.

As rate = change in concentration per time, its units are **mol dm^{-3} s^{-1}**.

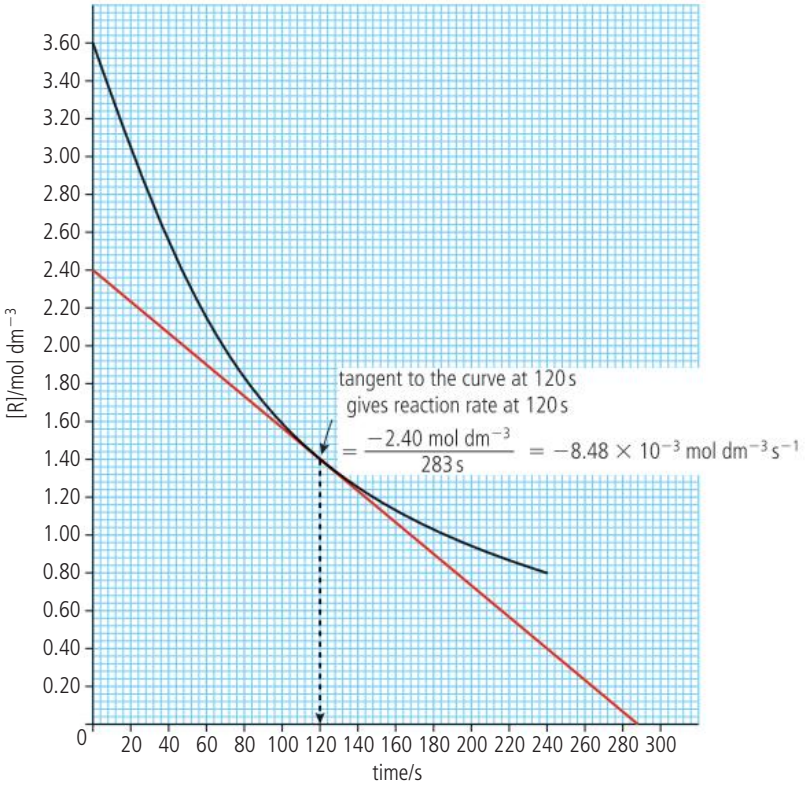
Figure 3 represents graphs of two different reactions showing the change in concentration of reactant against time.



R2.2 Figure 3 Reactant concentration against time for two different reactions, A and B.

We can see that the concentration of reactants is decreasing more quickly in reaction A than in reaction B – the curve is steeper. The steepness, or gradient, of the curve is a measure of the change in concentration per unit time, in other words, the rate of the reaction.

Because the graphs are curves and not straight lines, the gradient is not constant and so can only be given for a particular value of time. We can measure this by drawing a tangent to the curve at the specified time point and measuring its gradient. This is shown in Figure 4 for the time at 120 s. Note that the gradient of this graph is negative as the reactant concentration is decreasing, but rate is expressed as a positive value.



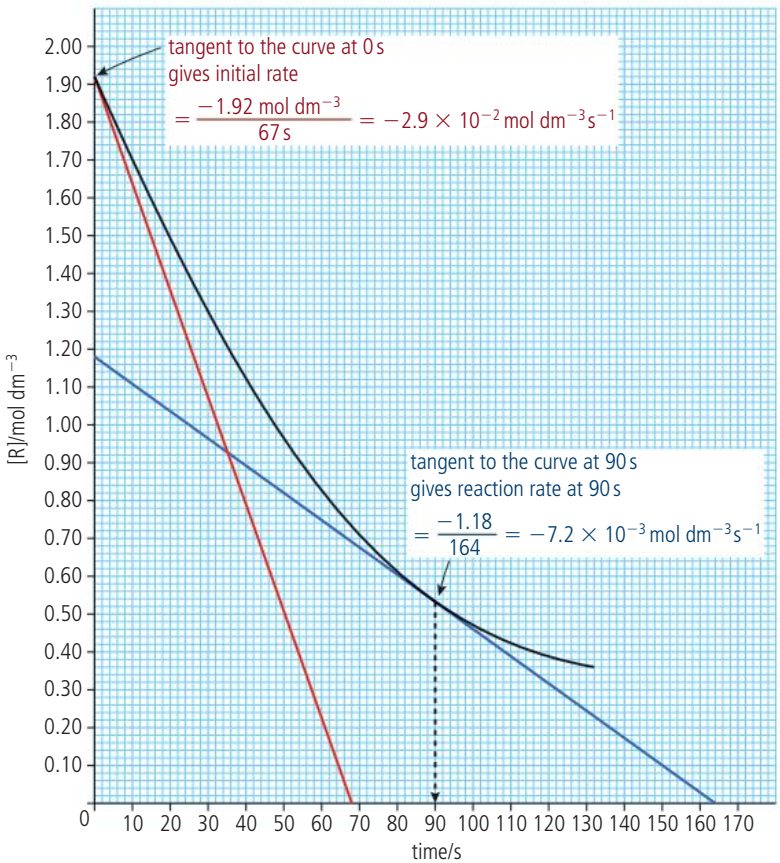
R2.2 Figure 4 Measuring the gradient of the tangent to the curve at time t = 120 s. The measured rate of the reaction is 8.48×10^{-3} mol dm^{-3} s^{-1} at this time. Note that, by convention, rate is always expressed as a positive value.

The shape of the curve indicates that the rate of the reaction is not constant during the reaction, but is greatest at the start and slows down as the reaction proceeds. This is illustrated in Figure 5, which shows the calculation of reaction rate at two different times during a reaction.

$t = 0\,s$; rate $= 2.9 \times 10^{-2}\,mol\,dm^{-3}\,s^{-1}$

$t = 90\,s$; rate $= 7.2 \times 10^{-3}\,mol\,dm^{-3}\,s^{-1}$

You will get a more accurate value for the slope of the tangent if you draw it as long as you reasonably can, so that the '*y*' value (concentration) and the '*x*' value (time) are as large as possible.



R2.2 Figure 5 Measuring the gradient of the tangent to the curve at two different times during a reaction. The rate decreases as the reaction proceeds.

Note the difference between the two instructions 'draw a graph' and 'sketch a graph'. *Drawing* is based on actual data so scales must be chosen appropriately and data points and units clearly marked; *sketching* is a way of showing a trend in the variables, without reference to specific data. Note that in both cases, the axes must be clearly labelled with the dependent variable on the *y*-axis and the independent variable on the *x*-axis.

The rate is greatest at the start because this is when the reactant concentration is highest. The effect of concentration on reaction rate is discussed later in this chapter. Because of this variation in rate as a reaction proceeds, in order to compare the rates of reactions under different conditions, it is common to compare the **initial rate** of each reaction by taking the tangent to the curve at $t = 0$. As we will see later in this chapter, initial rate data are very useful in analysing the effect of concentration on rate.

The rate of a reaction is not constant during a reaction, but is greatest at the start and decreases as the reaction proceeds.

Measuring rates of reaction uses different techniques depending on the reaction

Choosing whether to measure the change in concentration of reactants or products, and the technique with which to measure that change, really depends on what is the most convenient for a particular reaction. This is different for different reactions. In most cases the concentration is not measured directly, but is measured by means of a signal that is related to the changing concentration. If, for example, a reaction forms a coloured precipitate as a product, the change in colour could be measured. If a reaction gives off a gas, then the change in volume or change in mass could be measured. The raw data collected using these 'signals' will be in a variety of units, rather than as concentrations measured in mol dm^{-3} directly. This is generally not a problem, as it still enables us to determine the rate of the reaction. Many of the experiments used here can be carried out using data-logging devices. Some examples of common techniques in relation to specific reactions are discussed below.

Tool 1, 3, Inquiry 2 – Concentration changes in reactions are not usually measured directly. What methods are used to provide data to determine the rate of reactions?

Nature of Science

Although the chemical reactions between individual molecules cannot be observed directly, there are many indirect methods for investigating these processes in order to develop explanations for what is happening. As with all of chemistry, the validity of these theories is dependent on the extent to which they are supported by experimental data and their ability to make accurate predictions.

TOK

Note that the balanced equation of a reaction gives us no information about its rate. We can obtain this information only from experimental (empirical) data. Is there a fundamental difference between knowledge claims based on conclusions from theoretical data and those based on experimental data?

Change in volume of gas produced

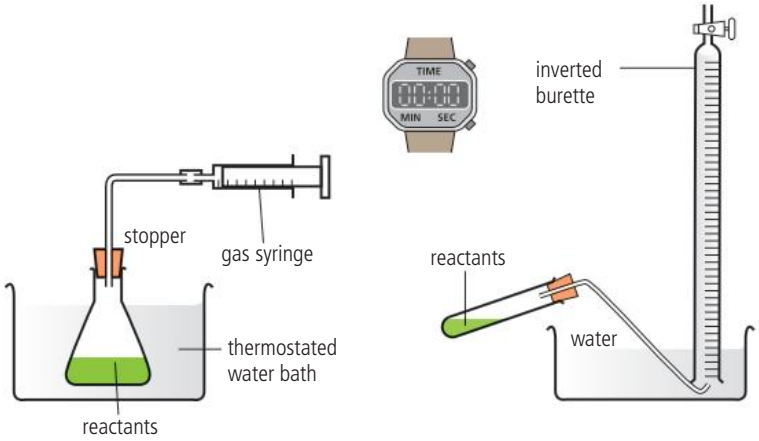
This is a convenient method if one of the products is a gas. Collecting the gas and measuring the change in volume at regular time intervals enables a graph to be plotted of volume against time. A **gas syringe** can be used for this purpose. It consists of a ground glass barrel and plunger. The plunger moves outwards as the gas collects and the barrel is calibrated to record the volume directly. Alternatively, the gas can be collected by displacement of water from an inverted burette. Note though that the displacement method can only be used if the gas collected has low solubility in water. Data loggers are also available for continuous monitoring of volume change against time. The rate of reaction of a metal with dilute acid to release hydrogen gas can be followed in this way.

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

Challenge yourself

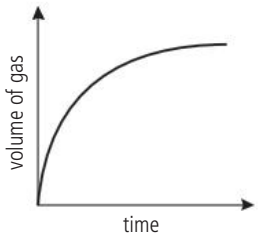
1. Most gases are less soluble in warm water than in cold water, so using warm water may help to reduce a source of error when collecting a gas by displacement of water. But what new error might this create?

Experiments to measure rate of reaction by following change in volume against time.



When you take a glass of cold water from the refrigerator and leave it by your bed overnight, you may notice bubbles of gas have formed by morning. This is because the gas (mostly dissolved oxygen) has become less soluble as the temperature of the water has increased.

Volume of gas against time. The reaction has ended when the curve reaches a plateau.

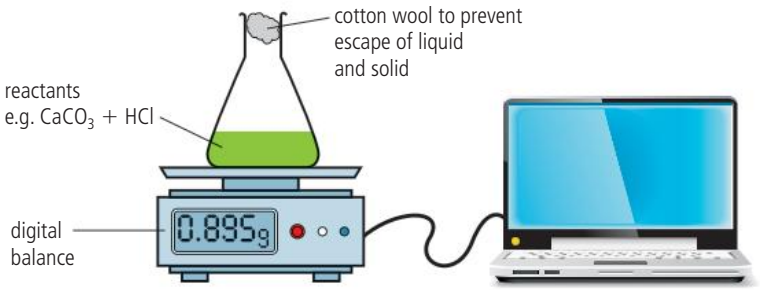


Change in mass

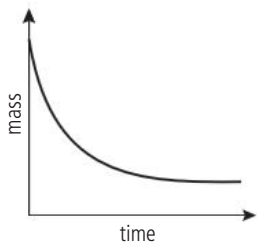
Many reactions involve a change in mass, and it may be convenient to measure this directly. If the reaction is giving off a gas, the corresponding decrease in mass can be measured by standing the reaction mixture directly on a balance. This method is unlikely to work well where the evolved gas is hydrogen, as it is too light to give significant changes in mass. The method allows for continuous readings, so a graph can be plotted directly of mass against time. For example, the release of carbon dioxide from the reaction between a carbonate and dilute acid can be followed in this way.

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

Experiment to measure rate of reaction by following change in mass against time.

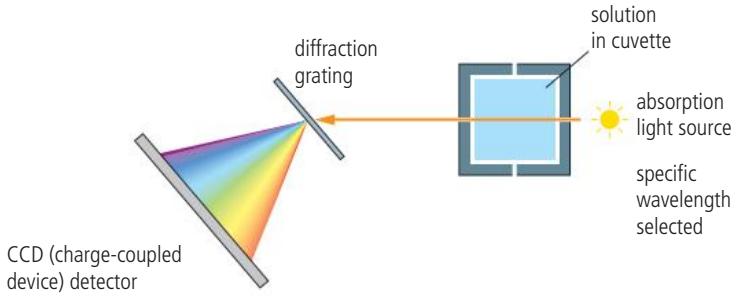


Mass against time. The reaction has ended when the curve reaches a plateau.



Change in transmission of light: colorimetry/spectrophotometry

This technique can be used if one of the reactants or products is coloured and so gives characteristic absorption in the visible region (wavelengths about 320–800 nm). Sometimes an indicator can be added to generate a coloured compound that can then be followed in the reaction. A colorimeter or spectrophotometer works by passing light of a selected wavelength through the solution being studied and measuring the intensity of the light transmitted by the reaction components. As the concentration of the coloured compound increases, it absorbs proportionally more light, so less is transmitted. A photocell generates an electric current according to the amount of light transmitted and this is recorded on a meter or connected to a computer.



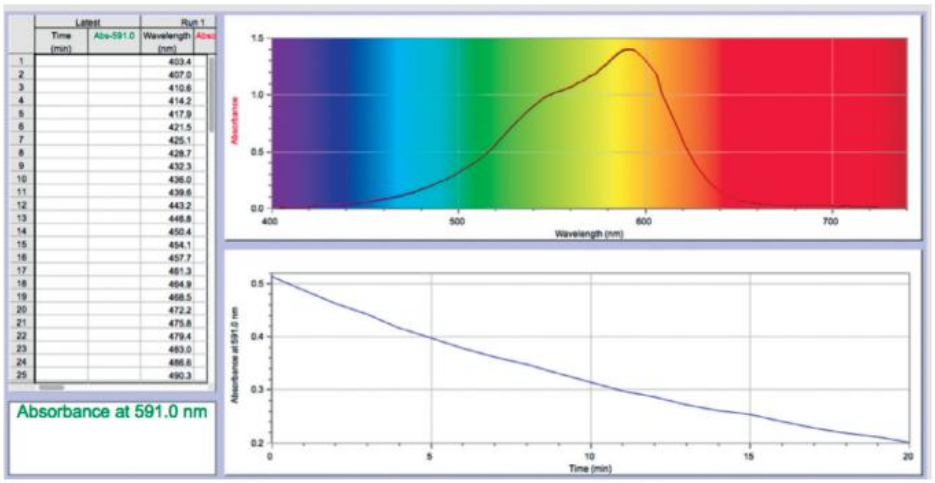
A spectrophotometer measures absorbance, which directly relates to concentration. Light of a specific wavelength is selected from an internal source and passed through the solution placed in the cuvette. The transmitted light passes through a diffraction grating, then the diffracted light is collected and changed into a digital signal by the charge-coupled device (CCD) detector.

The method allows for continuous readings to be made, so a graph of absorbance against time can be plotted directly. It is possible to convert the absorbance values into concentrations using a standard curve based on readings of known concentration. Often, however, it is sufficient to record absorbance itself (or transmittance, which is inversely proportional to absorbance) as a function against time.

For example, the reaction between the dye crystal violet and sodium hydroxide solution can be written in an abbreviated form as follows:

$$CV^+ + OH^- \rightarrow CVOH$$

The initial crystal violet solution (CV^+) is coloured but this slowly changes to a colourless solution as the product (CVOH) is formed. So we can determine the rate of product formation by measuring the *decrease in absorbance* that occurs as the coloured reactant is depleted. The figure shows data from this reaction, with absorbance at 591 nm measured against time.



Results of an experiment to determine the rate of reaction by following change in absorbance against time using a digital spectrophotometer.

An example of the use of a calibration curve to determine concentration from absorbance data is outlined in Structure 3.1.

Change in concentration measured using titration

In some reactions it may be possible to measure the concentration of one of the reactants or products by titrating it against a known 'standard' (see Structure 1.4). However, because this technique involves chemically changing the reaction mixture, it cannot be done continuously as the reaction proceeds. Instead, samples must be withdrawn from the reaction mixture at regular time intervals and then analysed by titration. A problem here is that the process of titration takes time, during which the reaction mixture in the sample will continue to react. To overcome this, a technique known as **quenching** can be used, where a substance is introduced which effectively stops the reaction in the sample at the moment it is withdrawn. It is rather like obtaining a 'freeze frame' shot of the reaction at a particular interval of time. In order to see how concentration changes as the reaction proceeds, it is necessary to repeat this process at several intervals of time.

For example, the reaction between H_2O_2 and acidified KI yields I_2, which can be titrated against sodium thiosulfate, $Na_2S_2O_3$, to determine its concentration. Sodium carbonate, Na_2CO_3, is used to quench the reaction by neutralizing the added acid.

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

Change in concentration measured using conductivity

The total electrical conductivity of a solution depends on the total concentration of its ions and on their charges. If this changes when reactants are converted to products, it can provide a convenient method to follow the progress of the reaction. Conductivity can be measured directly using a conductivity meter which involves immersing inert electrodes in the solution. As with colorimetry, the apparatus can be calibrated using solutions of known concentration so that the readings can be converted into the concentrations of the ions present.

For example, in the reaction:

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

the sharp decrease in the concentration of ions (12 on the reactants side and 0 on the products side) will give a corresponding decrease in the electrical conductivity of the solution as the reaction proceeds.

Non-continuous methods of detecting change during a reaction: 'clock reactions'

Sometimes it is difficult to record the continuous change in the rate of a reaction. In these cases, it may be more convenient to measure the time it takes for a reaction to reach a certain chosen fixed point – that is, something observable which can be used as an arbitrary 'end point' by which to stop the clock. The time taken to reach this point for the same reaction under different conditions can then be compared and used as a means of judging the different rates of the reaction. So in contrast to the first five techniques of measuring rate of reaction where time is the independent variable, detecting a change in a clock reaction uses time as a dependent variable.

Tool 1 – What experiments measuring reaction rates might use time as (i) a dependent or (ii) an independent variable?

Note that the limitation of this method is that the data obtained give only an average rate over the time interval.

For example, the following can be measured:

- the time taken for a certain size piece of magnesium ribbon to react completely with dilute acid, until it is no longer visible

$$Mg(s) + 2HCl\,(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

- the time taken for a solution of sodium thiosulfate with dilute acid to become opaque by the precipitation of sulfur, so that a cross viewed through paper is no longer visible

$$Na_2S_2O_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + SO_2(aq) + H_2O(l) + S(s)$$



Recording the increase in opaqueness during a reaction. Sodium thiosulfate (left) is a clear liquid, which reacts with hydrochloric acid (upper centre) to form an opaque solution (right). A cross (left) drawn onto paper is placed under the reaction beaker to allow the end point to be confirmed. The experiment is timed from when the reactants are mixed until the cross disappears from sight.

SKILLS

Investigating rates of reaction. Full details of how to carry out this experiment with a worksheet are available in the eBook.

In all these reactions, the goal is to measure change in concentration against time. This allows a comparison of reaction rates under different conditions. But because the rate is dependent on temperature, it is essential to control the temperature throughout these experiments. It is sometimes suitable to carry out the reactions in a thermostatically controlled water bath.

Exercise

Q1. Consider the following reaction.

$$2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$

Describe three different ways in which you could measure the rate of this reaction.

Q2. Which units are used to express the rate of a reaction?

A $mol\,dm^{-3}\,time$ **B** $mol^{-1}\,dm^3\,time^{-1}$

C $mol\,dm^{-3}\,time^{-1}$ **D** $mol\,time^{-1}$

Q3. The reaction between calcium carbonate and hydrochloric acid is carried out in an open flask. Measurements are made to determine the rate of the reaction.

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

(a) Suggest three different types of data that could be collected to measure the rate of this reaction.

(b) Explain how you would expect the rate of the reaction to change with time and why.

Q4. The following data were collected for the reaction $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$ at 390 °C.

$[H_2O_2]$ / mol dm^{-3}	Time / s	$[H_2O_2]$ / mol dm^{-3}	Time / s
0.200	0	0.070	120
0.153	20	0.063	140
0.124	40	0.058	160
0.104	60	0.053	180
0.090	80	0.049	200
0.079	100		

Draw a graph of concentration against time and determine the reaction rate after 60 s and after 120 s.

SKILLS

Modelling rate of reaction: collisions in the court. Full details of how to carry out this activity with a worksheet are available in the eBook.

Reactivity 2.2.2 – Collision theory

Reactivity 2.2.2 – Species react as a result of collisions of sufficient energy and proper orientation.

Explain the relationship between the kinetic energy of the particles and the temperature in kelvin, and the role of collision geometry.

	Structure 1.1 – What is the relationship between the kinetic molecular theory and collision theory?

TOK

The Kelvin scale of temperature gives a natural measure of the average kinetic energy of molecules in a gas, whereas the Celsius scale is based on the properties of water. Are physical properties such as temperature invented or discovered?

Species react as a result of collisions

Kinetic energy and temperature

Since the early 18th century, scientists have developed theories to explain the fact that gases exert a pressure. These theories developed alongside a growing understanding of the atomic and molecular nature of matter, and were extended to include the behaviour of particles in all states of matter. Today they are summarized as the **kinetic molecular theory of matter** (see Structure 1.1).

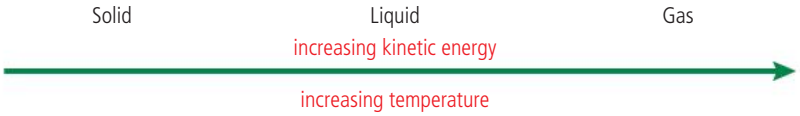
The essence of the kinetic molecular theory is that particles in a substance move randomly as a result of the **kinetic energy** that they possess. Because of the random nature of these movements and collisions, not all particles in a substance at any one time have the same values of kinetic energy, but will instead have a range of values. A convenient way to describe the kinetic energy of a substance is therefore to take the *average* of these values, and this is directly related to its **absolute temperature** – that is, its temperature measured in kelvin.

Increasing temperature therefore means an increase in the average kinetic energy of the particles of a substance. As we supply a substance with extra energy by heating it, we raise the average kinetic energy of the particles and so also raise its temperature. When we compare the behaviour of the particles in the three states of matter from solid, through liquid, to gas, the differences are a result of this increase in the average kinetic energy of the particles.



A puddle of water evaporates, even on a cold day, because a small proportion of molecules on the surface have enough kinetic energy to vaporize. This demonstrates that the particles in a substance must have a range of values of kinetic energy as described by kinetic molecular theory.

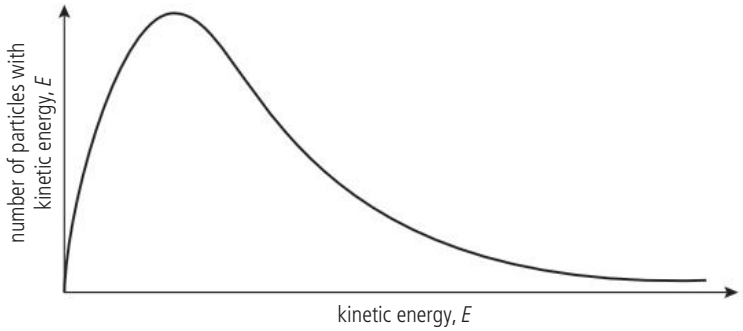
For a given substance this can be summarized as follows:



Temperature in kelvin (K) is proportional to the average kinetic energy of the particles in a substance.

The Maxwell–Boltzmann energy distribution curve

The fact that particles in a gas at a specific temperature show a range in their values of kinetic energy is expressed by the **Maxwell–Boltzmann energy distribution curve**.



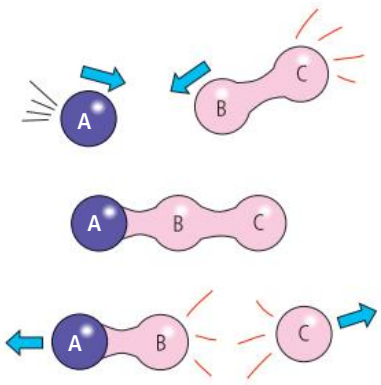
The Maxwell–Boltzmann energy distribution curve.

Like other distribution curves, this shows the number of particles having a specific value of kinetic energy (or the probability of that value occurring) plotted against the values for kinetic energy. The area under the curve represents the total number of particles in the sample.

Although their names are linked in the famous energy distribution curve discussed here, James Clerk Maxwell and Ludwig Boltzmann had very different outlooks on life. Maxwell was a Scottish physicist, known for his curiosity and humour. His wife worked alongside him in many of his experiments. Boltzmann, an Austrian, was prone to depression and took his own life, seemingly believing that his work was not valued. Nonetheless, as peers during the 19th century, they refined and developed each other's ideas, culminating in the distribution curve that bears their two names.

The nature of collisions between particles

When reactants are placed together, the kinetic energy that their particles possess causes them to collide with each other. The energy of these collisions may result in some bonds within the reactants being broken, and some new bonds forming. As a result, products form and the reaction 'happens'. This explanation of chemical reactions is known as collision theory.



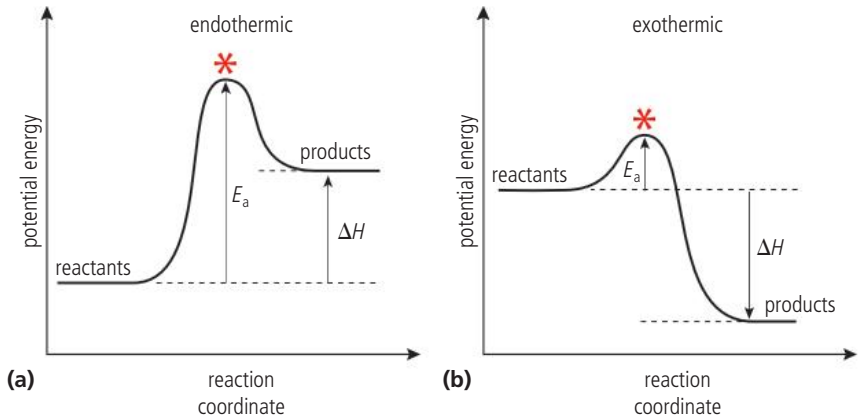
Particles react by colliding with sufficient kinetic energy and in the correct orientation.

It follows that the rate of the reaction will depend on the number of collisions between particles that are 'successful', that is, which lead to the formation of products. But a very important point is that *not all collisions will be successful*. There are two main factors that influence this:

- energy of collision and
- geometry of collision.

Energy of collision

In order for a collision to lead to a reaction, the particles must have a certain minimum value for their kinetic energy, known as the **activation energy**, E_a. This energy is necessary for overcoming repulsion between molecules, and often for breaking some bonds in the reactants before they can react. When this energy is supplied, the reactants achieve the **transition state** from which products can form. The activation energy therefore represents an energy barrier for the reaction, and it has a different value in different reactions.

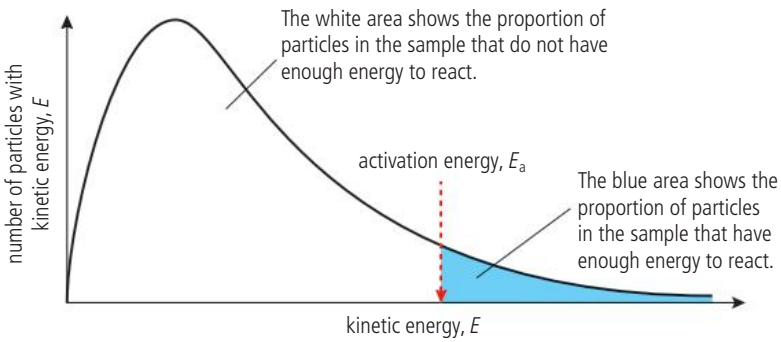


Energy path of a reaction with the activation energy for **(a)** endothermic and **(b)** exothermic reactions. * represents the transition state.

Activation energy (E_a) is defined as the minimum value of kinetic energy that particles must have before they are able to react.

We can think of the activation energy as a 'threshold value' – a bit like a pass mark in an examination: values greater than this mark achieve a pass, lower values do not achieve a pass. The activation energy threshold similarly determines which particles react and which do not. So only particles that have a kinetic energy value greater than the activation energy will have successful collisions. Note that particles with lower values of kinetic energy may still collide, but these collisions will not be 'successful' in the sense of causing a reaction.

It therefore follows that the rate of the reaction depends on the proportion of particles that have values for kinetic energy greater than the activation energy.



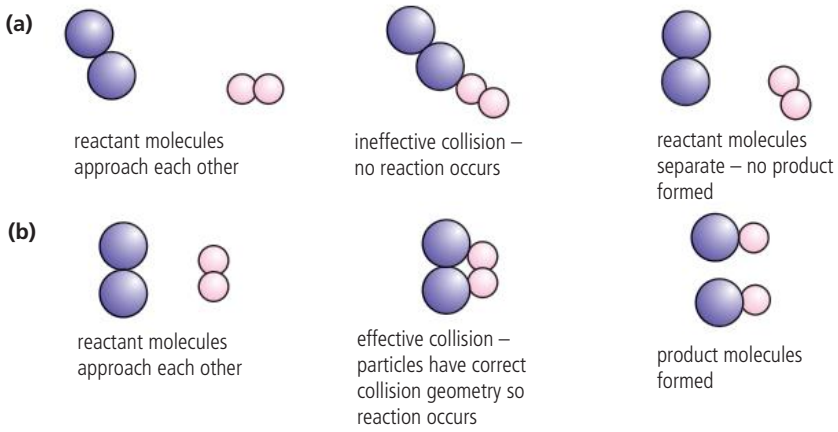
Maxwell–Boltzmann energy distribution curve showing how the activation energy, E_a, distinguishes between particles that have greater or lesser values of the kinetic energy required to react.

The magnitude of the activation energy varies greatly from one reaction to another, and it is an important factor in determining the overall rate of the reaction. In general, reactions with high activation energy proceed more slowly than those with low activation energy as fewer particles will have the required energy for a successful collision.

HL Later in this chapter, we will learn how activation energy can be calculated.

Geometry of collision

Because collisions between particles are random, they are likely to occur with the particles in many different orientations. In some reactions, this can be crucial in determining whether or not the collisions will be successful, and therefore what proportion of collisions will lead to a reaction.



The effect of collision geometry. In **(a)** the particles do not have the correct collision geometry and no reaction occurs. In **(b)** the particles collide with the correct geometry, enabling products to form.

We can now summarize the collision theory as follows. The rate of a reaction depends on the frequency of collisions that occur between particles possessing both:

- values of kinetic energy greater than the activation energy and
- appropriate collision geometry.

Understanding this theory will help us to investigate and explain the factors that increase the rate of reaction.

In order to react, particles must collide with kinetic energy greater than the activation energy and have the correct collision geometry.

Nature of Science

The collision between a small number of reacting species resulting in chemical change has not been observed directly. Instead, collision theory is based on an application of kinetic molecular theory and theory of how chemical reactions occur through bond-breaking and bond-making. In science, theories generally accommodate the assumptions and premises of other theories in this way. The fact that collision theory helps to explain the observed effects of factors influencing the rate of reactions adds to its validity. The theory enables chemists to make predictions about the impact of different factors on the rates of specific reactions, which has important applications in many branches of chemistry such as industry, biochemistry and environmental chemistry.

Structure 1.1 – What is the relationship between the kinetic molecular theory and collision theory?

Exercise

Q5. Which statement is correct for a collision between reactant particles that leads to reaction?

A Colliding particles must have different energy.

B Colliding particles must have the same energy.

C Colliding particles must have kinetic energy greater than the average kinetic energy.

D Colliding particles must have kinetic energy greater than the activation energy.

Q6. Which of the following determine whether a reaction will occur?

I. the orientation of the molecules
II. the energy of the molecules
III. the volume of the container

A I and II **B** I and III **C** II only **D** I, II and III

Q7. If we compare two reactions, one which requires the simultaneous collision of three molecules and the other which requires a collision between two molecules, which reaction would you expect to be faster? Explain why.

Reactivity 2.2.3, 2.2.4 and 2.2.5 – Factors that influence the rate of reaction

Reactivity 2.2.3 – Factors that influence the rate of a reaction include pressure, concentration, surface area, temperature and the presence of a catalyst.

Predict and explain the effects of changing conditions on the rate of a reaction.

	Tool 1 – What variables must be controlled in studying the effect of a factor on the rate of a reaction? Nature of Science, Tool 3, Inquiry 3 – How can graphs provide evidence of systematic and random error?

Reactivity 2.2.4 – Activation energy, E_a, is the minimum energy that colliding particles need for a successful collision leading to a reaction.

Construct Maxwell–Boltzmann energy distribution curves to explain the effect of temperature on the probability of successful collisions.

Reactivity 2.2.5 – Catalysts increase the rate of reaction by providing an alternative reaction pathway with lower E_a.

Sketch and explain energy profiles with and without catalysts for endothermic and exothermic reactions.

Construct Maxwell–Boltzmann energy distribution curves to explain the effect of different values for E_a on the probability of successful collisions.

Biological catalysts are called enzymes. The different mechanisms of homogeneous and heterogeneous catalysts will not be assessed.	Reactivity 2.3 – What is the relative effect of a catalyst on the rate of the forward and backward reactions? HL Structure 3.1 – What are the features of transition elements that make them useful as catalysts?

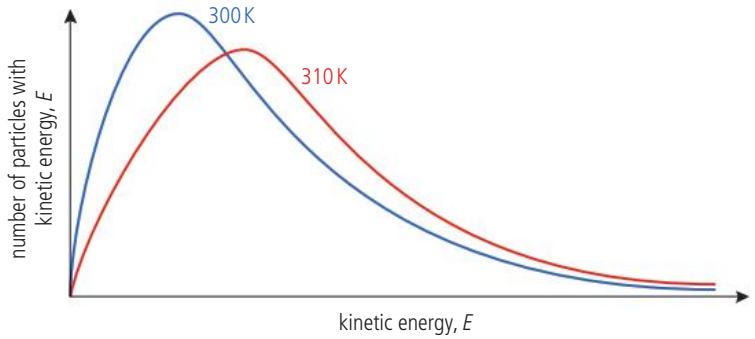
Be careful not to confuse the question of 'how fast?' a reaction goes with the question of 'how far?' it goes. We are discussing only the first question here. The question of how far a reaction goes, which influences the *yield* of the reaction, will be discussed in Reactivity 2.3.

Temperature, concentration, pressure, surface area and the use of a catalyst can influence the rate of reaction

From the collision theory, we know that any factor which increases the number of successful collisions will increase the rate of the reaction. We will investigate five such factors here.

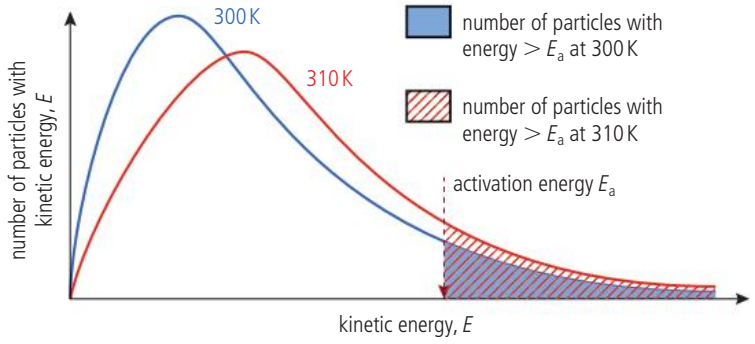
Temperature

Increasing the **temperature** causes an increase in the average kinetic energy of the particles. We can see this by comparing Maxwell–Boltzmann energy distribution curves of the same sample of particles at two different temperatures.



Maxwell–Boltzmann distribution curves for a sample of gas at 300 K and 310 K. At the higher temperature, the curve has shifted to the right and become broader, showing a larger number of particles with higher values for kinetic energy.

The area under the two curves is equal as this represents the total number of particles in the sample. But at the higher temperature, more of the particles have higher values for kinetic energy and the peak of the curve shifts to the right. In Figure 6, we can see how this shift increases the proportion of particles that have values for kinetic energy greater than that of the activation energy.



R2.2 Figure 6 Maxwell–Boltzmann energy distribution curves for a sample of gas at two different temperatures, showing the higher proportion of particles with kinetic energy greater than the activation energy at the higher temperature.

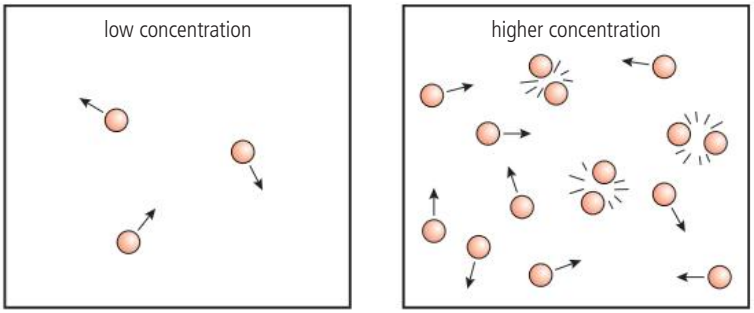
So, as temperature increases, there is an increase in collision frequency due to the higher kinetic energy, but more importantly, there is an increase in the number of collisions involving particles with the necessary activation energy to overcome the activation energy barrier. Consequently, there is an increase in the frequency of *successful* collisions and so an increase in the rate of reaction. Many reactions approximately double their reaction rate for every 10 °C increase in temperature.

HL Later in this chapter we will explore this further through a study of the mathematical relationship between temperature and rate of reaction.

Concentration

Increasing the **concentration** of reactants increases the rate of reaction. This is because as concentration increases, the frequency of collisions between reactant particles increases, as shown in Figure 7. The frequency of successful collisions therefore increases too.

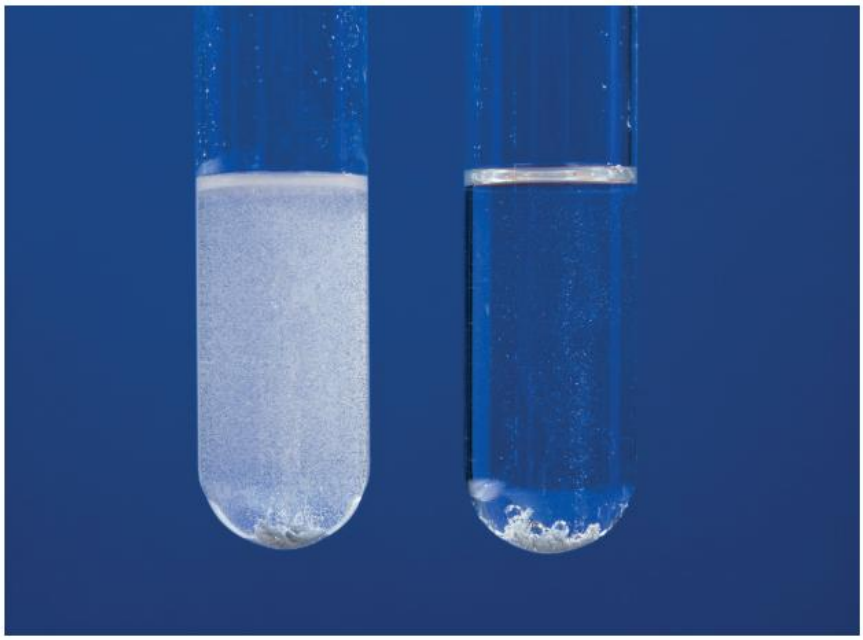
i Specimens of the extinct mammal the mammoth, dated as 10 000 years old, have been found perfectly preserved in the Arctic ice, whereas for individual specimens of a similar age found in California, only bones remain. This is an illustration of the effect of the cold temperature in the Arctic decreasing the rate of the reactions of decay. The same concept is used in the process of refrigerating or freezing food to preserve it.



R2.2 Figure 7 Effect of concentration on collision frequency.

When particles are closer together they have a greater chance of colliding.

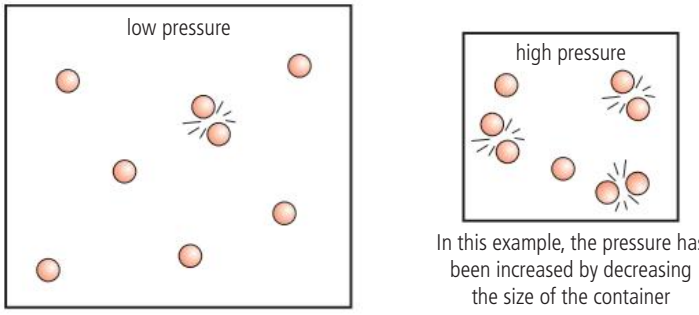
We can see the effect of concentration by following the rate of a reaction as it progresses. As reactants are used up, their concentration falls and the rate of the reaction decreases, giving the typical rate curves we saw in Figures 1 and 2.



The effect of concentration on the rate of reaction between zinc and sulfuric acid. The tube on the left has a more concentrated solution of the acid, the tube on the right has a more dilute solution. The product, hydrogen gas, is seen collecting much more quickly in the presence of the more concentrated acid.

Pressure

For reactions involving gases, increasing **pressure** increases the rate of reaction. This is because the higher pressure compresses the gas, effectively increasing its concentration. This will increase the frequency of collisions.



At the same temperature, the box on the right has a higher pressure and a greater collision frequency.

In this example, the pressure has been increased by decreasing the size of the container

Surface area

Increasing the **surface area** of reactants increases the rate of reaction. This is important in heterogeneous reactions where the reactants are in different phases, such as a solid reacting with a solution. Subdividing a large particle into smaller parts increases the total surface area and therefore allows more contact and a higher probability of collisions between the reactants. You may know, for example, how much easier it is to start a fire using small pieces of wood, rather than a large log – it is because with the small pieces there is more contact between the wood and the oxygen with which it is reacting. In reactions involving solids in solutions, stirring may help to increase the surface area of the solid by ensuring individual particles are spread throughout the solution and do not aggregate at the bottom of the container. This increases the rate of reaction.

The effect of particle size can be demonstrated in the reaction between marble ($CaCO_3$) and hydrochloric acid. When marble chips are replaced with powder, the effervescence caused by carbon dioxide release is much more vigorous.

This effect of particle size on reaction rate can be quite dramatic. It has been responsible for many industrial accidents involving explosions of flammable dust powders – for example, coal dust in mines and flour in mills.

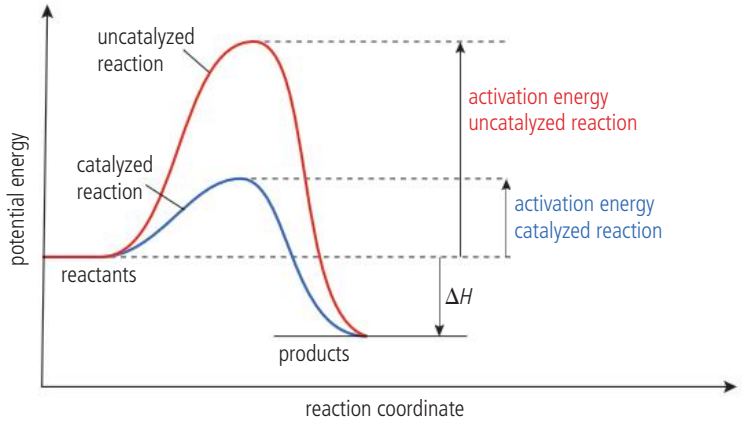


Coal dust explosion experiment at Altofts Colliery, Yorkshire, UK. Health and safety research in the UK started with investigations in the early 20th century into safety in mines. Experiments were carried out at locations such as Altofts Colliery, helping to determine that coal dust was explosive under certain circumstances.

Catalyst

A **catalyst** is a substance that increases the rate of a chemical reaction without itself undergoing chemical change. Most catalysts work by providing an alternative route for the reaction that has a lower activation energy.

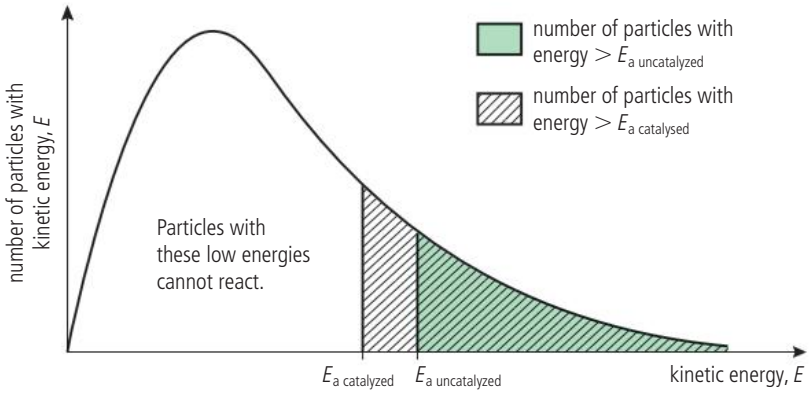
Effect of a catalyst on lowering the activation energy of a reaction.



This means that without increasing the temperature, a larger number of particles will now have values of kinetic energy greater than the activation energy, and so will be able to undergo successful collisions. Think again of activation energy as being like the pass mark in an examination: the effect of the catalyst is like lowering the pass mark. This means that with the same work in the tests, a higher number of people would be able to achieve a pass!

Figure 8 uses the Maxwell–Boltzmann distribution to show how a catalyst increases the proportion of particles having values of kinetic energy greater than the activation energy.

R2.2 Figure 8 Effect of catalyst on increasing the proportion of particles able to react.



A catalyst is a substance that increases the rate of a chemical reaction without itself undergoing permanent chemical change.

Reactivity 2.3 – What is the relative effect of a catalyst on the rate of the forward and backward reactions?

HL Structure 3.1 – What are the features of transition elements that make them useful as catalysts?

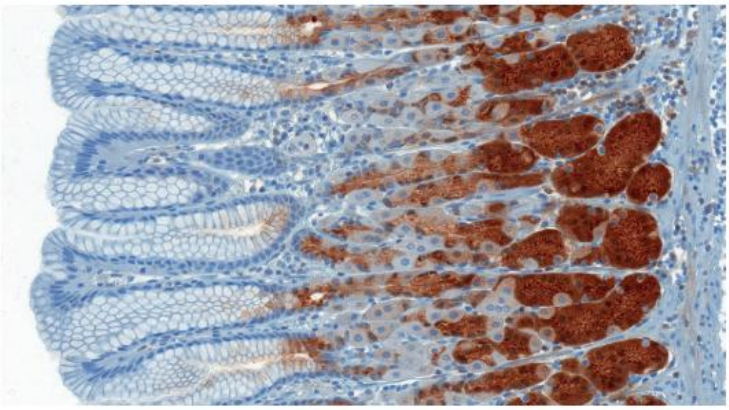
Catalysts bring about an equal reduction in the activation energy of both the forward and the reverse reactions, so they do not change the position of equilibrium or the yield (seen in Reactivity 2.3). However, because of their ability to increase the *rate* of reactions, they influence the rate of formation of products and so play an essential role in the efficiency of many industrial processes. Without catalysts, many reactions would proceed too slowly, or would have to be conducted at such high temperatures that they would simply not be worthwhile. This is why the discovery of the 'best' catalyst for a particular reaction is a very active area of research, and often the exact specification of a catalyst used in an industrial process is a matter of secrecy.

HL Transition metals are particularly common catalysts in industry given their ability to show variable oxidation states as well as using 3d and 4s electrons to form weak bonds with reactant molecules (see Structure 3.1 for more detail).



A catalytic converter containing transition metal catalysts such as platinum, palladium and rhodium. This device catalyses reactions that convert the toxic emissions from an internal combustion engine into less harmful ones. It is estimated that catalytic converters can reduce pollution emissions by 90% without loss of engine performance or fuel economy.

Every *biological* reaction is controlled by a catalyst, known as an **enzyme**. Thousands of different enzymes exist as they are each specific for a particular biochemical reaction. Enzymes are finding increasingly widespread uses in many domestic and industrial processes, from biological detergents to acting as 'biosensors' in medical studies. Some of these applications, such as cheese making, are centuries old, but others are developing rapidly, constituting the field known as **biotechnology**.



Catalysis is also an important aspect of Green Chemistry, which seeks to reduce the negative impact of chemical processes on the environment. Catalysts can replace stoichiometric reagents, and can greatly enhance the selectivity of processes. As they are effective in very small quantities and can frequently be reused, catalysts do not contribute to the chemical waste, and so they increase the atom economy.

Challenge yourself

2. Catalysts can be categorized as 'homogeneous' or 'heterogeneous'. A homogeneous catalyst is in the same phase as the reactants. For example, gaseous chlorine radicals catalyse the breakdown of ozone in the stratosphere. A heterogeneous catalyst, such as solid vanadium(V) oxide in the reaction between gaseous sulfur dioxide and oxygen, is in a different phase to the reactants. Can you identify which type of catalyst might be more difficult to recover after a reaction and suggest a possible approach for doing so?

Catalytic reforming is the process by which linear hydrocarbons are converted into branched or cyclic molecules that burn more smoothly. The development of this process is thought to have played a major role in the Second World War. Aircraft fuel using such hydrocarbons increased the performance of the European allies' planes to the point where they were able to gain victory in the skies.

Biological catalysts are called enzymes.

A microscopic cross-section of glands found in the stomach. The pepsinogen digestive enzyme is shown in brown. It is converted by gastric acid into the active enzyme pepsin which catalyses the breakdown of proteins into small units of amino acids called peptides.

SKILLS

The effect of a catalyst. Full details of how to carry out this experiment with a worksheet are available in the eBook.

Nature of Science

Depletion of the protective ozone layer in the stratosphere has been caused largely by the catalytic effects of CFCs and nitrogen oxides. These chemicals are produced from a variety of sources and often have their most destructive effect far from the country of their origin. International action and cooperation have played an important part in reducing the effects of ozone depletion, and continuing adherence by all countries to international treaties is essential.

Inquiry-based skills for investigating rate of reaction

Identification of controlled variables

Given the range of factors that can affect the rate of reaction, we must be careful to identify the relevant controlled variables when planning an investigation. For example, when investigating the effect of temperature on the reaction between hydrochloric acid, HCl(aq), and magnesium, Mg(s), we would need to ensure that the same concentration of acid is used in each trial as well as using the same sized magnesium strip to control the surface area.

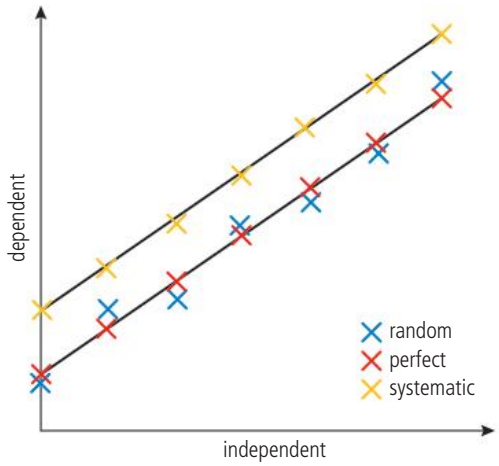
Tool 1 – What variables must be controlled in studying the effect of a factor on the rate of a reaction?

When identifying variables to be controlled, it can be helpful to first consider the factors that affect rate of reaction, such as concentration, surface area and temperature, and then the specific details of your measurement technique. For example, when using a light sensor to measure the rate of formation of a precipitate in a reaction, you would need to ensure that the position of the sensor and light source are the same during all trials. This approach is crucial to obtaining valid data from an investigation.

Evidence for systematic and random errors in graphs

As well as identifying the effect of a given variable on the rate of reaction, graphs can also be used to provide evidence of systematic and random errors.

We can evaluate the fit of a trend line or curve by applying the coefficient of determination, R^2 (pronounced 'R squared'). An R^2 value will fall between 0 and 1, where 1 indicates that the trend line or curve passes perfectly through all data points. This value can be calculated automatically on most graph-plotting software.



In a perfect data set, all data points would be positioned on the trend line. A systematic error produces a displaced straight line above or below the expected position. Random errors lead to points on both sides of the trend line.

Systematic error occurs when all measurements are higher, or all measurements are lower, than the expected value. This leads to inaccuracy in the final results. Random errors occur in individual measurements due to limitations in measurement equipment (uncertainty), changes in the surroundings, misinterpreted measurements or an insufficient number of repeat trials. These can lead to imprecision in collected data.



Nature of Science, Tool 3, Inquiry 3 – How can graphs provide evidence of systematic and random error?

Exercise

Q8. Which of the following statements is correct?

A A catalyst increases the rate of the forward reaction only.

B A catalyst increases the rate of the forward and backward reactions.

C A catalyst increases the yield of product formed.

D A catalyst increases the activation energy of a reaction.

Q9. Which statements are correct for the effects of catalyst and temperature on the rate of reaction?

	Adding a catalyst	Increasing the temperature
A	collision frequency increases	collision frequency increases
B	activation energy decreases	collision frequency increases
C	collision frequency increases	activation energy increases
D	activation energy increases	activation energy decreases

Q10. In the reaction between marble (calcium carbonate) and hydrochloric acid, which set of conditions would give the highest rate of reaction?

$$CaCO_3(s) + 2HCl \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

A marble chips and 1.0 mol dm^{-3} HCl

B marble powder and 1.0 mol dm^{-3} HCl

C marble chips and 0.1 mol dm^{-3} HCl

D marble powder and 0.1 mol dm^{-3} HCl

Q11. A sugar cube cannot be ignited with a match, but a sugar cube coated in ashes will ignite. Suggest a reason for this observation.

Q12. Catalytic converters are now used in most cars to convert some components of exhaust gases into less environmentally damaging molecules. One of these reactions converts carbon monoxide and nitrogen monoxide into carbon dioxide and nitrogen. The catalyst usually consists of metals such as platinum or rhodium.

(a) Write an equation for this reaction.

(b) Explain why it is important to reduce the concentrations of carbon monoxide and nitrogen monoxide released into the atmosphere.

(c) Why do you think the converter sometimes consists of small ceramic beads coated with the catalyst?

(d) Suggest why the converter usually does not work effectively until the car engine has warmed up.

(e) Discuss whether the use of catalytic converters in cars solves the problem of car pollution.

HL

Reactivity 2.2.6, 2.2.7 and 2.2.8 – Reaction mechanisms

Reactivity 2.2.6 – Many reactions occur in a series of elementary steps. The slowest step determines the rate of the reaction. Evaluate proposed reaction mechanisms and recognize reaction intermediates. Distinguish between intermediates and transition states, and recognize both in energy profiles of reactions.	
Include examples where the rate-determining step is not the first step. Proposed reaction mechanisms must be consistent with kinetic and stoichiometric data.	Reactivity 3.4 – Which mechanism in the hydrolysis of halogenoalkanes involves an intermediate?
Reactivity 2.2.7 – Energy profiles can be used to show the activation energy and transition state of the rate-determining step in a multistep reaction. Construct and interpret energy profiles from kinetic data.	
Reactivity 2.2.8 – The molecularity of an elementary step is the number of reacting particles taking part in that step. Interpret the terms 'unimolecular', 'bimolecular' and 'termolecular'.	

Most reactions involve a series of elementary steps

TOK

The study of kinetics enables us to accumulate evidence in support of a particular reaction mechanism. This is an example of inductive reasoning, discussed in the TOK chapter. But there may be alternative reaction pathways that are also consistent with the data. In the examples given here, can you suggest alternative possible reaction mechanisms and what further evidence might support them?

Most reactions that occur at a measurable rate occur as a series of simple steps, each involving a small number of particles, as described in the collision theory discussed earlier in this chapter. This sequence of steps is known as the **reaction mechanism**. The individual steps, called **elementary steps**, usually cannot be observed directly, so the mechanism is in effect a *theory* about the sequence of events in progressing from reactants to products. Chemists derive evidence to support such reaction mechanisms from many sources, and the study of kinetic and stoichiometric data often gives very important clues. It is worth noting though, that while kinetic evidence can help to support a particular mechanism, we cannot *prove* it to be correct – only that it is consistent with the observed data.

Often the products of a single step in the mechanism are used in a subsequent step. They exist only as reaction **intermediates**, not as final products. The sum of the individual steps in the mechanism must equal the overall equation for the reaction and intermediates on both sides cancel out.

For example, in the reaction:

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

It has been shown that the mechanism involves the following elementary steps:

step 1: $NO_2(g) + \cancel{NO_2(g)} \rightarrow NO(g) + \cancel{NO_3(g)}$

step 2: $\cancel{NO_3(g)} + CO(g) \rightarrow \cancel{NO_2(g)} + CO_2(g)$

overall reaction: $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

The overall reaction is obtained by cancelling molecules that appear on both sides.

NO_3 is an intermediate in this reaction, being produced and consumed in different steps, so it does not appear in the overall equation.

The term **molecularity** is used in reference to an elementary step to indicate the number of reactant species involved. So **unimolecular** refers to an elementary step that involves a single reactant particle, and **bimolecular** refers to an elementary step with two reactant particles. In the NO_2 + CO reaction above, both the elementary steps are bimolecular. Because of collision theory, and the extremely low probability of more than two particles colliding at the same time with sufficient energy and in the correct orientation, **termolecular** reactions (those that involve three reactant particles) are rare.

Nature of Science

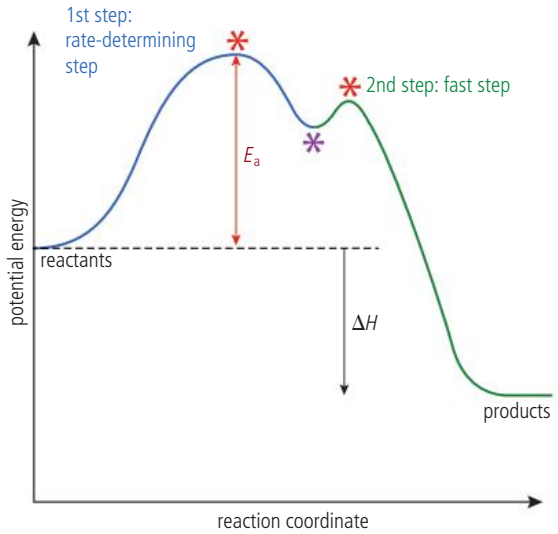
The simultaneous collision of three particles with sufficient energy and the correct orientation is so unlikely statistically that reaction mechanisms usually exclude termolecular reactions and propose instead a stepwise mechanism. In this way, scientists are applying the principle of Occam's razor – that theories need to be as simple as possible while maximizing explanatory power.

The rate-determining step is the slowest step in the reaction mechanism

When city planners are trying to improve traffic flow through a particular area, they always look at the place where traffic is moving the most slowly – perhaps a crowded junction or a merge lane. They know that this is the place that is limiting the overall flow. Similarly, in chemical reactions that involve several steps, the overall rate of reaction is determined by the slowest step in the sequence. This is therefore called the **rate-determining step**. Products of the reaction can only appear as fast as the products of this elementary step. So the rate-determining step determines the overall rate of the reaction.

The slowest step in a reaction mechanism is called the rate-determining step. This step determines the overall rate of the reaction.

Energy profiles can be used to illustrate the progress of a multistep reaction. An example is shown in Figure 9.



R2.2 Figure 9 Energy profile showing a two-step reaction. The * show transition states and the * shows the intermediate.

The rate-determining step is the step in a reaction mechanism that has the highest activation energy.

An intermediate is a species that exists for a finite period of time during a chemical reaction so could in theory be detected and isolated during a multistep reaction. A transition state exists only as bonds are being broken and formed in the formation of products from reactants so cannot be detected or isolated.

The two maxima represent the transition states (as explained on page 586), and the minimum between them represents the intermediate species present after the first step. In this example, the activation energy of the first step is higher than that of the second step, so the first step will be the slowest step and will determine the rate of the reaction. The activation energy for the overall reaction is equal to the activation energy of this rate-determining step. Catalysts usually alter the reaction mechanism by providing an alternative pathway for the rate-determining step that has a lower activation energy.

Worked example

Sketch an energy profile for the exothermic reaction between 2-chloro-2-methylpropane, $(CH_3)_3CCl$, and the hydroxide ion, OH^-. The proposed reaction mechanism is shown below. (This is known as an S_N2 reaction and full details are discussed in Reactivity 3.4.)

Step 1 (*slow step*): $(CH_3)_3CCl \rightarrow (CH_3)_3C^+ + Cl^-$

Step 2 (*fast step*): $(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_3COH$

Overall reaction: $(CH_3)_3CCl + OH^- \rightarrow (CH_3)_3COH + Cl^-$

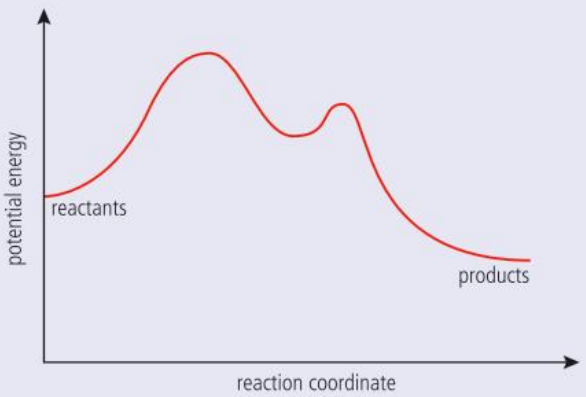
Solution

From the reaction mechanism we can see:

There are two steps in the mechanism and the $(CH_3)_3C^+$ ion is an intermediate (it is produced and then consumed in the following step).

The first step is the rate-determining step so will have a greater activation energy than the second step.

Draw an energy profile with *potential energy* on the *y*-axis and *reaction coordinate* on the *x*-axis as follows:



Note that because this is an exothermic reaction, the potential energy of the products has been drawn below that of the reactants.

Reactivity 3.4 – Which mechanism in the hydrolysis of halogenoalkanes involves an intermediate?

Exercise

Q13. Consider the following statements.

I. The slow step in a reaction mechanism is called the rate-determining step.

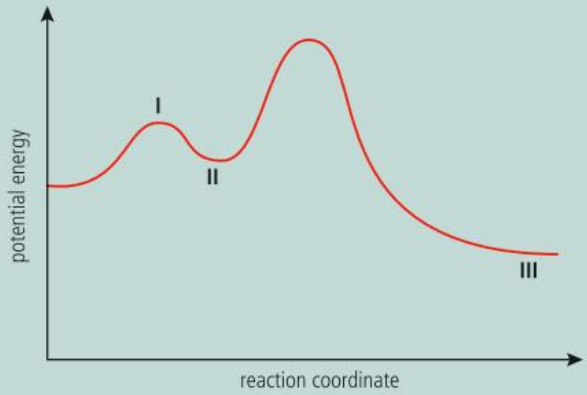
II. All reactions contain a transition state.

III. All reactions contain an intermediate.

Which statement(s) is/are correct?

A I only **B** I and II only **C** I and III only **D** II and III only

Q14. The energy profile below shows a two-step reaction mechanism.



Which of the following correctly labels I, II and III?

	I	II	III
A	transition state	intermediate	reactants
B	intermediate	transition state	reactants
C	transition state	intermediate	products
D	intermediate	transition state	products

Q15. In the following proposed mechanism for a reaction, identify any intermediates and deduce the overall reaction equation.

Step 1 (*slow step*): $NO_2 + F_2 \rightarrow NO_2F + F$

Step 2 (*fast step*): $NO_2 + F \rightarrow NO_2F$

Reactivity 2.2.9 and 2.2.10 – Rate equations

Reactivity 2.2.9 – Rate equations depend on the mechanism of the reaction and can only be determined experimentally.

Deduce the rate equation for a reaction from experimental data.

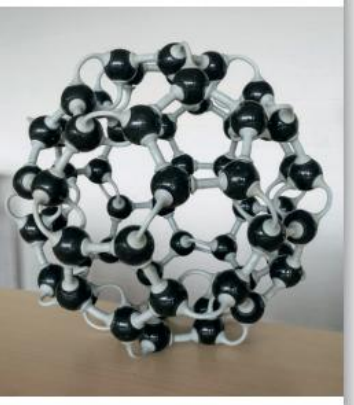
Reactivity 2.2.10 – The order of a reaction with respect to a reactant is the exponent to which the concentration of the reactant is raised in the rate equation.

The order with respect to a reactant can describe the number of particles taking part in the rate-determining step.

The overall reaction order is the sum of the orders with respect to each reactant.

Sketch, identify and analyse graphical representations of zero, first and second order reactions.

Concentration–time and rate–concentration graphs should be included. Only integer values for order of reaction will be assessed.	Tool 1, 3, Inquiry 2 – What measurements are needed to deduce the order of reaction for a specific reactant? Nature of Science – Why are reaction mechanisms only considered as 'possible mechanisms'?



The structure of oxidized buckminsterfullerene, $C_{60}O_3$, showing its three-oxygen bridge in red. Fullerenes are allotropes of carbon, made of a closed cage of hexagons and pentagons. The structures of fullerenes are discussed in Structure 2.2.

Rate equations are determined experimentally and depend on the mechanism of a reaction

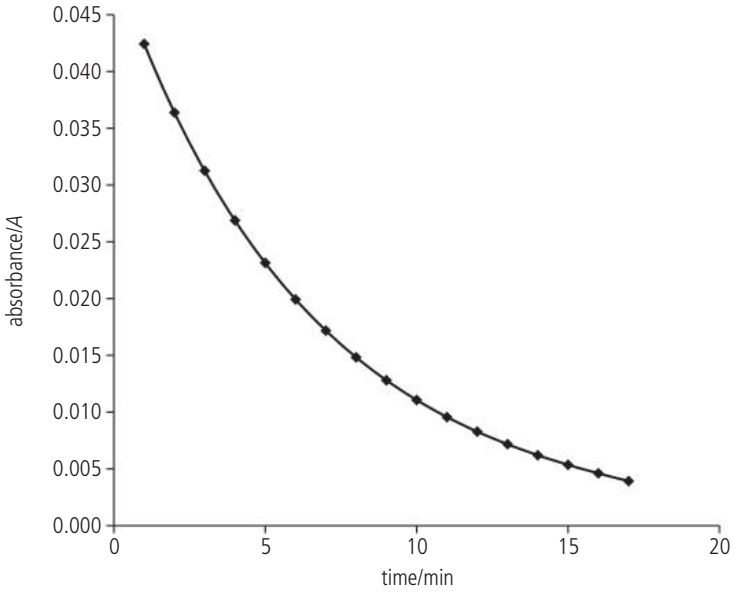
Determination of the rate equation

Let us look in more detail at some typical data from a study of the change in concentration of a reactant during a reaction. We will investigate an unusual but simple reaction in which an oxidized form of buckminsterfullerene (C_{60}, discussed in Structure 2.2) decomposes into $C_{60}O$ by releasing O_2 when its solution in methylbenzene is warmed to room temperature.

$$C_{60}O_3 \rightarrow C_{60}O + O_2$$

We can follow the reaction by recording the change in absorbance of light of a certain wavelength (as described on page 581) as this is directly proportional to the concentration of $C_{60}O_3$. In other words, observing absorbance as a function of time gives a measure of concentration as a function of time. The table and graph below show some experimental results.

Time / minutes	$C_{60}O_3$ absorbance at 23 °C	Time / minutes	$C_{60}O_3$ absorbance at 23 °C
3	0.04241	57	0.01106
9	0.03634	63	0.00955
15	0.03121	69	0.00827
21	0.02680	75	0.00710
27	0.02311	81	0.00616
33	0.01992	87	0.00534
39	0.01721	93	0.00461
45	0.01484	99	0.00395
51	0.01286		

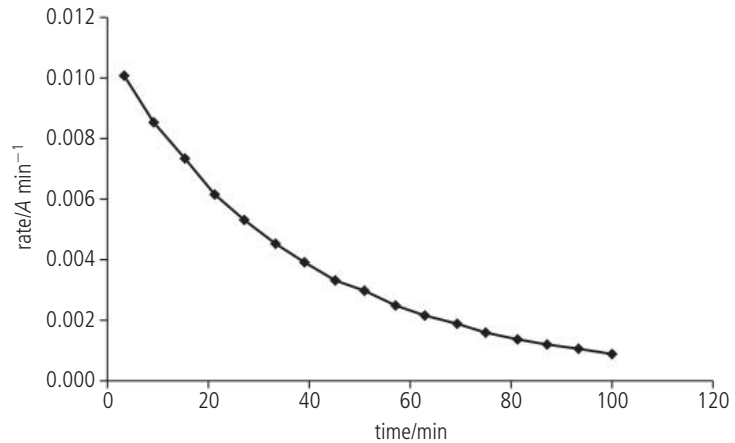


Absorbance–time graph for decomposition of $C_{60}O_3$.

In the first section of this chapter, we established that the rate of the reaction is equal to the rate of change in the concentration of $C_{60}O_3$.

$$\text{rate} = -\frac{\Delta[C_{60}O_3]}{\Delta t}$$

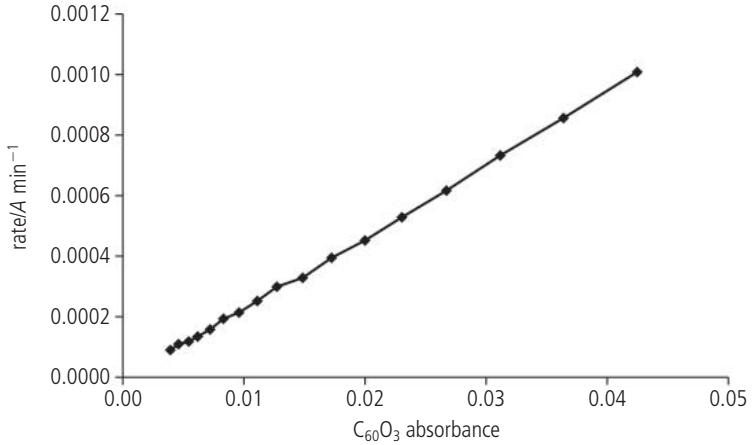
Note that the value for the change in concentration here is negative as concentration is decreasing, but by convention rate is expressed as a positive value. The rate can be evaluated at each time interval by measuring the gradient of the tangent to the curve at that particular value of time, or from the data table by calculating the change in absorbance divided by the change in time at each step. When the rate calculated in this way is plotted as a function of time, we obtain the graph shown in Figure 10.



R2.2 Figure 10 Rate–time graph for decomposition of $C_{60}O_3$.

The graph shows that the rate changes over the course of time, slowing down as the concentration of $C_{60}O_3$ decreases. This graph mirrors the absorbance–time graph for decomposition of $C_{60}O_3$ above, where absorbance also decreases with time. The similarity of the graph of concentration of $C_{60}O_3$ (shown by absorbance) against time with that of rate against time suggests that the rate must be related to the concentration at each time.

We can confirm this by plotting the rate of the reaction against the absorbance of $C_{60}O_3$, as shown in Figure 11.



R2.2 Figure 11 Rate–absorbance graph for $C_{60}O_3$ decomposition.

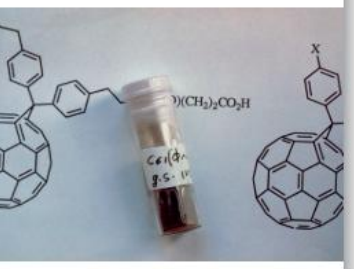
The straight-line graph obtained in Figure 11 confirms that the rate of the reaction is directly proportional to the concentration of the reactant, $C_{60}O_3$.

$$\text{reaction rate} \propto [C_{60}O_3]$$

This proportional relationship is converted into an equation by introducing a constant. So:

$$\text{reaction rate} = k\,[C_{60}O_3]$$

where k is the **rate constant**.



A di(phenylaminosuccinate) fullerene derivative being studied for antiviral activity.

Fullerene derivatives are currently being studied in AIDS research given their potential for antiviral activity. An example is the di(phenylaminosuccinate) fulleroid which has two phenylaminosuccinate chains added to a C_{61} fullerene 'ball'. This molecule alters two of the proteins that the human immunodeficiency virus (HIV) needs for reproduction, and has been shown to inhibit the growth of HIV in infected immune system cells.

This equation is known as the **rate equation** for this reaction. In this case, it is called a **first-order** rate equation because the concentration of the only reactant is raised to the power 1. It has been shown by experiment that the rate of all reactions can similarly be shown to depend on the concentration of one or more of the reactants, and that the exact relationship depends on the particular reaction.

Note that in other sources, the terms 'rate law' or 'rate expression' are commonly used in place of 'rate equation'.

In general, the rate is proportional to the product of the concentrations of the reactants, each raised to a power. For the reaction:

$$A + B \rightarrow \text{products}$$

$$\text{rate} \propto [A]^m[B]^n \text{ or rate} = k[A]^m[B]^n$$

The powers to which the concentrations of reactants are raised in the rate equation, m and n, are known as the **orders** of the reaction with respect to reactants A and B respectively. The **overall reaction order** for the reaction is the sum of the individual orders, $m + n$. The rate constant, k, has a fixed value for a particular reaction at a specified temperature. Once the value of k and the orders of the reaction are known, the rate equation enables us to calculate the rate of reaction at any concentration of reactants.

Worked example

The reaction:

$$2H_2(g) + 2NO(g) \rightarrow 2H_2O(g) + N_2(g)$$

is shown to be second order with respect to NO and first order with respect to H_2.

Give the rate equation for this reaction and its overall reaction order.

Solution

'Second order with respect to NO' means that the concentration of NO must be raised to the power 2 in the rate equation; 'first order for H_2' means that the concentration of H_2 must be raised to the power 1. When the exponent is 1, it is not usually shown. Therefore:

$$\text{rate} = k\,[NO]^2\,[H_2]$$

The overall reaction order = 2 + 1 = 3; it is a third-order reaction.

The order of reaction with respect to a particular reactant is the power to which its concentration is raised in the rate equation. The overall order for the reaction is the sum of the individual orders for all reactants.

The rate constant k is a constant for a particular reaction at a specified temperature.

The example above of the reaction between H_2 and NO illustrates the point that the orders of reaction with respect to reactants do not necessarily correspond to their coefficients in the reaction equation. The orders can in fact *only* be determined by experiment (empirically). The table below gives examples of some reaction equations and the empirically derived orders of the reactions with respect to individual reactants, and so the overall order. As you can see, there is no predictable relationship between the coefficients in the equation and the values for the order of reaction with respect to the reactants.

	Equation for the reaction	Order with respect to reactant 1	Order with respect to reactant 2	Overall order of the reaction
1	$H_2(g) + I_2(g) \rightarrow 2HI(g)$	H_2, 1st	I_2, 1st	2nd
2	$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$	H_2O_2, 1st	–	1st
3	$S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow 2SO_4^{2-}(aq) + I_2(aq)$	$S_2O_8^{2-}$, 1st	I^-, 1st	2nd
4	$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$	N_2O_5, 1st	–	1st

This apparent disconnect between the reaction equation and the rate equation begs the question: what *does* determine the order of the reaction? You will find the answer to this question after following the worked examples on the next page.

The rate equation for an overall reaction is determined by the reaction mechanism

As the rate of reaction depends on the rate-determining step, it follows that the rate equation for the overall reaction must depend on the rate equation for the rate-determining step. So how can this be determined?

Because the rate-determining step is an elementary step, a single molecular event, its rate equation comes directly from its molecularity. Collision theory informs us that the concentration of each reactant in the rate-determining step must appear in the

rate equation for that step, raised to the power of its coefficient in the equation. The table below shows the relationship between equations for elementary steps and their rate equations. (Remember, these relationships exist *only for elementary steps* and not for deriving the rate equation for the overall reaction from the stoichiometric coefficients.)

Equation for rate-determining step	Molecularity	Rate equation
A → products	unimolecular	rate = k [A]
2A → products	bimolecular	rate = k [A]^2
A + B → products	bimolecular	rate = k [A] [B]

The rate equation for the rate-determining step, predictable from its reaction equation, leads us to the rate equation for the overall reaction. If the rate-determining step is the first or only step in the mechanism then its rate equation is the same as the rate equation for the overall reaction.

Worked example

The reaction:

$$2NO_2Cl(g) \rightarrow 2NO_2(g) + Cl_2(g)$$

is believed to have the following mechanism.

step 1:	$NO_2Cl(g) \rightarrow NO_2(g) + Cl(g)$	slow: the rate-determining step
step 2:	$NO_2Cl(g) + Cl(g) \rightarrow NO_2(g) + Cl_2(g)$	fast
overall:	$2NO_2Cl(g) \rightarrow 2NO_2(g) + Cl_2(g)$	

Deduce the rate equation and the overall order of the reaction.

Solution

The rate equation for the overall reaction is that of step 1, the rate-determining step:

$$\text{rate} = k\,[NO_2Cl]$$

This is a first-order reaction.

When the rate-determining step is not the first step in the mechanism, it is a bit more complicated. In this case, its reactant concentrations will depend on an earlier step, so this must also be taken into account.

Worked example

For the reaction:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

the following reaction mechanism has been proposed.

step 1:	$NO(g) + NO(g) \rightarrow N_2O_2(g)$	fast
step 2:	$N_2O_2(g) + O_2(g) \rightarrow 2NO_2(g)$	slow: the rate-determining step
overall:	$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$	

Solution

So the rate depends on step 2 for which the rate equation is:

$$\text{rate} = k[N_2O_2][O_2]$$

However, N_2O_2 is an intermediate not a reactant so cannot appear in the rate equation. Because it is a product of step 1, the concentration of the intermediate depends on $[NO]^2$. Therefore, we can substitute this into the equation above.

So the rate equation for the overall reaction is:

$$\text{rate} = k[NO]^2[O_2]$$

It is a third-order reaction.

These examples explain why the order of the reaction with respect to each reactant is not linked to their coefficients in the overall equation for the reaction but is instead determined by their coefficients in the equation for the rate-determining step.

Perhaps you can now understand what it means for a reaction to be zero order with respect to a particular reactant. Although the reactant is required for the reaction to take place, we know that the concentration of this reactant does not affect the rate of the reaction – and this is because it does not take part in the rate-determining step. If a reactant does appear in the rate equation, then that reactant, or something derived from it, must take part in the rate-determining step.

The mechanisms given on the previous page are described as 'possible mechanisms' because they fit the empirical findings – that is, both the kinetic data and the overall stoichiometry of the reaction. Mechanisms that do not satisfy one of these criteria must be rejected. Remember though that we can go no further in accepting a mechanism than to state that it is consistent with the data; it cannot be proven to be correct.

In summary, we can see that kinetic data give us information about reaction mechanisms, and so give insights into the detailed processes of bond-making and bond-breaking. Good examples of this are covered in Reactivity 3.4 in the hydrolysis of halogenoalkanes, where the different mechanisms of the reactions for primary and tertiary molecules are interpreted in terms of differences in their bonding.

Nature of Science – Why are reaction mechanisms only considered as 'possible mechanisms'?

Evaluation of a proposed mechanism for a reaction involves checking that it is consistent with kinetic data and the overall stoichiometry of the reaction.

Remember, the coefficients in the balanced equation for the reaction do *not* give you information about the rate equation. This information can only be obtained from experimental data. This is in contrast with the equilibrium law which, as we will see in the next chapter, *is* based on the reaction's stoichiometry.

Graphical representations of reaction kinetics

In our study here we will investigate reactions where the order with respect to a particular reactant is zero, first, or second. In more complex reactions, other values for order are possible, including fractional and negative values. As we saw at the beginning of this section, it is possible to establish the order of a reaction with respect to a reactant from graphical representations of experimental data. However, as you will see below, concentration–time graphs do not lead to a clear distinction between first and second order. Rate–concentration graphs, on the other hand, clearly reveal the difference. Both are shown below for each case, with reference to a single reactant, A.

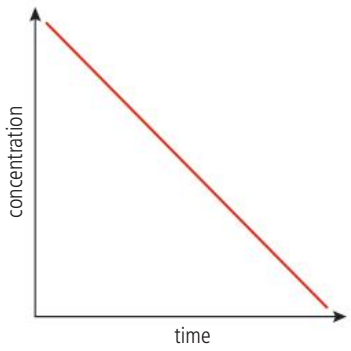
Zero-order reaction

Here the concentration of reactant A does not affect the rate of the reaction.

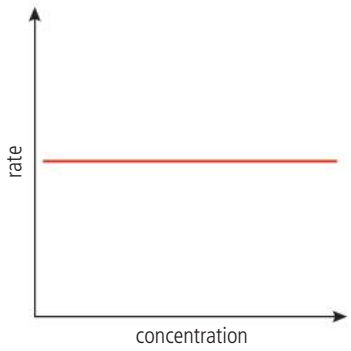
$$\text{rate} = k\,[A]^0 \text{ or rate} = k$$

Note that the rate constant is written with a lowercase *k*. Do not confuse this with equilibrium constants, in Reactivity 2.3, which are written with an uppercase *K*.

So the concentration–time graph is a straight line, showing a constant rate (Figure 12). The gradient of the line = *k*. The rate–concentration graph is a horizontal line (Figure 13).



R2.2 Figure 12 Concentration–time graph for a zero-order reaction.



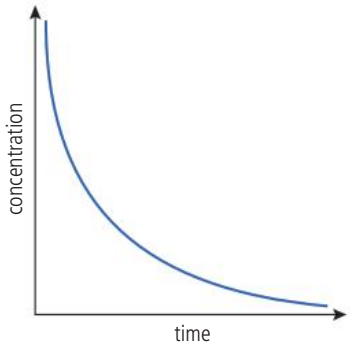
R2.2 Figure 13 Rate–concentration graph for a zero-order reaction.

First-order reaction

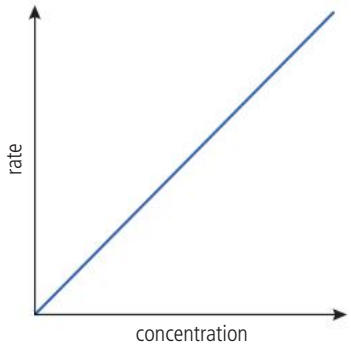
Here the rate is directly proportional to the concentration of A.

$$\text{rate} = k\,[\text{A}]$$

So the concentration–time graph is a curve showing rate decreasing with concentration (Figure 14). The rate–concentration graph is a straight line passing through the origin with gradient *k* (Figure 15).



R2.2 Figure 14 Concentration–time graph for a first-order reaction.



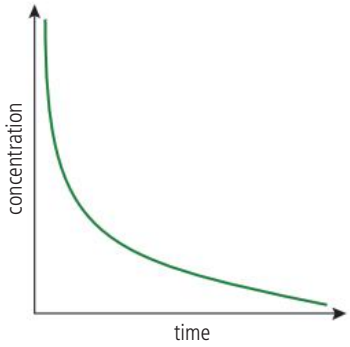
R2.2 Figure 15 Rate–concentration graph for a first-order reaction.

Second-order reaction

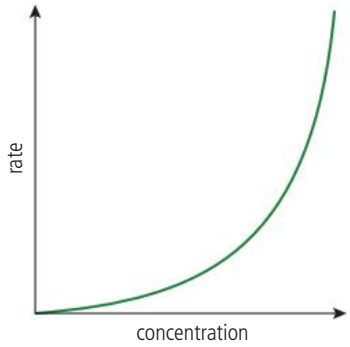
Here the rate is proportional to the square of the concentration of A.

$$\text{rate} = k\,[\text{A}]^2$$

So the concentration–time graph is also a curve, steeper at the start than the first-order graph and levelling off more quickly (Figure 16). The rate–concentration graph is a parabola, characteristic of the square function (Figure 17). The gradient here is proportional to the concentration and is initially zero.



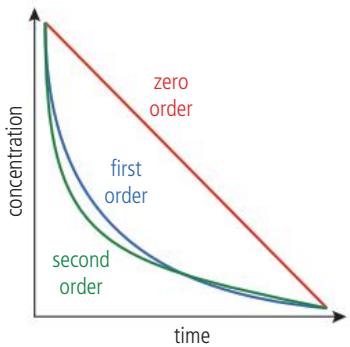
R2.2 Figure 16 Concentration–time graph for a second-order reaction.



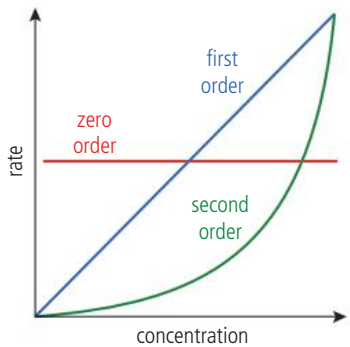
R2.2 Figure 17 Rate–concentration graph for a second-order reaction.

Summary

The relationships of concentration–time and rate–concentration graphs for zero-, first-, and second-order reactions are shown together in Figures 18 and 19 for comparison.



R2.2 Figure 18 Concentration–time graphs for zero-, first-, and second-order reactions.



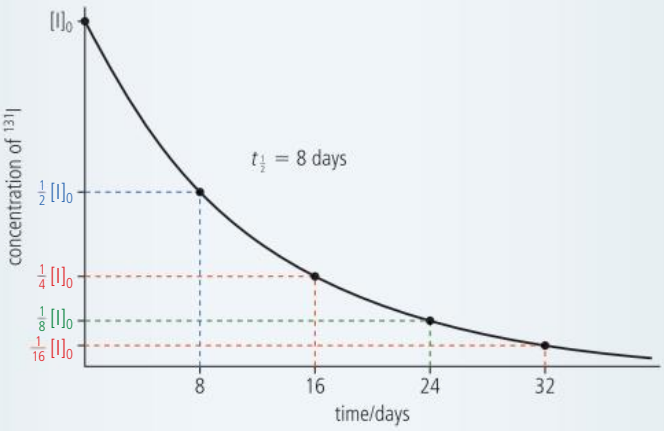
R2.2 Figure 19 Rate–concentration graphs for zero-, first-, and second-order reactions.

Remember that because the orders of reaction can only be deduced experimentally, we will always need to make time and concentration measurements to do so. Graphical presentation of this data can then allow the calculation of the rate of reaction at specific concentrations.

Tool 1, 3, Inquiry 2 – What measurements are needed to deduce the order of reaction for a specific reactant?

Challenge yourself

3. Radioactive decay is always a first-order process. Therefore, if we measure the time it takes for the concentration of a radioactive isotope to decrease to half its original value, we find that this interval is independent of the starting concentration. This value, known as the half-life, $t_{½}$, for the reactant, is therefore a constant, as shown in the figure on the next page.



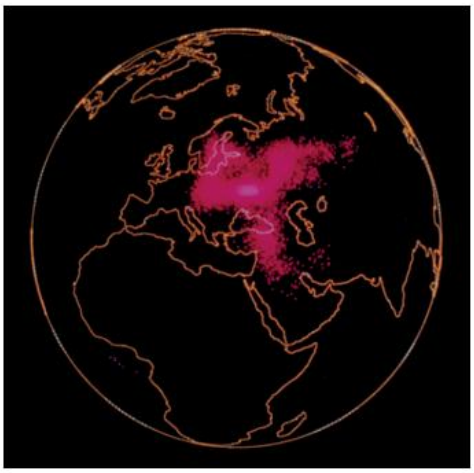
First-order radioactive decay of iodine-131 showing constant half-life. Iodine-131 is used in the diagnosis and treatment of thyroid cancer.

Given that $t_{½}$ for ^{131}I is 8 days, calculate the mass of ^{131}I remaining after 24 days in a sample initially containing 0.680 g.

The rate of decay of a radioactive isotope, a first-order process, can be quantified by calculating the time taken for the concentration of a sample to decrease by half. This value, known as half-life, *t*½ , is constant and found to be independent of the starting concentration. Half-life values of different isotopes vary enormously from 4.5 billion years for uranium-238 to milliseconds for carbon-17. The duration of the half-life is of prime relevance in assessing the health dangers associated with radioactivity. When the nuclear facility in Chernobyl, Ukraine, exploded in April 1986, many different isotopes were released. Of these, iodine-131 had decayed almost completely after about six weeks, but caesium-137 with a half-life of 30 years, and strontium-90 with a half-life of 29 years, will remain in the soil and concentrate in food chains for over 300 years. These are considered to be the most devastating consequence of the accident.

Determination of the overall order of a reaction

Methods for determining the overall order of a reaction depend on determining the order with respect to each reactant in turn. There are two main methods for doing this, although only one of these, the initial rates method, is covered at this level. It is discussed here with respect to two reactants, denoted 'A' and 'B' in these examples.



Computer simulation of the distribution of radioactivity in the northern hemisphere six days after the accident at the Chernobyl nuclear power station. High-altitude winds carried radioactivity over the Middle Eastv while lower-level winds carried radioactivity north over Scandinavia and west over Poland.

Initial rates method

This involves carrying out a number of separate experiments with different starting concentrations of reactant A, and measuring the initial rate of each reaction. The concentrations of other reactants are held constant so that the effect of [A] on reaction rate can be seen. The process can then be repeated for reactant B.

By analysing the data, the order of the reaction can be deduced as follows.

- If changing the concentration of A has no effect on the rate, the reaction must be zero order with respect to A.
- If changes in the concentration of A produce directly proportional changes in the rate of the reaction, the reaction must be first order with respect to A. In other words, in a first-order reaction, doubling the concentration of A leads to doubling of the rate, tripling [A] leads to a tripling of the rate, and so on.
- If changes in the concentration of A lead to the square of that change in the rate of the reaction, then the reaction must be second order with respect to A. For example, doubling [A] would lead to a four-fold increase in the rate of reaction, and tripling [A] would lead to a nine-fold increase in the rate.

Worked example

Use the data in the table below to work out the order of reaction with respect to reactants A and B, and so write the rate equation for this reaction.

Experiment number	Initial concentrations / mol dm^{-3}		Initial rate of reaction / mol dm^{-3} s^{-1}
	[A]	[B]	
1	0.10	0.10	2.0×10^{-4}
2	0.20	0.10	4.0×10^{-4}
3	0.30	0.10	6.0×10^{-4}
4	0.30	0.20	2.4×10^{-3}
5	0.30	0.30	5.4×10^{-3}

Solution

The concentration of B is constant in the first three experiments, so we can use these to deduce the effect of A on the rate of the reaction. We can find the change in rate by dividing one value by the other. Comparing experiments 1 and 2, doubling [A] leads to a doubling of the rate; from experiments 1 and 3, tripling [A] leads to a tripling of the rate. So the reaction must be first order with respect to A as the rate is proportional to [A].

The concentration of A is held constant in the last three experiments, so these are used to deduce the effect of B on the rate. Comparing experiments 3 and 4, doubling [B] leads to a quadruple (2^2) change in the rate; comparing experiments 3 and 5, tripling [B] leads to a nine-fold (3^2) change in the rate. So the reaction must be second order with respect to B as the rate is proportional to $[B]^2$.

Therefore, the rate equation for this reaction is rate = $k[A][B]^2$.

The table below summarizes the deductions used in analysing data of this type.

	Change in rate of zero-order reaction	Change in rate of first-order reaction	Change in rate of second-order reaction
[A] doubles	no change	rate doubles (×2)	rate ×4
[A] triples	no change	rate triples (×3)	rate ×9
[A] quadruples	no change	rate quadruples (×4)	rate ×16

Use of the integrated form of the rate equation

In more advanced studies of kinetics, mathematical analysis involving calculus is used. By taking the integrated form of the rate equation, direct graphical analysis of functions of concentration against time leads to identification of the order. This is not covered in this course.

Nature of Science

Chemical kinetic data are derived entirely from experiment, and cannot be deduced from knowledge of the reaction's stoichiometry. This requires objectivity on the part of the researcher, as results can sometimes be different from what might be expected. Kinetic data, when interpreted alongside stoichiometric data, can provide valuable insights into the nature of chemical change.

Exercise

Q16. Write the rate equation for each of the reactions in the table on the previous page.

Q17. The rate equation for the reaction:

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

is rate = k [NO][O_3]. What is the order with respect to each reactant and what is the overall order?

Q18. The reaction:

$$CH_3Cl(aq) + OH^-(aq) \rightarrow CH_3OH(aq) + Cl^-(aq)$$

is found to be second order overall. Give three possible rate equations consistent with this finding.

Q19. If the reaction:

$$NO_2(g) + CO(g) \rightarrow CO_2(g) + NO(g)$$

occurs by a one-step collision process, what would be the expected rate equation for the reaction?

Q20. The reaction:

$$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$$

is shown experimentally to be second order with respect to NO_2. Is this consistent with the following mechanism?

$NO_2 + NO_2 \rightarrow NO_3 + NO$ slow: the rate-determining step

$NO_3 + NO \rightarrow 2NO + O_2$ fast

Q21. Which statement or statements about the following reaction at 450 °C is/are correct?

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

I. The reaction must involve a collision between one O_2 and two SO_2 molecules.

II. Every collision between SO_2 and O_2 will produce SO_3.

III. The rate-determining step is the slowest step of the reaction.

A I and III **B** II only **C** III only

D None of the statements is correct.

Q22. If the mechanism of a reaction is:

$AB_2 + AB_2 \rightarrow A_2B_4$ slow

$A_2B_4 \rightarrow A_2 + 2B_2$ fast

(a) What is the overall equation for the reaction?

(b) What is the rate equation for this reaction?

(c) What units will the rate constant have in this equation?

Q23. The reaction between NO_2 and F_2 gives the following rate data at a certain temperature. What is the order of reaction with respect to NO_2 and F_2?

$[NO_2]$ / mol dm^{-3}	$[F_2]$ / mol dm^{-3}	Rate / mol dm^{-3} min^{-1}
0.1	0.2	0.1
0.2	0.2	0.4
0.1	0.4	0.2

	NO_2 order	F_2 order
A	first	first
B	first	second
C	second	first
D	second	second

Q24. The following data were obtained for the reaction of NO(g) with O_2(g) to form NO_2(g) at 25 °C.

Experiment	[NO] / mol dm^{-3}	$[O_2]$ / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.30	0.20	2.0×10^{-3}
2	0.30	0.40	4.0×10^{-3}
3	0.60	0.80	3.2×10^{-2}

Calculate the order with respect to the two reactants and write the rate equation for the reaction.

Q25. If a reaction $A + 2B \rightarrow$ products has the rate equation rate $= k[A]^2$, deduce the rates in experiments 2 and 3 in the table below.

Experiment	[A] / mol dm^{-3}	[B] / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}
1	0.01	0.01	3.8×10^{-3}
2	0.02	0.01	
3	0.02	0.02	

Reactivity 2.2.11 – The rate constant, *k*

Reactivity 2.2.11 – The rate constant, *k*, is temperature dependent and its units are determined from the overall order of the reaction.	
Solve problems involving the rate equation, including the units of *k*.	
	Reactivity 3.4 – What are the rate equations and units of *k* for the reactions of primary and tertiary halogenoalkanes with aqueous alkali?

Determining the units and value of the rate constant, *k*

Units of *k* vary depending on the overall order of the reaction

The table below shows how the rate constant *k* has different units, depending on the overall order of the reaction. Note that these examples measure rate per second, so this would have to be changed if the rate given were, for example, per minute.

Zero order	First order	Second order	Third order
rate = k	rate = k [A]	e.g. rate = k [A]^2	e.g. rate = k [A]^3
k = units of rate = mol dm^{-3} s^{-1}	$k = \frac{\text{units of rate}}{\text{units of concentration}}$ $= \frac{\text{mol dm}^{-3}\text{ s}^{-1}}{\text{mol dm}^{-3}}$ = s^{-1}	$k = \frac{\text{units of rate}}{(\text{units of concentration})^2}$ $= \frac{\text{mol dm}^{-3}\text{ s}^{-1}}{(\text{mol dm}^{-3})^2}$ = mol^{-1} dm^3 s^{-1}	$k = \frac{\text{units of rate}}{(\text{units of concentration})^3}$ $= \frac{\text{mol dm}^{-3}\text{ s}^{-1}}{(\text{mol dm}^{-3})^3}$ = mol^{-2} dm^6 s^{-1}

Once we have identified a rate equation, we can deduce the overall order of reaction and identify the units of *k*. For example, the rate equations for the reaction between primary and tertiary halogenoalkanes with aqueous hydroxide ions are shown below.

Halogenoalkane	Rate equation	Overall order of reaction	Units of *k*
Primary	rate = k [halogenoalkane] [OH$^-$]	Second order	mol^{-1} dm^3 s^{-1}
Tertiary	rate = k [halogenoalkane]	First order	s^{-1}

Reactivity 3.4 – What are the rate equations and units of *k* for the reactions of primary and tertiary halogenoalkanes with aqueous alkali?

Make sure that you include the correct units for *k* in all calculations. You should check that the units are consistent with the data, so that the rate will always have the units of *concentration time*$^{-1}$.

Reactions which are zero order overall are relatively uncommon. They occur when the rate of the reaction is independent of the concentration of the reactants. An example would be the decomposition of gaseous ammonia using a catalyst of heated platinum.

$$2NH_3(g) \xrightarrow{Pt(s)} N_2(g) + 3H_2(g)$$

The rate depends on the number of NH_3 molecules attached to the surface of the catalyst, which is very small relative to the total number of NH_3 molecules. So increasing the concentration of the reactant will not affect the rate.

The value of *k* can be calculated from the rate equation when the concentrations of reactants and the corresponding rate are known

Once the rate equation has been derived, we can calculate the value of *k* using the concentration of reactants and the corresponding rate of reaction.

Worked example

A reaction has the rate equation, rate = $k\,[A]^2[B]$.

Calculate the value of k, including units, for the reaction when the concentrations of both A and B are 2.50×10^{-2} mol dm^{-3} and the reaction rate is 7.75×10^{-5} mol dm^{-3} min^{-1}.

Solution

Substituting the values into the rate equation gives:

$$7.75 \times 10^{-5}\,\text{mol dm}^{-3}\,\text{min}^{-1} = k(2.50 \times 10^{-2}\,\text{mol dm}^{-3})^2 \times (2.50 \times 10^{-2}\,\text{mol dm}^{-3})$$

Therefore

$$k = \frac{7.75 \times 10^{-5}\,\text{mol dm}^{-3}\,\text{min}^{-1}}{(2.50 \times 10^{-2})^3(\text{mol dm}^{-3})^3}$$

$$= 4.96\,\text{mol}^{-2}\,\text{dm}^6\,\text{min}^{-1}$$

Exercise

Q26. Give the units of k in each of the rate equations below:

(a) rate = $k\,[NO_2]^2$ **(b)** rate = $k\,[CH_3CH_2Br]$ **(c)** rate = $k\,[NH_3]^0$

(d) rate = $k\,[NO]^2\,[Br_2]$ **(e)** rate = $k\,[H_2]\,[I_2]$

Q27. The reaction $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$ has a value of $k = 6.9 \times 10^{-4}\,s^{-1}$ at a certain temperature. Deduce the rate equation for this reaction.

Q28. A reaction involving A and B is found to be zero order with respect to A and second order with respect to B. When the initial concentrations of A and B are 1.0×10^{-3} mol dm^{-3} and 2.0×10^{-3} mol dm^{-3} respectively, the initial rate of the reaction is 4.5×10^{-4} mol dm^{-3} min^{-1}. Calculate the value and units of the rate constant for the reaction.

Reactivity 2.2.12 and 2.2.13 – The Arrhenius equation

Reactivity 2.2.12 – The Arrhenius equation uses the temperature dependence of the rate constant to determine the activation energy.

Describe the qualitative relationship between temperature and the rate constant.

Analyse graphical representations of the Arrhenius equation, including its linear form.

The Arrhenius equation and its linear form are given in the data booklet.	

Reactivity 2.2.13 – The Arrhenius factor, A, takes into account the frequency of collisions with proper orientations.

Determine the activation energy and the Arrhenius factor from experimental data.

i The term 'rule of thumb', used to describe a guideline or rough measure, is of unknown origin. The phrase exists in other languages including Scandinavian languages, Dutch, Turkish, and Persian, and it is likely that it refers to one of the numerous ways that thumbs have been used to estimate things.



The flight of insects like this common wasp depends on the release of energy from chemical reactions in their cells. The rate of these reactions is affected significantly by changes in the external temperature, slowing down when it is cooler. This is why wasps are only active during the warmer months, and why it is so much easier to swat a fly, for example, on a cold day.



Laboratory temperature sensor. The sensor is at the end of the metal rod and has been placed in a beaker of ice. Data-logging devices like this allow continuous temperature measurements to be made and analysed on a computer.

The Arrhenius equation is used to determine the activation energy of a reaction

The rate constant, *k*, is temperature dependent

Earlier in this chapter, we learned that the rate of reactions increases with increasing temperature, and that the common relationship is that a 10 °C increase in temperature leads to a doubling of the rate. This is often referred to as a rule of thumb, not a law of nature, as there are many reactions that respond very differently to temperature changes. In this section, we will find out more about why this is so.

From the rate equations developed earlier in the chapter we know that the rate of reaction depends on two things: the rate constant, *k*, and the concentrations of reactants, raised to a power. Since increasing temperature does not change the values of reactant concentrations, its effect must therefore be on the value of *k*. So *k* is a general measure of the rate of a reaction at a particular temperature.

We have also used collision theory to explain the effect of increasing temperature on reaction rate: principally, that by increasing the number of collisions that involve particles having the necessary activation energy, E_a, a greater proportion of collisions leads to reaction. Maxwell–Boltzmann energy distribution curves can be used to show the changing distribution of kinetic energies with increasing temperature, as we saw on page 589. From this, we can predict that the value of the activation energy will determine the extent of the change in the number of particles that can react at higher temperature. When the activation energy is large, a temperature rise will cause a significant increase in the number of particles that can react. On the other hand, a low value for activation energy will mean that the same temperature rise will have a proportionately smaller effect on the reaction rate. Thus the temperature dependence of *k* depends on the value of the activation energy.

Clearly, a mathematical relationship must exist between temperature, the rate constant and the activation energy. We will explore this below.

The temperature dependence of the rate constant is expressed in the Arrhenius equation

Svante Arrhenius showed that the fraction of molecules with energy greater than the activation energy, E_a, at temperature *T* is proportional to the expression $e^{\frac{-E_a}{RT}}$ where *R* is the gas constant (= 8.31 J K^{-1} mol^{-1}) and *T* is the absolute temperature (in K). This must mean that the reaction rate, and therefore the rate constant are also proportional to this value. So we can write

$$k \propto e^{\frac{-E_a}{RT}} \text{ or } k = Ae^{\frac{-E_a}{RT}}$$

where *A* is the **Arrhenius factor**, often called the **frequency factor** or **pre-exponential factor**. It takes into account the frequency with which successful collisions will occur based on collision geometry. It is a constant for a reaction and has units the same as *k* (and so varies depending on the order of the reaction).

The equation $k = Ae^{\frac{-E_a}{RT}}$ is known as the **Arrhenius equation** and is given in Section 1 of the data booklet.

Using the Arrhenius equation to calculate activation energy

Simple manipulations of the Arrhenius equation give equations which can be used to calculate activation energy from experimental data.

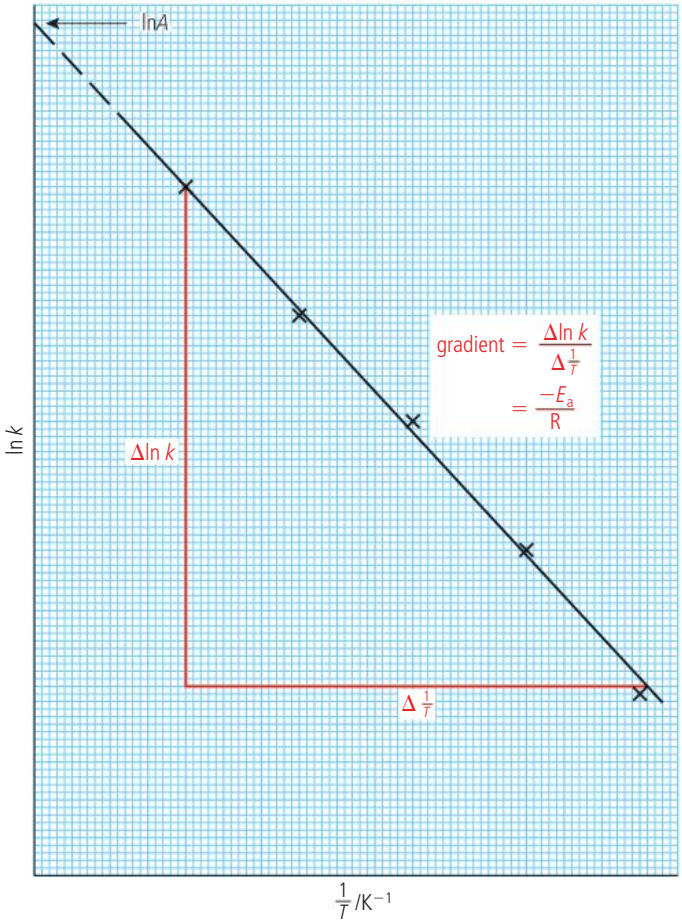
The equation of a straight line

If we take the natural logarithm (logarithm to base e) of both sides of the Arrhenius equation, we find that:

$$\ln k = -\frac{E_a}{RT} + \ln A$$

This is a form of the equation for a straight line: $y = mx + c$

So a graph of $\ln k$ (on the y-axis) against $\frac{1}{T}$ (on the x-axis) will give a straight line with gradient (m) $= -\frac{E_a}{R}$. This is known as an **Arrhenius plot** and an example is shown in Figure 20.

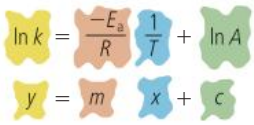


R2.2 Figure 20 An Arrhenius plot showing that $\ln k$ versus $\frac{1}{T}$ gives a straight line with intercept $\ln A$ on the y-axis and gradient $= -\frac{E_a}{R}$.

As R is a constant (8.31 J K^{-1} mol^{-1}), it is therefore a simple operation to derive E_a from the measured gradient of this graph.

$$\text{gradient} = -\frac{E_a}{R}$$

Therefore, E_a (in J mol^{-1}) = − measured gradient (in K) × 8.31 (in J K^{-1} mol^{-1}).



The Arrhenius equation can be manipulated into the form of the equation for a straight line.

SKILLS

Calculation of the activation energy of a reaction. Full details of how to carry out this experiment with a worksheet are available in the eBook.

Worked example

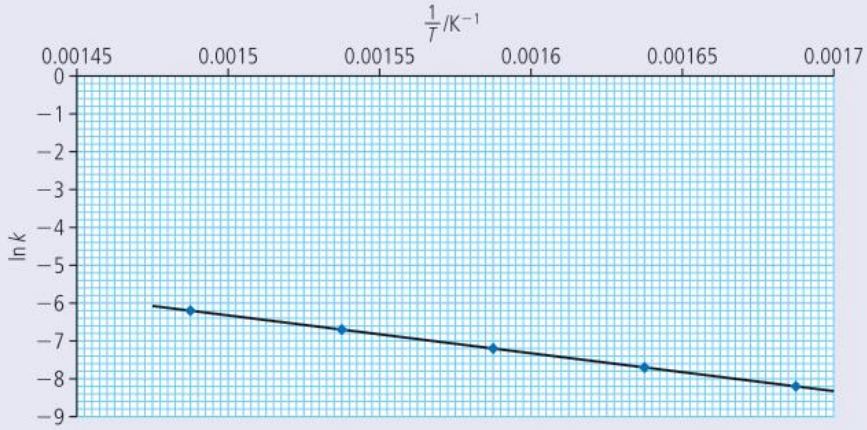
The following data were collected for a reaction.

Rate constant / s^{-1}	Temperature / °C
2.88×10^{-4}	320
4.87×10^{-4}	340
7.96×10^{-4}	360
1.26×10^{-3}	380
1.94×10^{-3}	400

Determine the activation energy for the reaction in kJ mol^{-1} by a graphical method.

Solution

Convert the values of k to ln$k$ and the values for temperature to $\frac{1}{T}$ (remember to convert °C to K by adding 273). Draw an Arrhenius plot of ln$k$ against $\frac{1}{T}$ and measure its gradient.



measured gradient = −9518.65 K

$$\text{gradient} = -\frac{E_a}{R}$$

$$E_a(\text{J mol}^{-1}) = 9518.65(\text{K}) \times 8.31(\text{J K}^{-1}\,\text{mol}^{-1})$$

Therefore $E_a = 79100\,\text{J mol}^{-1} = 79.1\,\text{kJ mol}^{-1}$

When calculating E_a from graphical data, the units associated with your value will be in J mol^{-1}. This can be converted to kJ mol^{-1} by dividing by 1000.

By comparing the manipulated Arrhenius equation, $\ln k = -\frac{E_a}{RT} + \ln A$, with the equation for a straight line, $y = mx + c$, we can also determine that the y-intercept = ln$A$.

Rearranging this equation gives $A = e^{(y\text{-intercept})}$

Worked example

In an Arrhenius plot of ln k against $\frac{1}{T}$ the y-intercept was found to be $-1.20\,s^{-1}$. Calculate the Arrhenius factor from this data. Assume that it is a first-order reaction.

Solution

As we know that the y-intercept = $\ln A$, we can rearrange this equation to give $A = e^{(y\text{-intercept})}$

Substituting the y-intercept gives $A = e^{-1.20} = 0.301\ s^{-1}$

Note that the units of A will be identical to the units of the rate constant. So for a first-order reaction this will be s^{-1}.

Solving simultaneous equations

Activation energy can also be calculated from values of the rate constant, k, at only two temperatures. The formula is derived as follows:

At temperature T_1 where the rate constant is k_1:

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A$$

At temperature T_2 where the rate constant is k_2:

$$\ln k_2 = -\frac{E_a}{RT_2} + \ln A$$

By subtracting the second equation from the first, we can derive the following equation:

$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

This equation is given in Section 1 of the data booklet.

Worked example

The table below shows rate constants for the gas-phase decomposition of hydrogen iodide at two different temperatures.

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

Temperature / °C	Rate constant / mol dm^{-3} s^{-1}
283	3.52×10^{-7}
508	3.95×10^{-2}

Calculate the activation energy for the reaction.

Solution

Convert temperatures in °C to K: $T_1 = 556$ K and $T_2 = 781$ K.

Substituting the values into the equation:

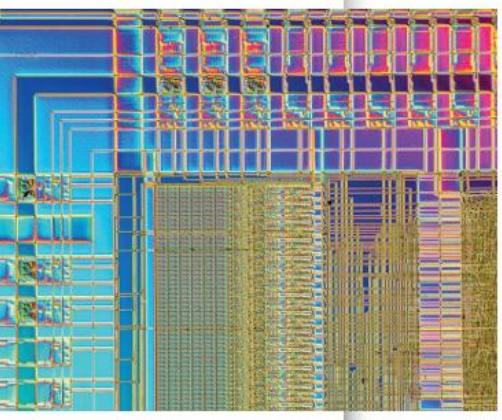
$$\ln\left(\frac{k_1}{k_2}\right) = \left(\frac{E_a}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{3.52 \times 10^{-7}\ \text{mol dm}^{-3}\ \text{s}^{-1}}{3.95 \times 10^{-2}\ \text{mol dm}^{-3}\ \text{s}^{-}}\right)^1 = \frac{E_a}{8.31\ \text{J K}^{-1}\ \text{mol}^{-1}}\left(\frac{1}{781\ \text{K}} - \frac{1}{556\ \text{K}}\right)$$

$$E_a = 1.87 \times 10^5\ \text{J mol}^{-1} = 187\ \text{kJ mol}^{-1}$$

Nature of Science

The effect of increasing temperature on increasing the rate of reaction is widely observed and broadly understood qualitatively in terms of the kinetic molecular theory and collision theory. But the significance of the Arrhenius equation is that it proposes a quantitative model to explain the effect of temperature change on reaction rate, which leads to testable predictions.



A laptop memory chip. The Arrhenius equation is used in research on the temperature dependence of memory devices.

So the Arrhenius equation enables us to calculate the activation energy of a reaction. The relationship also supports the observation that increasing the temperature by 10 K (which is of course the same as an increase of 10 °C) doubles the value of the rate constant and hence the rate of reaction when the activation energy is in a fairly narrow range around 50 kJ mol^{-1}. This is the situation for a large number of common reactions, so the rule of thumb is justified. But for reactions that have particularly large or particularly small values for activation energy, we find that the rise in temperature has a very different effect on the rate constant. This is applied in materials research, where the temperature sensitivity of reactions is crucial. For example, research into the temperature dependence of memory devices such as laptop memory chips is based on the Arrhenius equation and helps manufacturers predict the memory retention under different conditions.

Exercise

Q29. Consider the following statements.

I. The rate constant of a reaction increases with increase in temperature.

II. Increase in temperature decreases the activation energy of the reaction.

III. The term A in the Arrhenius equation $\left(k = Ae^{\frac{-E_a}{RT}}\right)$ relates to the geometric requirements of the collisions.

Which statement(s) is/are correct?

A I only **B** I and II only **C** I and III only **D** II and III only

Q30. To what does A refer in the Arrhenius equation $k = Ae^{\frac{-E_a}{RT}}$?

A activation energy **B** kinetic energy

C rate constant **D** collision geometry

Q31. The rate of a chemical reaction increases with increasing temperature. This increase in rate is due to:

I. an increase in the collision rate

II. an increase in the activation energy

III. an increase in the rate constant

A I and II only **B** I and III only **C** II and III only **D** I, II and III

Q32. Rate constants for the reaction

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

are given below.

At 700 K, $k = 1.30\,\text{mol}\,\text{dm}^{-3}\,\text{s}^{-1}$

At 800 K, $k = 23.0\,\text{mol}\,\text{dm}^{-3}\,\text{s}^{-1}$

Calculate the value of the activation energy in kJ mol^{-1}.

HL end

Guiding Question revisited

How can the rate of a reaction be controlled?

In this chapter we have explored collision theory and investigative techniques to show:

- The rate of reaction is expressed as the change in concentration of a particular reactant or product per unit time. It has units of mol dm^{-3} s^{-1}.
- Rate of reaction can be measured indirectly using different experimental techniques. The choice of technique will depend on the changes that occur during a specific reaction such as the production of a gas, the formation of a precipitate, or changes in the colour or electrical conductivity of a solution.
- The rate at a specific point in a reaction can be calculated from the gradient of a tangent on a graph of concentration, volume, absorbance or mass against time.
- For a reaction to occur, species must collide with sufficient kinetic energy and proper orientation. These collisions are known as 'successful' collisions.
- The minimum energy required for a successful collision is called the activation energy, E_a.
- The use of a catalyst and increases in pressure, concentration, surface area and temperature lead to an increase in the frequency of successful collisions per unit time and so increase the rate of a reaction.
- Catalysts increase the rate of reaction by providing an alternative reaction pathway with a lower E_a. This effect can be represented in a reaction energy profile.
- Maxwell–Boltzmann distribution curves can be used to explain the effect of changing temperature and the use of a catalyst on the probability of successful collisions occurring.

HL

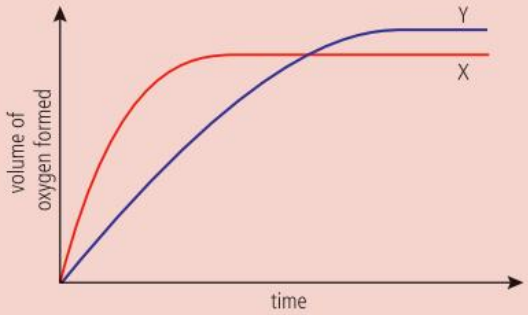
- Many reactions occur in a series of elementary steps. The slowest step determines the rate of reaction. We can represent single and multistep reactions in energy profiles that show the activation energy and transition state of each step.
- The molecularity of an elementary step is the number of reacting particles taking place in the rate-determining step. The terms unimolecular, bimolecular and termolecular are used for one, two and three reacting particles respectively.
- Experimentally determined rate equations can provide evidence about reaction mechanisms and the rate constant at a given temperature.
- The order of reaction with respect to a reactant is the exponent to which the concentration of the reactant is raised in the rate equation. This exponent tells us the number of each particle taking part in the rate-determining step.
- The overall order of reaction is the sum of the orders with respect to each reactant. This determines the value and units of the rate constant, k, at a given temperature.
- The Arrhenius equation uses the temperature dependence of the rate constant to determine the activation energy. Graphical techniques can be used to calculate the activation energy for a reaction.
- The Arrhenius factor, A, takes into account the frequency of collisions with proper orientations. It can also be calculated using experimental data.

HL end

Practice questions

1. Curve X on the graph shows the volume of oxygen formed during the catalytic decomposition of a 1.0 mol dm^{-3} solution of hydrogen peroxide:

$$2H_2O_2(aq) \rightarrow O_2(g) + 2H_2O(l)$$



Which change would produce curve Y?

A adding water

B adding some 0.1 mol dm^{-3} hydrogen peroxide solution

C using a different catalyst

D lowering the temperature

2. Which changes increase the rate of the reaction below?

$$C_4H_{10}(g) + Cl_2(g) \rightarrow C_4H_9Cl(l) + HCl(g)$$

I. increase of pressure

II. increase of temperature

III. removal of HCl(g)

A I and II only **B** I and III only **C** II and III only **D** I, II and III

3. Which experimental procedure could be used to determine the rate for the following reaction?

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

A measure the change in electrical conductivity in a given time

B measure the change in mass in a given time

C record the time taken for the formation of a precipitate

D measure the change in volume of gas produced in a given time

4. The catalyst manganese(IV) oxide, $MnO_2(s)$, increases the rate of the decomposition reaction of hydrogen peroxide, $H_2O_2(aq)$. Which statements about MnO_2 are correct?

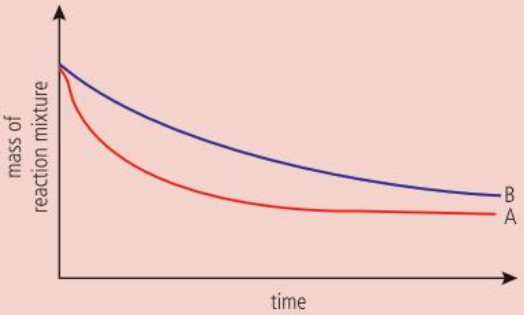
I. The rate is independent of the particle size of MnO_2.

II. MnO_2 provides an alternative reaction pathway for the decomposition with a lower activation energy.

III. All the MnO_2 is present after the decomposition of the hydrogen peroxide is complete.

A I and II only **B** I and III only **C** II and III only **D** I, II and III

5. The graph below was obtained when zinc carbonate reacted with dilute hydrochloric acid under two different conditions, denoted as experiments A and B.



(a) Write an equation including state symbols for the reaction occurring. (2)

(b) Explain why the mass of the reaction mixture decreases in both cases. (1)

(c) Make reference to collision theory to explain the shape of curve A. (3)

(d) Describe the measurements that could be made from the graph to compare the initial rates of the reactions in A and B. Comment on the results expected. (3)

(e) The concentration of hydrochloric acid used in experiments A and B was the same. Suggest three possible differences in the conditions of experiments A and B. (3)

(f) For each of the conditions given in **(e)**, explain why it would affect the rate of the reaction. (6)

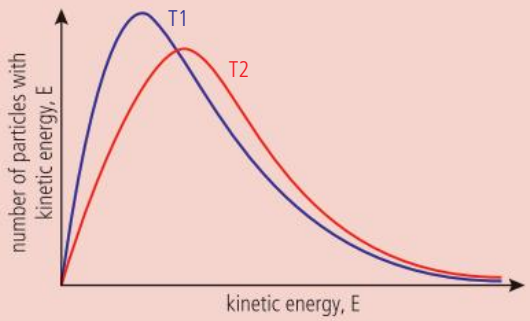
(g) The experiment was repeated using zinc metal in place of zinc carbonate.

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

Describe the differences you would expect in the results, and evaluate whether this is likely to be a satisfactory method for following the rate of reaction. (2)

(Total 20 marks)

6. The figure below shows a Maxwell–Boltzmann distribution curve for a sample of a gas at two different temperatures, T1 and T2.



(a) Deduce the relative values of T1 and T2. (1)

(b) Make reference to your answer to (a) to explain the differences in the shape of the two graphs. (2)

(c) 'A catalyst provides a reaction route with a lower activation energy, and so increases the rate of reaction.'

Justify this statement by means of a suitably labelled Maxwell-Boltzmann distribution curve, showing the proportion of reacting particles with and without a catalyst. (4)

(d) Explain why catalysts increase the rate of reaction but have no effect on:

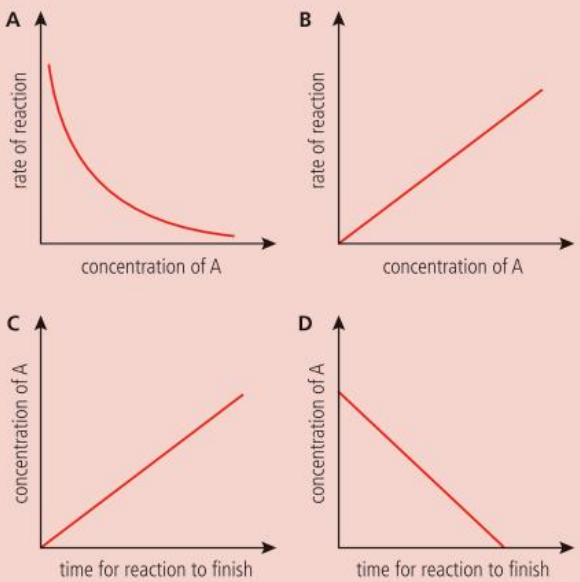
(i) the enthalpy change

(ii) the stoichiometric yield of a product. (4)

(Total 11 marks)

HL

7. Which graph represents a reaction that is first order with respect to reactant A?



8. Bromine and nitrogen(II) oxide react according to the following equation.

$$Br_2(g) + 2NO(g) \rightarrow 2NOBr(g)$$

Which rate equation is consistent with the experimental data?

$[Br_2]$ / mol dm^{-3}	[NO] / mol dm^{-3}	Rate / mol dm^{-3} s^{-1}
0.10	0.10	1.0×10^{-6}
0.20	0.10	4.0×10^{-6}
0.20	0.40	4.0×10^{-6}

A rate = $k[Br_2]^2[NO]$

B rate = $k[Br_2][NO]^2$

C rate = $k[Br_2]^2$

D rate = $k[NO]^2$

9. Which step is the rate-determining step of a reaction?

A the step with the lowest activation energy

B the final step

C the step with the highest activation energy

D the first step

10. Consider the following reaction:

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

A proposed reaction mechanism is:

$NO(g) + NO(g) \rightleftharpoons N_2O_2(g)$	fast
$N_2O_2(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$	slow
$N_2O(g) + H_2(g) \rightarrow N_2(g) + H_2O(g)$	fast

What is the rate equation?

A rate = $k[H_2][NO]^2$

B rate = $k[N_2O_2][H_2]$

C rate = $k[NO]^2[H_2]^2$

D rate = $k[NO]^2[N_2O_2]^2[H_2]$

11. What happens when the temperature of a reaction increases?

A the activation energy increases

B the rate constant increases

C the enthalpy change increases

D the order of the reaction increases

12. Consider the following reaction:

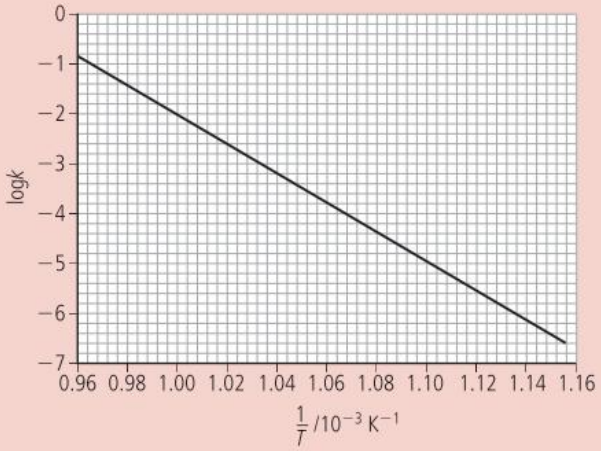
$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

At $T < 227\,^{\circ}C$ the rate equation is rate = $k[NO_2]^2$. Which of the following mechanisms is consistent with this rate equation?

A	$NO_2 + NO_2 \rightleftharpoons N_2O_4$	fast
	$N_2O_4 + 2CO \rightarrow 2NO + 2CO_2$	slow
B	$NO_2 + CO \rightarrow NO + CO_2$	slow
C	$NO_2 \rightarrow NO + O$	slow
	$CO + O \rightarrow CO_2$	fast
D	$NO_2 + NO_2 \rightarrow NO_3 + NO$	slow
	$NO_3 + CO \rightarrow NO_2 + CO_2$	fast

13. Consider the following graph of ln*k* against $\frac{1}{T}$ (temperature in kelvin) for the second-order decomposition of N_2O into N_2 and O.

$$N_2O \rightarrow N_2 + O$$



(a) State how the rate constant, *k*, varies with temperature, *T*. (1)

(b) Determine the activation energy, E_a, for this reaction. (3)

(c) The *y*-intercept on this graph was found to be 28.1. Determine the Arrhenius factor, *A*, for this reaction. (2)

(d) The rate equation for this reaction is rate = $k[N_2O]^2$ and the rate constant is 0.244 $dm^3 mol^{-1} s^{-1}$ at 750 °C. A sample of N_2O of concentration 0.200 mol dm^{-3} is allowed to decompose. Calculate the rate when 10% of the N_2O has reacted. (2)

(Total 8 marks)

14. Andy and Suhailah were asked to investigate the kinetics involved in the iodination of propanone. They were given the following equation by their teacher.

$$CH_3COCH_3(aq) + I_2(aq) \xrightarrow{H^+(aq)} CH_2ICOCH_3(aq) + HI(aq)$$

Andy's hypothesis was that the rate will be affected by changing the concentrations of the propanone and the iodine, as the reaction can happen without a catalyst. Suhailah's hypothesis was that, because the catalyst is involved in the reaction, the concentrations of the propanone, iodine and the hydrogen ions will all affect the rate.

They carried out several experiments varying the concentration of one of the reactants or the catalyst whilst keeping other concentrations and conditions the same and obtained the results below.

Experiment	Composition by volume of mixture / cm^3				Initial rate / mol $dm^{-3} s^{-1}$
	1.00 mol dm^{-3} $CH_3COCH_3(aq)$	water	1.00 mol dm^{-3} $H^+(aq)$	5.00 × 10^{-3} mol dm^{-3} I_2 in KI	
1	10.0	60.0	10.0	20.0	4.96 × 10^{-6}
2	10.0	50.0	10.0	30.0	5.04 × 10^{-6}
3	5.0	65.0	10.0	20.0	2.47 × 10^{-6}
4	10.0	65.0	5.0	20.0	2.51 × 10^{-6}

(a) Explain why Andy and Suhailah added water to the mixtures. (1)

(b) **(i)** Deduce the order of reaction for each substance and the rate equation from the results. (2)

(ii) Comment on whether Andy's or Suhailah's hypothesis is correct. (1)

(c) Using the data from Experiment 1, determine the concentration of the substances used and the rate constant for the reaction including its units. (3)

(d) **(i)** This reaction uses a catalyst. Sketch and annotate the Maxwell–Boltzmann energy distribution curve for a reaction with and without a catalyst on labelled axes. (3)

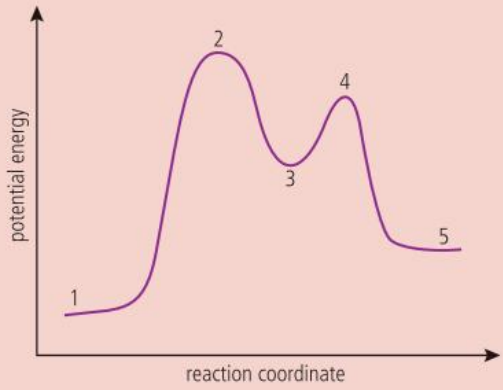
(ii) Describe how a catalyst works. (1)

(Total 11 marks)

15. The diagram shows a potential energy profile for a reaction.
The reaction occurs by the following mechanism.

Step 1: $W + XY \rightarrow WY + X$

Step 2: $WY + Z \rightarrow W + YZ$



(a) Deduce the equation for the overall reaction. (1)

(b) Identify points 1–5 on the energy profile as reactants, products, transition state or intermediate. (3)

(c) Identify the species present at each step points 1–5 on the energy profile. (3)

(d) Determine which step is the rate-determining step and deduce the rate equation for the overall reaction. (2)

(e) Consider whether the reaction is catalysed, and if so, identify the catalyst. (1)

(f) Add labelled arrows to the diagram to show the activation energy, E_a, and the enthalpy change, ΔH. (2)

(Total 12 marks)

HL end



REACTIVITY

2.3 How far? The extent of chemical change

An agricultural landscape in the Netherlands. Our ability to feed a growing global population has been dependent on our ability to mass produce plant fertilizer. Industrial scale production of ammonia, an essential starting material in the production of fertilizer, was made possible through an understanding of reversible reactions and the factors that can be used to influence them. Specifically, the Haber process uses high pressures and a temperature of about 450 °C to maximize the conversion of nitrogen and hydrogen gas into ammonia.

Guiding Question

How can the extent of a reversible reaction be influenced?

Imagine that you are part of the way along an escalator (a moving staircase) that is moving up, and you decide to run down it. If you can run down at exactly the same speed as the escalator is moving up, you will have no *net* (overall) movement. So, if someone were to take a picture of you at regular time intervals, it would seem as if you were not moving at all. Of course, in reality both you and the escalator *are* moving, but because there is no net change neither movement is observable. In chemical reactions a similar phenomenon occurs when a reaction takes place at the same rate as its reverse reaction, so no net change is observed. This is known as a **state of dynamic equilibrium**.

In this chapter, we explore some of the features of the equilibrium state and learn how this enables us to predict how far reactions will proceed under different conditions. Industrial processes rely significantly on this type of study to determine the conditions that will maximize the yield of product.

HL Use of the **equilibrium law** enables us to quantify reaction components, and the **equilibrium constant** and **Gibbs energy change** (seen in Reactivity 1.4) can be used to measure the position of equilibrium in such reactions.

Equilibrium studies are also important in many biochemical and environmental processes, such as predicting the solubility of gases in the blood and knowing how certain chemicals in the atmosphere may react together to form pollutants that contribute to climate change.

Reactivity 2.3.1 – Dynamic equilibrium

Reactivity 2.3.1 – A state of dynamic equilibrium is reached in a closed system when the rates of forward and backward reactions are equal.

Describe the characteristics of a physical and chemical system at equilibrium.

A state of dynamic equilibrium is reached in a closed system

In this section we will think about how **dynamic equilibrium** is reached in both a **physical system,** in which we consider changes of state, and a **chemical system**, in which we consider **reversible** chemical reactions.



Snow and ice-covered peak in the Cordillera Huayhuash, Peru. Equilibrium considerations help explain the relationship between water vapour in the clouds and precipitations in the form of liquid (rain) and solid (snow) at different temperatures and pressures.

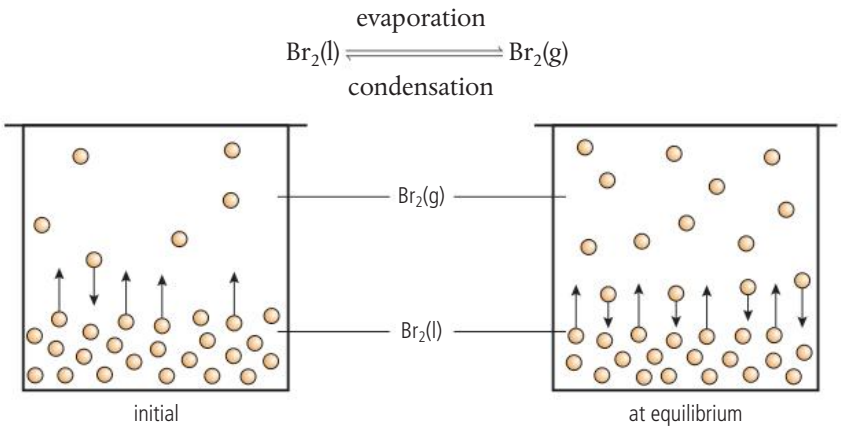
Physical systems

Consider what happens when some bromine, Br_2, is placed in a sealed container at room temperature.

As bromine is a **volatile** liquid, with a boiling point close to room temperature, a significant number of particles (molecules of Br_2) will have enough energy to escape from the liquid state and form vapour in the process known as **evaporation**. As the container is sealed, the bromine vapour cannot escape and so its concentration will increase. Some of these vapour molecules will collide with the surface of the liquid, lose energy, and become liquid in the process known as **condensation**.

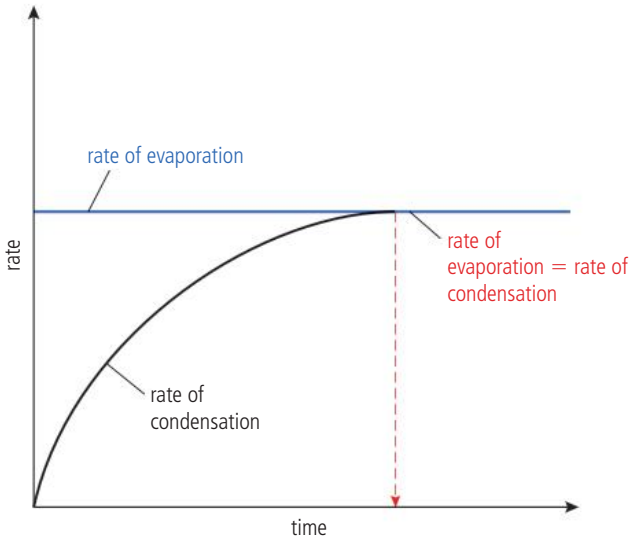


▲ Bromine stored in a sealed jar. The system is in dynamic equilibrium, so the concentrations of liquid and vapour do not change at constant temperature.



▲ Establishing dynamic equilibrium in the evaporation of bromine. Equilibrium is established when the rate of evaporation equals the rate of condensation.

The rate of condensation increases with the increase in concentration of vapour, as more vapour particles collide with the surface of the liquid. Eventually, the rate of condensation is equal to the rate of evaporation, and at this point there will be no net change in the amounts of liquid and gas present (Figure 1). We say that the system has reached **equilibrium**. This will only occur in a **closed system**, where the $Br_2(g)$ cannot escape as vapour but may condense back into the liquid.



R2.3 Figure 1 The rate of evaporation and condensation as liquid–vapour equilibrium is established in a closed system. The rate of evaporation is constant as the surface area remains the same, while the rate of condensation increases as the concentration of vapour increases. Equilibrium is established when the two rates are equal.

Chemical systems

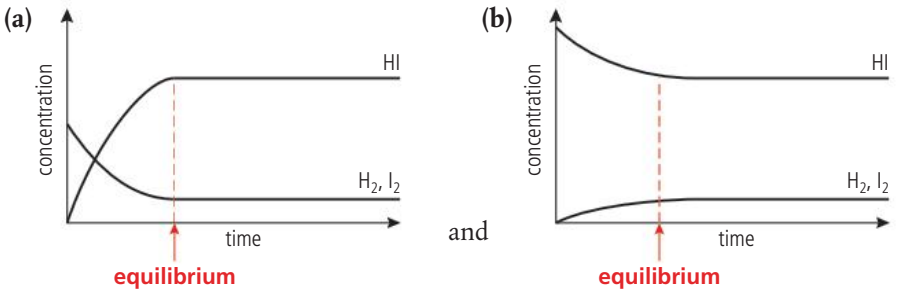
Consider the reaction of dissociation between hydrogen iodide (HI) and its elements hydrogen (H_2) and iodine (I_2). Hydrogen and hydrogen iodide are both colourless, whereas iodine is released as a purple gas.

$$\underset{\text{colourless gas}}{2HI(g)} \rightleftharpoons \underset{\text{colourless gas}}{H_2(g)} + \underset{\text{purple gas}}{I_2(g)}$$

If we carry out this reaction starting with hydrogen iodide in a sealed container, there will at first be an increase in the purple colour owing to the production of iodine gas. But after a while this increase in colour will stop, and it may appear that the reaction too has stopped. In fact, what has happened is that the rate of the dissociation of HI is fastest at the start when the concentration of HI is greatest and falls as the reaction proceeds. Meanwhile, the reverse reaction, which initially has a zero rate because there is no H_2 or I_2 present, starts slowly and increases in rate as the concentrations of H_2 and I_2 increase. Eventually, the rate of dissociation of HI becomes equal to the rate of the reverse reaction of association between H_2 and I_2, so the concentrations remain constant. This is why the colour in the flask remains the same. At this point, equilibrium has been reached. The equilibrium is described as **dynamic** because both forward and backward reactions are still occurring.

If we were to analyse the contents of the flask at this point, we would find that HI, H_2 and I_2 would all be present and that if there were no change in conditions, their concentrations would remain constant over time. We refer to this as the **equilibrium mixture**.

If we reversed the experiment and started with H_2 and I_2 instead of HI, we would find that eventually an equilibrium mixture would again be achieved in which the concentrations of H_2, I_2 and HI would remain constant. These relationships are shown in Figure 2.



R2.3 Figure 2 Equilibrium is reached when the concentrations of reactants and products become constant. Note that the same equilibrium mixture is reached whether you start (a) from a mixture of H_2 and I_2 or (b) from pure HI.

The equilibrium state has specific characteristics

In studies of equilibria, we are dealing with reversible reactions – that is, reactions that occur in both directions. The convention is to describe the reaction from left to right (reactants to products) as the **forward reaction**, and the reaction from right to left (products to reactants) as the **backward** or **reverse reaction**. The symbol ⇌ is used to show that the reaction is an equilibrium reaction.

Bromine is the only non-metallic element that is liquid at room temperature. It is extremely toxic and takes its name from a Greek word meaning stench.



Heated iodine crystals in a stoppered flask. Iodine is a crystalline solid at room temperature, but sublimes on heating to form a purple gas.

TOK

The study of chemical change often involves both the macroscopic and submicroscopic scales. What might this suggest about the role of imagination and intuition in the creation of hypotheses in the natural sciences?

Strictly speaking, all reactions can be considered as equilibrium reactions. However, in many cases, the equilibrium mixture consists almost entirely of products – that is, it is considered to have gone virtually to completion. By convention we use the symbol → rather than the equilibrium symbol in these cases. Combustion reactions, for example, are considered irreversible given the relative stability of the products compared to the reactants. In other reactions there may be so little product formed that it is undetectable and we consider the reaction to have effectively not happened.

Make sure that you use the equilibrium symbol ⇌ when writing equations for reactions where the reverse reactions are significant. For example, it must be used when explaining the behaviour of weak acids and bases (Reactivity 3.1).

At equilibrium the rate of the forward reaction is equal to the rate of the backward reaction.

$$\text{reactants} \underset{\text{backward reaction}}{\overset{\text{forward reaction}}{\rightleftharpoons}} \text{products}$$



The Dragon spacecraft, first launched by the American company SpaceX in 2010, uses the combustion reaction between monomethyl hydrazine and the oxidizing agent dinitrogen tetroxide to produce thrust and orientate the spacecraft during a mission.

$$4CH_3NHNH_2 + 5N_2O_4 \rightarrow 9N_2 + 4CO_2 + 12H_2O$$

The strong N≡N bonds and C=O bonds found in the products make them significantly more stable than the reactants, and so the reaction can be considered non-reversible.

The examples of physical and chemical systems discussed above have shown that at equilibrium the rate of the forward reaction is equal to the rate of the backward reaction.

These reactions have also shown some of the main features of the equilibrium state, and these can now be summarized as they apply to *all* reactions at equilibrium.

	Characteristics of a physical and a chemical system at equilibrium	Explanation
1	Equilibrium is dynamic	The reaction has not stopped, but both forward and backward reactions are still occurring at the same rate.
2	Equilibrium is achieved in a closed system	A closed system has no exchange of matter with the surroundings, so equilibrium is achieved where both reactants and products can react and recombine with each other.
3	The concentrations of reactants and products remain constant at equilibrium	They are being produced and destroyed at an equal rate.
4	At equilibrium there is no change in macroscopic properties	Macroscopic properties are observable properties such as colour and density. These do not change as they depend on the concentrations of the components of the mixture.
5	Equilibrium can be reached from either direction	The same equilibrium mixture will result under the same conditions, no matter whether the reaction is started with all reactants, all products, or a mixture of both.

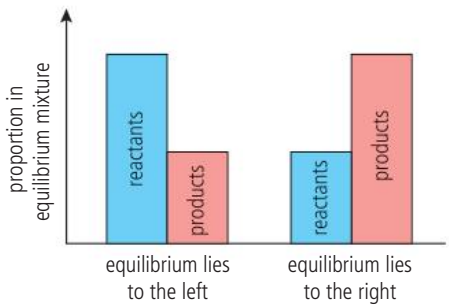
It is important to understand that even though the concentrations of reactant and product are *constant* at equilibrium, this in no way implies that they are *equal*. In fact, most commonly there will be a much higher concentration of either reactant or product in the equilibrium mixture, depending both on the reaction and on the conditions. For example, we can see in Figure 2 that when the dissociation of HI reaches equilibrium, there is a higher concentration of HI than of H_2 and I_2.

Challenge yourself

1. A closed system is defined differently in different disciplines. In thermodynamics, it means that no matter can be exchanged with the surroundings, but energy can flow. To what extent can the Earth be considered a closed system?

Think back to the moving staircase analogy in the introduction to this chapter, where the top and bottom of the escalator represent reactants and products respectively. It would be possible for you to be 'at equilibrium' near the top of the staircase, near the bottom, or anywhere in between. As long as you were moving at the same speed as the staircase, you would still have no net change in position.

The proportion of reactant and product in the equilibrium mixture is referred to as its **equilibrium position**. Reactions where the mixture contains predominantly products are said to 'lie to the right' and reactions with predominantly reactants are said to 'lie to the left'.



It is, however, often useful to be able to capture this information mathematically to compare the equilibrium mixtures of different reactions and the effect of different conditions. In the next section we will look at how this is done.

Nature of Science

At equilibrium, no change is observed on the macroscopic level, although particles are reacting at the submicroscopic level. These changes can be deduced using techniques such as isotopic labelling, which allow the progress of a specific reactant to be followed. Our power of understanding is enhanced by contributions from instrumentation and sensors that may gather information beyond human sense perception.

Exercise

Q1. Which statements are correct for a reaction at equilibrium?

I. The forward and reverse reactions both continue.

II. The rates of the forward and reverse reactions are equal.

III. The concentrations of reactants and products are equal.

A I and II only **B** I and III only **C** II and III only **D** I, II and III

TOK What are the differences between theories and analogies as forms of explanation?

SKILLS Conceptualize equilibrium with 'water races'. Full details of how to carry out this experiment with a worksheet are available in the eBook.

Describing the position of equilibrium

Sometimes you may see the equilibrium sign written with unequal arrows such as ⇌. This is used to represent the reaction that lies in favour of products. Likewise, ⇌ is used to represent a reaction that lies in favour of reactants.

Q2. Which statement is always true for a chemical reaction that has reached equilibrium at constant temperature?

A The yield of product(s) is greater than 50%.

B The rate of the reverse reaction is lower than that of the forward reaction.

C The amounts of reactants and products do not change.

D Both forward and reverse reactions have stopped.

Q3. Which statement is *not* true for a mixture of ice and water at equilibrium at constant temperature?

A The rates of melting and freezing are equal.

B The amounts of ice and water are equal.

C The same position of equilibrium can be reached by cooling water and by heating ice.

D There is no observable change in the system.

Reactivity 2.3.2 and 2.3.3 – Equilibrium law

Reactivity 2.3.2 – The equilibrium law describes how the equilibrium constant, *K*, can be determined from the stoichiometry of a reaction.

Deduce the equilibrium constant expression from an equation for a homogeneous reaction.

Reactivity 2.3.3 – The magnitude of the equilibrium constant indicates the extent of a reaction at equilibrium and is temperature dependent.

Determine the relationships between *K* values for reactions that are the reverse of each other at the same temperature.

Include the extent of reaction for: $K \ll 1, K < 1, K = 1, K > 1, K \gg 1$.	Reactivity 3.1 – How does the value of *K* for the dissociation of an acid convey information about the strength of the acid?

The equilibrium constant, *K*, can be predicted from the reaction stoichiometry

Consider the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

If we were to carry out a series of experiments on this reaction with different starting concentrations of H_2, I_2, and HI, we could wait until each reaction reached equilibrium and then measure the composition of each equilibrium mixture. Here are some typical results obtained at 440 °C.

Experiment I

	Initial concentration / mol dm^{-3}	Equilibrium concentration / mol dm^{-3}
H_2	0.100	0.0222
I_2	0.100	0.0222
HI	0.000	0.156

Experiment II

	Initial concentration / mol dm^{-3}	Equilibrium concentration / mol dm^{-3}
H_2	0.000	0.0350
I_2	0.0100	0.0450
HI	0.350	0.280

Experiment III

	Initial concentration / mol dm^{-3}	Equilibrium concentration / mol dm^{-3}
H_2	0.0150	0.0150
I_2	0.000	0.0135
HI	0.127	0.100

At a glance, the data may not appear to show any pattern. However, there is a predictable relationship among the different compositions of these equilibrium mixtures, and the key to discovering it is in the stoichiometry of the reaction equation.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

If we take the equilibrium concentrations and process them in the following way:

$$\frac{[HI]^2_{eqm}}{[H_2]^1_{eqm}[I_2]^1_{eqm}}$$

2 = coefficient of HI in the reaction equation

1 = coefficient of H_2 in the reaction equation

1 = coefficient of I_2 in the reaction equation

we find the following results:

Experiment I $\quad \dfrac{(0.156)^2}{0.0222 \times 0.0222} = 49.4$

Experiment II $\quad \dfrac{(0.280)^2}{0.035 \times 0.0450} = 49.8$

Experiment III $\quad \dfrac{(0.100)^2}{0.0150 \times 0.0135} = 49.4$

Clearly, this way of processing the equilibrium data produces a constant value within the limits of experimental accuracy. The constant is known as the equilibrium constant, ***K***. It has a fixed value for this reaction at a specified temperature.

In fact, every reaction has its own particular value of *K* which can be derived in a similar way. This finding is described by the equilibrium law.

- First we use the balanced reaction equation to write the **equilibrium constant expression**.

For the reaction:

$$aA + bB \rightleftharpoons cC + dD$$

the equilibrium constant expression

$$K = \frac{[C]^c_{eqm}[D]^d_{eqm}}{[A]^a_{eqm}[B]^b_{eqm}}$$

- The value for *K* can then be determined by substituting the equilibrium concentrations of all reactants and products into this equation.

Remember square brackets [ ] are commonly used to show concentration in mol dm^{-3}.

The equilibrium law states that the equilibrium constant, *K*, has a fixed value for a particular reaction at a specified temperature. The only thing that changes the value of *K* for a reaction is the temperature.

As *K* is calculated using the concentrations of reactants and products, it is commonly stated as K_c in other sources. The 'c' stands for 'concentration'.

Many sources give units for K which are a multiple of mol dm^{-3}, depending on the stoichiometry of the reaction. In fact, this is not fully correct, as the terms in the equilibrium expression are really a thermodynamic quality known as 'activity' that has no units. For this reason, we are omitting units in the values of K here, and you will not be required to include them in IB examination answers.

Note:

- The equilibrium constant expression has the concentrations of products in the numerator and the concentrations of reactants in the denominator.
- Each concentration is raised to the power of its coefficient in the balanced equation. (Where the power is equal to one, it is not shown.)
- Where there is more than one reactant or product, the terms are multiplied together.

Worked example

Write the equilibrium constant expression for the following reactions.

(i) $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$

(ii) $Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}(aq)$

Solution

(i) $K = \dfrac{[H_2O]^2}{[H_2]^2[O_2]}$

(ii) $K = \dfrac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4}$

The equilibrium constant expression will only give the value of K when the concentrations used in the equation are the *equilibrium* concentrations for all reactants and products. Strictly speaking, the subscript 'eqm' should always be used in the equation, but by convention this is generally left out. However, make completely sure that the only values you substitute into an equation to calculate K are the equilibrium concentrations.

The magnitude of K gives information on the extent of reaction

Different reactions have different values of K. What does this value tell us about a particular reaction?

As the equilibrium constant expression puts products in the numerator and reactants in the denominator, a high value of K will mean that at equilibrium there are proportionately more products than reactants. In other words, such an equilibrium mixture lies to the right and the reaction goes almost to completion. By contrast, a low value of K must mean that there are proportionately fewer products with respect to reactants, so the equilibrium mixture lies to the left and the reaction has barely taken place.

Consider the following three reactions and their K values measured at 550 K.

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $\quad K = 2$

$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$ $\quad K = 10^{10}$

$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$ $\quad K = 10^{18}$

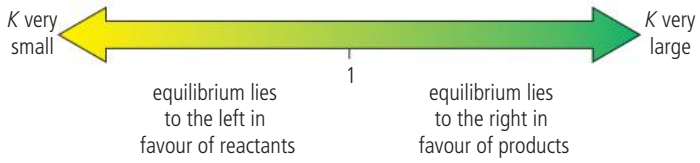
The large range in their K values tells us about the differing **extents** of these reactions. We can deduce that the reaction between H_2 and Cl_2 has taken place the most fully at this temperature, while H_2 and I_2 have reacted the least.

The equilibrium constant expressions described here apply to homogeneous reactions, that is, reactions where reactants and products are in the same phase, as gases, liquids, or in solution. It is good practice always to include state symbols in your equations to ensure this is being applied correctly.

Challenge yourself

2. Why do you think the reactions of the three halogens, Cl_2, Br_2 and I_2, with H_2 have such different values for their equilibrium constant at the same temperature? What can you conclude about the strength of bonding in the three hydrogen halides?

A good rule of thumb to apply to these situations is that if $K \gg 1$, the reaction is considered to go almost to completion (very high conversion of reactants into products), and if $K \ll 1$, the reaction hardly proceeds.



The smaller the value of *K*, the further the equilibrium mixture lies to the left. The larger the value of *K*, the further the equilibrium mixture lies to the right.

This can be summarized as follows.

Value of *K*	Extent of reaction
$K \ll 1$	Reaction hardly proceeds
$K < 1$	Equilibrium lies towards the reactants
$K = 1$	Significant amounts of both reactants and products at equilibrium
$K > 1$	Equilibrium lies towards the products
$K \gg 1$	Reaction goes almost to completion

Note that the magnitude of *K* does not give us any information on the *rate* of the reaction. It informs us of the nature of the equilibrium mixture, but not how quickly the equilibrium state will be achieved.

The value of *K* can be particularly useful to consider the dissociation of an acid in solution. Weak acids undergo very little dissociation so will have very low values of *K* whereas a stronger acid will dissociate to a greater extent, producing a larger value of *K*.

HL This will be explored in more detail in Reactivity 3.1.

Reactivity 3.1 – How does the value of *K* for the dissociation of an acid convey information about its strength?

Relationships between *K* values for reactions that are the reverse of each other at the same temperature

As *K* is defined with products in the numerator and reactants in the denominator, each raised to the power of their stoichiometric coefficients in the balanced equation, we can manipulate the value of *K* according to changes made to these terms. For this discussion we will consider the generic reaction:

$$aA + bB \rightleftharpoons cC + dD$$

for which the equilibrium constant is:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The reverse reaction

$$cC + dD \rightleftharpoons aA + bB$$

defines the products as reactants and vice versa. We will denote its equilibrium constant as K'.

$$K' = \frac{[A]^a[B]^b}{[C]^c[D]^d}$$

The magnitude of the equilibrium constant *K* gives information about the extent of reaction at a particular temperature, but not about how fast it will achieve the equilibrium state.

We can see that $K' = \frac{1}{K}$ or $K' = K^{-1}$.

In other words, the equilibrium constant for a reaction is the reciprocal of the equilibrium constant for its reverse reaction.

Worked example

The equilibrium constant for the reaction

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

is 0.040 at a certain temperature. What would be the value of the equilibrium constant, K', for the reverse reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

at the same temperature?

Solution

The value of K' is the reciprocal of K.

So $K' = \frac{1}{K}$ or K^{-1}.

$\therefore K' = \frac{1}{0.040} = 25$

This manipulation of the value of K is summarized below.

	Effect on equilibrium expression	Effect on K
inversing the reaction	inverts the expression	$\frac{1}{K}$ or K^{-1}

Challenge yourself

3. We can also express the relationship between K and K' for multiples of a reaction. Doubling the reaction coefficients squares the equilibrium expression, $K' = K^2$, and halving the reaction coefficients square roots the equilibrium expression, $K'' = \sqrt{K}$.

At a given temperature, the reaction

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

has a value of $K = 278$. Determine values of K for the following reactions at this temperature.

(a) $4SO_2(g) + 2O_2(g) \rightleftharpoons 4SO_3(g)$

(b) $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$

(c) $6SO_3(g) \rightleftharpoons 6SO_2(g) + 3O_2(g)$

Exercise

Q4. Write the equilibrium constant expression for the following reactions:

(a) $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

(b) $4NH_3(g) + 7O_2(g) \rightleftharpoons 4NO_2(g) + 6H_2O(g)$

(c) $CH_3Cl(aq) + OH^-(aq) \rightleftharpoons CH_3OH(aq) + Cl^-(aq)$

Q5. Write the equations for the reactions represented by the following equilibrium constant expressions:

(a) $K = \dfrac{[NO_2]^2}{[N_2O_4]}$ **(b)** $K = \dfrac{[CO][H_2]^3}{[CH_4][H_2O]}$

Q6. Write the equilibrium constant expressions for the following chemical reactions:

(a) fluorine gas and chlorine gas combine to form $ClF_3(g)$

(b) NO dissociates into its elements

(c) methane, CH_4, and steam react to form carbon monoxide and hydrogen.

Q7. When the following reactions reach equilibrium at a given temperature, does the equilibrium mixture contain mostly reactants or mostly products? Assume that the values for K are applicable at the given temperature.

(a) $N_2(g) + 2H_2(g) \rightleftharpoons N_2H_4(g)$ $K = 7.4 \times 10^{-26}$

(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K = 2.7 \times 10^{-18}$

(c) $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ $K = 6.0 \times 10^{13}$

Q8. At 298 K, the equilibrium concentrations in the reaction mixture:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

are $[N_2O_4] = 1.62\,mol\,dm^3$ and $[NO_2] = 1.80\,mol\,dm^{-3}$.

Determine the value of the equilibrium constant, K.

Q9. At a given temperature, the reaction

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

has a value of $K = 278$. Determine the value of K for the *reverse* reaction at this temperature.

Reactivity 2.3.4 – Le Châtelier's principle

Reactivity 2.3.4 – Le Châtelier's principle enables the prediction of the qualitative effects of changes in concentration, temperature and pressure to a system at equilibrium. Apply Le Châtelier's principle to predict and explain responses to changes of systems at equilibrium.	
Include the effects on the value of K and on the equilibrium composition. Le Châtelier's principle can be applied to heterogeneous equilibria such as: $X(g) \rightleftharpoons X(aq)$	Reactivity 2.2 – Why do catalysts have no effect on the value of K or on the equilibrium composition?

SKILLS

Observations of shifts in the position of chemical equilibria. Full details of how to carry out this experiment with a worksheet are available in the eBook.

Henri-Louis Le Châtelier was a French chemist who published his equilibria principle in 1884. Among other research, he also investigated the possibility of ammonia synthesis, but abandoned his efforts after suffering a devastating explosion in his laboratory. After Haber's later elucidation of the conditions required in the reaction, Le Châtelier realized that he had been very close to the discovery himself. Later in his life, he noted 'It was the greatest blunder of my career'.

When a system at equilibrium is subjected to a change, it will respond in such a way as to minimize the effect of the change.

A system at equilibrium will respond when subjected to a change

A system remains at equilibrium so long as the rate of the forward reaction equals the rate of the backward reaction. But as soon as this balance is disrupted by any change in conditions that unequally affects the rates of these reactions, the equilibrium condition will no longer be met. It has been shown, however, that equilibria respond in a predictable way to such a situation based on a principle known as **Le Châtelier's principle**. This states that *a system at equilibrium when subjected to a change will respond in such a way as to minimize the effect of the change*. Simply put, this means that whatever we do to a system at equilibrium, the system will respond in the opposite way. Add something, and the system will react to remove it; remove something, and the system will react to replace it. After a while, a new equilibrium will be established and this will have a different composition from the earlier equilibrium mixture. Applying the principle, therefore, enables us to predict the qualitative effect of typical changes that occur to systems at equilibrium.

Changes in concentration

Suppose an equilibrium is disrupted by an increase in the concentration of one of the reactants. This will cause the rate of the forward reaction to increase while the backward reaction will not be affected, so the reaction rates will no longer be equal. When equilibrium re-establishes itself, the mixture will have new concentrations of all reactants and products, and the equilibrium will have shifted in favour of products. The value of K will be unchanged. This is in keeping with the prediction from Le Châtelier's principle: the addition of reactant causes the system to respond by removing reactant – this favours the forward reaction and so shifts the equilibrium to the right.



Experiment to show the effect of changing the concentration of chloride ions on the cobalt chloride equilibrium reaction:

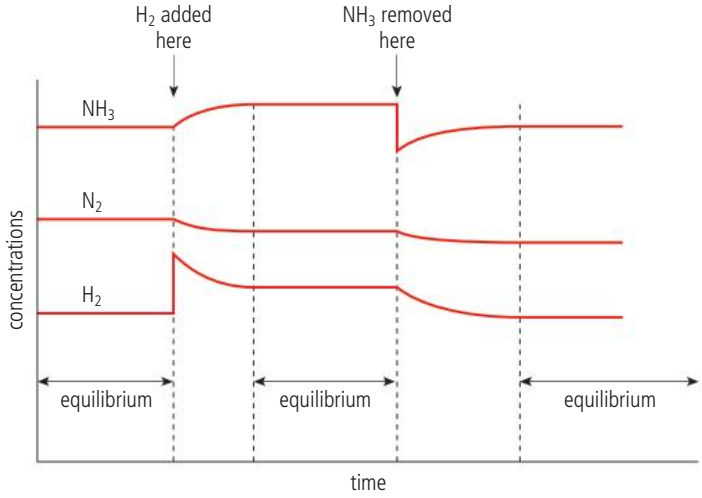
$[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \rightleftharpoons CoCl_4^{2-}(aq) + 6H_2O(l)$

The flask on the left has a low concentration of chloride ions, giving the pink colour of the complex ion with water. As the concentration of chloride ions is increased, the equilibrium shifts to the right, changing the colour from pink to blue. Adding water would shift the equilibrium in the opposite direction. Cobalt chloride is often used to test for the presence of water because of this colour change.

Similarly, the equilibrium could be disrupted by a decrease in the concentration of product by removing product from the equilibrium mixture. As the rate of the backward reaction is now decreased, there will be a shift in the equilibrium in favour of the products. A different equilibrium position will be achieved, but the value of K will be unchanged. Again, this confirms the prediction from Le Châtelier's principle: removal of product causes the system to respond by making more product – this favours the forward reaction and so shifts the equilibrium to the right.

The graph in Figure 3 illustrates these disruptions to equilibrium for the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$



R2.3 Figure 3 Effects of the addition of reactant and removal of product on the equilibrium $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. When H_2 is added, the rate of the forward reaction with N_2 increases and more NH_3 is formed. The equilibrium shifts to the right. When NH_3 is removed, the rate of the backward reaction decreases, and again, the equilibrium shifts to the right producing more NH_3. After each change, a new equilibrium mixture is achieved but *K* remains constant.

After H_2 is added, the concentrations of N_2 and H_2 decrease (in a 1:3 ratio in keeping with their reaction stoichiometry), while the concentration of NH_3 rises (in a 2:1 ratio relative to N_2) as the rate of the forward reaction increases and the equilibrium shifts to the right. The new equilibrium mixture has a higher concentration of products. In the second part of the graph, removal of NH_3 from the equilibrium mixture causes a decrease in the concentrations of N_2 and H_2 as they react to form more NH_3.

Often in an industrial process, the product will be removed as it forms. This ensures that the equilibrium is continuously pulled to the right, increasing the yield of product.

Applying Le Châtelier's principle, can you think what concentration changes would cause an equilibrium to shift to the left? The answer is either an increase in concentration of product or a decrease in concentration of reactant.

Changes in pressure

Equilibria involving gases will be affected by a change in pressure if the reaction involves a change in the number of molecules. This is because there is a direct relationship between the number of gas molecules and the pressure exerted by a gas in a fixed volume. So if such a reaction at equilibrium is subject to an increase in pressure, the system responds to decrease this pressure by favouring the side with the smaller number of molecules. Conversely, a decrease in pressure will cause a shift in the equilibrium position to the side with the larger number of molecules of gas. A different equilibrium position will be achieved but the value of *K* will be unchanged, so long as the temperature remains the same.

For example, consider the reaction used in the production of methanol:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

In total, there are three molecules of gas on the left side and one molecule of gas on the right side. So for this reaction, high pressure will shift the equilibrium to the right, in favour of the smaller number of molecules, which increases the yield of CH_3OH.

Changes in pressure or volume will affect the position of equilibrium of a reaction if it involves a change in the number of gas molecules.

Note that many common equilibrium reactions do not involve a change in the number of gas molecules and so are not affected by changes in pressure. For example, the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

has two molecules of gas on both sides of the equation. Changing the pressure for this reaction will affect the rate of the reaction but not the position of equilibrium or the value of *K*.

Changes in concentration, pressure or volume may change the position of equilibrium, but have no effect on the value of *K*.

When ΔH is given for an equilibrium reaction, by convention its sign refers to the forward reaction. So a negative sign for ΔH means that the forward reaction is exothermic, and the backward reaction is endothermic.

Changes in temperature

We have noted that *K* is temperature dependent, so changing the temperature will change *K*. However, in order to predict *how K* will change we must examine the enthalpy changes (see Reactivity 1.1) of the forward and backward reactions. Remember that an exothermic reaction releases energy (ΔH is negative), whereas an endothermic reaction absorbs energy (ΔH is positive). The enthalpy changes of the forward and backward reactions are equal and opposite to each other.

So if we apply Le Châtelier's principle, including the energy change in the chemical reaction, we can predict how the reaction will respond to a change in temperature.

Consider the reaction

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \quad \Delta H = -57 \text{ kJ mol}^{-1}$$
brown colourless

The negative sign of ΔH tells us that the forward reaction is exothermic and so releases heat. If this reaction at equilibrium is subjected to a decrease in temperature, the system will respond by producing heat and it does this by favouring the forward exothermic reaction. This means that the equilibrium will shift to the right, in favour of the product, N_2O_4. A new equilibrium mixture will be achieved and the value of *K* will increase. So here we can see that the reaction will give a higher yield of products at a lower temperature.

Conversely, increasing the temperature favours the backward, endothermic, reaction, and so shifts the equilibrium to the left, decreasing the value of *K*. The reaction mixture becomes a darker colour as the concentration of NO_2 increases.



Experiment to show the effect of temperature on the reaction that converts NO_2 (brown) to N_2O_4 (colourless). As the temperature is increased, more NO_2 is produced and the gas becomes darker, as seen in the tube on the left. With a decrease in temperature (the tube on the right), the equilibrium shifts to the right, producing more N_2O_2, and the gas becomes paler.

The table below illustrates the effect of temperature on the value of *K* for this reaction.

Temperature / K	*K* for $2NO_2(g) \rightleftharpoons N_2O_4(g)$
273	1300
298	170

Even though, in this case, a lower temperature will produce an equilibrium mixture with a higher proportion of products, remember from Reactivity 2.2 that low temperature also causes a lower rate of reaction. And so, although a higher yield will be produced eventually, it may simply take too long to achieve this for practical and economic considerations if this was an industrial-scale reaction. We will come back to this point later in this chapter.

Now consider the following reaction:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \quad \Delta H = +181 \text{ kJ mol}^{-1}$$

In this case, we can see that the forward reaction is endothermic and so absorbs heat. So here the effect of a decreased temperature will be to favour the backward exothermic reaction. Therefore, the equilibrium will shift to the left in favour of reactants, and *K* will decrease. At higher temperatures, the forward, endothermic, reaction is favoured, so the equilibrium shifts to the right and *K* will increase.

The table below illustrates the effect of temperature on the value of *K* for this reaction.

Temperature / K	K for $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$
298	4.5×10^{-31}
900	6.7×10^{-10}
2300	1.7×10^{-3}

Challenge yourself

4. Use information from this section to explain why there is very little NO in the atmosphere under ordinary conditions, and why severe air pollution is often characterized by a brownish haze.

The reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ takes place in motor vehicles where the heat released by combustion of the fuel is sufficient to cause the nitrogen and oxygen gases from the air to combine. Unfortunately, the product, NO, is toxic, and, worse still, quickly becomes converted into other toxins that form the components of acid rain and smog. It is therefore of great interest to vehicle manufacturers to find ways of lowering the temperature during combustion in order to reduce the production of NO in the reaction above.

These examples illustrate that, unlike changes in concentration and pressure, changes in temperature *do* cause the value of *K* to change. An increase in temperature increases the value of *K* for an endothermic reaction and decreases the value of *K* for an exothermic reaction. This is because changes in temperature have a different effect on the rates of the forward and backward reactions due to their different activation energies, as discussed in Reactivity 2.2. In the next chapter, we will use this fact to explain why the pH of pure water is temperature dependent.

TOK

Combustion reactions are generally described as exothermic, but the reaction

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

is endothermic. When is it appropriate to refer to an 'exception to a rule', and when does the rule need to be reconsidered?

Addition of a catalyst

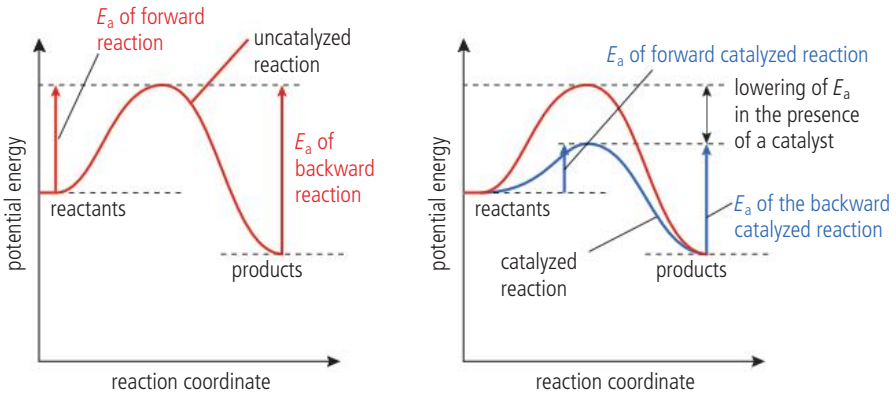
Catalysts are widely used in industrial processes to increase the rate of product formation, and are involved in every single biochemical reaction where they are known as enzymes.

As we learn in Reactivity 2.2, a catalyst speeds up the rate of a reaction by providing an alternative reaction pathway that has a transition state with a lower activation energy, E_a. This increases the number of particles that have sufficient energy to react without raising the temperature.

Because the forward and backward reactions pass through the same transition state, a catalyst lowers the activation energy by the same amount for the forward and backward reactions. So the rate of both these reactions will be increased by the same factor, as shown in Figure 4. The catalyst will therefore have no effect on the position of equilibrium, or on the value of *K*. In other words, the catalyst will not increase the equilibrium yield of product in a reaction. It will, however, speed up the attainment of the equilibrium state and so cause products to form more quickly. Catalysts are

Increasing the temperature causes an increase in the value of *K* for an endothermic reaction and a decrease in the value of *K* for an exothermic reaction.

generally not shown in the reaction equation or in the equilibrium constant expression as they are not chemically changed at the end of the reaction and have no effect on the equilibrium concentrations.



R2.3 Figure 4 The effect of a catalyst in lowering the activation energy of both forward and backward reactions.

Reactivity 2.2 – Why do catalysts have no effect on the value of *K* or on the equilibrium composition?

Catalysts do not change the position of equilibrium or the equilibrium yield of a single reaction, but they enable the equilibrium mixture to be achieved more quickly.

Catalysts are widely used in industrial processes to increase the rate of product formation and are involved in every single biochemical reaction. One of the key principles of Green Chemistry is that catalytic reagents, chosen to be as selective as possible, are superior to stoichiometric reagents as they are not consumed in the reaction.

Summary

We can now summarize the effects of concentration, pressure, temperature and catalyst on the position of equilibrium and on the value of *K*.

Effect of …	Change in position of equilibrium	Change in value of K
1 concentration	changes	no change
2 pressure	changes if reaction involves a change in the number of gas molecules	no change
3 temperature	changes	changes
4 catalyst	no change	no change

A particular reaction at a specified temperature can have many different possible equilibrium positions, but only one value for the equilibrium constant *K*.

It is worth noting that although we have only seen examples of homogeneous equilibria (in the gaseous phase) in this section, we can also apply Le Châtelier's principle to heterogeneous equilibria involving reactants and products in gaseous and aqueous states.

Consider, for example, a fizzy drink bottle which contains an equilibrium between dissolved carbon dioxide and gaseous carbon dioxide.

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

When the bottle is opened, releasing some of the gaseous CO_2, the equilibrium shifts to the left. We can see this change occur in the formation of CO_2 bubbles. Once the cap is placed back onto the bottle, a new equilibrium composition will be formed but the equilibrium constant will remain the same.



The fizzing we see when we open carbonated drinks is caused by a shift in equilibrium from aqueous carbon dioxide to gaseous carbon dioxide: $CO_2(g) \rightleftharpoons CO_2(aq)$

If the system remains open, the equilibrium continues to shift to the left until no dissolved carbon dioxide remains and the drink becomes flat.

Applying Le Châtelier's principle

In reactions involving the manufacture of a chemical, it is obviously a goal to obtain as high a conversion of reactant to product as possible. Application of Le Châtelier's principle enables chemists to choose conditions that will cause the equilibrium to lie to the right and so help to achieve this. But the *yield* of a reaction is only part of the consideration. The *rate* is also clearly of great significance as it would be of limited value if a process were able to claim a high equilibrium yield of product, but take several years to achieve this. The economics of the process will depend on considerations of both the equilibrium and the kinetics of the reaction – in other words, on how far and how fast the reaction will proceed. Sometimes these two criteria work against each other, and so the best compromise must be reached. Two case studies of industrial processes are discussed here.

Note that you are not expected to learn specific conditions for any reaction, so there is no need to focus on the names of catalysts, specific temperature used, etc. But you should be able to apply an understanding of equilibria to any given example, and predict the conditions likely to be effective.

It is estimated that over 150 million tonnes of ammonia, NH_3, are produced worldwide every year. Approximately 80% of this ammonia is used to make fertilizers, notably ammonium nitrate, NH_4NO_3. Other uses include synthesis of textiles such as nylon and powerful explosives. In August 2020, a major explosion occurred in the Port of Beirut after 2750 tonnes of confiscated ammonium nitrate was ignited by a fire in an adjacent warehouse. Accidents such as this in industrial plants raise many questions regarding health and safety, storage, and handling of chemicals, and the balance of responsibility between companies, governments, and individuals.



The Port of Beirut explosion killed over 200 people and caused up to $15 billion in property damage.

Fritz Haber and Carl Bosch developed the process for the industrial synthesis of ammonia from its elements, and the first factory for ammonia production opened in Germany in 1913, just before the First World War. This development enabled the continued production of explosives when imports of nitrate, used for producing nitric acid and explosives such as TNT, were barred through blockaded ports. This effectively enabled Germany to continue its war efforts for another four years. Haber was awarded the Nobel Prize in Chemistry in 1918. In many ways history has recorded this as a controversial choice – not only had Haber's work helped to prolong the war, he had also been responsible for the development and use of chlorine as the first poison gas.

Worked example

The Haber process is based on the reaction:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -93\,kJ\,mol^{-1}$$

Deduce the conditions that would maximize the conversion of reactants to products in this reaction.

Solution

The following information can be derived from this equation:

- all reactants and products are gases
- there is a change in the number of gas molecules as the reaction proceeds: four gas molecules on the left and two on the right
- the forward reaction is exothermic so releases heat; the backward reaction is endothermic so absorbs heat.

Application of Le Châtelier's principle to this reaction enables us to consider the optimum conditions for converting reactants to products.

- Concentration: we would need to *increase* the concentration of the reactants nitrogen and hydrogen by adding more to the reaction vessel (in the molar ratio 1:3 in accordance with their stoichiometry in the equation) and *decrease* the concentration of ammonia by removing it as it forms. These changes would both shift the equilibrium to the right.
- Pressure: as the forward reaction involves a decrease in the number of gas molecules, it will be favoured by a *high pressure*.
- Temperature: as the forward reaction is exothermic, it will be favoured by a lower temperature. However, too low a temperature would cause the rate of reaction to be uneconomically slow, and so a *moderate temperature* is used as a compromise.
- Catalyst: a catalyst does not affect the position of equilibrium but will speed up the rate of production and so help to compensate for the moderate temperature used. An iron-based catalyst is used in the Haber process.

In fact, the Haber process achieves a conversion of H_2 and N_2 into NH_3 of only about 10–20% per pass through the reactor. After separation of the NH_3 product, the unconverted reactants are recycled to the reactor to obtain an overall yield of about 95%. This recycling of unconverted reactants is commonly used in industrial processes and allows processes with low equilibrium yield to be made commercially viable. Designing processes that prevent or minimize waste is the first of the 12 principles of Green Chemistry.



Tractor applying a chemical solution of fertilizer to the soil. Ammonium salts such as ammonium nitrate and sulfate are particularly effective fertilizers as they supply the nitrogen needed by plants and are readily soluble. It is estimated that without the use of ammonium fertilizers, 2 billion people would starve.

Nature of Science

Scientific discoveries often have significant economic, ethical and political implications. Some of these may be unintended consequences of the discovery, such as the environmental degradation caused by the excess use of nitrate fertilizers as an outcome of the Haber process. This raises the question of who must take moral responsibility for the applications of scientific discoveries. The process of science includes risk-benefit analyses, risk assessment, and ethical considerations, but sometimes the full consequences cannot be predicted and do not become known until much later.

Challenge yourself

5. Consider the atom economy of the Haber process described here using the formula:

$$\%\ \text{atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100$$

Explain how the atom economy is different from the reaction yield.

In a similar manner to the Haber process, the production of methanol involves an exothermic homogeneous reaction in the gaseous state with more molecules of gas on the left side of the equation:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \quad \Delta H = -90\,\text{kJ mol}^{-1}$$

Again, Le Châtelier's principle can be used to consider the pressure and temperature conditions that will optimize the conversion of reactants to products.

	Condition used	Reasoning
Pressure	High pressure	The forward reaction involves a reduction in the number of molecules of gas from three molecules of reactant to one molecule of product. High pressure will shift the equilibrium to the right.
Temperature	Moderate temperature	The forward reaction is exothermic so a low temperature will increase the equilibrium yield but decrease the rate. A moderate temperature is used as a compromise.

A catalyst will also be used to increase the rate of reaction although it has no impact on the position of equilibrium.

Methanol, CH_3OH, is used as a **chemical feedstock** to make other chemicals. A high proportion is converted into methanal, HCHO, which is then converted into plastics, paints, explosives, and plywood. Methanol is used as a laboratory solvent, as an antifreeze agent, and in the process of producing biodiesel fuel from fats. Interest has also focused on the potential of methanol as an energy storage molecule in the so-called 'methanol economy'. In on-going efforts to reduce dependence on imported fossil fuels, China has greatly increased production capacity and consumption of methanol for its transportation sector. In 2021, China had over 20 000 methanol taxis in operation.

Drivers stand beside the first batch of M100 (pure methanol) taxis in China's Shaanxi province in 2018.



The Contact process is an industrially significant reaction used to produce sulfuric acid, H_2SO_4. One step in this process is shown below.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H = -198\,kJ\,mol^{-1}$$

As we have seen throughout this section, Le Châtelier's principle can be used to predict the conditions that will maximize the production of sulfur trioxide in this step. More sulfuric acid by mass is produced worldwide than any other chemical. It has been found that the production of sulfuric acid closely mirrors historical events such as major wars that affect a country's economy. For this reason, some economists use sulfuric acid production as a measure of a country's industrial strength. Sulfuric acid is used directly or indirectly in nearly all industrial processes, including the production of fertilizers, detergents and paints, and in ore processing, steel production, and water treatment. Approximately 250 million tonnes of sulfuric acid are produced annually across all continents.

Exercise

Q10. The manufacture of sulfur trioxide can be represented by the equation below:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H = -198\,kJ\,mol^{-1}$$

What happens when a catalyst is added to an equilibrium mixture from this reaction?

A The rate of the forward reaction increases and that of the reverse reaction decreases.

B The rates of both forward and reverse reactions increase.

C The value of ΔH increases.

D The yield of sulfur trioxide increases.

Q11. What will happen to the position of equilibrium and the value of the equilibrium constant when the temperature is increased in the following reaction?

$$Br_2(g) + Cl_2(g) \rightleftharpoons 2BrCl(g) \quad \Delta H = +14\,kJ\,mol^{-1}$$

	Position of equilibrium	Value of equilibrium constant
A	shifts towards the reactants	decreases
B	shifts towards the reactants	increases
C	shifts towards the products	decreases
D	shifts towards the products	increases

Q12. Which changes will shift the position of equilibrium to the right in the following reaction?

$$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$$

I. adding a catalyst

II. decreasing the oxygen concentration

III. increasing the volume of the container

A I and II only **B** I and III only **C** II and III only **D** I, II and III

Q13. For each of the following reactions, predict in which direction the equilibrium will shift in response to an increase in pressure:

(a) $2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$

(b) $CO(g) + 2H_2 \rightleftharpoons CH_3OH(g)$

(c) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

Q14. How will the equilibrium

$$CH_4(g) + 2H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g) \quad \Delta H = +ve$$

respond to the following changes?

(a) addition of $H_2(g)$

(b) addition of $CH_4(g)$

(c) a decrease in the volume of the container

(d) removal of $CS_2(g)$

(e) increase in temperature

Q15. The reaction

$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g) \quad \Delta H = -566\,kJ\,mol^{-1}$$

takes place in catalytic converters in cars. If this reaction is at equilibrium, will the amount of CO increase, decrease or stay the same when:

(a) the pressure is increased by decreasing the volume?

(b) the pressure is increased by adding $O_2(g)$?

(c) the temperature is increased?

(d) a platinum catalyst is added?

Q16. In the Haber process for the synthesis of ammonia, what effects does the catalyst have?

	Rate of formation of $NH_3(g)$	**Amount of $NH_3(g)$ formed**
A	increases	increases
B	increases	decreases
C	increases	no change
D	no change	increases

Q17.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H = -200\,kJ\,mol^{-1}$$

According to the above information, what temperature and pressure conditions produce the greatest amount of SO_3?

	Temperature	**Pressure**
A	low	low
B	low	high
C	high	high
D	high	low

Q18. Predict how you would expect the value of *K* for the exothermic Haber process to change as the temperature is increased. Explain the significance of this in terms of the reaction yield.

HL

Reactivity 2.3.5 – The reaction quotient, *Q*

Reactivity 2.3.5 – The reaction quotient, *Q*, is calculated using the equilibrium expression with non-equilibrium concentrations of reactants and products.

Calculate the reaction quotient *Q* from the concentrations of reactants and products at a particular time, and determine the direction in which the reaction will proceed to reach equilibrium.

The reaction quotient, *Q*, enables us to predict the direction of reaction

Remember that the value of *K* is calculated by substituting the *equilibrium* concentrations of all reactants and products into the equilibrium constant expression. Any other values used will not give the equilibrium value *K* for that reaction at that temperature.

This in itself can be useful. If we take the concentrations of the reactants and products at one moment in time when the reaction is not at equilibrium, and substitute these into the equilibrium constant expression, we obtain a value known as the **reaction quotient**, ***Q***. As time passes and the reaction continues, the concentrations of all reaction components change and eventually reach the equilibrium concentrations. In other words, the value of *Q* changes in the direction of *K*. This enables us to predict the direction in which the reaction will proceed.

For example, if we again consider the reaction:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

for which $K = 49.5$ at 440 °C, as we saw earlier in this chapter.

The table shows experimental data for the concentrations of the reaction components from experiments I and II at a time when the reaction mixture was not at equilibrium.

	Experiment I: concentration at time t / mol dm^{-3}	Experiment II: concentration at time t / mol dm^{-3}
H_2	0.0500	0.0250
I_2	0.0500	0.0350
HI	0.100	0.300

The equilibrium constant expression $= \dfrac{[HI]^2}{[H_2][I_2]}$

Experiment I, time t $\quad Q = \dfrac{(0.100)^2}{(0.0500)(0.0500)} = 4.00$

Experiment 2, time t $\quad Q = \dfrac{(0.300)^2}{(0.0250)(0.0350)} = 103$

In experiment I, $Q < K$ and so Q must increase as the reaction moves towards equilibrium. This means that the net reaction must be to the right, in favour of products.

In experiment II, $Q > K$ and so Q must decrease as the reaction moves towards equilibrium. This means that the net reaction must be to the left, in favour of reactants.



Hydrogen gas (left) reacts with iodine gas (middle) to produce colourless hydrogen iodide gas (right).

The reaction quotient, *Q*, is a measure of the relative amounts of reactants and products present in a reaction at a particular time. Its value is determined from substituting concentrations of reaction components, all measured at the same time, into the equilibrium expression.

We can summarize the use of the reaction quotient, Q, in determining the direction of reaction as follows:

- if $Q = K$, the reaction is at equilibrium, no net reaction occurs
- if $Q < K$, the reaction proceeds to the right in favour of products
- if $Q > K$, the reaction proceeds to the left in favour of reactants.

Note that the value of Q for a reaction does not have a fixed value as it can be measured at any point in time, whereas the value of K for a reaction is a constant at a specified temperature.

Worked example

The equilibrium constant K for the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

is 1.7×10^2 at 500 K.

Determine whether the reaction mixture is at equilibrium when the concentrations of the components at this temperature are as follows:

$[N_2] = 1.50$

$[H_2] = 1.00$

$[NH_3] = 8.00$.

If it is not at equilibrium, state and explain in which direction the reaction will proceed.

Solution

First write the equilibrium constant expression.

$$\frac{[NH_3]^2}{[N_2][H_2]^3}$$

Calculate the value of Q at these conditions by substituting the given concentration values into the equilibrium expression.

$$Q = \frac{(8.00)^2}{(1.50)(1.00)^3} = 42.67$$

Compare the value of Q at the given conditions with K.

$$42.67 < 1.7 \times 10^2$$

Therefore, the reaction is not at equilibrium. It will proceed to the right in favour of products, as the value of Q must increase to be equal to K at equilibrium.

Nature of Science

Knowledge of how systems at equilibrium respond to change has many applications, as we have seen with some industrial processes. Le Châtelier's principle is a useful predictive tool for this purpose and has the advantage of being effective and relatively simple to apply. But it has some disadvantages too. Firstly, it leads only to qualitative predictions of the system's response. In some cases, such as investigations of when a precipitate will form in aqueous solution, this is insufficient. Secondly, Le Châtelier's principle offers no *explanation* for the response – it predicts *what* will happen, but not *why*.

On the other hand, use of the reaction quotient, Q, to predict the consequence of change can often provide an effective explanation. As disturbances in concentration or pressure change the value of Q, the system responds as Q progresses towards K. Changes in temperature are different because they change the value of K as the forward and backward reactions respond differently to temperature changes. In this case, the system responds as Q progresses towards the new value of K. Scientific explanations often draw on different approaches and theories in this way. So long as the approaches do not contradict each other, together they can clarify and strengthen the understanding.

Exercise

Q19. The equilibrium constant, K, for the reaction:

$$H_2O(g) + Cl_2O(g) \rightleftharpoons 2HOCl(g)$$

is 0.0900 at 298 K.

Determine whether the following sets of conditions represent an equilibrium mixture for the reaction at this temperature.

	$[H_2O]$	$[Cl_2O]$	$[HOCl]$
(a)	0.100	0.100	1.00
(b)	0.49	0.040	0.042
(c)	0.19	0.00033	0.083

Q20. The equilibrium constant for the reaction:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

is 1.00 at 298 K.

Determine the reaction quotient, Q, using the non-equilibrium concentrations below and determine the direction in which the reaction will proceed to reach equilibrium.

$[CO(g)] = 2.00\,mol\,dm^{-3}$

$[H_2O(g)] = 2.00\,mol\,dm^{-3}$

$[CO_2(g)] = 4.00\,mol\,dm^{-3}$

$[H_2(g)] = 4.00\,mol\,dm^{-3}$

Reactivity 2.3.6 – Quantifying the composition of equilibrium

Reactivity 2.3.6 – The equilibrium law is the basis for quantifying the composition of an equilibrium mixture.	
Solve problems involving values of K and initial and equilibrium concentrations of the components of an equilibrium mixture.	
When K is very small, the approximation $[reactant]_{initial} \approx [reactant]_{eqm}$ should be understood. The use of quadratic equations is not expected. Only homogeneous equilibria will be assessed.	Reactivity 3.1 – How does the equilibrium law help us to determine the pH of a weak acid, weak base or a buffer solution?

The equilibrium law can be used to solve problems involving *K* and initial and equilibrium concentrations

So far we have learnt how to derive the equilibrium constant *K* from the equation for a reaction and have considered in qualitative terms what its value tells us about the composition of an equilibrium mixture. We will now take this further by quantifying these values.

There are two processes involved here, which we will consider in turn:

- calculation of the equilibrium constant, *K*
- calculation of the concentrations of reactants and products present at equilibrium.

As we will see, the equilibrium constant expression is the key to all these calculations.

In the examples here, we will consider only **homogeneous equilibria**, that is, those where reactants and products are all in the same phase, as gases or as solutions.

TOK

The study of systems at equilibrium uses mathematics. Does this indicate that the systems are inherently mathematical, or have we constructed the mathematics to fit the system?

Calculating the equilibrium constant from initial and equilibrium concentrations

If we know the equilibrium concentrations of all reactants and products in a reaction, we can simply substitute these into the equilibrium expression to calculate *K* as we did earlier in the chapter. The first step in such a calculation is always to write the equilibrium expression from the chemical equation.

Worked example

Hydrogen can be prepared by the combination of carbon monoxide and water at 500 °C. At equilibrium, the concentrations in the reaction mixture were found to be:

CO	$0.150\,\text{mol dm}^{-3}$	H_2	$0.200\,\text{mol dm}^{-3}$
H_2O	$0.0145\,\text{mol dm}^{-3}$	CO_2	$0.0200\,\text{mo dm}^{-3}$

Calculate the equilibrium constant for the reaction at this temperature.

Solution

First write the equation for the reaction, making sure it is correctly balanced:

$$CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g)$$

Next write the equilibrium expression:

$$K = \frac{[H_2][CO_2]}{[CO][H_2O]}$$

Now substitute the given values for each component:

$$K = \frac{(0.200)(0.0200)}{(0.150)(0.0145)} = 1.84$$

Remember to check that the precision of your answer is consistent with the data given in the question – the answer here must be given to three significant figures.

More commonly, we may first have to work out the value for the equilibrium concentration for one or more reactants or products from data on initial concentrations and equilibrium concentrations of other components. The important thing here is to be sure that only *equilibrium* concentrations are substituted into the equilibrium expression.

The steps given below will help you to do this. These steps will be a useful guide through many calculations in this chapter and the work on acids and bases that follows.

1. Write the balanced equation.
2. Under the equation, write in the values of the concentrations of each component using three rows: *initial*, *change* and *equilibrium*.
   - *Initial* represents the concentration originally placed in the flask; unless stated otherwise, we assume the initial product concentration is zero.
   - *Change* represents the amount that reacts to reach equilibrium. A minus sign for reactants represents a decrease in concentration as they are used up, and a plus sign for products represents an increase in concentration as they form. The changes that occur must be in the same ratio as the coefficients in the balanced equation, so if we know one of the change values, we can deduce the others.
   - *Equilibrium* represents the concentration present in the equilibrium mixture. This can be calculated by applying the amount of change to the initial concentration for each component.

     equilibrium concentration = initial concentration ± change in concentration
3. Write the expression for K from the balanced equation. Substitute the values for equilibrium concentration and calculate K.

Worked example

A student placed 0.20 mol of $PCl_3(g)$ and 0.10 mol of $Cl_2(g)$ into a 1 dm^3 flask at 350 °C. The reaction, which produced PCl_5, was allowed to come to equilibrium, at which time it was found that the flask contained 0.12 mol of PCl_3. What is the value of K for this reaction?

Solution

Step 1 Write the balanced equation for the reaction.

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

Step 2 Insert the data under the equation in the three rows for initial, change and equilibrium. In this example, the numbers in black are data that were given in the question and numbers in blue have been derived as explained below.

	$PCl_3(g)$	+	$Cl_2(g)$	$\rightleftharpoons$	$PCl_5(g)$
initial (mol dm^{-3})	0.20		0.10		0.00
change (mol dm^{-3})	–0.08		–0.08		+0.08
equilibrium (mol dm^{-3})	0.12		0.02		0.08

The change in concentration of PCl_3, the amount that reacted to reach equilibrium, is 0.20 – 0.12 = 0.08. It is given a minus sign to show that the concentration decreases by this amount. As PCl_3 and Cl_2 react in a 1:1 ratio and form a 1:1 ratio of PCl_5, the same change in concentration must apply to Cl_2 and PCl_5. The equilibrium concentrations are calculated by applying the change amount to the initial values.

Step 3 $K = \frac{[PCl_5]}{[PCl_3][Cl_2]} = \frac{0.08}{0.12 \times 0.02} = 33$

The example above involved a 1 dm^3 reaction volume, so we could use the given amounts in mol directly as concentration in mol dm^{-3}. Sometimes though, we will need to calculate concentrations from given amounts and volumes. For example, if the data were given for a 3 dm^3 volume, we would need to divide the amounts in mol by 3 to express this as mol dm^{-3}. The volume must also be taken into account in this way when the reaction involves a change in the number of molecules of gas.

Worked example

The oxidation of NO to form NO_2 occurs during the formation of smog. When 0.60 mol of NO was reacted with 0.60 mol of O_2 in a 2 dm^3 container at 500 °C, the equilibrium mixture was found to contain 0.20 mol of NO_2. Calculate the equilibrium constant for the reaction at this temperature.

Solution

Step 1 Write the equation: $2NO + O_2 \rightleftharpoons 2NO_2$

Step 2 Insert the data from the question under the equation. Note that because the volume is 2 dm^3, the amounts must be divided by 2 to give concentration as mol dm^{-3}. As before, derived data are shown in blue, with explanations for these below.

	$2NO$	+	O_2	$\rightleftharpoons$	$2NO_2$
initial (mol dm^{-3})	0.30		0.30		0.00
change (mol dm^{-3})	–0.10		–0.05		+0.10
equilibrium (mol dm^{-3})	0.20		0.25		0.10

The change in concentration of NO_2, the amount that had formed at equilibrium, is +0.10. From the stoichiometry of the reaction, for every 2 moles of NO_2 that form, 2 moles of NO and 1 mole of O_2 are used. Therefore, we can deduce the corresponding changes in concentration for NO and O_2 and use these values to calculate the equilibrium concentrations of all components.

Step 3 $K = \frac{[NO_2]^2}{[NO]^2[O_2]} = \frac{(0.10)^2}{(0.20)^2 \times 0.25} = 1.0$



Aerial view over Los Angeles showing a thick smog. The formation of smog involves several chemical equilibria including those involving nitrogen and sulfur oxides.

Do not miss out the step showing the equilibrium constant expression. It will help to ensure you substitute the values correctly, and even if you make a mistake with the numbers, you can still get credit for this part of your answer.

Calculating equilibrium concentrations from the equilibrium constant

If we know the value of K and the equilibrium concentrations of all but one of the components, we can calculate the remaining equilibrium concentration simply by substituting the values into the equilibrium expression.

Worked example

The reaction:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

has $K = 0.500$ at 350 K. If the concentrations at equilibrium are:

CO $0.200\,mol\,dm^{-3}$

H_2 $0.155\,mol\,dm^{-3}$

what is the equilibrium concentration of CH_3OH?

Solution

Write the equilibrium expression:

$$K = \frac{[CH_3OH]}{[CO][H_2]^2}$$

Substitute the data from the question and solve the equation to give the unknown concentration.

$$0.500 = \frac{[CH_3OH]}{(0.200)(0.155)^2}$$

Therefore $[CH_3OH] = 0.00240\,mol\,dm^{-3}$ or $2.40 \times 10^{-3}\,mol\,dm^{-3}$

A more complex situation arises when we need to calculate equilibrium concentrations given K and initial concentrations. Here we use algebra to deduce the concentrations that have reacted to reach equilibrium and so calculate the equilibrium concentrations. The process developed in the previous section will also help to set the data out clearly here.

Worked example

The equilibrium constant K for the reaction

$$SO_3(g) + NO(g) \rightleftharpoons NO_2(g) + SO_2(g)$$

was found to be 6.78 at a specified temperature. If the initial concentrations of NO and SO_3 were both $0.0300\,mol\,dm^{-3}$, what would be the equilibrium concentration of each component?

Solution

To calculate the equilibrium concentrations of the reactants and products, we need to know how much has reacted, in other words the change in concentration:

let the change in concentration of NO = $-x$

therefore change in concentration of SO_3 = $-x$

and change in concentration of both NO_2 and SO_2 = $+x$ (due to the 1:1 stoichiometry)

Insert the relevant data from the question under the equation:

	$SO_3(g)$	+ $NO(g) \rightleftharpoons$	$NO_2(g)$	+ $SO_2(g)$
initial ($mol\,dm^{-3}$)	0.0300	0.0300	0.00	0.00
change ($mol\,dm^{-3}$)	$-x$	$-x$	$+x$	$+x$
equilibrium ($mol\,dm^{-3}$)	$0.0300 - x$	$0.0300 - x$	x	x

Write the equilibrium expression and substitute the equilibrium concentrations.

$$K = \frac{[NO_2][SO_2]}{[SO_3][NO]} = \frac{x^2}{(0.300 - x)^2} = 6.78$$

This can be solved by taking the square root of both sides of the equation and collecting the terms in x.

$$\frac{x}{0.0300 - x} = \sqrt{6.78} = 2.60$$

$$x(1 + 2.60) = 2.60 \times 0.0300 = 0.0780$$

$$x = \frac{0.0780}{3.60} = 0.0217$$

The equilibrium concentration of each component can now be calculated using the value for x.

$[SO_3] = 0.0300 - 0.0217 = 0.00830\,mol\,dm^{-3}$

$[NO] = 0.0300 - 0.0217 = 0.0083\,mol\,dm^{-3}$

$[NO_2] = 0.0217\,mol\,dm^{-3}$

$[SO_2] = 0.0217\,mol\,dm^{-3}$

Note that the number of significant figures given in the calculated values reflects those in the data provided in the question. In this case, 3.

Always look for a way to simplify calculations of this type, for example, by taking the square root of both sides of the equation. If you think you need to use the quadratic equation to solve equilibria calculations at this level, you have almost certainly made a mistake or have missed a simplifying step – so go back and look again.

Do not make the mistake of stopping when you have calculated x. The question asks for the equilibrium concentrations so you must substitute the value for x in the expressions you derived for the equilibrium concentrations to give the final answer.

Calculating equilibrium concentrations when *K* is very small

In some reactions, the value of K is very small, less than 10^{-3}. As we learnt in Reactivity 2.3, this represents a reaction in which the forward reaction has hardly proceeded and the equilibrium mixture consists almost entirely of reactants. In other words, the change in reactant concentrations is close to zero, as the equilibrium concentrations of the reactants are approximately equal to their initial concentrations:

$$[\text{reactant}]_{\text{initial}} \approx [\text{reactant}]_{\text{equilibrium}}$$

This situation is common in the study of weak acids and bases as they dissociate only slightly in solution to form small amounts of $H^+(aq)$ and $OH^-(aq)$ ions respectively. Determining values for $[H^+]$ and $[OH^-]$ using the approximation above allows us to calculate pH and pOH values for a weak acid, weak base or a buffer solution as discussed in Reactivity 3.1.

TOK

We often make assumptions in scientific calculations to simplify the mathematics. What kind of justification is required to do so?

Reactivity 3.1 – How does the equilibrium law help us to determine the pH of a weak acid, weak base or a buffer solution?

Worked example

The thermal decomposition of water has a very small value of K. At 1000 °C, $K = 7.3 \times 10^{-18}$ for the reaction

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$$

A reaction is set up at this temperature with an initial H_2O concentration of 0.10 mol dm^{-3}. Calculate the H_2 concentration at equilibrium.

When using approximations of this type given a very small value of K, be sure to note in your answer where you are making the approximation and why it is justified.

Solution

We need to know the change in concentration of H_2, so we could assign this as x. But from the stoichiometry of the reaction, this would make the change in $[O_2] = \frac{1}{2}x$. So it will make the calculation easier if we proceed as follows:

Let change in concentration of $H_2 = 2x$

Therefore change in concentration of $O_2 = x$

So change in concentration of $H_2O = -2x$ (due to the 2:2:1 stoichiometry)

Insert the relevant data from the question under the equation.

	$2H_2O(g)$	$\rightleftharpoons$	$2H_2(g)$	+	$O_2(g)$
initial (mol dm^{-3})	0.10		0.00		0.00
change (mol dm^{-3})	$-2x$		$+2x$		$+x$
equilibrium (mol dm^{-3})	$0.10 - 2x \approx 0.10$		$2x$		x

The approximation $[H_2O]_{initial} \approx [H_2O]_{equilibrium}$ follows from the very small value of K.

The approximation made in this calculation that $[\text{reactant}]_{initial} \approx [\text{reactant}]_{equilibrium}$ assumes that the value of x is extremely small, so that subtracting x (or in this case $2x$) from the initial concentration will not make a difference to the result within the precision used. You can check this assumption against your answer: subtracting 5.3×10^{-7} from 0.10 will still give 0.10 when rounded to this precision. Note though that multiplying or dividing by x, however small its value, will make a significant difference to the answer, so the values of x on the numerator in the K expression must be retained through the calculation.

Write the equilibrium expression and substitute the equilibrium concentrations.

$$K = \frac{[H_2]^2[O_2]}{[H_2O]^2} = \frac{(2x)^2 x}{(0.10)^2} = 7.3 \times 10^{-18}$$

This can now be solved for x.

$$4x^3 = (7.3 \times 10^{-18}) \times (0.010) = 7.3 \times 10^{-20}$$

$$x = 2.632 \times 10^{-7}$$

As a rule of thumb, when $K < 10^{-3}$, approximations of this type are justified.

The equilibrium concentration of H_2 can now be calculated.

$[H_2]_{equilibrium} = 2x = 5.3 \times 10^{-7}$ mol dm^{-3}

Exercise

Q21. The dissociation of hydrogen iodide into its elements takes place in a 1.00 dm^3 container at 440 °C. When 1.00 mole of hydrogen iodide is used, it is found to have decreased to 0.78 moles at equilibrium.

(a) Calculate the equilibrium constant for this reaction at this temperature.

(b) Deduce whether the dissociation reaction is endothermic or exothermic, given that at 600 °C the value of K is 0.04.

Q22. The reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ is carried out in a closed container with initial concentrations of both reactants of 1.6 mol dm^{-3}. K for the reaction is 1.7×10^{-3}.

Calculate the concentration of NO(g) at equilibrium.

Q23. **(a)** The reaction $CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g)$ was studied at 550°C. When 4.0 moles of CO and 6.4 moles of H_2O were introduced into a 1 dm^3 vessel, the equilibrium mixture was found to contain 3.2 moles of both H_2 and CO_2.

Calculate the concentrations of CO and H_2O at equilibrium and the value of K.

(b) At the same temperature and pressure, a different experiment was found to have 4.0 moles of both CO and H_2O, and 3.0 moles of both H_2 and CO_2 present in the mixture after a period of reaction. Show mathematically that this mixture had not reached equilibrium, and in which direction it will react.

Reactivity 2.3.7 – Measuring the position of equilibrium

Reactivity 2.3.7 – The equilibrium constant and Gibbs energy change, ΔG, can both be used to measure the position of an equilibrium reaction.	
Calculations using the equation $\Delta G^{\ominus} = -RT \ln K$. The equation is given in the data booklet.	Reactivity 1.4 – How can Gibbs energy be used to explain which of the forward or backward reaction is favoured before reaching equilibrium?

Gibbs energy change can be used to measure the position of equilibrium

Different reactions have widely differing values of their equilibrium constant K, reflecting the range in the direction and extent of the chemical reaction. In some cases, such as the ionization of water, the reaction barely takes place, while other reactions, such as the combustion of methane, go almost to completion. What determines this fundamental difference between reactions?

To answer this, we will revisit some of the thermodynamic concepts we learnt in Reactivity 1.4. Remember that the Gibbs energy change, ΔG, is a measure of the work that is available from a system and can be calculated for a particular composition of reactants and products in a reaction mixture using $\Delta G = G_{products} - G_{reactants}$.
Its sign is used to predict the spontaneity of the reaction at this specific composition.

ΔG = negative ⇒ reaction proceeds in the forward direction

ΔG = positive ⇒ reaction proceeds in the backward direction

$\Delta G = 0$ ⇒ reaction is at equilibrium **($G_{products} = G_{reactants}$)**

Reactivity 1.4 – How can Gibbs energy be used to explain which of the forward or backward reaction is favoured before reaching equilibrium?

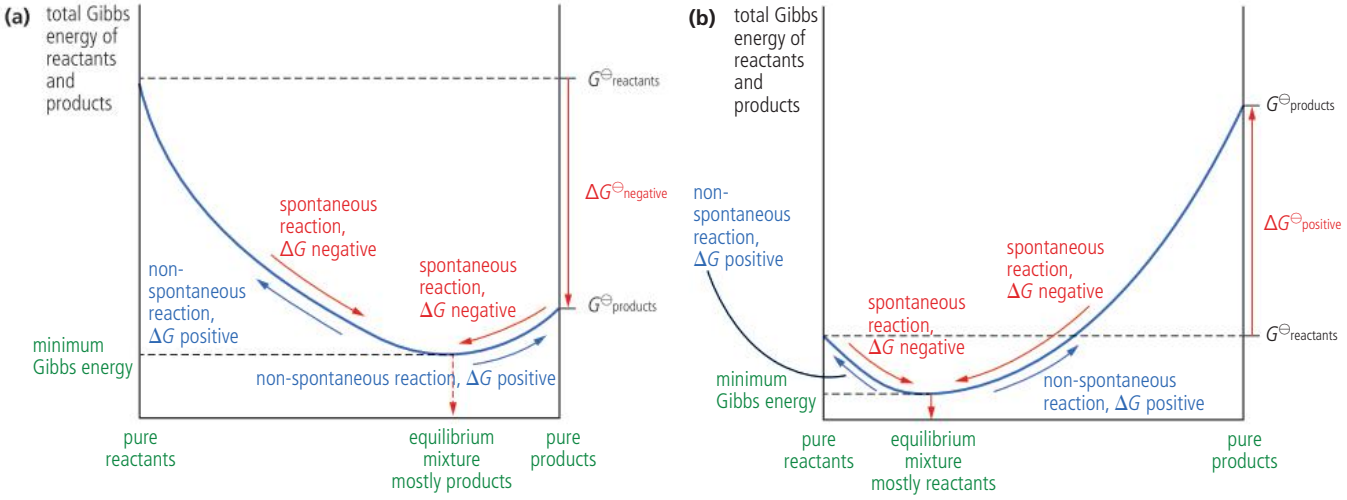
Note that Gibbs energy is also commonly referred to as 'Gibbs free energy' or simply 'free energy' in other sources.

Consider what happens to the total Gibbs energy during a reaction, such as when a fully charged battery is used until it is fully discharged (dead).

- At the start of the reaction, the total Gibbs energy of the reactants is greater than that of the products so a lot of work is available. ΔG is negative and the reaction proceeds in the forward direction.
- As the battery discharges, the reaction continues converting reactants to products. So the total Gibbs energy of the reactants decreases while the Gibbs energy of the products increases. ΔG becomes less negative and less work is available.
- The system reaches equilibrium when the total Gibbs energies of the reactants and products are equal and no work can be extracted from the system. The battery is dead.

As the reaction progresses, there is a decrease in the total Gibbs energy as work is done by the system. Figure 5 shows that this occurs whether the reaction starts with pure reactants or with pure products. Because the Gibbs energy decreases in both directions, the reaction must go through a composition that corresponds to the minimum value of Gibbs energy. This is the equilibrium state where the net reaction stops. The relative amounts of reactants and products at equilibrium, the composition of this equilibrium mixture, is determined by the difference in Gibbs energy between the reactants and products.

Equilibrium occurs when a reaction mixture is at the minimum value of Gibbs energy.



R2.3 Figure 5 The total Gibbs energy for different compositions of reaction mixtures **(a)** and **(b)**. Starting with either pure reactants or pure products, the Gibbs energy decreases as the reaction moves towards equilibrium. In **(a)** $G^{\ominus}_{reactants} > G^{\ominus}_{products}$ so $\Delta G^{\ominus}$ is negative for the reaction and it progresses forward towards equilibrium. The equilibrium mixture consists largely of products. In **(b)** $G^{\ominus}_{reactants} < G^{\ominus}_{products}$ so $\Delta G^{\ominus}$ is positive for the reaction and very little reaction occurs before equilibrium. The equilibrium mixture consists largely of reactants.

The position of equilibrium corresponds to a maximum value of entropy for the system.

The decrease in total Gibbs energy during the reaction appears as work done by the system or as an increase in entropy. Therefore, the system has the highest possible value of entropy when Gibbs energy is at a minimum – in other words, at equilibrium.

So $\Delta G^{\ominus}$ can be used to predict the spontaneity of a reaction and the position of equilibrium as follows:

- A reaction with a value of $\Delta G^{\ominus}$ that is both large and negative appears to occur spontaneously and has an equilibrium mixture with a high proportion of products.
- A reaction with a value of $\Delta G^{\ominus}$ that is large and positive appears to be non-spontaneous as only very small amounts of product form. It has an equilibrium mixture that is predominantly reactants.

K can be calculated from thermodynamic data

We have now identified two terms that relate to the position of equilibrium:

- K, the equilibrium constant
- $\Delta G^{\ominus}$, the change in standard Gibbs energy.

Clearly, these terms must be related to each other. The equation which shows this relationship is derived from the principles of thermodynamics.

$$\Delta G^{\ominus} = -RT \ln K$$

This equation is given in Section 1 of the data booklet. In this equation, $\Delta G^{\ominus}$ is the standard Gibbs energy change of the reaction; R is the gas constant ($8.31\,J\,K^{-1}\,mol^{-1}$), T is the absolute temperature, in kelvin, and $\ln K$ is the natural logarithm of the equilibrium constant, K.

From this equation, we can deduce relationships between $\Delta G^{\ominus}$ and K for a reaction. These are summarized below.

$\Delta G^{\ominus}$	$\ln K$	K	Equilibrium mixture
$\Delta G^{\ominus}$ negative	$\ln K$ positive	$K > 1$	mainly products
$\Delta G^{\ominus}$ positive	$\ln K$ negative	$K < 1$	mainly reactants
$\Delta G^{\ominus} = 0$	$\ln K = 0$	$K = 1$	appreciable amounts of both reactants and products

The equation can also be used to calculate the equilibrium constant from the standard Gibbs energy change of a reaction and vice versa. This can be useful in situations where the equilibrium constant is difficult to measure directly, for example, because a reaction may be too slow to reach equilibrium, or where the amounts of some of the components are too small to measure.

Worked example

The esterification reaction that produces ethyl ethanoate has a Gibbs energy change $\Delta G = -4.38\,kJ\,mol^{-1}$.

$$CH_3COOH(aq) + C_2H_5OH(aq) \rightleftharpoons CH_3COOC_2H_5(aq) + H_2O(aq)$$

Calculate the value of the equilibrium constant of this reaction at 298 K.

Solution

$$\Delta G^{\ominus} = -RT \ln K$$

$$\therefore -4.38 \times 1000\,J\,mol^{-1} = -(8.31\,J\,K^{-1}\,mol^{-1}) \times (298\,K) \times \ln K$$

$$\ln K = \frac{4380\,J\,mol^{-1}}{2478\,J\,mol^{-1}} = 1.77$$

$$\therefore K = e^{1.77} = 5.87$$

As the units for $\Delta G^{\ominus}$ are commonly given as $kJ\,mol^{-1}$ and the units for the gas constant are $J\,K^{-1}\,mol^{-1}$, we must convert

- *either* the gas constant to 0.00831 **kJ** $K^{-1}\,mol^{-1}$
- *or* the value of $\Delta G^{\ominus}$ to **J** mol^{-1}

so that we have consistent units for energy when using $\Delta G^{\ominus} = -RT \ln K$.

The equilibrium constant for a reaction is determined by the sign and value of its Gibbs energy change, $\Delta G^\ominus$, through the equation $\Delta G^\ominus = -RT \ln K$.

We have now answered the question about what determines the fact that different reactions have such different values of equilibrium constant. The answer is the value of $\Delta G^\ominus$. Remember from Reactivity 1.4 that this in turn depends on the values of enthalpy change ($\Delta H^\ominus$) and entropy change ($\Delta S^\ominus$) for the reaction.

Nature of Science

In essence, Le Châtelier's principle can be summarized as a system that is stressed when it is disturbed from its position of lowest Gibbs energy, responding by spontaneously relaxing back to this lowest energy state, the equilibrium position. The principle is sometimes used to describe negative feedback cycles, and links are made to other disciplines such as politics and economics. Although these applications may be useful in a general sense to enhance understanding, they must be subject to the checks and balances of the scientific process if they are to be claimed as scientifically valid. Without evidence that is testable and therefore falsifiable, these extensions of the principle have no scientific basis and might be considered as pseudoscience.



Rusting of iron is a slow reaction that proceeds in the forward direction. It has a high equilibrium constant but a small rate constant.

Rate of reaction and equilibrium

Rusting of iron is a complex process, but it can be represented by the equation:

$$4Fe(s) + 3O_2(g) \rightleftharpoons 2Fe_2O_3(s)$$

This is a heterogeneous equilibrium, so we will not derive the equilibrium expression here. We can, however, calculate the value of the equilibrium constant from $\Delta G^\ominus = 1490 \times 10^6$ J, using the equation $\Delta G^\ominus = -RT \ln K$. This gives a value of $K = 10^{261}$. This very large value indicates that this is a thermodynamically favourable reaction, which will proceed towards completion. Clearly $\Delta G^\ominus$ is large and negative. But we know that rusting is a slow process, which can take years to complete.

This is an example of the magnitude of the equilibrium constant giving no information on the rate of reaction. Nonetheless, a study of the relative values of the rate constants for the forward and backward steps can help to explain some aspects of equilibria and Le Châtelier's principle.

We will consider a reaction that we will assume occurs in a single step. In other words, the overall reaction is an elementary bimolecular reaction (see Reactivity 2.2).

$$A + B \rightleftharpoons C + D$$

In this case (and only in this case), we can write the rate laws for the forward and backward reactions from the stoichiometry of the reaction.

$$\text{rate of forward reaction} = k[A][B]$$

$$\text{rate of backward reaction} = k'[C][D]$$

where k = rate constant for the forward reaction and k' = rate constant for the backward reaction.

The equilibrium constant expression for this reaction is:

$$K = \frac{[C][D]}{[A][B]}$$

At equilibrium, the rate of the forward reaction = rate of backward reaction, so

$$k[A][B] = k'[C][D]$$

Rearranging this gives

$$\frac{k}{k'} = \frac{[C][D]}{[A][B]} \text{ or } \frac{k}{k'} = \frac{[C][D]}{[A][B]} \text{ or } K = \frac{k}{k'}$$

In other words, the equilibrium constant is the ratio of the rate constants of the forward and backward reactions. From this we can deduce the following:

- If $k \gg k' \Rightarrow K$ is large and the reaction progresses towards completion.
- If $k \ll k' \Rightarrow K$ is small and the reaction barely takes place.
- Increasing the concentration of reactants increases the rate of the forward reaction and so shifts the equilibrium to the right. Increasing the concentration of products increases the rate of the backward reaction and so shifts the equilibrium to the left. The value of the equilibrium constant stays constant because concentration changes do not affect the values of the rate constants.
- Adding a catalyst increases the values of k and k' by the same factor, so the ratio of their values, the equilibrium constant, is not affected.
- From the Arrhenius equation, $k = Ae^{\frac{-E_a}{RT}}$, the activation energy of the forward and backward reactions is different, and so they are differently affected by temperature. For an endothermic reaction, in which E_a(forward reaction) > E_a(backward reaction), the increase in temperature has a greater effect on increasing k than k', so K increases as temperature increases.

The position of equilibrium is determined by the relative values of the rate constants of the forward and backward reactions.

Nature of Science

Le Châtelier's principle enables qualitative predictions about changes to systems at equilibrium to be made, but we rely on thermodynamics for an explanation of these changes. Several seemingly different approaches can be used, but because they are applications of the same thermodynamic and kinetic concepts, they support the same conclusions. Quantitative measurements provide evidence for equilibrium theory and enable us to make calculations of related variables.

Exercise

Q24. Which of the following correctly describes the entropy and Gibbs energy of a system at equilibrium?

	Entropy S	Gibbs energy G
A	maximum value	maximum value
B	minimum value	maximum value
C	maximum value	minimum value
D	minimum value	minimum value

Q25. What is the sign of ΔG for a reaction when:

(a) $K = 1$

(b) $K > 1$

(c) $K < 1$

Q26. (a) The ionization of water has an equilibrium constant 1.00×10^{-14} at 298 K.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

Calculate ΔG for this reaction at this temperature.

(b) At 313 K the equilibrium constant has a value of 2.92×10^{-14}. What can you conclude about the enthalpy change, ΔH, of the reaction?

HL end

Guiding Question revisited

How can the extent of a reversible reaction be influenced?

In this chapter we have considered the following features of reversible reactions:

- A dynamic equilibrium is reached:
  - in a closed physical or chemical system;
  - when the rates of forward and backward reactions are equal and the concentrations of reactants and products remain constant.
- The equilibrium constant, *K*, can be determined from the stoichiometry of a reaction and the equilibrium concentrations of reactants and products.
- The magnitude of *K* indicates the extent of reaction at a given temperature.
- The equilibrium law:
  - states that every reaction will have a particular value of *K* at a given temperature;
  - can be used to quantify the composition of an equilibrium mixture.
- Le Châtelier's principle can be used to predict changes in equilibrium position when a system is subject to changes in concentration, pressure and temperature. It states that *a system at equilibrium when subjected to a change will respond in such a way as to minimize the effect of the change*. Therefore:
  - an increase in concentration of reactants will shift the equilibrium towards the products and vice versa; *K* remains unchanged;
  - an increase in pressure will shift the equilibrium towards the side of the reaction with the least gaseous molecules and vice versa; *K* remains unchanged;
  - an increase in temperature will shift the equilibrium in the endothermic direction and vice versa; *K* changes at different temperatures;
  - the use of a catalyst has no effect on the position of equilibrium as it increases the forward and backward rate by equal amounts; *K* remains unchanged.

HL

- The reaction quotient, *Q*, is calculated using non-equilibrium concentrations and can be used to predict the direction in which the reaction will proceed to reach equilibrium.
- The equilibrium constant and standard Gibbs energy change, $\Delta G^\ominus$, of a reaction can both be used to measure the position of equilibrium:
  - when $\Delta G^\ominus$ is negative, $K > 1$ and the equilibrium mixture will contain mostly products;
  - when $\Delta G^\ominus$ is positive, $K < 1$ and the equilibrium mixture will contain mostly reactants;
  - when $\Delta G^\ominus = 0$, $K = 1$ and the equilibrium mixture will contain appreciable amounts of both reactants and products.

- The relationship between $\Delta G^{\ominus}$ and K is summarized in the equation $\Delta G^{\ominus} = -RT \ln K$.

HL end

Practice questions

1. Which statement about chemical equilibria implies they are dynamic?

A The position of equilibrium constantly changes.

B The rates of forward and backward reactions change.

C The reactants and products continue to react.

D The concentrations of the reactants and products continue to change.

2. The reaction below represents the equilibrium established between gaseous and aqueous carbon dioxide in a carbonated soft drinks bottle.

$$CO_2(g) \rightleftharpoons CO_2(aq)$$

The bottle is opened for a short period of time allowing some $CO_2(g)$ to escape before the lid is placed back on. What is the effect of this change on the position of equilibrium and the concentration of $CO_2(aq)$?

	Position of equilibrium	$[CO_2(aq)]$
A	shifts to the left	decreases
B	shifts to the right	increases
C	shifts to the left	increases
D	shifts to the right	decreases

3. What is the effect of an increase of temperature on the yield and the equilibrium constant for the following reaction?

$$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(l) \quad \Delta H = -128 \text{ kJ mol}^{-1}$$

	Yield	Equilibrium constant
A	increases	increases
B	increases	decreases
C	decreases	increases
D	decreases	decreases

4. Consider the equilibrium between methanol, $CH_3OH(l)$, and methanol vapour, $CH_3OH(g)$.

$$CH_3OH(l) \rightleftharpoons CH_3OH(g)$$

What happens to the position of equilibrium and the value of K as the temperature decreases?

	Position of equilibrium	Value of K
A	shifts to the left	decreases
B	shifts to the left	increases
C	shifts to the right	decreases
D	shifts to the right	increases

5. An increase in temperature increases the amount of chlorine present in the following equilibrium.

$$PCl_5(s) \rightleftharpoons PCl_3(l) + Cl_2(g)$$

What is the best explanation for this?

A The higher temperature increases the rate of the forward reaction only.

B The higher temperature increases the rate of the reverse reaction only.

C The higher temperature increases the rate of both reactions but the forward reaction is affected more than the reverse.

D The higher temperature increases the rate of both reactions but the reverse reaction is affected more than the forward.

6. Consider the following reversible reaction.

$$Cr_2O_7^{2-}(aq) + H_2O(l) \rightleftharpoons 2CrO_4^{2-}(aq) + 2H^+(aq)$$

What will happen to the position of equilibrium and the value of *K* when more H^+ ions are added at constant temperature?

	Position of equilibrium	Value of *K*
A	shifts to the left	decreases
B	shifts to the right	increases
C	shifts to the right	does not change
D	shifts to the left	does not change

7. Consider this equilibrium reaction in a sealed container:

$$H_2O(g) \rightleftharpoons H_2O(l)$$

What will be the effect on the equilibrium of increasing the temperature from 20 °C to 30 °C?

A More of the water will be in the gaseous state at equilibrium.

B More of the water will be in the liquid state at equilibrium.

C At equilibrium the rate of condensation will be greater than the rate of evaporation.

D At equilibrium the rate of evaporation will be greater than the rate of condensation.

8. Which statement is correct for the equilibrium:

$$H_2O(l) \rightleftharpoons H_2O(g)$$

in a closed system at 100 °C?

A All the $H_2O(l)$ molecules have been converted to $H_2O(g)$.

B The rate of the forward reaction is greater than the rate of the reverse reaction.

C The rate of the forward reaction is less than the rate of the reverse reaction.

D The pressure remains constant.

9. **(a)** Consider the following equilibrium:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad \Delta H = -198\,kJ\,mol^{-1}$$

(i) Deduce the equilibrium constant expression, *K*, for the reaction. (1)

(ii) State and explain the effect of increasing the pressure on the yield of sulfur trioxide. (2)

(iii) State and explain the effect of increasing the temperature on the yield of sulfur trioxide. (2)

(iv) State the effects of a catalyst on the forward and reverse reactions, on the position of equilibrium, and on the value of *K*. (3)

(b) HL When a mixture of 0.100 mol NO, 0.051 mol H_2, and 0.100 mol H_2O was placed in a 1.0 dm^3 flask at 300 K, the following equilibrium was established:

$$2NO(g) + 2H_2(g) \rightleftharpoons N_2(g) + 2H_2O(g)$$

At equilibrium, the concentration of NO was found to be 0.062 mol dm^{-3}. Determine the equilibrium constant, *K*, of the reaction at this temperature. (4)

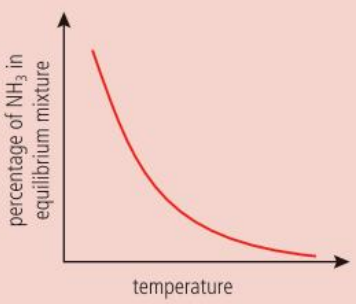
(Total 12 marks)

10. The Haber process enables the large-scale production of ammonia needed to make fertilizers.

The equation for the Haber process is given below.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

The percentage of ammonia in the equilibrium mixture varies with temperature.



(a) Use the graph to deduce whether the forward reaction is exothermic or endothermic and explain your choice. (2)

(b) State and explain the effect of increasing the pressure on the yield of ammonia. (2)

(c) Deduce the equilibrium constant expression, *K*, for the reaction. (1)

(d) HL A mixture of 1.00 mol N_2 and 3.00 mol H_2 was placed in a 1.0 dm^3 flask at 400 °C. When the system was allowed to reach equilibrium, the concentration of NH_3 was found to be 0.062 mol dm^{-3}. Determine the equilibrium constant, *K*, of the reaction at this temperature. (3)

(e) HL Iron is used as a catalyst in the Haber process. State the effect of a catalyst on the value of *K*. (1)

(Total 9 marks)

11. An example of a homogeneous reversible reaction is the reaction between hydrogen and iodine.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

(a) Outline the characteristics of a homogeneous chemical system that is in a state of equilibrium. (2)

(b) Deduce the expression for the equilibrium constant, *K*. (1)

(c) Predict what would happen to the position of equilibrium if the pressure was increased from 1 atm to 2 atm. (1)

(d) The value of *K* at 500 K is 160 and the value of *K* at 700 K is 54. Deduce what this information tells us about the enthalpy change of the forward reaction. (1)

(e) Determine the value of the equilibrium constant, K', for the reverse reaction at 500 K. (1)

(f) HL At a temperature just above 700 K it is found that when 1.60 mol of hydrogen and 1.00 mol of iodine are allowed to reach equilibrium in a 4.00 dm^3 flask, the amount of hydrogen iodide formed in the equilibrium mixture is 1.80 mol. Determine the value of the equilibrium constant at this temperature. (4)

(g) The reaction can be catalyzed by adding platinum metal. State and explain what effect the addition of platinum would have on the value of the equilibrium constant. (2)

(Total 12 marks)

HL

12. 0.50 mol of $I_2(g)$ and 0.50 mol of $Br_2(g)$ are placed in a closed flask. The following equilibrium is established.

$$I_2(g) + Br_2(g) \rightleftharpoons 2IBr(g)$$

The equilibrium mixture contains 0.80 mol of IBr(g). What is the value of *K*?

A 0.64

B 1.3

C 2.6

D 64

13. Consider the following equilibrium reaction.

$$Cl_2(g) + SO_2(g) \rightleftharpoons SO_2Cl_2(g)$$

$\Delta H = -84.5\,kJ\,mol^{-1}$

In a 1.00 dm^3 closed container, at 375 °C, 8.60×10^{-3} mol of SO_2 and 8.60×10^{-3} mol of Cl_2 were introduced. At equilibrium, 7.65×10^{-4} mol of SO_2Cl_2 was formed.

(a) Deduce the equilibrium constant expression, K, for the reaction. (1)

(b) Determine the value of the equilibrium constant, K. (3)

(c) If the temperature of the reaction is changed to 300 °C, predict, stating a reason in each case, whether the equilibrium concentration of SO_2Cl_2 and the value of K will increase or decrease. (3)

(d) If the volume of the container is changed to 1.50 dm^3, predict, stating a reason in each case, how this will affect the equilibrium concentration of SO_2Cl_2 and the value of K. (3)

(e) Suggest, stating a reason, how the addition of a catalyst at constant pressure and temperature will affect the equilibrium concentration of SO_2Cl_2. (2)

(Total 12 marks)

14. **(a)** Calculate the value of $\Delta G^\ominus$ for a reaction in which $K = 1$. (1)

(b) Nitrogen oxide, NO, is oxidized in the air to NO_2.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

At 298 K, the value of K for this reaction is 1.7×10^{12}. Calculate the value of $\Delta G^\ominus$ for the reaction in kJ mol^{-1} and comment on the position of equilibrium at this temperature. (3)

(Total 4 marks)

15. The equilibrium constant K for the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

is 1.7×10^2 at 500 K.

Determine whether the reaction mixture is at equilibrium when the concentrations of the components at this temperature are as follows:

$[N_2] = 0.500$

$[H_2] = 0.400$

$[NH_3] = 3.00$.

If it is not at equilibrium, state and explain in which direction the reaction will proceed. (3)

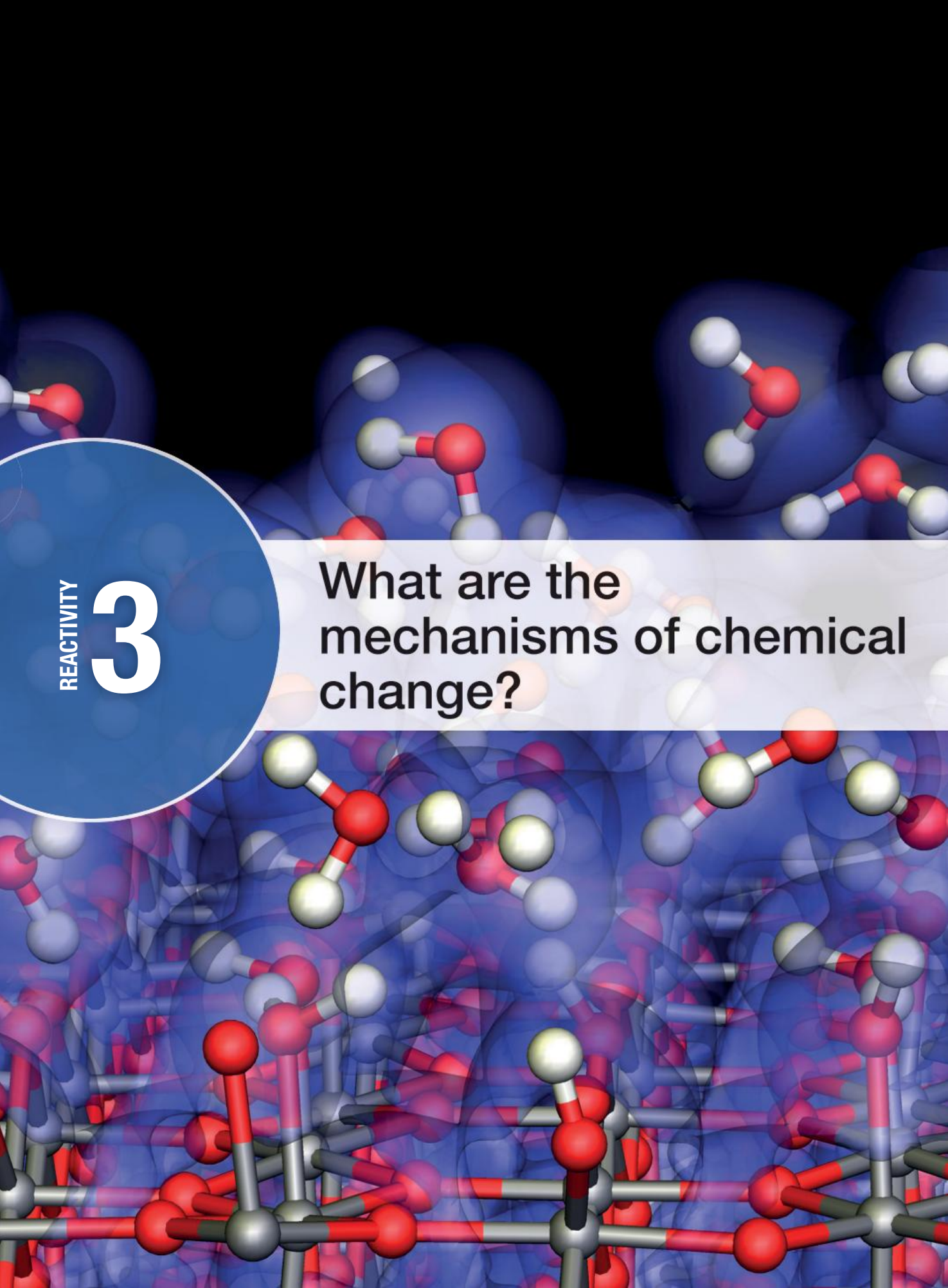
(Total 3 marks)

HL end

REACTIVITY

3

What are the mechanisms of chemical change?





A water-titanium dioxide model produced from molecular dynamics calculations which simulated proton transfer for water. The structure and charge density of H_2O molecules are shown across the centre, and the TiO_2 surface is shown across the bottom. The atoms are colour-coded: hydrogen (white), oxygen (red) and titanium (grey). The charge density (electron cloud) is purple. TiO_2 is a widely used catalyst in solar cells and fuel cells. Understanding the mechanism of its reaction with H_2O is key to further development of its role in photocatalytic mechanisms.

Reaction mechanisms refer to how chemical reactions proceed at the molecular level. Many reactions involve more than one step, and in these cases the mechanism is shown as a sequence where the product of one step is the reactant for the next.

Although there are many ways in which reaction mechanisms can be classified, there are only four fundamental types of reaction based on the behaviour of subatomic particles.

- Proton transfer reactions include the range of acid–base reactions and neutralization.
- Electron transfer reactions include all oxidation–reduction processes.
- Electron-sharing reactions include reactions between radicals.
- Electron-pair-sharing reactions include the reactions of electrophiles and nucleophiles, which are also characterized as Lewis acid–base reactions.

We will consider each of these types of reaction in turn in this Topic. As you study these examples, try to keep in mind the fundamental processes occurring at the molecular level. It is the particulate nature of the structure of the reactants that determines the reaction mechanisms.

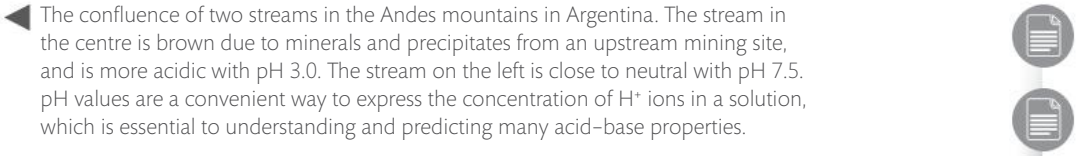
Given the infinite number of different chemical reactions, it is helpful to realize that they can be categorized in this relatively simple way based on the transfer or sharing of subatomic particles between reactants.



REACTIVITY

3.1 Proton transfer reactions





The confluence of two streams in the Andes mountains in Argentina. The stream in the centre is brown due to minerals and precipitates from an upstream mining site, and is more acidic with pH 3.0. The stream on the left is close to neutral with pH 7.5. pH values are a convenient way to express the concentration of H^+ ions in a solution, which is essential to understanding and predicting many acid–base properties.

Guiding Question

What happens when protons are transferred?

Hydrogen atoms are the simplest atoms, containing just one proton and one electron. When they ionize by losing the electron and forming H^+, all that is left is the proton. H^+ is therefore equivalent to a proton, and we can use these two terms interchangeably.

When a proton is transferred in a reaction:

- the reactant loses H^+ so loses a positive charge
- the product gains H^+ and so gains a positive charge.

This type of reaction will therefore only be possible between certain species – reactants that can release H^+, and products that have a lone pair that can accommodate an additional H^+. This behaviour is known as Brønsted–Lowry acid–base behaviour.

In this chapter, we will identify species that can undergo proton transfer reactions, and learn how these reactions can be predicted and followed with reference to the pH and pOH scales. Different acids and bases share some common properties, but differ in their strength depending on their equilibria in aqueous solution. It is strongly recommended that you are familiar with the study of equilibria from Reactivity 2.3 before starting this chapter.

Acid–base chemistry is central to topics such as air and water pollution, how climate change affects the chemistry of the oceans, the action of drugs in the body, food science and many aspects of cutting-edge research.

Reactivity 3.1.1 and 3.1.2 – Brønsted–Lowry acids and bases

Reactivity 3.1.1 – A Brønsted–Lowry acid is a proton donor and a Brønsted–Lowry base is a proton acceptor. Deduce the Brønsted–Lowry acid and base in a reaction.	
A proton in aqueous solution can be represented as both $H^+(aq)$ and $H_3O^+(aq)$. The distinction between the terms 'base' and 'alkali' should be understood.	Nature of Science, Reactivity 3.4 – Why has the definition of acid evolved over time?

Reactivity 3.1.2 – A pair of species differing by a single proton is called a conjugate acid–base pair. Deduce the formula of the conjugate acid or base of any Brønsted–Lowry base or acid.	
	Structure 2.1 – What are the conjugate acids of the polyatomic anions listed in Structure 2.1?

Brønsted–Lowry theory describes acids and bases in terms of proton transfer

Early theories to define acids and bases

The French chemist Lavoisier proposed in 1777 that oxygen was the 'universal acidifying principle'. He believed that an acid could be defined as a compound of oxygen and a non-metal. In fact, the name he gave to the newly discovered gas *oxygen* means 'acid-former'. This theory, however, had to be dismissed when the acid HCl was proven to be made of hydrogen and chlorine only – no oxygen. To hold true, of course, any definition of an acid has to be valid for *all* acids.

A big step forward came in 1887 when the Swedish chemist Arrhenius suggested that an acid could be defined as a substance that dissociates in water to form hydrogen ions (H^+) and anions, while a base dissociates into hydroxide (OH^-) ions and cations. He also recognized that the hydrogen and hydroxide ions could form water, and the cations and anions could form a salt. In a sense, Arrhenius was very close to the theory that is widely used to explain acid and base properties today, but his focus was only on aqueous systems. A broader theory was needed to account for reactions occurring without water, and especially for the fact that some insoluble substances show base properties.

Svante August Arrhenius (1859–1927) wrote up his ideas on acids dissociating into ions in water as part of his doctoral thesis while he was a student at Stockholm University. But his theory was not well received and he was awarded the lowest possible class of degree. Later, his work gradually gained recognition and he received one of the earliest Nobel Prizes in Chemistry in 1903.

Arrhenius may be less well known as the first person documented to predict the possibility of global warming as a result of human activity. In 1896, aware of the rising levels of CO_2 caused by increased industrialization, he calculated the likely effect of this on the temperature of the Earth. Today, over 100 years later, the significance of this relationship between increasing CO_2 and global temperatures is recognized as a major threat to ecosystems and life on Earth.

Nature of Science

The evolution of theories to explain acid–base chemistry and develop general principles is a fascinating tale of the scientific process in action. Some theories have arisen and been disproved, such as Lavoisier's early definition of an acid as a compound containing oxygen. Falsification of an idea is an essential aspect of the scientific process. Other theories have proved to be too limited in application, such as Arrhenius' theory which could not be generalized beyond aqueous solutions.

On the other hand, the Brønsted–Lowry theory, alongside an alternative broader theory known as Lewis theory that is described in Reactivity 3.4, has stood the test of time and experimentation. This indicates that it has led to testable predictions which have supported the theory, and enabled wide ranging applications to be made.

Nature of Science, Reactivity 3.4 – Why has the definition of acid evolved over time?

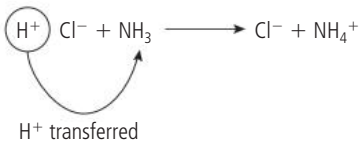
Brønsted–Lowry theory developed from independent work by two chemists

In 1923 two chemists, Martin Lowry of Cambridge, England, and Johannes Brønsted of Copenhagen, Denmark, working independently, published similar conclusions regarding the definitions of acids and bases. Their findings overcame the limitations of Arrhenius' work and have become established as the **Brønsted–Lowry theory**.

This theory focuses on the transfer of H^+ ions during an acid–base reaction: acids donate H^+, while bases accept H^+. For example, in the reaction between hydrogen chloride, HCl, and ammonia, NH_3, to form ammonium chloride, NH_4Cl, we can see that HCl transfers H^+ to NH_3.

$$HCl + NH_3 \rightleftharpoons NH_4^+ + Cl^-$$

NH_4Cl is an ionic compound containing NH_4^+ and Cl^- ions.



HCl acts as an acid and donates H^+, NH_3 acts as a base and accepts H^+.



Reaction between vapours of HCl and NH_3 forming the white smoke of ammonium chloride NH_4Cl.
$HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$

Challenge yourself

1. From physical properties that you observe in the photo, what might be another way of classifying this reaction?

As we learned on page 671, H^+ is a proton and the two terms can be used interchangeably.

Therefore the Brønsted–Lowry theory can be stated as:

- a Brønsted–Lowry acid is a proton (H^+) donor
- a Brønsted–Lowry base is a proton (H^+) acceptor.

Nature of Science

Brønsted and Lowry's work on acid–base theory is a good example of what is sometimes referred to as 'multiple independent discovery'. This refers to cases where similar discoveries are made by scientists at almost the same time, even though they have worked independently from each other. Examples include the independent discovery of calculus by Newton and Leibniz, the formulation of the mechanism for biological evolution by Darwin and Wallace, and derivation of the pressure–volume relationships of gases by Boyle and Mariotte. Nobel Prizes in Chemistry are commonly awarded to more than one person working in the same field, who may have made the same discovery independently. Multiple independent discoveries are likely increasing as a result of communication technology, which enables scientists who may be widely separated geographically to have access to a common body of knowledge as the basis for their research.

When a discovery is made by more than one scientist at about the same time, ethical questions can arise, such as whether the credit belongs to one individual or should be shared, and whether there are issues regarding intellectual property and patent rights. Historically, these issues have been settled in very different ways in different cases. Nonetheless, the peer review process in science aims to ensure that credit is correctly awarded to the scientist or scientists responsible for a discovery, and that published work represents a new contribution to work in that field.

Does competition between scientists help or hinder the production of knowledge?

TOK

Worked example

Deduce the Brønsted–Lowry acid and base in the following reactions. Consider only the forward reactions here.

1. $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
2. $H_2PO_4^-(aq) + HCO_3^-(aq) + \rightleftharpoons HPO_4^{2-}(aq) + H_2CO_3(aq)$

Solution

1. $NH_3(aq)$ accepts H^+ to become $NH_4^+(aq)$ ∴ $NH_3(aq)$ is the Brønsted–Lowry base.

   $H_2O(l)$ donates H^+ to become $OH^-(aq)$ ∴ $NH_3(aq)$ is the Brønsted–Lowry acid.

2. $H_2PO_4^-(aq)$ donates H^+ to become $HPO_4^{2-}(aq)$ ∴ $H_2PO_4^-(aq)$ is the Brønsted–Lowry acid.

   $HCO_3^-(aq)$ accepts H^+ to become $H_2CO_3(aq)$ ∴ $HCO_3^-(aq)$ is the Brønsted–Lowry base.

A Brønsted–Lowry acid is a proton (H^+) donor. A Brønsted–Lowry base is a proton (H^+) acceptor.

Reacting species in Brønsted–Lowry acid–base reactions form conjugate pairs

Conjugate acid–base pairs differ by one proton

The act of donating cannot happen in isolation – there must always be something present to play the role of acceptor. In Brønsted–Lowry theory, an acid can therefore only behave as a proton donor if there is also a base present to accept the proton.

Consider the acid–base reaction between a generic acid HA and base B:

$$HA + B \rightleftharpoons A^- + BH^+$$

We can see that HA acts as an acid, donating a proton to B while B acts as a base, accepting the proton from HA. But if we look also at the reverse reaction, we can pick out another acid–base reaction: here, BH^+ is acting as an acid, donating its proton to A^- while A^- acts as a base accepting the proton from BH^+. In other words, acid HA has reacted to form the base A^-, while base B has reacted to form acid BH^+.

conjugate acid–base pair

$$HA + B \rightleftharpoons A^- + BH^+$$

conjugate acid–base pair

Acids react to form bases and vice versa. The acid–base pairs related to each other in this way are called **conjugate acid–base pairs**, and you can see that they *differ by just one proton*. It is important to be able to recognize these pairs in a Brønsted–Lowry acid–base reaction.

One example of a conjugate pair is H_2O and H_3O^+, which is found in all acid–base reactions in aqueous solution. The reaction:

$$H_2O(l) + H^+(aq) \rightleftharpoons H_3O^+(aq)$$

occurs when a proton released from an acid readily associates with H_2O molecules, forming H_3O^+. In other words, protons become hydrated. H_3O^+ is variously called the hydroxonium ion, the oxonium ion, or the hydronium ion and is always the form of hydrogen ions in aqueous solution. However, for most reactions it is convenient simply to write it as $H^+(aq)$. Note that in this pair H_3O^+ is the conjugate acid and H_2O is its conjugate base.

Note that $H_3O^+(aq)$ and $H^+(aq)$ are both used to represent a proton in aqueous solution.

Lowry described the ready hydration of the proton as 'the extreme reluctance of the hydrogen nucleus to lead an isolated existence'.

Worked example

Label the conjugate acid–base pairs in the following reaction:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

Solution

CH_3COOH / CH_3COO^-
acid base
conjugate pair

H_2O / H_3O^+
base acid
conjugate pair

When writing the conjugate acid of a base, add one H^+. When writing the conjugate base of an acid, remove one H^+. Remember to adjust the charge by the 1^+ removed or added.

Deducing the formulas of conjugate acids and bases

In a conjugate pair the acid always has one proton more than its conjugate base, so this makes it easy to predict the formula of the corresponding conjugate for any given acid or base.

Worked example

1. Write the conjugate base for each of the following.
   (a) H_3O^+ **(b)** NH_3 **(c)** H_2CO_3
2. Write the conjugate acid for each of the following.
   (a) NO_2^- **(b)** OH^- **(c)** CO_3^{2-}

Solution

1. To form the base from these species, remove one H^+
   (a) H_2O **(b)** NH_2^- **(c)** HCO_3^-
2. To form the acid from these species, add one H^+
   (a) HNO_2 **(b)** H_2O **(c)** HCO_3^-

The acid and base in a conjugate acid–base pair differ by just one proton.

If we look at the polyatomic ions listed in Structure 2.1, we see that most of the ions can act as Brønsted–Lowry bases by accepting H^+ and forming Brønsted–Lowry acids.

Structure 2.1 – What are the conjugate acids of the polyatomic ions listed in Structure 2.1?

Polyatomic ion	Conjugate acid
hydroxide, OH^-	H_2O
nitrate, NO_3^-	HNO_3
hydrogencarbonate, HCO_3^-	H_2CO_3
carbonate, CO_3^{2-}	HCO_3^-
sulfate, SO_4^{2-}	HSO_4^-
phosphate, PO_4^{3-}	HPO_4^{2-}

Ammonium, NH_4^+, which is also a polyatomic ion listed in Structure 2.1, cannot accept H^+ to form a conjugate acid. It instead loses H^+, and so acts as a Brønsted–Lowry acid and forms its conjugate base, NH_3. Which of the polyatomic ions above can also function as a Brønsted–Lowry acid?

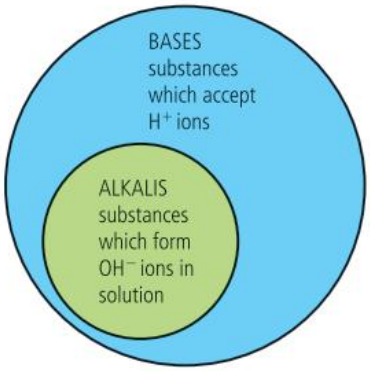
Brønsted–Lowry bases are defined as any species which can accept a proton. A smaller group, the **alkalis**, are soluble bases which dissolve in water to release the hydroxide ion, OH^-.

For example:

$$K_2O(s) + H_2O(l) \rightarrow 2K^+(aq) + 2OH^-(aq)$$

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

$$HCO_3^-(aq) \rightleftharpoons CO_2(g) + OH^-(aq)$$



The relationship between alkalis and bases.

Alkalis are bases that dissolve in water to form the hydroxide ion, OH^-.

Exercise

Q1. Deduce the formula of the conjugate acid of each of the following:

(a) SO_3^{2-} **(b)** CH_3NH_2 **(c)** $C_2H_5COO^-$

(d) NO_3^- **(e)** F^- **(f)** HSO_4^-

Q2. Deduce the formula of the conjugate base of each of the following:

(a) H_3PO_4 **(b)** CH_3COOH **(c)** H_2SO_3

(d) HSO_4^- **(e)** OH^- **(f)** HBr

Q3. For each of the following reactions, identify the Brønsted–Lowry acids and bases and the conjugate acid–base pairs:

(a) $CH_3COOH + NH_3 \rightleftharpoons NH_4^+ + CH_3COO^-$

(b) $CO_3^{2-} + H_3O^+ \rightleftharpoons H_2O + HCO_3^-$

(c) $NH_4^+ + NO_2^- \rightleftharpoons HNO_2 + NH_3$

Reactivity 3.1.3 – Amphiprotic species

Reactivity 3.1.3 – Some species can act as both Brønsted–Lowry acids and bases.	
Interpret and formulate equations to show acid–base reactions of these species.	
	Structure 3.1 – What is the periodic trend in the acid–base properties of metal and non-metal oxides? Structure 3.1 – Why does the release of oxides of nitrogen and sulfur into the atmosphere cause acid rain?

Some species can act as both Brønsted–Lowry acids and bases

You may be surprised to see water described in the answers to the Worked examples on page 676 as a base (Q1, part a), and as an acid (Q2, part b), as you are probably not used to thinking of water as an acid, or as a base, but rather as a neutral substance. The point is that Brønsted–Lowry theory describes acids and bases in terms of how they react together, so it all depends on what water is reacting with.

Consider the following:

$$\underset{\text{acid}}{CH_3COOH} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{base}}{CH_3COO^-} + \underset{\text{acid}}{H_3O^+}$$

$$\underset{\text{base}}{NH_3} + \underset{\text{acid}}{H_2O} \rightleftharpoons \underset{\text{acid}}{NH_4^+} + \underset{\text{base}}{OH^-}$$

So with CH_3COOH, water acts as a Brønsted–Lowry base, and with NH_3 it acts as a Brønsted–Lowry acid.

Notice that water is not the only species that can act as both an acid and as a base. For example, in the Worked example below, we can deduce similar behaviour with HCO_3^-.

Worked example

Write equations to show HCO_3^- acting **(a)** as a Brønsted–Lowry acid and **(b)** as a Brønsted–Lowry base.

Solution

(a) to act as an acid, it donates H^+

$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(l)$

(b) to act as a base, it accepts H^+

$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$

Amphoteros is a Greek word meaning 'both'. For example, *amphi*bians are adapted both to water and to land.

Substances that can act as both Brønsted–Lowry acids and bases in this way are said to be **amphiprotic**. What are the features that enable these species to have this 'double identity'?

- To act as a Brønsted–Lowry acid, they must be able to dissociate and release H^+.
- To act as a Brønsted–Lowry base, they must be able to accept H^+, which means they must have a lone pair of electrons.

An amphiprotic substance is one which can act as both a proton donor and a proton acceptor.

So substances that are amphiprotic according to Brønsted–Lowry theory must possess both a lone pair of electrons and hydrogen that can be released as H^+.

Challenge yourself

2. At ambient temperature, the polyatomic ion $OH^-(aq)$ may not be considered truly amphiprotic as its basic properties dominate – losing H^+ in solution is unlikely due to the instability of O^{2-} in water. However, when a metal hydroxide such as magnesium hydroxide is heated, it decomposes as follows:

$$Mg(OH)_2(s) \rightarrow MgO(s) + H_2O(g)$$

Derive the ionic form of this reaction to analyse how the hydroxide ion is showing amphiprotic behaviour here.

Nature of Science

Terminology in science has to be used appropriately according to the context. *Amphiprotic* specifically relates to Brønsted–Lowry acid–base theory, where the emphasis is on the transfer of a proton. The term *amphoteric*, on the other hand, has a broader meaning as it is used to describe a substance which can act as an acid and as a base, including reactions that do not involve the transfer of a proton. For example, as described in Structure 3.1, aluminium oxide is an amphoteric oxide because it reacts with both dilute acids and alkalis. We will see in Reactivity 3.4 that this acid–base behaviour is best described by a different theory, the Lewis theory. Note that all amphiprotic substances are also amphoteric, but the converse is not true. The fact that the two terms exist reflects the fact that different theories are used to describe acid–base reactions.

Structure 3.1 – What is the periodic trend in the acid–base properties of metal and non-metal oxides?

Structure 3.1 – Why does the release of oxides of nitrogen and sulfur into the atmosphere cause acid rain?

We can recognize trends in acidic and basic behaviour related to the periodic table. Moving left to right across a period, the oxides transition from basic metal oxides through **amphoteric** oxides which are able to react with both acids and bases, to acidic oxides. For example, in period 3:

Na_2O MgO	Al_2O_3	SiO_2 P_4O_{10} SO_2 Cl_2O
basic metal oxides	amphoteric oxide	acidic non-metal oxides

- The basic metal oxides react with an acid to form a salt and water.

  $Na_2O(s) + 2HCl(aq) \rightarrow 2NaOH(aq) + 2H_2O(l)$

- Al_2O_3 is amphoteric because it reacts both with an acid and with a base to form a salt and water.

  $Al_2O_3(s) + 3H_2SO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 3H_2O(l)$

  $Al_2O_3(s) + 3H_2O(l) + 2OH^-(aq) \rightarrow 2Al(OH)_4^-$

- The non-metal oxides form weak acids in solution.

  $SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3(aq)$

  $H_2SO_3(aq) \rightleftharpoons 2H^+(aq) + SO_3^{2-}(aq)$

Nitrogen and sulfur both form several different oxides, known as NO_x and SO_x, which are released from the burning of fossil fuels, especially coal and heavy oil. As we see above for SO_2, they react with moisture in the atmosphere to form weak acids such as sulfurous and nitrous acids. These weak acids can react further to form stronger acids, resulting in a complex mixture of pollutants in the atmosphere. For example:

$$2NO_2(g) + H_2O(l) \rightarrow HNO_2(aq) + HNO_3(aq)$$

This lowers the pH causing **acid rain,** defined as when the pH of precipitation has been lowered to less than 5.6. Acid rain is a major environmental problem, causing a negative impact on structural materials, lakes and rivers, and plant life, especially coniferous forests.



Test tubes containing normal rainwater (left) and acid rain (right) with universal indicator solution added to show acidity. The normal rainwater has a pH of above 5.6, while the acid rain has a lower pH; in this example it is pH 4.0.

TOK

How might developments in scientific knowledge trigger political controversies or controversies in other areas of knowledge?



Woodland devastated by the effects of acid rain in the Czech Republic, near the border with Germany. Emissions of oxides of sulfur and nitrogen from industry have caused this widespread death of trees. This is one of the most polluted parts of central Europe.

i

The Danish chemist Søren Peder Lauritz Sorensen (1868–1939) developed the pH concept in 1909, originally proposing that it be formulated as *p*H. He did not account for his choice of the letter 'p' though it has been suggested to originate from the German word *potenz* for power. It could equally well derive from the Latin, Danish, or French terms for the same word.

$pH = -\log_{10}[H^+]$
$[H^+] = 10^{-pH}$

Exercise

Q4. Show by means of equations how the anion in K_2HPO_4 is amphiprotic.

Q5. **(a)** Explain with an equation why normal rainwater is acidic because it dissolves CO_2 from the atmosphere.

(b) Formulate equations to show how sulfur dioxide released into the atmosphere can be oxidized to sulfur trioxide, which then dissolves in water to form sulfuric acid.

(c) Suggest why adding lime, calcium oxide, to stream water may help to reduce the effects of acid rain.

Q6. Suggest why the elimination of burning coal as a fuel is an important goal of many countries and international organizations.

Reactivity 3.1.4 – The pH scale

Reactivity 3.1.4 – The pH scale can be used to describe the $[H^+]$ of a solution: $pH = -\log_{10}[H^+]$; $[H^+] = 10^{-pH}$ Perform calculations involving the logarithmic relationship between pH and $[H^+]$.	
Include the estimation of pH using universal indicator, and the precise measurement of pH using a pH meter/probe. The equations for pH are given in the data booklet.	Tools 1, 2, 3 – What is the shape of a sketch graph of pH against $[H^+]$? Nature of Science, Tool 2 – When are digital sensors (e.g. pH probes) more suitable than analogue methods (e.g. pH paper/solution)?

pH is a logarithmic expression of $[H^+]$

Chemists realized a long time ago that it would be useful to have a quantitative scale of acid strength based on the concentration of hydrogen ions. As the majority of acids encountered are weak, the hydrogen ion concentration expressed directly as mol dm^{-3} produces numbers with large negative exponents. For example, the H^+ concentration in our blood is 4.6×10^{-8} mol dm^{-3}. Such numbers are not very user-friendly when it comes to describing and comparing acids. The introduction of the pH scale in 1909 by Sorensen led to wide acceptance owing to its ease of use. It is defined as follows:

$$pH = -\log_{10}[H^+]$$

In other words, pH is the negative number to which the base 10 is raised to give the $[H^+]$. This can also be expressed as:

$$[H^+] = 10^{-pH}$$

- A solution that has $[H^+] = 0.1$ mol $dm^{-3} \Rightarrow [H^+] = 10^{-1}$ mol $dm^{-3} \Rightarrow pH = 1$.
- A solution that has $[H^+] = 0.01$ mol $dm^{-3} \Rightarrow [H^+] = 10^{-2}$ mol $dm^{-3} \Rightarrow pH = 2$.

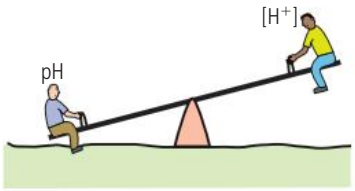
The pH scale has distinct features

pH numbers are usually positive and have no units

Although the pH scale is theoretically an infinite scale and can extend into negative numbers, most common acids and bases will have positive pH values and fall within the range pH 0–14. This corresponds to $[H^+]$ in the range 1.0 mol dm^{-3} to 10^{-14} mol dm^{-3}.

The pH number is inversely related to $[H^+]$

Solutions with a higher $[H^+]$ have a lower pH and vice versa. So stronger and more concentrated acids have a lower pH, while weaker and more dilute acids have a higher pH.



The inverse relationship between pH and H^+.

A change of one pH unit represents a 10-fold change in $[H^+]$

This means that increasing the pH by one unit represents a decrease in $[H^+]$ by 10 times; and decreasing by one pH unit represents an increase in $[H^+]$ by 10 times.

Worked example

If the pH of a solution is changed from 3 to 5, deduce how the hydrogen ion concentration changes.

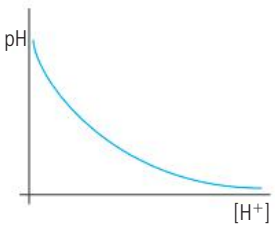
Solution

$pH = 3 \Rightarrow [H^+] = 10^{-3}$ mol dm^{-3} $\quad$ $pH = 5 \Rightarrow [H^+] = 10^{-5}$ mol dm^{-3}

So $[H^+]$ has changed by 10^{-2} or decreased by a factor of 100.

The inverse logarithmic relationship between pH and $[H^+]$ can be illustrated by following the change in pH as the $[H^+]$ of a solution is increased. We can observe the following:

- as $[H^+]$ in a solution increases, the pH value decreases
- for each increase of 10 times in $[H^+]$, the pH will decrease by 1 unit.



The inverse logarithmic relationship between pH and $[H^+]$.

Logarithmic scales are used in other disciplines where they can help in the presentation of data. In medicine, the logarithmic decay of levels of drugs in the blood against time is used. In seismic studies, the Richter scale is a logarithmic expression of the relative energy released during earthquakes. In sense perception, the decibel scale of sound intensity and the scale for measuring the visible brightness of stars (their magnitude) are also logarithmic scales.

Tools 1, 2, 3 – What is the shape of a sketch graph of pH against $[H^+]$?

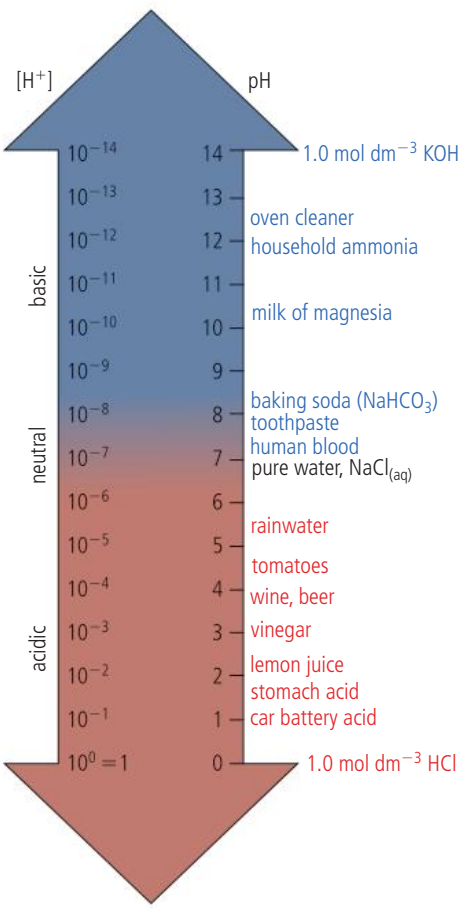
Note that a sketch graph shows labelled axes but without units. The graph shows the overall relationship between two variables but without plotted data points.

Nature of Science

The use of a logarithmic scale to represent data enables a wide range of values to be presented as a smaller range of simpler numbers. We see here that the pH scale takes a range of hydrogen ion concentrations from 10^{0} to 10^{-14} and effectively compresses it to a much smaller scale of numbers, 0–14. On page 78, we see that the use of a logarithmic scale to represent ionization energies similarly makes a wide range of data easier to interpret. In cases of exponential change, a log base scale shows the data as a straight line, so outliers where the change is greater or less than exponential can be easily identified.

But use of a logarithmic scale can also be misleading, as it can obscure the scale of change if not interpreted correctly. For example, a small change in pH represents a dramatic difference in the hydrogen ion concentration of a solution. Keep this in mind when you read reports of changes in pH, for example, of rainfall as a result of pollution. A reported change from pH 5.5 to pH 4.5 may not sound much, but in fact it represents a *tenfold increase* in the hydrogen ion concentration – hugely significant to the acidic properties. The pH of our blood is carefully controlled by chemicals called buffers to remain at 7.4, and a change of only half a pH unit on either side of this can be fatal. Communication of data in science takes different forms and uses different scales and must always be interpreted in the context used.

The pH scale at 298 K and pH values of some common substances.



Measuring pH

An easy way to estimate pH is with universal indicator paper or solution. The substance tested will give a characteristic colour, which can then be compared with a colour chart supplied with the indicator. Narrower-range indicators give a more accurate reading than broad-range indicators. The use of indicators is an analogue method which always depends on the user's interpretation of the colour, and so is somewhat subjective. Indicators are useful for estimations and comparisons of pH, rather than for precise measurements.



The pH scale and universal indicator solution. The tubes contain solutions of pH 0–14 from left to right, with added universal indicator.

A more objective and usually more accurate means is by using a **pH meter** that directly reads the H^+ concentration through a special electrode. pH meters can record to an accuracy of several decimal places. They must, however, be calibrated before each use with a buffer solution and standardized for the temperature, as pH is a temperature-dependent measurement.



Digital pH meter being used to measure the pH of a chemical solution. The tip of the probe is immersed in the liquid, which is weakly acidic (pH 5.8). The probe's tip contains electrodes that measure the electrical potential of the hydrogen ions, which is directly related to pH.

Nature of Science, Tool 2 – When are digital sensors (e.g. pH probes) more suitable than analogue methods (e.g. pH paper/solution)?

SKILLS

Use of a pH meter and universal indicator to measure pH. Full details of how to carry out this experiment with a worksheet are available in the eBook.

pH calculations

From the equations of the relationship between pH and $[H^+]$ we can:

- calculate the value of pH from a known concentration of H^+
- calculate the concentration of H^+ from a given pH.

The pH scale is a measure of $[H^+]$ and so may appear to be more suited for the measurement of acids than bases. But we can use the same scale to describe the alkalinity of a solution. As you can see below, this is because the relationship between $[H^+]$ and $[OH^-]$ is inverse in aqueous solutions, and so lower $[H^+]$ means higher $[OH^-]$ and vice versa. Therefore, the scale of pH numbers represents a range of values from strongly acidic through to strongly alkaline.

pH 0	pH 7	pH 14
←		→
increasing $[H^+]$ increasing acidity	neutral at 298 K	increasing $[OH^-]$ increasing alkalinity

In pH calculations you will need to be able to work out logarithms to base 10, and anti-logarithms. Make sure that you are familiar with these operations on your calculator.



The colours of the flowers of hydrangea plants (*Hydrangea macrophyll*) depend on the availability of aluminium ions, Al^{3+}, which react with the plant's pigments. A lower pH makes aluminium ions more easily absorbed, and the flowers are blue. A higher pH keeps the aluminium ions locked in insoluble form unavailable to plants, and the flowers are pink. The pink flower on the left was grown at pH 6.5, the blue flower on the right at pH 5.0, and the purple flower in the middle at pH 5.8, so both colours are present.

Challenge yourself

3. Derive equations to show why aluminium sulfate, when added to water, gives a cloudy appearance and has a low pH. You may find it helpful to read page 773.
4. Suggest why some gardeners water hydrangea flowers with a weak solution of vinegar.

Note that the logarithms used in all the work on acids and bases are logarithms to base 10 (log). Do not confuse these with natural logarithms, to base e, (ln).

Worked example

A sample of lake water was analysed at 298 K and found to have $[H^+] = 3.2 \times 10^{-5}\,mol\,dm^{-3}$. Calculate the pH of this water and comment on its value.

Solution

$pH = -\log_{10}[H^+]$

$= -\log_{10}(3.2 \times 10^{-5}) = -(-4.49485)$

$pH = 4.49$

At 298 K this pH < 7, and the lake water is therefore acidic.

The rule to follow for significant figures in logarithms is that *the number of decimal places in the logarithm should equal the number of significant figures in the number.* In other words, the number to the left of the decimal place in the logarithm is not counted as a significant figure (this is because it is derived from the exponential part of the number). In this example, the number given has two significant figures (3.2) and so the answer is given to two decimal places (.49).

Worked example

Human blood has a pH of 7.40. Calculate the concentration of hydrogen ions present.

Solution

$[H^+] = 10^{-pH}$

$= 10^{-7.40} = 4.0 \times 10^{-8}$

$[H^+] = 4.0 \times 10^{-8}\,mol\,dm^{-3}$

Exercise

Q7. What happens to the pH of an acid when 10 cm^3 of the acid is added to 90 cm^3 of water?

Q8. Beer has a hydrogen ion concentration of 1.9×10^{-5} mol dm^{-3}. What is its pH?

Q9. What is the pH of a 0.01 mol dm^{-3} solution of HCl which dissociates fully?

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

Q10. Lake water was found to have a concentration of H^+ ions of 3.2×10^{-5} mol dm^{-3}. Calculate the pH and determine if the lake water is acidic, basic, or neutral at 298 K.

Q11. Soil water found in a limestone area has a pH of 8.3. What is its concentration of H^+ ions?

Q12. Suggest why it is more convenient to express acidity in pH values rather than by concentration of hydrogen ions.

Reactivity 3.1.5 – The ion product constant of water

Reactivity 3.1.5 – The ion product constant of water, K_w, shows an inverse relationship between $[H^+]$ and $[OH^-]$. $K_w = [H^+][OH^-]$	
Recognize solutions as acidic, neutral and basic from the relative values of $[H^+]$ and $[OH^-]$.	
The equation for K_w and its value at 298 K are given in the data booklet.	Reactivity 2.3 – Why does the extent of ionization of water increase as temperature increases?

The ionization of water produces H^+ and OH^- ions



Victoria Falls on the Zimbabwe–Zambia border. It is estimated that 6.25×10^8 dm^3 of water flows over the falls every second. According to the ionization constant discussed here, for every billion of these molecules only two are ionized, and that proportion gets even smaller at lower temperatures.

As the majority of acid–base reactions involve ionization in aqueous solution, it is useful to consider the role of water in more detail. Water itself does ionize, albeit only very slightly at normal temperatures and pressures, so we can write an equilibrium expression for this reaction.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

Therefore $$K = \frac{[H^+][OH^-]}{[H_2O]}$$

The concentration of water can be considered to be constant due to the fact that so little of it ionizes, and it can therefore be combined with K to produce a modified equilibrium constant known as $\mathbf{K_w}$.

$K[H_2O] = [H^+][OH^-]$

Therefore $K_w = [H^+][OH^-]$

K_w is known as the **ionic product constant of water** and has a fixed value at a specified temperature. At 298 K, $K_w = 1.00 \times 10^{-14}$.

We are using $H^+(aq)$ throughout this chapter as a simplified form of $H_3O^+(aq)$. This is acceptable in most situations, but do not forget that H^+ in aqueous solution always exists as $H_3O^+(aq)$.

Water is a pure liquid so its concentration is just a function of its density, which is 1.00 g cm^{-3}.
Using $n = \frac{m}{M}$ gives $n(H_2O) = \frac{1000\,g\,dm^{-3}}{18\,g\,mol^{-1}} = 55\,mol\,dm^{-3}$

The value $K_w = 1.00 \times 10^{-14}$ at 298 K is given in the data booklet.

In pure water, because $[H^+] = [OH^-]$, it follows that $[H^+] = \sqrt{K_w}$

So at 298 K, $[H^+] = 1.00 \times 10^{-7}$, which gives pH = 7.00.

This is consistent with the widely known value for the pH of water at room temperature.

The relationship between H^+ and OH^- is inverse

Because the product $[H^+] \times [OH^-]$ gives a constant value, it follows that the concentrations of these ions must have an inverse relationship. In other words, in aqueous solutions the higher the concentration of H^+, the lower the concentration of OH^- and vice versa. Solutions are defined as acidic, neutral, or basic according to their relative concentrations of these ions as shown below.

		at 298 K
Acidic solutions are defined as those in which	$[H^+] > [OH^-]$	pH < 7
Neutral solutions are defined as those in which	$[H^+] = [OH^-]$	pH = 7
Alkaline solutions are defined as those in which	$[H^+] < [OH^-]$	pH > 7

So if we know the concentration of either H^+ or OH^-, we can calculate the other from the value of K_w.

$K_w = [H^+][OH^-]$

$$[H]^+ = \frac{K_w}{[OH]^-} \text{ and } [OH]^- = \frac{K_w}{[H]^+}$$

Worked example

A sample of blood at 298 K has $[H^+] = 4.60 \times 10^{-8}$ mol dm^{-3}.

Calculate the concentration of OH^- and state whether the blood is acidic, neutral, or basic.

Solution

At 298 K, $K_w = 1.00 \times 10^{-14} = [H^+][OH^-]$

So $[OH]^- = \frac{1.00 \times 10^{-14}}{4.60 \times 10^{-8}} = 2.17 \times 10^{-7}$ mol dm^{-3}

As $[OH^-] > [H^+]$ the solution is basic.

The concentrations of H^+ and OH^- are inversely proportional in an aqueous solution.

K_w is temperature dependent

The ionic product constant of water, K_w, was derived on page 686.

$$K_w = [H^+]\,[OH^-] = 1.00 \times 10^{-14} \text{ at } 298\text{ K}$$

As K_w is an equilibrium constant, its value must be temperature dependent. The reaction for the dissociation of water is endothermic as it involves bond breaking. This means that:

- an increase in temperature will shift the equilibrium to the right, which will increase the value of K_w. The concentrations of $H^+(aq)$ and $OH^-(aq)$ increase, and so pH decreases
- a decrease in temperature will shift the equilibrium to the left, which will decrease the value of K_w. The concentrations of $H^+(aq)$ and $OH^-(aq)$ decrease, and so pH increases.

Some data to illustrate these trends are given in the table.

Temperature / °C	K_w	$[H^+]$ in pure water ($\sqrt{K_w}$)	pH of pure water ($-\log_{10}[H^+]$)
0	1.5×10^{-15}	0.39×10^{-7}	7.47
10	3.0×10^{-15}	0.55×10^{-7}	7.27
20	6.8×10^{-15}	0.82×10^{-7}	7.08
25	1.0×10^{-14}	1.00×10^{-7}	7.00
30	1.5×10^{-14}	1.22×10^{-7}	6.92
40	3.0×10^{-14}	1.73×10^{-7}	6.77
50	5.5×10^{-14}	2.35×10^{-7}	6.63

In other words, the pH of pure water is 7.00 only when the temperature is 298 K. Note that at temperatures above and below this, despite changes in the pH value, water is still a neutral substance as its $H^+(aq)$ concentration is equal to its $OH^-(aq)$ concentration. It does not become acidic or basic as we heat it or cool it respectively!

The temperature dependence of K_w means that the temperature should always be stated alongside pH measurements.

SKILLS

The pH of water at different temperatures. Full details of how to carry out this experiment with a worksheet are available in the eBook.

Reactivity 2.3 – Why does the extent of ionization of water increase as temperature increases?

TOK

Because many people are so familiar with the value 7.00 as the pH of water, it is often more difficult to convince them that water with a pH of greater or less than this is still neutral. Can you think of other examples where entrenched prior knowledge might hinder a fuller understanding of new knowledge? Are we likely to misinterpret experimental data when it does not fit with our expectations based on prior knowledge?

Exercise

Q13. A sample of pure water is found to have a pH of 7.3. What can you deduce about the temperature at which the measurement was made?

Q14. An aqueous solution of baking soda, $NaHCO_3$, has a concentration of OH^- ions of 7.8×10^{-6} mol dm^{-3} at 298 K. Determine its concentration of hydrogen ions.

Q15. At body temperature, 37 °C, the value of K_w is 2.4×10^{-14}. Determine the concentration of H^+ ions and the pH of pure water at this temperature.

Q16. An aqueous solution has a pH of 9 at 25 °C. What are its concentrations of H^+ and OH^- ions?

Q17. For each of the following aqueous solutions at 298 K, calculate $[OH^-]$ from $[H^+]$ or $[H^+]$ from $[OH^-]$. Classify each solution as acidic, basic, or neutral.

(a) $[H^+] = 3.4 \times 10^{-9}$ mol dm^{-3}

(b) $[OH^-] = 0.010$ mol dm^{-3}

(c) $[OH^-] = 1.0 \times 10^{-10}$ mol dm^{-3}

(d) $[H^+] = 8.6 \times 10^{-5}$ mol dm^{-3}

Q18. A sample of blood has $[H^+] = 4.6 \times 10^{-8}$ mol dm^{-3} at 298 K. Determine its concentration of OH^- ions and state whether the sample is acidic, basic or neutral.

Q19. For each of the following biological fluids, calculate the pH from the given concentration of H^+ or OH^- ions at 298 K.

(a) bile: $[OH^-] = 8 \times 10^{-8}$ mol dm^{-3}

(b) gastric juice: $[H^+] = 10^{-2}$ mol dm^{-3}

(c) urine: $[OH^-] = 6 \times 10^{-10}$ mol dm^{-3}

Reactivity 3.1.6 – Strong and weak acids and bases

Reactivity 3.1.6 – Strong and weak acids and bases differ in the extent of ionization.	
Recognize that acid–base equilibria lie in the direction of the weaker conjugate.	
HCl, HBr, HI, HNO_3 and H_2SO_4 are strong acids, and group 1 hydroxides are strong bases. The distinction between strong and weak acids or bases and concentrated and dilute reagents should be covered.	Reactivity 2.3 – How would you expect the equilibrium constants of strong and weak acids to compare? Reactivity 1.1 – Why does the acid strength of the hydrogen halides increase down group 17? Tool 1, Inquiry 2 – What physical and chemical properties can be observed to distinguish between weak and strong acids or bases of the same concentration?

The strength of an acid or base depends on its extent of ionization

Brønsted–Lowry acids and bases dissociate in solution. Acids produce H^+ ions and bases produce OH^- ions. As a result, their aqueous solutions exist as equilibrium mixtures containing both the undissociated form and the ions. As we will see, the position of this equilibrium is what defines the strength of an acid or a base.

Consider the acid dissociation reaction:

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$$

If this acid dissociates fully, its equilibrium lies to the right and it will exist virtually entirely as ions in solution. It is said to be a **strong acid**. For example:

$$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

Hydrochloric acid, HCl, is a strong acid so it dissociates fully. This means that the reverse reaction can be considered to be negligible and so the reaction is usually written without the equilibrium sign.

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

If, on the other hand, the acid dissociates only partially, its equilibrium lies to the left and the undissociated form dominates. It is said to be a **weak acid**. For example:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

Ethanoic acid, CH_3COOH, is a weak acid so it dissociates only partially. Here it is essential to use the equilibrium sign in its dissociation reaction.

Strong acids are good proton donors. As their dissociation reactions go virtually to completion, their conjugate bases are not readily able to accept a proton. For example, the strong acid HCl reacts to form the conjugate base Cl^- which shows virtually no basic properties.

$HCl(aq)$	+	$H_2O(l)$	$\rightarrow$	$H_3O^+(aq)$	+	$Cl^-(aq)$
strong acid		base		conjugate acid		conjugate base

Weak acids are poor proton donors. As their dissociation reactions are equilibria which lie to the left, in favour of reactants, their conjugate bases are readily able to accept a proton. For example, the weak acid CH_3COOH reacts to form the conjugate base CH_3COO^-, which is a stronger base than Cl^-.

$CH_3COOH(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	$CH_3COO^-(aq)$
weak acid		base		conjugate acid		conjugate base

So acid dissociation reactions favour the production of the weaker conjugate.

In a similar way, bases can be described as strong or weak on the basis of the extent of their ionization. For example, NaOH is a **strong base** because it ionizes fully:

$$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$$



Common household acids and bases. From left to right: Drano contains sodium hydroxide, vitamin C is ascorbic acid, muriatic acid is hydrochloric acid, white vinegar contains ethanoic acid and Windex contains ammonia. If these were all present in the same concentration, what would be the increasing order of their pH values?

Strong acids and strong bases ionize almost completely in solution. Weak acids and weak bases ionize only partially in solution.

Its dissociation is written without equilibrium signs. Note that it is the OH^- ions that show Brønsted–Lowry base behaviour by accepting protons.

On the other hand, NH_3 is a **weak base** as it ionizes only partially, so its equilibrium lies to the left and the concentration of ions is low.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Strong bases are good proton acceptors; they react to form conjugates that do not show acidic properties. Weak bases are poor proton acceptors; they react to form conjugates with stronger acidic properties than the conjugates of strong bases. Base ionization reactions favour the production of the weaker conjugate.

In writing the ionization reactions of weak acids and bases, it is essential to use the equilibrium sign.

The strength of an acid or base is therefore a measure of how readily it dissociates in aqueous solution. This is an inherent property of a particular acid or base, dependent on its bonding. Do not confuse acid or basic *strength* with its *concentration*, which is a variable depending on the number of moles per unit volume, according to how much solute has been added to the water. Note, for example, it is possible for an acid or base to be strong but present in a dilute solution, or weak and present in a concentrated solution.

Be careful not to confuse two different pairs of opposites:

- strong and weak acids or bases refer to their extent of dissociation
- concentrated and dilute refer to the ratio of solute and water in the solution.

Weak acids and bases are much more common than strong acids and bases

It is useful to know which of the common acids and bases are strong and which are weak. Fortunately this is quite easy as there are very few common examples of strong acids and bases, so this short list can be committed to memory. You will then know that any other acids and bases you come across are likely to be weak.

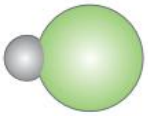
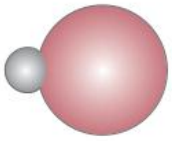
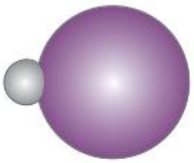
	Acid		Base	
common examples of strong forms	HCl	hydrochloric acid	LiOH	lithium hydroxide
	HBr	hydrobromic acid	NaOH	sodium hydroxide
	HI	hydroiodic acid	KOH	potassium hydroxide
	HNO_3	nitric acid		
	H_2SO_4	sulfuric acid		
some examples of weak forms	CH_3COOH and other organic acids	ethanoic acid	NH_3	ammonia
	H_2CO_3	carbonic acid	$C_2H_5NH_2$ and other amines	ethylamine
	H_3PO_4	phosphoric acid		

Note that amines such as ethylamine, $C_2H_5NH_2$, can be considered as organic derivatives of NH_3 in which one of the hydrogen atoms has been replaced by an alkyl (hydrocarbon) group. There are literally hundreds of acids and bases in organic chemistry, nearly all of which are weak in comparison with the strong inorganic acids listed here. Amino acids, the building blocks of proteins, as their name implies, contain both the basic $–NH_2$ amino group and the –COOH carboxylic acid group. The 'A' in DNA deoxyribonucleic acid, the store of genetic material, stands for 'acid'; in this case, the acidic component is phosphate groups.

Strong and weak acids differ in the extent of their dissociation, and therefore in their equilibrium constants. At equilibrium, strong acids have a high concentration of product, the ionized form, and therefore have large equilibrium constants. Weak acids, with low concentration of product at equilibrium, will have much smaller equilibrium constants.

Reactivity 2.3 – How would you expect the equilibrium constants of strong and weak acids to compare?

The strength of a Brønsted–Lowry acid depends on the ease with which it dissociates to release H^+ ions. In turn this depends on the strength of the bond that has to be broken to release H^+. If we consider the hydrogen halides, as the halogen atom increases in size going down group 17, this increases the length of the H–halogen bond. Longer bonds are weaker bonds that need less energy to break. So the acid strength of the hydrogen halides increases down the group: HF < HCl < HBr < HI.

	Bond length /nm	Bond strength /kJ mol^{-1}
HF 	0.02	568.0
HCl 	0.127	432.0
HBr 	0.141	366.3
HI 	0.161	298.3



Reactivity 1.1 – Why does the acid strength of the hydrogen halides increase down group 17?

Distinguishing between strong and weak acids and bases

Due to their greater ionization in solution, strong acids and strong bases will contain a *higher concentration of ions* than weak acids and weak bases. This then can be used as a means of distinguishing between them. Note though that such comparisons will only be valid when solutions of the same concentration (mol dm^{-3}) are compared at the same temperature. We will consider here three properties that depend on the concentration of ions and so can be used for this purpose.

Tool 1, Inquiry 2 – What physical and chemical properties can be observed to help you distinguish between weak and strong acids or bases of the same concentration?

Electrical conductivity

Electrical conductivity of a solution depends on the concentration of mobile ions. Strong acids and strong bases will therefore show higher conductivity than weak acids and bases – as long as solutions of the same concentration are compared. This can be measured using a conductivity meter or probe, or by using the conductivity setting on a pH meter.

SKILLS
Conductivity of strong and weak acid/bases. Full details of how to carry out this experiment with a worksheet are available in the eBook.



The different rates of reaction between calcium carbonate and three acids of different strength at the same concentration. The strongest acid is on the left and the weakest on the right. The carbonate reacts with each acid to produce carbon dioxide gas, which can be seen as bubbles in the solution. The stronger the acid, the more vigorous the reaction – the left test tube fizzes whilst the right one bubbles very gently. What variables must be kept constant in order for this to be a valid comparison of acid strength?

Rate of reaction

The reactions of acids with bases described on page 694 depend on the concentration of H^+ ions. They will therefore happen at an increased rate with stronger acids.

These different rates of reactions may be an important consideration, for example, regarding safety in the laboratory, but they usually do not provide an easy means of quantifying data to distinguish between weak and strong acids.

pH

Because it is a measure of the H^+ concentration, the pH scale can be used directly to compare the strengths of acids, provided they are of equal molar concentration. The stronger the acid of a fixed concentration, the lower the pH value. Universal indicator or a pH meter can be used to measure pH.

Exercise

Q20. Ammonia, NH_3, acts as a weak Brønsted–Lowry base when dissolved in water.

Write an equation for this reaction and outline what is meant by the term 'weak' in the context of the equilibrium position of this reaction.

Q21. Which of the following 1 mol dm^{-3} solutions will be the poorest conductor of electricity?

A HCl

B CH_3COOH

C NaOH

D NaCl

Q22. Which methods will distinguish between equimolar solutions of a strong base and a strong acid?

I. Add magnesium to each solution and look for the formation of gas bubbles.

II. Add aqueous sodium hydroxide to each solution and measure the temperature change.

III. Use each solution in a circuit with a battery and lamp and see how brightly the lamp glows.

A I and II only

B I and III only

C II and II only

D I, II and III

Q23. Which acid in each of the following pairs has the stronger conjugate base?

(a) H_2CO_3 or H_2SO_4 **(b)** HCl or HCOOH

Reactivity 3.1.7 – Neutralization reactions

Reactivity 3.1.7 – Acids react with bases in neutralization reactions. Formulate equations for the reactions between acids and metal oxides, metal hydroxides, hydrogencarbonates and carbonates.	
Identify the parent acid and base of different salts. Bases should include ammonia, amines, soluble carbonates and hydrogencarbonates; acids should include organic acids.	Tool 1, Structure 1.1 – How can the salts formed in neutralization reactions be separated? Reactivity 1.1 – Neutralization reactions are exothermic. How can this be explained in terms of bond enthalpies? Reactivity 3.2 – How could we classify the reaction that occurs when hydrogen gas is released from the reaction between an acid and a metal?

Neutralization reactions occur when acids and bases react together

Nature of Science

Classification leading to generalizations is an important aspect of studies in science. Historically, groups of substances such as acids were classified together because they were shown to have similar chemical properties. Over time it was recognized that many substances share these acidic properties, and so the classification broadened. Similarly, grouping of compounds as bases and alkalis occurred on the basis of experimental evidence for their properties.

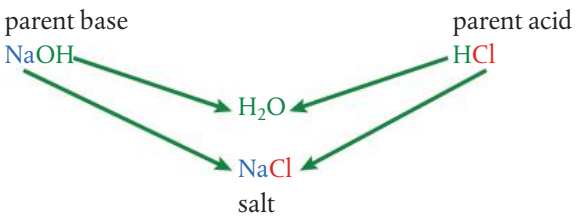
TOK To what extent do the classification systems we use in the pursuit of knowledge affect the conclusions that we reach?

Brønsted–Lowry acids release H^+ ions, and soluble bases, alkalis, release OH^- ions. The reaction between H^+ ions and OH^- ions to form H_2O is known as a **neutralization** reaction.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

During the reaction, an ionic compound called a **salt** also forms, as the hydrogen of the acid is replaced by a metal ion or another positive ion.

For example, sodium chloride, NaCl, known as common salt, is derived from the acid HCl by reaction with a base that contains Na, such as NaOH. The terms **parent acid** and **parent base** are sometimes used to describe this relationship between an acid, a base, and their salt.



In acid–base theory, the words ionization and dissociation are often used interchangeably as acid dissociation always leads to ion formation.

When acids react with reactive metals, they also form salts as the hydrogen in the acid is replaced by the metal. But in these reactions, there is no transfer of a proton, H^+, as the hydrogen is released as the gas, H_2. Here the hydrogen ions are becoming electrically neutral by accepting electrons while the metal is being ionized by electron loss. For example, in the reaction between magnesium metal and hydrochloric acid:

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

$$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^- \quad \text{electron loss} = \text{oxidation}$$

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \quad \text{electron gain} = \text{reduction}$$

These reactions are therefore redox reactions, and cannot be described by Brønsted–Lowry acid–base theory.

Reactivity 3.2 – How could we classify the reaction that occurs when hydrogen gas is released from the reaction between an acid and a metal?

acid + base → salt + water

Metal oxides and metal hydroxides are bases which react with acids to produce a salt and water.

For example:

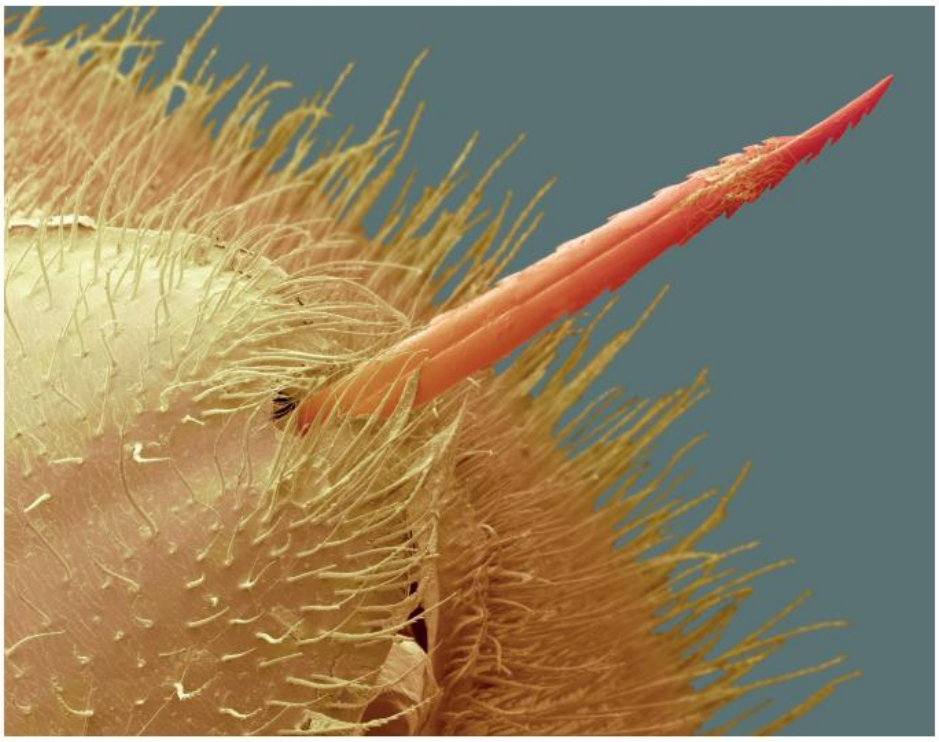
$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

$$2CH_3COOH(aq) + CuO(s) \rightarrow Cu(CH_3COO)_2(aq) + H_2O(l)$$

$$2HBr(aq) + Mg(OH)_2(aq) \rightarrow 2H_2O(l) + MgBr_2(aq)$$

Ammonia solution, NH_4OH, is also a soluble base which reacts with acids to form a salt and water.

$$HNO_3(aq) + NH_4OH(aq) \rightarrow NH_4NO_3(aq) + H_2O(l)$$



Coloured scanning electron micrograph (SEM) of the end of the abdomen of a bee, showing the needle-like stinger. The stinger is used to inject venom. Bee stings are slightly acidic, and so have traditionally been treated by using a mild alkali such as baking soda ($NaHCO_3$). Wasp stings, on the other hand, are claimed to be alkaline, and so are often treated with the weak acid, ethanoic acid (CH_3COOH), found in vinegar. There is, however, dispute over these claims as the pH of wasp stings is actually very close to neutral.

When you need to choose a base in solution to make a specific salt, it is useful to know some simple solubility rules.

- The only soluble carbonates and hydrogencarbonates are NH_4CO_3, Na_2CO_3, $NaHCO_3$, K_2CO_3, $KHCO_3$, and $Ca(HCO_3)_2$.
- The only soluble hydroxides are NH_4OH, LiOH, NaOH, and KOH.

Neutralization reactions occur when an acid and base react together to form a salt and water. They are exothermic reactions.

acid + carbonate → salt + water + carbon dioxide

Metal carbonates and hydrogencarbonates react with acids to produce a salt, water and carbon dioxide.

For example:

$$2HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

$$H_2SO_4(aq) + Na_2CO_3(aq) \rightarrow Na_2SO_4(aq) + H_2O(l) + CO_2(g)$$

$$CH_3COOH(aq) + KHCO_3(aq) \rightarrow KCH_3COO(aq) + H_2O(l) + CO_2(g)$$

These reactions can also be represented as ionic equations:

$$2H^+(aq) + CO_3^{2-}(aq) \rightarrow H_2O(l) + CO_2(g)$$

$$H^+(aq) + HCO_3^-(aq) \rightarrow H_2O(l) + CO_2(g)$$

The reactions involve a gas being given off, so they visibly produce bubbles, known as **effervescence**.

$$NaHCO_3(s) + CH_3COOH(aq) \rightarrow NaCH_3COO(aq) + CO_2(g) + H_2O(l)$$



Kitchen chemistry. Baking soda ($NaHCO_3$) and vinegar (CH_3COOH) react together in a powerful acid–base reaction, releasing carbon dioxide gas.
$NaHCO_3(s) + CH_3COOH(aq) \rightarrow NaCH_3COO(aq) + CO_2(g) + H_2O(l)$

Rainwater dissolves some CO_2 from the air to form a weak solution of carbonic acid, H_2CO_3.

$$H_2O(l) + CO_2(g) \rightleftharpoons H_2CO_3(aq)$$

Greater pressure, found underground in beds of limestone rock, $CaCO_3$, causes CO_2 to dissolve more readily, increasing the acidity of the solution. This then reacts with the $CaCO_3$:

$$H_2CO_3(aq) + CaCO_3(s) \rightleftharpoons Ca(HCO_3)_2(aq)$$

$CaCO_3$ is virtually insoluble but calcium hydrogencarbonate, $Ca(HCO_3)_2$, is soluble and washes away, causing caves to form in limestone regions. Inside the cave where the pressure is lower, the reaction above is reversed as less CO_2 dissolves, so $CaCO_3$ comes out of solution and precipitates. This causes the formations known as stalactites and stalagmites.



Stalactites hanging from the roof of a limestone cave in Kangaroo Island, Australia. Stalactites are formed from $CaCO_3$ precipitating out of solution, as the water dripping from the cave dissolves less CO_2 and loses acidity.

Reactions of rainwater on $CaCO_3$ rocks gives rise to 'hard water', that is water containing elevated levels of Ca^{2+} ions, in limestone areas.

When rainwater dissolves acidic gases from industrial emissions in the atmosphere, its pH is lowered further and it is known as 'acid rain'. This causes widespread damage including the erosion of carbonates such as marble structures.



The effect of acid rain eroding marble structures on a building in New York, USA, is shown on the right. The image on the left shows the structure after restoration to its original state.

Tool 1, Structure 1.1 – How can the salts formed in neutralization reactions be separated?

Neutralization reactions generally form aqueous solutions of salts. The pure salt can be separated by filtration followed by evaporation, as described in Structure 1.1.

Reactivity 1.1 – Neutralization reactions are exothermic. How can this be explained in terms of bond enthalpies?

In a neutralization reaction between an acid and a base, the net reaction is the formation of H_2O from its ions. (The other ions are called **spectator ions** as they do not change during the reaction and so can be cancelled out.)

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

For every mole of H_2O that forms, 2 moles of O–H bonds are made. As bond-making is an exothermic process, the overall reaction is also exothermic, releasing energy. For reactions between all strong acids and strong bases, the enthalpy of neutralization, expressed per mole of H_2O formed, is very similar – approximately $\Delta H = -57\ kJ\ mol^{-1}$, reflecting the fact that the overall reaction is the same in all cases, the formation of water.

Challenge yourself

5. Why do neutralization reactions involving weak acids or weak bases give different values for their enthalpy of neutralization compared with strong acids and bases?



Indigestion tablets effervescing as they dissolve in a glass of water to release CO_2. These antacids neutralize acids in the digestive system, which helps to reduce pain and inflammation.

Neutralization reactions can be useful to help reduce the effect of an acid or a base. For example, treatment for acid indigestion often involves using 'antacids' which contain a mixture of weak bases such as magnesium hydroxide and aluminium hydroxide. In places where the soil has become too acidic, the growth of many plants will be restricted. Adding a weak alkali such as lime, CaO, can help to reduce the acidity and hence increase the fertility of the soil.

Exercise

Q24. Write equations for the following reactions:

(a) sulfuric acid and copper oxide

(b) nitric acid and sodium hydrogencarbonate

(c) phosphoric acid and potassium hydroxide

(d) hydrochloric acid and methylamine

Q25. Which of the following is/are formed when a metal oxide reacts with a dilute acid?

I. a metal salt

II. water

III. carbon dioxide gas

A I only **B** I and II only **C** II and III only **D** I, II and III

Q26. Suggest by name a parent acid and parent base that could be used to make the following salts. Write equations for each reaction.

(a) sodium nitrate

(b) ammonium chloride

(c) copper sulfate

(d) potassium methanoate

Reactivity 3.1.8 – pH curves

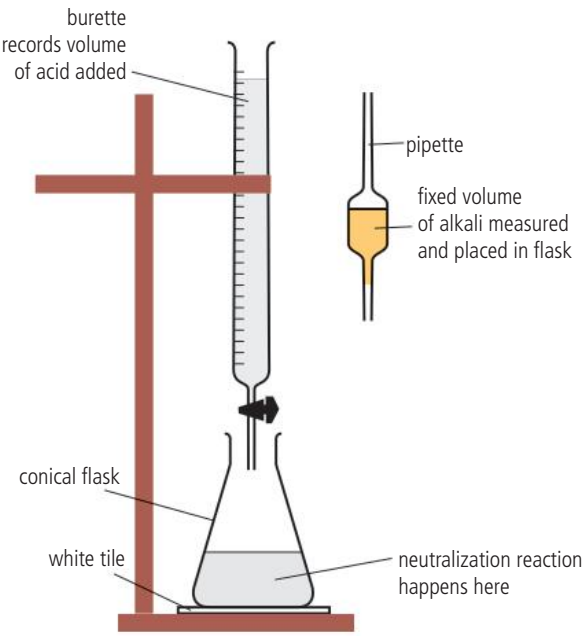
Reactivity 3.1.8 – pH curves for neutralization reactions involving strong acids and bases have characteristic shapes and features.	
Sketch and interpret the general shape of the pH curve.	
Interpretation should include the intercept with the pH axis and equivalence point. Only monoprotic neutralization reactions will be assessed.	Structure 1.4 – Why is the equivalence point sometimes referred to as the stoichiometric point? Tools 1 and 3, Structure 1.3 – How can titration be used to calculate the concentration of an acid or base in solution?

In the following section, we will study the pH curves of the reactions between strong acids and strong bases. The reactions between different combinations of strong and weak acids and bases are described on pages 693–696. To make comparisons of the curves easier, these examples all use:

- 0.10 mol dm^{-3} solutions of all acids and bases
- an initial volume of 50.0 cm^3 of acid in the conical flask with base added from the burette
- monoprotic acids and bases which all react in a 1:1 ratio, so that equivalence is achieved at equal volumes for these equimolar solutions (i.e. when 50.0 cm^3 of base has been added to the 50.0 cm^3 of acid).

pH curves can be generated from acid–base titrations

The neutralization reactions between acids and bases described previously can be investigated quantitatively using a technique called **acid–base titration**. Titration is one of the most widely used procedures in chemistry (Figure 1). Quality control of food and drink production, health and safety checks in the cosmetic industry, and clinical analysis in medical services are just some examples of its use. Controlled volumes of one reactant are added gradually from a **burette** to a fixed volume of the other reactant that has been carefully measured using a **pipette** and placed in a conical flask. The reaction between acid and base takes place in the flask until the **equivalence point** or **stoichiometric point** is reached, where they exactly neutralize each other. A pH meter or an indicator is used to detect the exact point at which equivalence is reached.



R3.1 Figure 1 Simple titration apparatus.



A pH meter recording change in pH during a titration. The conical flask contains sodium hydroxide solution, NaOH(aq), and the burette contains hydrochloric acid, HCl, known as the **titrant**. The change in pH with volume of titrant added is used to generate a pH curve.

When a base is added to an acid in the neutralization reaction, there is a change in pH as we would expect. But this change does not show a linear relationship with the volume of base added, partly due to the logarithmic nature of the pH scale. The easiest way to follow the reaction is to record pH using a pH meter or data-logging device as a function of volume of base added and plot these values as **pH curves**.

It is found that in most titrations, a big jump in pH occurs at equivalence, and this is known as the **point of inflection**. The equivalence point is determined as being half way up this jump.

The equivalence point in a titration can also be determined using an acid–base indicator, which is chosen to change colour at the pH of the equivalence point. The use of indicators in titration is discussed further on pages 719–721.



Addition of base from the burette to an acid in the conical flask containing indicator. As the neutralization reaction happens, the change in the pH of the reaction mixture causes a change in the colour of the indicator. Dropwise addition of the base ensures that an accurate measure of the equivalence point can be made.

At the equivalence point, the acid and base have exactly neutralized each other, so the solution contains salt and water only. The reacting ratio of acid to base to reach this point is determined by the *stoichiometry* of the neutralization reaction. For example:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl\,(aq) + H_2O(l)$$

Equivalence point when 1 mole acid : 1 mole base

$$2HCl(aq) + Ba(OH)_2\,(aq) \rightarrow BaCl_2(aq) + H_2O(l)$$

Equivalence point when 2 moles acid : 1 mole base

pH curve of strong acid and strong base

For example:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

pH at equivalence = 7

The calculations in the table on the next page are a sample to show the reasons for the shape of the pH curve. In this example, we assume full dissociation because these are strong acids and bases. Note also that as the base is added to the acid, neutralization of some of the acid occurs, while excess acid remains – until equivalence where the amounts of acid and base have fully reacted. After equivalence, the mixture contains excess base. As the volume changes during the addition, this must be taken into account in determining the concentrations.

As the volume of base added increases, we can see how the resulting pH changes.

Structure 1.4 – Why is the equivalence point sometimes referred to as the stoichiometric point?

SKILLS

Titration can be used to determine the concentration of one solution (acid or base), when the concentration of the other solution in the neutralization reaction is accurately known.

Tools 1 and 3, Structure 1.3 – How can titration be used to calculate the concentration of an acid or a base in solution?

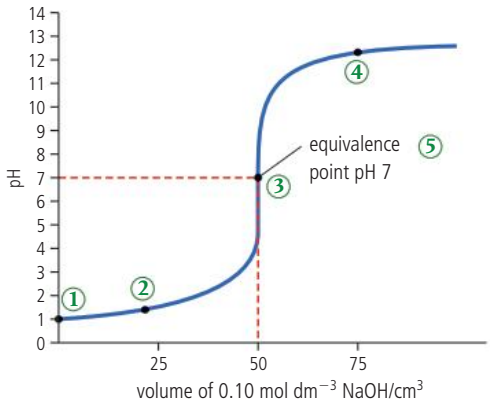
SKILLS

Acid–base titrations using a pH sensor – identifying the equivalence point. Full details of how to carry out this experiment with a worksheet are available in the eBook.

Volume of base added				
0.00 cm^3 (flask contains acid only)	25.00 cm^3 (flask contains excess acid)	49.00 cm^3 (flask contains excess acid)	50.00 cm^3 (contents of flask at equivalence)	51.00 cm^3 (flask contains excess base)
$[acid]_{initial}$ = 0.10 mol dm^{-3} $[H^+]$ = 1 × 10 mol dm^{-3} **pH = 1.0**	n(acid initial) = cV = 0.10 × 0.050 = 0.0050 mol n(base added) = cV = 0.10 × 0.0250 = 0.00250 mol n(acid remaining) = 0.0050 − 0.00250 = 0.00250 mol $n(H^+)$ = 0.00250 mol new volume = 0.0750 dm^3 so $[H^+]$ = 0.0333 mol dm^{-3} **pH = 1.5**	n(acid initial) = 0.0050 mol n(base added) = cV = 0.10 × 0.0490 = 0.00490 mol n(acid remaining) = 0.0050 − 0.00490 = 0.00010 mol $n(H^+)$ = 0.00010 mol new volume = 0.0990 dm^3 so $[H^+]$ = 0.00101 mol dm^{-3} **pH = 3.0**	**All of the acid has been neutralized by the base; the solution contains NaCl + H_2O only** **pH = 7.0**	n(base added) = cV = 0.10 × 0.0510 = 0.00510 mol n(base remaining) = 0.00510 − 0.0050 = 0.00010 mol $n(OH^-)$ = 0.00010 mol new volume = 0.101 dm^3 so $[OH^-]$ = 0.00099 mol dm^{-3} so pOH = 3 **pH = 11.0**

The curve obtained by continuous measurement with a pH probe shows the **pH curve** of these pH changes over the full range of addition of base (Figure 2).

R3.1 Figure 2 pH curve for strong acid–strong base.



The following points can be deduced from the graph as marked:

1. initial pH = 1, pH of strong acid
2. pH changes only gradually until equivalence
3. very sharp jump in pH at equivalence: from pH 3 to pH 11
4. after equivalence, the curve flattens out at a high value, pH of strong base
5. **pH at equivalence** = 7.

One drop of solution delivered from a burette has a volume of about 0.05 cm^3.

SKILLS

Most burettes have 0.1 cm^3 as the smallest division, so on this analogue scale you should record all readings to one half of this, that is ±0.05 cm^3.

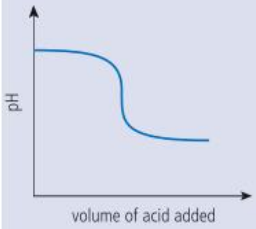
Exercise

Q27. What is the pH of the solution formed when a strong acid is exactly neutralized by a strong base? What is the name of this point in a titration?

Q28. Give the equation for the neutralization reaction that occurs during the titration of aqueous dilute nitric acid with potassium hydroxide solution. If the acid is placed in the conical flask and has a concentration of 0.01 mol dm^{-3}, what will be the intercept with the pH axis at the start of the titration?

Q29. In a titration, the equivalence point is reached when 10.00 cm^3 of 0.01 mol dm^{-3} NaOH have been added to 12.00 cm^3 of HCl. What is the concentration of the acid?

pH curves can equally well be described in terms of the addition of an acid to a base, in which case the curves will be the inverse.



Be sure to check which way round the data are given when answering questions on this topic.

HL

Reactivity 3.1.9 – The pOH scale

Reactivity 3.1.9 – The pOH scale describes the $[OH^-]$ of a solution. **$pOH = -\log_{10}[OH^-]$; $[OH^-] = 10^{-pOH}$** Interconvert $[H^+]$, $[OH^-]$, pH and pOH values.	
The equations for pOH are given in the data booklet.	

pH and pOH scales are interrelated

The pH scale simplifies the expression of the H^+ concentration in a solution and makes it easier to compare different solutions in terms of their H^+ content. The same rationale can be applied to the OH^- ions in a solution. Like H^+ ions, OH^- ions are often present in low concentrations in solutions and so when expressed as mol dm^{-3} they have negative exponents that can be awkward to work with. The parallel scale, known as the **pOH scale**, is therefore used to describe the OH^- content of solutions.

- $pOH = -\log_{10}[OH^-]$
- $pH = -\log_{10}[H^+]$
- $[OH^-] = 10^{-pOH}$
- $[H^+] = 10^{-pH}$

The equations for pH and pOH are given in the data booklet.

As this is a negative logarithmic scale like pH, it has the same features:

- pOH numbers are positive and have no units
- the pOH number is inversely related to the $[OH^-]$
- a change of one pOH unit represents a tenfold change in $[OH^-]$.

From the relationship $[H^+]\,[OH^-] = K_w = 1.00 \times 10^{-14}$ at 298 K, it follows that:

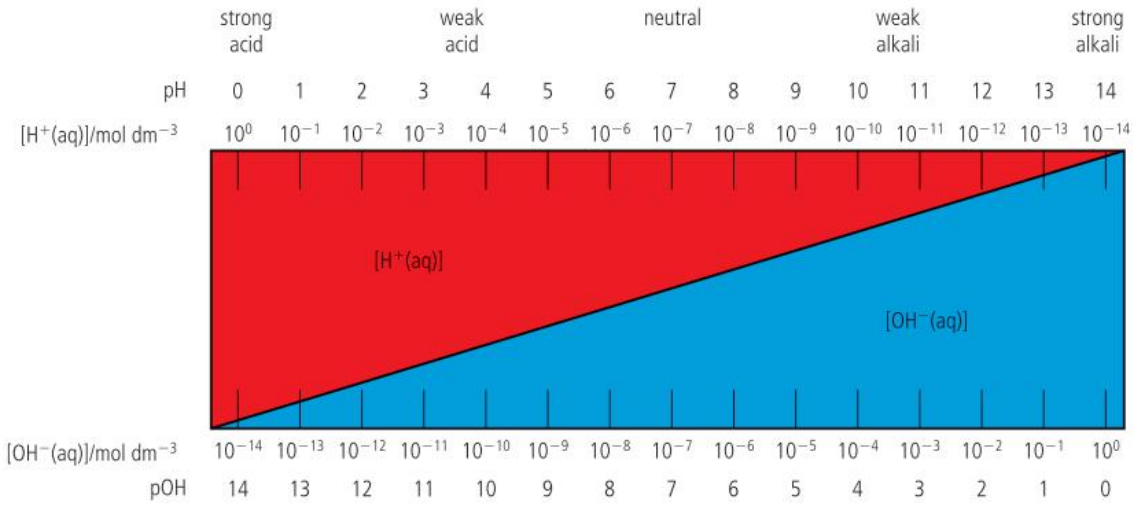
$$10^{-pH} \times 10^{-pOH} = 1.00 \times 10^{-14} \text{ at } 298\text{ K}$$

By taking the negative logarithm to base 10 of both sides, we get:

$$pH + pOH = 14.00 \text{ at } 298\text{ K}$$

In all aqueous solutions at 298 K: pH + pOH = 14

The relationships between pH, $[H^+]$, pOH, and $[OH^-]$ are shown in Figure 3.



R3.1 Figure 3 Relationship between $[H^+]$, $[OH^-]$, pH, and pOH at 298 K.

In the same way that the negative logarithm to base 10 of H^+ and OH^- are known as pH and pOH respectively, the same terminology can be applied to K_w to derive **pK_w**.

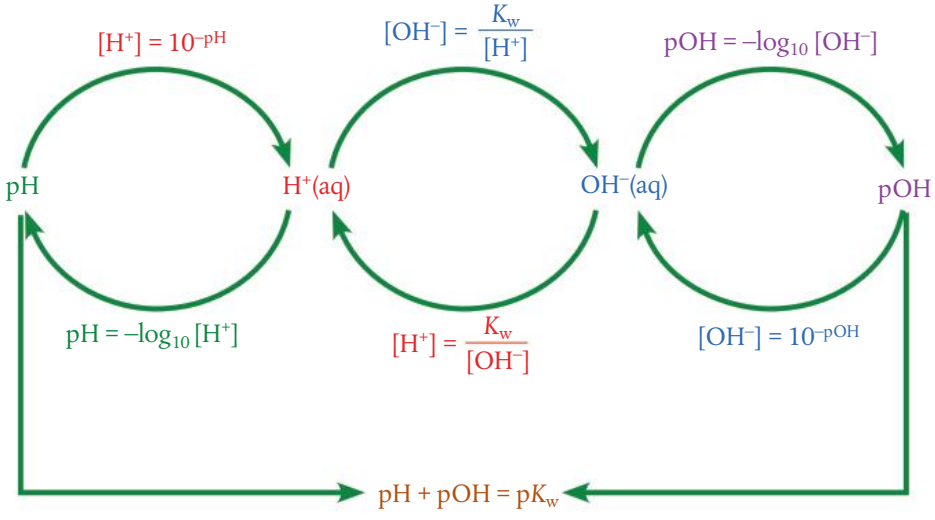
- $pK_w = -\log_{10}(K_w)$
- $K_w = 10^{-pK_w}$

So we can rewrite the expression above in a form that will apply to all temperatures:

$$pH + pOH = pK_w$$

pH + pOH = pK_w

Summary of the relationships between $[H^+]$, $[OH^-]$, pH, and pOH



A summary of the steps in interconversion between $[H^+]$, $[OH^-]$, pH, pOH and pK_w.

Worked example

Lemon juice has a pH of 2.90 at 25 °C. Calculate its $[H^+]$, $[OH^-]$ and pOH.

Solution

$[H^+] = 10^{-pH} = 10^{-2.90} = 1.3 \times 10^{-3}\,mol\,dm^{-3}$

pH + pOH = 14.00 at 298 K, so pOH = 14.00 – 2.90 = 11.10

$[OH^-] = 10^{-pOH} = 10^{-11.10} = 7.69 \times 10^{-12}\,mol\,dm^{-3}$

or $K_w = [H^+]\,[OH^-]$, so $1.00 \times 10^{-14} = (1.3 \times 10^{-3}) \times [OH^-]$

$[OH^-] = 7.69 \times 10^{-12}\,mol\,dm^{-3}$

Strong acids and bases: pH and pOH can be deduced from their concentrations

As we can assume full dissociation for strong acids and bases, we can deduce the ion concentrations and so calculate the pH or pOH directly from the initial concentration of the solution. Note that the pH and pOH are derived from the *equilibrium* concentrations of H^+ and OH^-. In these examples, we will use the same notation as in Reactivity 2.3, black for data that is given in the questions and blue for derived data.

Worked example

Calculate the pH of the following at 298 K:

(a) 0.10 mol dm^{-3} NaOH(aq)

(b) 0.15 mol dm^{-3} H_2SO_4(aq)

Solution

(a)

$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$

initial (mol dm^{-3})	0.10	
equilibrium (mol dm^{-3})		0.10

pOH = $-\log_{10}(0.10) = 1.0$, therefore pH = 13.0

(b)

$H_2SO_4(aq) \rightarrow 2H^+(aq) + SO_4^{2-}(aq)$

initial (mol dm^{-3})	0.15	
equilibrium (mol dm^{-3})		0.30

pH = $-\log_{10}(0.30) = 0.52$

Exercise

Q30. A solution of sodium hydroxide is prepared by adding distilled water to 6.0 g NaOH to make 1.0 dm^3 of solution. What is the pH of this solution? Assume that NaOH dissociates completely in solution:

$$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$$

Q31. At the temperature of the human body, 37 °C, the value of $K_w = 2.4 \times 10^{-14}$. Calculate $[H^+]$, $[OH^-]$, pH, pOH, and pK_w of water at this temperature. Is it acidic, basic or neutral?

Q32. The pH of a sample of milk is 6.77 at 298 K. Calculate its pOH, $[H^+]$, and $[OH^-]$. Deduce whether it is acidic, basic, or neutral.

Q33. Calculate the pH of the following solutions of strong acids and bases:

(a) 0.40 mol dm^{-3} HCl

(b) 3.7×10^{-4} mol dm^{-3} KOH

(c) 5.0×10^{-5} mol dm^{-3} $Ba(OH)_2$

Reactivity 3.1.10 and 3.1.11 – Acid and base dissociation constants

Reactivity 3.1.10 – The strengths of weak acids and bases are described by their K_a, K_b, pK_a or pK_b values.

Interpret the relative strengths of acids and bases from these data.

Reactivity 3.1.11 – For a conjugate acid–base pair, the relationship $K_a \times K_b = K_w$ can be derived from the expressions for K_a and K_b.

Solve problems involving these values.

The use of quadratic equations is not expected in calculations.	Reactivity 2.3 – How can we simplify calculations when equilibrium constants K_a and K_b are very small?

Dissociation constants express the strength of weak acids and bases

Weak acids and bases, unlike strong acids and bases, do not dissociate fully. This means we *cannot* deduce the concentrations of ions in their solutions from the initial concentrations, as the ion concentrations will depend on the extent of dissociation that has occurred. So we need some means of quantifying the extent of dissociation – and the process takes us back to equilibrium considerations.

The dissociation reactions of weak acids and weak bases can be represented as equilibrium expressions, each with their own equilibrium constant. The value of this constant will convey information about the position of equilibrium and therefore the extent of dissociation of the acid or base.

Consider the generic weak acid HA dissociating in water:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$K = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

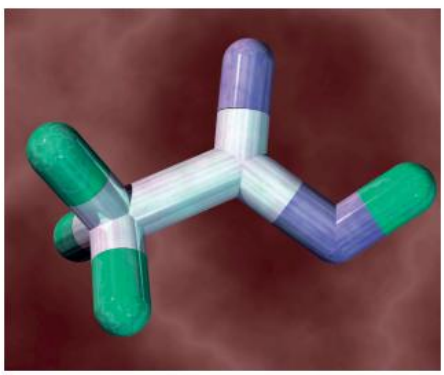
Given that the concentration of water is considered to be a constant, we can combine this with K to produce a modified equilibrium constant known as $\boldsymbol{K_a}$.

$$K[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

Therefore

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

K_a is known as the **acid dissociation constant**. It will have a fixed value for a particular acid at a specified temperature.



Computer model of a molecule of ethanoic acid, CH_3COOH. The atoms (tubes) are colour coded: carbon is white, hydrogen is green, and oxygen is purple. Ethanoic acid is a weak acid, and is used in many of the examples in this chapter. It is used in the production of plastics and also as a preservative.

As the value of K_a depends on the position of the equilibrium of acid dissociation, it gives a direct measure of the strength of an acid. *The higher the value of K_a at a particular temperature, the greater the dissociation, and so the stronger the acid.* Note that because K_a is an equilibrium constant, its value does not depend on the concentration of the acid or on the presence of other ions. We will return to this point in our study of buffer solutions on pages 723–732.

Similarly, we can consider the ionization of a base using the generic weak base B.

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

$$K = \frac{[BH^+][OH^-]}{[B][H_2O]}$$

Again, we can combine the constants to give a modified equilibrium constant $\boldsymbol{K_b}$.

$$K[H_2O] = \frac{[BH^+][OH^-]}{[B]}$$

Therefore

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

K_b is known as the **base dissociation constant**. It will have a fixed value for a particular base at a specified temperature.

As with K_a, the value of K_b relates to the position of the equilibrium and hence in this case to the strength of the base. *The higher the value of K_b at a particular temperature, the greater the ionization and hence the stronger the base.*

Note that the term **acid dissociation constant** is sometimes used interchangeably with the term **acid ionization constant**. You should be comfortable using and recognizing either term.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

The values of K_a and K_b are constant for a specific acid and base respectively, at a specified temperature. Their values give a measure of the strength of the acid or base.

Worked example

Write the expressions for K_a and K_b for the following acid and base.

(a) $CH_3COOH(aq)$ **(b)** $NH_3(aq)$

Solution

First write the equation for the equilibrium reactions – remembering that acids donate H^+ and bases accept H^+.

(a) $CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

(b) $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Exercise

Q34. Write the expressions for K_b for the following:

(a) $C_2H_5NH_2(aq)$

(b) $HSO_4^-(aq)$

(c) $CO_3^{2-}(aq)$

Q35. Place the following acids in order of increasing strength.

H_3PO_4 $K_a = 7.1 \times 10^{-3}$

HNO_2 $K_a = 7.1 \times 10^{-4}$

H_2SO_3 $K_a = 1.2 \times 10^{-2}$

Q36. Why do you think we do not usually use the concept of K_a and K_b to describe the strength of strong acids and bases?

Calculations involving K_a and K_b

The values of K_a and K_b enable us to compare the strengths of weak acids and bases, and to calculate ion concentrations present at equilibrium and so the pH and pOH values. Examples of these calculations are given below. Note that many of these questions are approached in a similar manner to those given in Reactivity 2.3. It is assumed here that you are familiar with that work, so it may be useful for you to refresh your memory before continuing.

The following points are to remind you of some key points and guide you in all the calculations that follow:

- The given concentration of an acid or base is its *initial* concentration – before dissociation occurs.
- The pH or pOH of a solution refers to the concentration of H^+ ions or OH^- ions at *equilibrium*.

- The concentration values substituted into the expressions for K_a and K_b must be the *equilibrium* values for all reactants and products.
- When the extent of dissociation is very small, when K_a or K_b has a very low value, it is appropriate to use the approximations:

$$[\text{acid}]_{\text{initial}} \approx [\text{acid}]_{\text{equilibrium}}$$
$$[\text{base}]_{\text{initial}} \approx [\text{base}]_{\text{equilibrium}}$$

This is because the extent of dissociation is so small, the concentration of the reactant – acid or base – is considered to be unchanged from its initial value at equilibrium.

Make sure you clearly state when an approximation is made in a calculation, and justify it in terms of the small value of *K*.

Reactivity 2.3 – How can we simplify calculations when equilibrium constants K_a or K_b are very small?

1 Calculation of K_a and K_b from pH and initial concentration

Worked example

Calculate K_a at 298 K for a 0.01 mol dm^{-3} solution of ethanoic acid (CH_3COOH). It has a pH of 3.4 at this temperature.

Solution

Write the equation for the dissociation of the acid. Insert the data in three rows: initial, change, and equilibrium. As in Reactivity 2.3, numbers in black are data that were given in the question, numbers in blue have been derived.

From the pH we get the $[H^+]$ at equilibrium:

pH 3.4 $\Rightarrow [H^+] = 10^{-3.4} = 4.0 \times 10^{-4}$ mol dm^{-3}

From the stoichiometry of the reaction we know that $[H^+] = [CH_3COO^-]$

	$CH_3COOH(aq)$	$\rightleftharpoons$	$CH_3COO^-(aq)$	+	$H^+(aq)$
initial (mol dm^{-3})	0.01		0.00		0.00
change (mol dm^{-3})	-4×10^{-4}		$+4 \times 10^{-4}$		$+4 \times 10^{-4}$
equilibrium (mol dm^{-3})	$0.01 - (4 \times 10^{-4})$ ≈ 0.01		4×10^{-4}		4×10^{-4}

The approximation $0.01 \approx 0.01 - (4 \times 10^{-4})$ is valid within the precision of these data.

Write the expression for K_a and substitute the equilibrium values.

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{(4 \times 10^{-4})^2}{0.01} = 1.6 \times 10^{-5}$$

Notice that the approximation is valid when subtracting a very small number (here 4×10^{-4}) from a larger number, as it only affects decimal points beyond the precision used. But when multiplying by the same very small number, we cannot make an approximation, as the effect on the result is very significant.

Worked example

Calculate the K_b for a 0.100 mol dm^{-3} solution of methylamine, CH_3NH_2, at 25 °C. Its pH is 11.80 at this temperature.

Solution

At 25 °C (298 K), pH + pOH = 14.00. Therefore pH 11.80 $\Rightarrow$ pOH = 2.20

$[OH^-] = 10^{-pOH} = 10^{-2.20} = 6.3 \times 10^{-3}$

From the stoichiometry of the reaction $[OH^-] = [CH_3NH_3^+]$

Justifiable approximations such as this can simplify calculations significantly. If a calculation looks as if it needs to use the quadratic equation to solve, look again – you have possibly missed making a valid approximation.

	$CH_3NH_2(aq)$	+ $H_2O(l)$ ⇌	$CH_3NH_3^+(aq)$	+ $OH^-(aq)$
initial (mol dm^{-3})	0.100		0.000	0.000
change (mol dm^{-3})	−0.00630		+0.00630	+0.00630
equilibrium (mol dm^{-3})	0.0937		0.00630	0.00630

$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_3]} = \frac{(0.00630)^2}{0.0937} = 4.22 \times 10^{-4}$$

2 Calculation of [H⁺] and pH, [OH⁻] and pOH from K_a and K_b

Worked example

A 0.75 mol dm^{-3} solution of ethanoic acid has a value for $K_a = 1.8 \times 10^{-5}$ at a specified temperature. What is its pH at this temperature?

Solution

To calculate pH we need to know [H⁺] at equilibrium, and therefore the amount of dissociation of the acid that has occurred: this is the 'change' amount in the reaction.

So let the change in concentration of $CH_3COOH = -x$

Therefore the change in concentration of CH_3COO^- and $H^+ = +x$

	$CH_3COOH(aq)$ ⇌	$CH_3COO^-(aq)$	+ $H^+(aq)$
initial (mol dm^{-3})	0.75	0.00	0.00
change (mol dm^{-3})	$-x$	$+x$	$+x$
equilibrium (mol dm^{-3})	$0.75 - x$ ≈ 0.75	x	x

As K_a is very small, x, the amount of dissociation, is also extremely small and it is valid to approximate $[CH_3COOH]_{initial} \approx [CH_3COOH]_{equilibrium}$.

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{x^2}{0.75} = 1.8 \times 10^{-5}$$

Therefore $x = \sqrt{1.8 \times 10^{-5} \times 0.75} = 3.7 \times 10^{-3}$

$[H^+] = 3.7 \times 10^{-3} \Rightarrow$ pH = 2.4

Worked example

A 0.20 mol dm^{-3} aqueous solution of ammonia has K_b of 1.8×10^{-5} at 298 K. What is its pH?

Solution

Let the change in concentration of $NH_3 = -x$

Therefore the change in concentration of NH_4^+ and $OH^- = +x$

	$NH_3(aq)$	+ $H_2O(l)$ ⇌	$NH_4^+(aq)$	+ $OH^-(aq)$
initial (mol dm^{-3})	0.20		0.00	0.00
change (mol dm^{-3})	$-x$		$+x$	$+x$
equilibrium (mol dm^{-3})	$0.20 - x$ ≈ 0.20		x	x

As K_b is very small, x, the amount of dissociation, is also extremely small, and so it is valid to approximate $[NH_3]_{initial} \approx [NH_3]_{equilibrium}$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x^2}{0.20} = 1.8 \times 10^{-5}$$

Therefore $x = \sqrt{1.8 \times 10^{-5} \times 0.20} = 1.9 \times 10^{-3}$

$[OH^-] = 1.9 \times 10^{-3}$

$pOH = -\log_{10}(1.9 \times 10^{-3}) = 2.72$

Therefore at 298 K, pH = 14.00 – 2.72 = 11.28

Exercise

Q37. The acid dissociation constant of a weak acid has a value of 1.0×10^{-5} mol dm^{-3}. What is the pH of a 0.1 mol dm^{-3} aqueous solution of HA?

A 2 **B** 3 **C** 5 **D** 6

Q38. Calculate the K_b of ethylamine, $C_2H_5NH_2$, given that a 0.10 mol dm^{-3} solution has a pH of 11.86.

Q39. What are the $[H^+]$ and $[OH^-]$ in a 0.10 mol dm^{-3} solution of an acid that has $K_a = 1.0 \times 10^{-7}$?



Stinging nettle plants. The leaves are covered in sharp hairs, which when touched inject a painful mixture of chemicals including the weak acid methanoic acid, HCOOH, into the skin. The stinging sensation can be relieved by rubbing the skin with leaves of a plant such as dock, which has a mildly basic sap and so helps to neutralize the acid.

pK_a and pK_b are logarithmic expressions of K_a and K_b

We have seen that K_a and K_b values give us a direct measure of the relative strengths of weak acids and bases. But as these values are characteristically very small, they usually involve dealing with numbers with negative exponents, which we have acknowledged before are clumsy to use as the basis for comparisons. They also span a wide range of values. So, in the same way as with the concentrations of H^+ and OH^- ions and K_w, and for the same reason, we can convert K_a and K_b values into their negative logarithms to the base 10, known as pK_a and pK_b.

- $pK_a = -\log_{10} K_a$
- $K_a = 10^{-pK_a}$
- $pK_b = -\log_{10} K_b$
- $K_b = 10^{-pK_b}$

Some examples of K_a and pK_a, and K_b and pK_b values are given below, all at 298 K.

Acid	Formula	K_a	pK_a
methanoic	HCOOH	1.8×10^{-4}	3.75
ethanoic	CH_3COOH	1.8×10^{-5}	4.76
propanoic	C_2H_5COOH	1.4×10^{-5}	4.87

Base	Formula	K_b	pK_b
ammonia	NH_3	1.8×10^{-5}	4.75
methylamine	CH_3NH_2	4.6×10^{-4}	3.34
ethylamine	$C_2H_5NH_2$	4.5×10^{-4}	3.35

Challenge yourself

6. Increasing the length of the carbon chain *decreases* the acid strength of the –COOH group but *increases* the basic strength of the $–NH_2$ group. Can you suggest why this is so? Hint: think about the electron density distributions in the molecules.

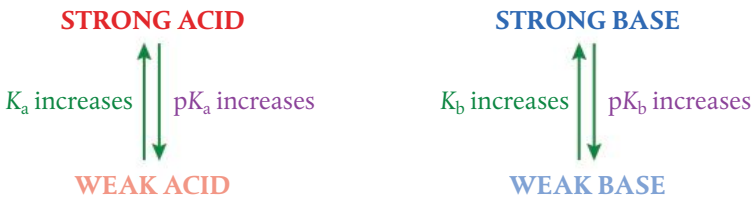
The following points follow from the table on the previous page and the table above.

1 **pK_a and pK_b numbers are usually positive and have no units.**

Although the derivation of K_a and K_b can be applied to any acid or base, it is useful mostly for weak acids and bases where the extent of dissociation is small. The fact that these have negative powers means that their pK_a and pK_b values will be positive, as we can see in the examples in the tables on the previous page and the table above.

2 **The relationship between K_a and pK_a and between K_b and pK_b is inverse.**

Stronger acids or bases with higher values for K_a or K_b have lower values for pK_a or pK_b.



3 **A change of one unit in pK_a or pK_b represents a tenfold change in the value of K_a or K_b.**

This is because the scale is logarithmic to base 10.

$pK_a = -\log_{10}K_a$; $K_a = 10^{-pK_a}$
$pK_b = -\log_{10}K_b$; $K_b = 10^{-pK_b}$

4 **pK_a and pK_b must be quoted at a specified temperature.**

This is because the values are derived from the temperature-dependent constants, K_a and K_b.

- The larger the pK_a, the weaker the acid.
- The larger the pK_b, the weaker the base.

The data booklet gives pK_a and pK_b values for a range of common weak acids and bases. These are the data commonly quoted to describe acid and base strengths, so in calculation questions, you may first need to convert pK_a or pK_b into K_a or K_b values. This is done by taking anti-logarithms, as we did with pH, pOH, and pK_w.

The relationship between K_a and K_b is reciprocal for a conjugate acid–base pair

Consider the K_a and K_b expressions for a conjugate acid–base pair HA and A^-:

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq) \qquad K_a = \frac{[H^+][A^-]}{[HA]}$$

$$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq) \qquad K_b = \frac{[HA][OH^-]}{[A^-]}$$

$$K_a \cdot K_b = \frac{[H^+][A^-]}{[HA]} \cdot \frac{[HA][OH^-]}{[A^-]}$$

Therefore $K_a \times K_b = [H^+] \times [OH^-] = K_w$

By taking negative logarithms of both sides:

$$pK_a + pK_b = pK_w$$

At 298 K, $K_w = 1.00 \times 10^{-14}$ so $pK_w = 14.00$

Therefore $pK_a + pK_b = 14.00$ at 298 K

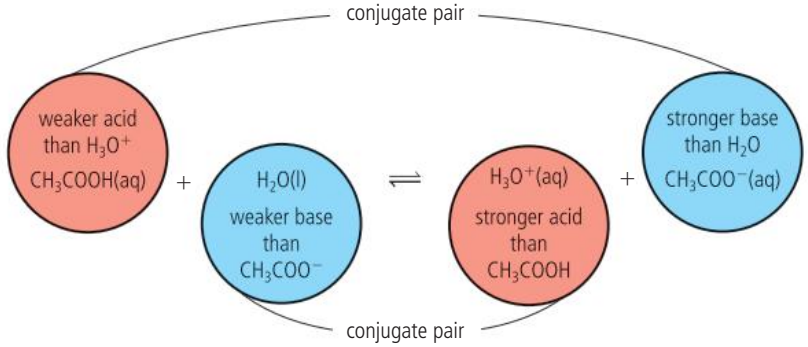
For any conjugate acid–base pair:
- $K_a \times K_b = K_w$
- $pK_a + pK_b = pK_w$
- $pK_a + pK_b = 14$ at 298 K

This relationship holds for any conjugate acid–base pair in aqueous solution. This means that from the value of K_a of the acid, we can calculate K_b for its conjugate base. It shows that the higher the value of K_a for the acid, the lower the value of K_b for its conjugate base. In other words, stronger acids have weaker conjugate bases, and vice versa. This gives a quantitative basis for the relative strengths of conjugate acid–base pairs, discussed qualitatively on page 689.

The relationship makes sense in the context of equilibrium positions. For a conjugate pair such as:

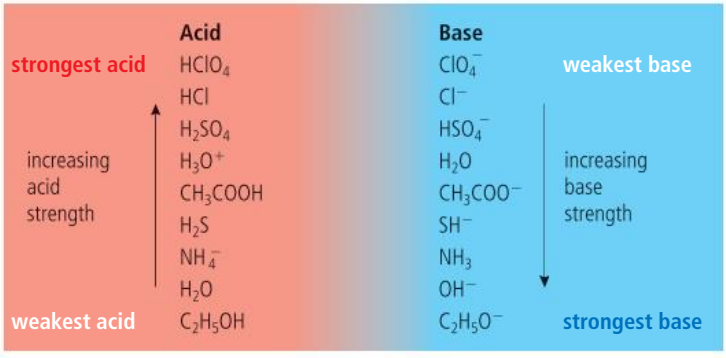
$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

the weaker the acid HA, the further this equilibrium lies to the left. This means the stronger the base A^-, because the greater its tendency to accept the proton. So acids and bases react to form the weaker conjugate, as illustrated in Figure 4.



R3.1 Figure 4 The reaction between CH_3COOH and H_2O. At equilibrium the mixture lies in favour of the weaker conjugates, the acid CH_3COOH and the base H_2O.

The inverse relationship between the strengths of acids and their conjugate bases is shown in Figure 5.



R3.1 Figure 5 The relative strengths of some acids and their conjugate bases in aqueous solution.

Nature of Science

The application of the equilibrium law to acid–base equilibria leads to a number of different derived equilibrium constants. These can be used to solve a wide range of numerical problems, which allow the strengths of acids and bases to be determined. Explanation of patterns and trends in the relative strengths of acids and bases is based on interpretations of their molecular structures. This flow of understanding and knowledge across a range of phenomena is central to the study of chemistry.

Exercise

Q40. A weak acid HA has a pK_a of 4.92. What will be the $[H^+]$ and pH of a 0.030 mol dm^{-3} solution of this acid?

Q41. What is the relationship between K_a and pK_a?

A $pK_a = -\log K_a$ **B** $pK_a = \frac{1.0 \times 10^{-14}}{K_a}$

C $pK_a = \log K_a$ **D** $pK_a = \frac{1.0}{K_a}$

Q42. The pK_a of HCN is 9.21 and that of HF is 3.17. Which is the stronger acid?

Q43. Look at the data in **Q42**. What are the pK_b values of CN^- and F^-? Which is the stronger base?

Q44. **(a)** The pK_a of ethanoic acid, CH_3COOH, at 298 K is 4.76. What is the pK_b of its conjugate base CH_3COO^-?

(b) The pK_a of methanoic acid, HCOOH, at 298 K is 3.75. Is its conjugate base weaker or stronger than the conjugate base of ethanoic acid?

Reactivity 3.1.12 – pH of salt solutions

Reactivity 3.1.12 – The pH of a salt solution depends on the relative strengths of the parent acid and base.	
Construct equations for the hydrolysis of ions in a salt, and predict the effect of each ion on the pH of the salt solution.	
Examples should include the ammonium ion NH_4^+, the carboxylate ion $RCOO^-$, the carbonate ion CO_3^{2-}, and the hydrogencarbonate ion HCO_3^-. The acidity of hydrated transition element ions and $Al^{3+}(aq)$ is not required.	

Ion hydrolysis determines the pH of a salt solution

The salt formed in a neutralization reaction is an ionic compound in which the cation is the conjugate acid of the parent base, and the anion is the conjugate base from the parent acid.

parent base	+	parent acid	→	salt	+	water
MOH	+	HA	→	M^+A^-	+	H_2O

Although salts are the products of a neutralization reaction, they do not all form neutral aqueous solutions. The pH of a salt solution depends on whether and to what extent their ions, the conjugate acids and bases, react with water and hydrolyse it, releasing H^+ or OH^- ions. The relative strengths of the conjugate acids and bases in the salt determine the extent of hydrolysis reactions and so the pH of the salt solution. As we saw on pages 710–711, the weaker the acid or base the stronger its conjugates, and vice versa.

Salt of strong acid and strong base – no hydrolysis

For example:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

pH approximately 7

The reaction between a strong acid and a strong base forms a salt in which both the conjugate acid and the conjugate base are weak. As a result, there is virtually no hydrolysis of ions, and the pH is close to neutral.

We saw this in the pH curve of a strong acid and a strong base on page 700, that the salt solution at equivalence has pH = 7.

Solutions of salts of strong acids with strong bases have a pH ≈ 7 at 298 K.

Salt of weak acid and strong base – anion hydrolysis

For example: $CH_3COOH(aq) + NaOH(aq) \rightarrow NaCH_3COO(aq) + H_2O(l)$

The anion CH_3COO^- in the salt is a conjugate base of the parent acid CH_3COOH. As this acid is weak, its conjugate base is strong enough to cause hydrolysis:

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

The release of OH^- causes the pH of the solution to *increase*.

Similarly, $$H_2CO_3 + NaOH(aq) \rightarrow NaHCO_3 + H_2O(l)$$

$$H_2CO_3 + 2NaOH(aq) \rightarrow Na_2CO_3(aq) + 2H_2O(l)$$

The anions HCO_3^- and CO_3^{2-} in these carbonate and hydrogencarbonate salts are conjugate bases of the weak parent acid H_2CO_3. These conjugate bases are strong enough to cause hydrolysis and release OH^- ions.

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

Solutions of salts of weak acids with strong bases have a pH > 7 at 298 K.

Salt of strong acid and weak base – cation hydrolysis

For example, $$HCl(aq) + NH_4OH(aq) \rightarrow NH_4Cl(aq) + H_2O(l)$$

The cation NH_4^+ in the salt is a conjugate acid of the parent base NH_4OH. As this base is weak, its conjugate is able to cause hydrolysis:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_4OH(aq) + H^+(aq)$$

The release of H^+ causes the pH of the solution to *decrease*.

Solutions of salts of strong acids with weak bases have a pH < 7 at 298 K.

Salt of weak acid and weak base

When a weak acid reacts with a weak base, a salt forms in which both the conjugates are relatively strong and carry out hydrolysis. The pH of the solution therefore depends on the relative K_a and K_b values of the acids and bases involved.

Summary

In summary, the pH of a salt solution depends on the relative hydrolysis of its anions and cations, which can be deduced from the relative strengths of the parent acids and bases. The table below summarizes this.

Neutralization reaction	Example of parent acid and base	Salt formed	Hydrolysis of ions	Type of salt solution	pH of salt solution
strong acid and strong base	$HCl(aq) + NaOH(aq)$	$NaCl(aq)$	neither ion hydrolyses	neutral	7
weak acid and strong base	$CH_3COOH(aq) + NaOH(aq)$ $H_2CO_3(aq) + NaOH(aq)$	$NaCH_3COO(aq)$ $NaHCO_3(aq)$ / $Na_2CO_3(aq)$	anion hydrolyses	basic	>7
strong acid and weak base	$HCl(aq) + NH_3(aq)$	$NH_4Cl(aq)$	cation hydrolyses	acidic	<7
weak acid and weak base	$CH_3COOH(aq) + NH_3(aq)$	$NH_4CH_3COO(aq)$	anion and cation hydrolyze	depends on relative strengths of conjugates	cannot generalize

- Salts of strong acids and strong bases are neutral.
- Salts of weak acids and strong bases are basic.
- Salts of strong acids and weak bases are acidic.



The destruction resulting from a large explosion of ammonium nitrate, NH_4NO_3, in Beirut, Lebanon in 2020. It was one of the biggest non-nuclear explosions in history and caused hundreds of fatalities and thousands of injuries. Ammonium nitrate is the salt of a strong acid and a weak base. It is used as a fertilizer and as an explosive.

Challenge yourself

7. Formulate equations for reactions that produce the salt ammonium nitrate from its parent acid and base and deduce the pH of its solution.
   At high temperatures, solid NH_4NO_3 decomposes to produce nitrogen, oxygen and water. Formulate equations for this reaction and suggest why it can be explosive.

Exercise

Q45. Predict for each salt in aqueous solution whether the pH will be greater than, less than, or equal to 7.

(a) $NaCl$ **(b)** $FeCl_3$

(c) $(NH_4)_2SO_4$ **(d)** Na_2CO_3

Q46. Which compound will dissolve in water to give a solution with a pH greater than 7?

A sodium chloride

B potassium carbonate

C ammonium nitrate

D lithium sulfate

Q47. Deduce whether the pH of the resulting salt solution will be greater than, less than, or equal to 7 when the following solutions exactly neutralize each other.

(a) $H_2SO_4(aq) + NH_3(aq)$

(b) $H_3PO_4(aq) + KOH(aq)$

(c) $HNO_3(aq) + Ba(OH)_2(aq)$

Q48. Show by means of equations how sodium hydrogencarbonate can increase the pH of a solution.

Reactivity 3.1.13 – pH curves revisited

Reactivity 3.1.13 – pH curves of different combinations of strong and weak monoprotic acids and bases have characteristic shapes and features.

Interpret the general shapes of pH curves for all four combinations of strong and weak acids and bases.

Interpretation should include intercept with the pH axis, equivalence point, buffer region points where pH = pK_a or pOH = pK_b.	Tool 1 – When collecting data to generate a pH curve, when should smaller volumes of titrant be added between each measurement?

This section takes the study of pH curves from pages 697–701 further by considering titrations between different combinations of strong and weak acids and bases. Our knowledge of the pH of salt solutions prepared from neutralization reactions between different combinations of acid and base discussed on pages 712–714 will be important in the interpretation of these curves. As before, we will make the comparisons simpler by using the same volumes and concentrations of reactants:

- 0.10 mol dm^{-3} solutions of all acids and bases
- an initial volume of 50.0 cm^3 of acid in the conical flask with base added from the burette
- monoprotic acids and bases which all react in a 1:1 ratio, so that equivalence is achieved at equal volumes for these equimolar solutions (i.e. when 50.0 cm^3 of base has been added to the 50.0 cm^3 of acid).

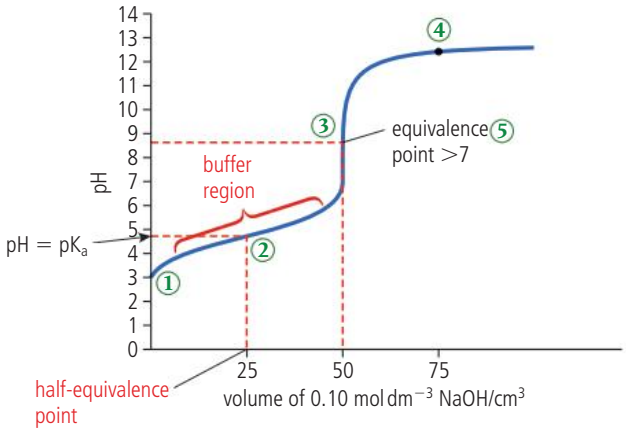
pH curve of weak acid and strong base

For example:

$$CH_3COOH(aq) + NaOH(aq) \rightarrow NaCH_3COO(aq) + H_2O(l)$$

pH at equivalence > 7 as the anion hydrolysis releases OH^-:
$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$

Titration curve for weak acid–strong base.



Note that acids and bases react in stoichiometric ratios, irrespective of whether they are weak or strong. In other words, equivalence is achieved with the same volume of alkali added to the strong acid, HCl, as to the weak acid, CH_3COOH, given that they are equimolar solutions.

The following points can be deduced from the graph as marked:

1. initial pH fairly high (pH of weak acid)
2. pH stays relatively constant until equivalence – labelled as buffer region
3. jump in pH at equivalence from about pH 7.0–11.0, which is not as much of a jump as for a strong acid–strong base titration
4. after equivalence, the curve flattens out at a high value (pH of strong base)
5. **pH at equivalence is > 7.**

The reaction mixture after the addition of 25 cm^3 of base is of particular interest. It is labelled as the **half-equivalence** point in the graph as it represents where exactly half of the acid has been neutralized by the base and converted into salt, while the other half of the acid in the flask remains unreacted. This mixture therefore has equal quantities of a weak acid and its salt, and is known as a **buffer**. We will discuss the special properties of these solutions on pages 723–730, but you can observe directly that the pH in this region is relatively resistant to change in pH on the addition of small amounts of base. This region of the graph is known as the **buffer region**.

The pH at the half-equivalence point gives us an easy way to calculate pK_a for the weak acid because at this point $[acid]_{eqm} = [salt]_{eqm}$.

Consider the equilibrium:

$$HA \rightleftharpoons H^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

As the acid is weak, we can assume that very little of it has ionized at equilibrium, and so

$$[acid]_{eqm} \approx [HA]_{initial}$$

Also we can assume that the salt is fully ionized, and so:

$$[\text{salt}]_{\text{eqm}} \approx [\text{A}^-]_{\text{eqm}}$$

Substituting into the equilibrium expression:

$$K_a = \frac{[\text{H}^+][\text{salt}]_{\text{eqm}}}{[\text{acid}]_{\text{eqm}}}$$

And as $[\text{acid}]_{\text{eqm}} = [\text{salt}]_{\text{eqm}}$ these terms cancel.

$\therefore K_a = [\text{H}^+]$ and $\text{p}K_a = \text{pH}$

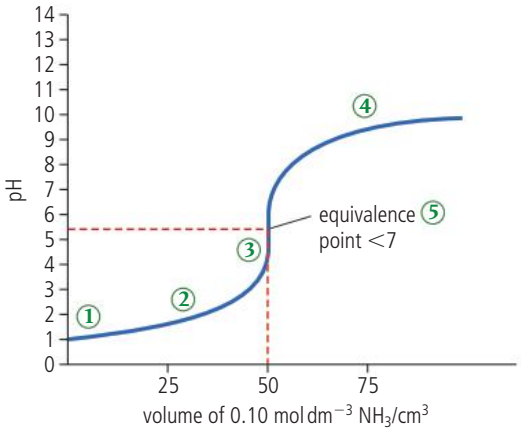
We can read the pH at the half-equivalence point directly from the graph, and so deduce the pK_a of the acid as shown. Note that a parallel calculation of pK_b can be done when a titration is carried out with acid added to base – in this case, at half-equivalence pK_b = pOH.

pH curve of strong acid and weak base

For example:

$$\text{HCl(aq)} + \text{NH}_3\text{(aq)} \rightarrow \text{NH}_4\text{Cl(aq)}$$

pH at equivalence < 7 as cation hydrolysis releases H^+:
$\text{NH}_4^+\text{(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{NH}_4\text{OH(aq)} + \text{H}^+\text{(aq)}$



Titration curve for strong acid–weak base.

The following points can be deduced from the graph as marked:

1. initial pH = 1 (strong acid)
2. pH stays relatively constant through the buffer region to equivalence
3. jump in pH at equivalence from about pH 3.0–7.0
4. after equivalence, the curve flattens out at a fairly low pH (pH of a weak base)
5. **pH at equivalence is < 7.**

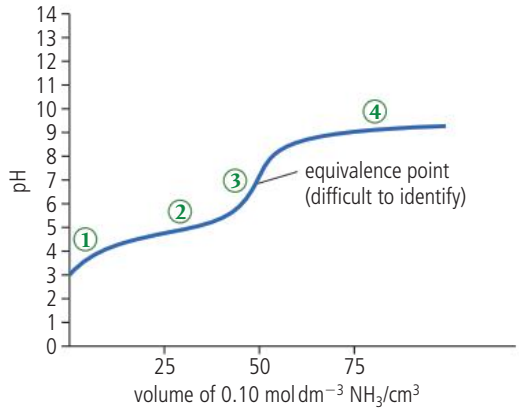
pH curve of weak acid and weak base

For example:

$$\text{CH}_3\text{COOH(aq)} + \text{NH}_3\text{(aq)} \rightleftharpoons \text{NH}_4\text{CH}_3\text{COO(aq)}$$

pH at equivalence is difficult to define.

Titration curve for weak acid–weak base.



The following points can be deduced from the graph:

① initial pH is fairly high (pH of weak acid)

② addition of base causes the pH to rise steadily

③ change in pH at the equivalence point is much less sharp than in the other titrations

④ after equivalence, the curve flattens out at a fairly low pH (pH of weak base).

This titration does not give a clearly defined equivalence point as there is no significant jump in pH to identify due to several equilibria being involved. For this combination of acid and base, it is better to use other techniques, such as conductimetric measurements, to determine the equivalence point.

Challenge yourself

8. What shape would you expect for a graph of conductivity against volume of acid added in a titration of a strong acid with a strong base? How could this be used to determine the equivalence point?

Tool 1 – When collecting data to generate a pH curve, when should smaller volumes of titrant be added between each measurement?

The graphs show that for all four different pH curves, the relationship between pH and the volume of titrant added is not linear. Close to the equivalence point, a small addition of titrant – often just one drop – causes a significant change in the pH. The pH curve will therefore be more accurate if smaller increments of titrant are added between each measurement at this point.

Exercise

Q49. Separate 20.0 cm^3 solutions of a weak acid and a strong acid of the same concentration are titrated with NaOH solution. Which will be the same for these two titrations?

I. initial pH

II. pH at equivalence point

III. volume of NaOH required to reach the equivalence point

A I only **B** II only

C I and II only **D** III only

Q50. Sketch a graph for the pH change as 0.1 mol dm^{-3} HCl(aq) is added to 25 cm^3 of 0.1 mol dm^{-3} NH_3(aq). Mark on your graph the pH at equivalence and the buffer region.

Q51. Titration experiments can be used to deduce the pK_a of a weak acid. Taking the neutralization reaction between CH_3COOH and NaOH as an example, show how the pK_a for the acid can be deduced from *two* different points on the titration curve.

Reactivity 3.1.14 and 3.1.15 – Acid–base indicators

Reactivity 3.1.14 – Acid–base indicators are weak acids, where the components of the conjugate acid–base pair have different colours. The pH of the end point of an indicator, where it changes colour, approximately corresponds to its pKa value.	
Construct equilibria expressions to show why the colour of an indicator changes with pH.	
The generalized formula HInd(aq) can be used to represent the undissociated form of an indicator. Examples of indicators with their pH range are given in the data booklet. Include universal indicator as a mixture of many indicators with a wide pH range of colour change.	Tool 1, Inquiry 2, Reactivity 3.2 – What are some of the similarities and differences between indicators used in acid–base titrations and in redox titrations?

Reactivity 3.1.15 – An appropriate indicator for titration has an end point range that coincides with the pH at the equivalence point.	
Identify an appropriate indicator for titration from the identity of the salt and the pH range of the indicator.	
Distinguish between the terms 'end point' and 'equivalence point'.	

Acid–base indicators signal change in pH

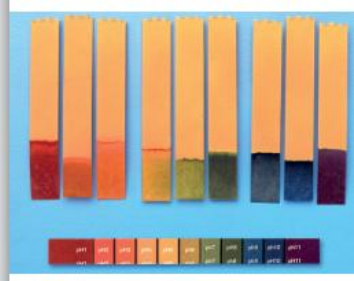
We learned on page 698 that acid–base indicators change colour according to the pH of the solution. They are therefore useful to signal a change in pH.

These indicators are themselves weak acids or weak bases in which the undissociated and dissociated forms have different colours. We will consider only indicators which are weak acids here, and use 'HInd' as a generic acidic indicator. HInd is a weak acid and so exists in equilibrium in solution as follows:

$$\underset{\text{colour A}}{HInd(aq)} \rightleftharpoons H^+(aq) + \underset{\text{colour B}}{Ind^-(aq)}$$

By applying Le Châtelier's principle, we can predict how this equilibrium will respond to a change in the pH of the medium.

- Increasing $[H^+]$: the equilibrium will shift to the left in favour of HInd.
- Decreasing $[H^+]$: the equilibrium will shift to the right in favour of Ind^-.



Universal indicator paper showing a range of colours in response to being dipped in solutions of different pH. The light green is neutral, the orange and red are increasingly acidic, whereas the dark green and purple are increasingly alkaline. Universal indicator is made of a mix of indicators so that it changes colour across the pH range. Other indicators change colour at a fixed end point, as described in this section.

In other words, at low pH colour A will dominate and at higher pH colour B will dominate.

For example, methyl orange is an indicator that is red when placed in a solution of acid such as HCl. As an alkali is added and the pH increases, the indicator changes to yellow. We can show this in an equation using HMet to represent the weak acid and Met^- to represent its conjugate base.

$$HMet(aq) \rightleftharpoons H^+(aq) + Met^-(aq)$$

Indicators are substances that change colour reversibly according to the pH of the solution.

Challenge yourself

9. What structural features might indicators possess that could explain the fact that they change colour on gain or loss of H^+?

Indicators change colour when the pH is equal to their pK_a

The change in colour of methyl orange, known as its **change point** or **end point**, happens in the range pH 3.1–4.4. What determines the pH at which this colour change occurs for an indicator?

We can answer this by considering the equilibrium expression for the above reaction.

The acid dissociation constant is defined as follows:

$$K_a = \frac{[H^+][Ind^-]}{[HInd]}$$

At the point where the equilibrium is balanced between the acid and its conjugate base, that is, where $[Ind^-] = [HInd]$, the indicator is exactly in the middle of its colour change. As these concentration values cancel in the equation:

$$K_a = \frac{[H^+]\cancel{[Ind^-]}}{\cancel{[HInd]}}$$

the expression becomes simplified as $K_a = [H^+]$ or $pK_a = pH$.

The end point of an indicator is the pH at which it changes colour. This occurs at the pH equal to its pK_a.

At this point, the addition of a very small volume of acid or base will shift the equilibrium as described above, and so cause the indicator to change colour – this is its end point. We can see from the equation above that this occurs at the pH equal to the pK_a of the indicator. It follows that different indicators, having different pK_a values, will have different end points and so will change colour at different pH values. A selection of indicator end points is given in Section 18 of the data booklet.

Remember that not all indicators change colour at pH 7. Different indicators change colour at a wide range of pH values, from acidic to basic.

The indicators discussed here are more correctly known as acid–base indicators to distinguish them from indicators used in redox titrations, known as redox indicators. While acid–base titrations follow the transfer of protons from acid to base, redox titrations follow the transfer of electrons from reducing agent to oxidizing agent. The indicators used in both cases signal the equivalence point by changing colour. In acid–base titrations the indicator is always added as an additional component to the reaction mixture, whereas in redox titrations the reaction itself may be accompanied by a colour change, so an external indicator is not always needed. For example, acidified $KMnO_4$ changes colour from purple to colourless as it is reduced, so the reaction acts as its own indicator to signal the equivalence point.



Methyl orange indicator changes colour when added to an acid or alkali. It turns red in acid (left) and yellow in alkali (right).

Tool 1, Inquiry 2, Reactivity 3.2 – What are some of the similarities and differences between indicators used in acid–base titrations and in redox titrations?

Indicators can be used to signal the equivalence point in titrations

Because indicators give us a visible cue when pH changes, they can be used to identify the equivalence points in titrations, given that this is the place where the pH changes most dramatically. An indicator will be effective in signalling the equivalence point of a titration *when its end point coincides with the pH at the equivalence point*. This means that different indicators must be used for different titrations, depending on the pH at the equivalence point.

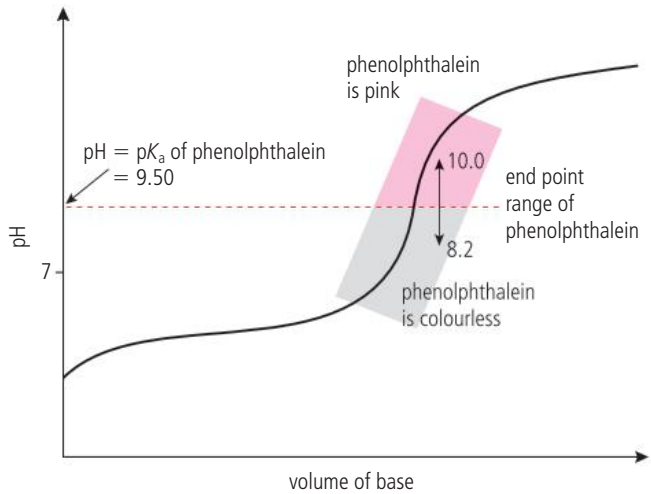
The following steps will help you to choose an appropriate indicator for a particular titration.

1. Determine what combination of weak and strong acid and base are reacting together.
2. Deduce the pH of the salt solution at equivalence from the nature of the parent acid and base.
3. Consult data tables to choose an indicator with end point in the range of the equivalence point.

For example, in the titration of a weak acid with a strong base the equivalence point occurs in the range pH 7–11. An appropriate indicator would therefore be one whose end point lies in this range, such as phenolphthalein (end point range 8.2–10.0) as shown in Figure 6.

Make sure that you do not confuse the terms 'equivalence point' and 'end point'.
- The equivalence point is where stoichiometrically equal amounts of acid and base have neutralized each other.
- The end point is the pH at which the indicator changes colour.

A titration is set up so that the pH of these two points coincides.



R3.1 Figure 6 A weak acid–strong base titration showing how phenolphthalein will change colour and so effectively signal when equivalence is reached.

The table below gives examples of suitable indicators for different titrations.

Reactants in titration	pH range at equivalence	Example of suitable indicators	pK_a	End point range of indicator and colour change
strong acid + strong base	3–11	phenolphthalein	9.60	8.3–10.0 colourless to pink
		methyl orange	3.70	3.1–4.4 red to yellow
weak acid + strong base	7–11	phenolphthalein	9.50	8.2–10.0 colourless to pink
		phenol red	7.90	6.8–8.4 yellow to red
strong acid + weak base	3–7	methyl orange	3.46	3.2–4.4 red to yellow
		bromophenol blue	4.20	3.0–4.6 yellow to blue
weak acid + weak base	this combination of acid and base does not give a significant change in pH at equivalence, so there is no suitable indicator to use here			

Our eyes are able to identify the distinct colour of one form of an indicator (e.g. HInd) when the ratio of its concentration to that of the other form (Ind^-) is about 10:1. So for a transition to be observed from the colour of HInd to the colour of Ind^- at the end point, the ratio of these concentrations must change from 10:1 to 1:10. This represents a range of two pH units. This is why there is a range of ±1 pH units on either side of the value of pK_a at which the eye can definitely notice the colour change occurring. This is given as the **end point range** in the table.

When an indicator is used to detect the equivalence point in a titration, a few drops of it are added to the solution in the conical flask at the start of the procedure. As the other solution is added from the burette and the neutralization reaction occurs, the exact volume where the indicator changes colour can be recorded as the equivalence point. A difference of just one drop of added solution from the burette should produce the change in colour. A good indicator is one that gives a distinct or sharp colour change at the equivalence point.

Nature of Science

Chemical indicators are a valuable tool in quantitative analysis using titrations, but cannot produce pH curves as they do not provide continuous data. pH and conductivity meters and probes provide these data, and improvements in technology have increased their precision. This has led chemists to a better understanding of the ionic changes occurring during neutralization reactions. pH curves have an unusual mathematical form which can be explained by the underlying chemistry and the interpretation of logarithmic scales.

Exercise

Q52. Which statement about indicators is always correct?

A The mid point of an indicator's colour change is at pH = 7.

B The pH range is greater for indicators with higher pK_a values.

C The colour red indicates an acidic solution.

D The pK_a value of an indicator is within its pH range.

Q53. Bromocresol green has a pH range of 3.8–5.4 and changes colour from yellow to blue as the pH increases.

(a) Of the four types of titration shown in the table on page 720, state in which two of these this indicator could be used.

(b) Suggest a value for the pK_a of this indicator.

(c) What colour will the indicator be at pH 3.6?

Reactivity 3.1.16 – Buffer solutions

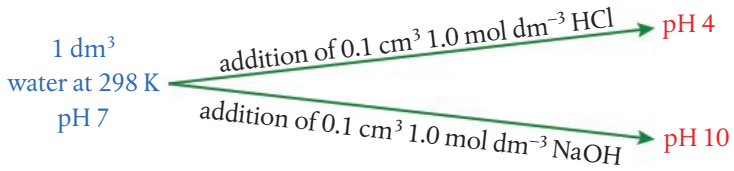
Reactivity 3.1.16 – A buffer solution is one that resists change in pH on the addition of small amounts of acid or alkali.	
Describe the composition of acidic and basic buffers and explain their actions.	
	Reactivity 2.3 – Why must buffer solutions be composed of weak acid or base conjugate systems, not of strong acids or bases?

Buffer solutions help to reduce fluctuations in pH

A buffer refers to something that acts to reduce the impact of one thing on another – a little bit like a shock absorber. For example, buffers in the computer world are areas shared by hardware devices that operate at different speeds. In acid–base chemistry, a buffer acts to reduce the pH impact of added acid or base on a chemical system. It is defined as follows:

A buffer solution is resistant to changes in pH on the addition of small amounts of acid or alkali.

To understand the importance of buffers, it is useful to see how added acid or alkali changes the pH of a non-buffered solution. This is shown below.



Note the volume of acid or alkali added here is only 0.1 cm^3 – just a few drops – yet the pH is changed by 3 units. Evidently, water is very vulnerable to significant fluctuations in its pH and this can have major impacts on chemical reactions in aqueous solutions. Biological systems are able to operate efficiently only within a narrow range of pH, principally because of the effect that pH change has on enzyme action which controls all biochemical reactions. These systems are therefore dependent on buffers, and mammalian blood is an excellent example of a complex natural buffer. Ocean chemistry also includes effective buffer systems, which help to maintain the conditions suitable for life. Many chemical processes such as chemical analysis, synthetic industries and the calibration of instruments depend on effective buffering.

Ocean water has a pH around 8–9, controlled by several buffer systems. The carbonate and hydrogencarbonate ions, existing in equilibrium: $CO_3^{2-} + H+ \rightleftharpoons HCO_3^-$, are crucial to the buffering action. The ocean has the capacity to absorb huge amounts of CO_2 from the atmosphere, so acts as a CO_2 'sink'. But as CO_2 dissolves in the ocean, it makes the water more acidic, releasing H^+ that shifts the equilibrium and reduces the concentration of CO_3^{2-}. Coral reefs are directly affected by this, because they depend on the carbonate ion to build their structures, and have shown serious decline with decreasing carbonate levels. A major concern is that the decrease in pH of the water may set up a feedback loop, reducing the ocean's buffering capacity and so diminishing its ability to take up additional CO_2 from the atmosphere. Many climate scientists believe that ocean acidification is potentially the most serious of all predicted outcomes of increase in atmospheric CO_2.

Note that although buffers maintain the pH close to a set value, they do not all work at pH 7. Different buffer solutions can be made to buffer at almost any pH.

How buffers work

There are two main types of buffer solution – acidic buffers that maintain the pH at a value less than 7, and basic buffers that maintain the pH at a value greater than 7. We will see that both are a *mixture* of two solutions, composed in such a way that they each contain the *two* species of a conjugate acid–base pair. The key to understanding their buffering action is to focus on the equilibria in the solutions and to pick out the species that respond to added H^+ and OH^-. These are shown in red on the next pages.

pH buffers are not the only type of buffer in physical science. Other examples include thermal buffers that help to maintain a constant temperature, and mineral redox buffers which help to stabilize oxidation states in natural rock systems. But buffering pH is by far the most common application, and so the term 'buffer' in chemistry is generally used synonymously with 'pH buffer'.

When giving the definition of a buffer, be sure to include the '*small amount*' for the added acid or alkali. Otherwise you imply that buffers have infinite ability to maintain the pH, which is not the case.



Biodiversity of coral species in Heron Island, Great Barrier Reef, Australia.
Corals depend on carbonate ions in the ocean to build their hard structures made from calcium carbonate.
In many parts of the world, coral reefs are threatened by changes in the ocean chemistry, especially the loss of buffering capacity and decreasing pH that is a result of increasing atmospheric carbon dioxide.

Acidic buffers

Composition of the buffer solution

A buffer solution is made by mixing an aqueous solution of a weak acid with a solution of its salt of a strong alkali. For example:

$$\underset{\text{weak acid}}{CH_3COOH(aq)} \quad \text{and} \quad \underset{\substack{\text{salt of weak acid}\\ \text{with strong alkali}}}{NaCH_3COO(aq)}$$

The following equilibria exist in this aqueous mixture:

$$\text{(i)} \quad CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

$CH_3COOH(aq)$ is a weak acid, so the equilibrium lies to the left.

$$\text{(ii)} \quad NaCH_3COO(aq) \rightarrow Na^+(aq) + CH_3COO^-(aq)$$

$NaCH_3COO(aq)$ is a soluble salt, so is fully dissociated in solution.

Therefore the mixture contains relatively high concentrations of both CH_3COOH and CH_3COO^-, that is, an acid and its conjugate base. These can be considered as 'reservoirs', ready to react with added OH^- and H^+ respectively in neutralization reactions.

Response to added acid and base

- Addition of acid (H^+):

  H^+ will combine with the base CH_3COO^- to form CH_3COOH, therefore removing most of the added H^+.

  $$CH_3COO^-(aq) + H^+(aq) \rightleftharpoons CH_3COOH(aq)$$

- Addition of base (OH^-):

  OH^- will combine with the acid CH_3COOH to form CH_3COO^- and H_2O, so removing most of the OH^-.

  $$CH_3COOH(aq) + OH^-(aq) \rightleftharpoons CH_3COO^-(aq) + H_2O(l)$$

Consequently, as the added H^+ and OH^- are used in these reactions, they do not persist in the solution and so the pH is largely unchanged.

A buffer solution is resistant to changes in pH on the addition of small amounts of acid or alkali.



Bottle containing a buffer solution for maintaining pH at 10.00. Note the fact that this is temperature dependent. Buffers are often supplied as concentrate or as tablets and can be diluted to give a larger volume. Dilution does not change the ratio of acid to salt or base to salt, so the pH remains constant whatever the volume.

Basic buffers

Composition of the buffer solution

Made by mixing an aqueous solution of a weak base with its salt of a strong acid. For example:

$$\underset{\text{weak base}}{NH_3(aq)} \quad \text{and} \quad \underset{\substack{\text{salt of weak base}\\ \text{with strong acid}}}{NH_4Cl(aq)}$$

The following equilibria exist in solution:

$$\text{(i)} \quad NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$NH_3(aq)$ is a weak base, so equilibrium lies to the left.

$$\text{(ii)} \quad NH_4Cl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

$NH_4Cl(aq)$ is a soluble salt, so is fully dissociated in solution.

So here the mixture contains relatively high concentrations of both $NH_3(aq)$ and $NH_4^+(aq)$, that is, a base and its conjugate acid. These species will again act as reservoirs, ready to react with added H^+ and OH^- respectively in neutralization reactions.

Response of buffer to added acid or alkali

- Addition of acid (H^+):

  H^+ will combine with the base NH_3 to form NH_4^+, therefore removing most of the added H^+.

$$NH_3(aq) + H^+ \rightleftharpoons NH_4^+(aq)$$

- Addition of base (OH^-):

  OH^- will combine with the acid NH_4^+ and form NH_3 and H_2O, so removing most of the OH^-.

$$NH_4^+(aq) + OH^-(aq) \rightleftharpoons NH_3(aq) + H_2O(l)$$

So, as with the acidic buffer, the removal of the added H^+ and OH^- by reactions with the components of the buffer solution means that they do not persist in the solution and so do not alter the pH.

In summary

Buffer solutions are a mixture containing both an acid and a base of a weak conjugate pair. The buffer's acid neutralizes added alkali, and the buffer's base neutralizes added acid, and so pH change is resisted.

These reactions depend on the reversible nature of the equilibria of the weak acid or base conjugate systems within the buffer solution, as this enables them to respond to changes in $[H^+]$ and $[OH^-]$. Strong acids or bases, because they ionize completely, do not exist as equilibria in solution, so cannot carry out reversible reactions to respond to both added $[H^+]$ and $[OH^-]$ ions. This is why buffers can only be composed of weak acids and bases.

SKILLS

Preparing a buffer solution. Full details of how to carry out this experiment with a worksheet are available in the eBook.

Reactivity 2.3 – Why must buffer solutions be composed of weak acid or base conjugate systems, not of strong acids or bases?

Exercise

Q54. Which mixture would produce a buffer solution when dissolved in 1.0 dm^3 of water?

A 0.50 mol of CH_3COOH and 0.50 mol of NaOH
B 0.50 mol of CH_3COOH and 0.25 mol of NaOH
C 0.50 mol of CH_3COOH and 1.00 mol of NaOH
D 0.50 mol of CH_3COOH and 0.25 mol of $Ba(OH)_2$

Q55. A buffer solution can be prepared by adding which of the following to 50 cm^3 of 0.10 mol dm^{-3} $CH_3COOH(aq)$?

I. 50 cm^3 of 0.10 mol dm^{-3} $NaCH_3COO(aq)$
II. 25 cm^3 of 0.10 mol dm^{-3} $NaOH(aq)$
III. 50 cm^3 of 0.10 mol dm^{-3} $NaOH(aq)$

A I only **B** I and II only **C** II and III only **D** I, II and III

Reactivity 3.1.17 – Buffer composition and pH

Reactivity 3.1.17 – The pH of a buffer solution depends on both:

- **the pK_a or pK_b of its acid or base**
- **the ratio of the concentration of acid or base to the concentration of the conjugate base or acid.**

Solve problems involving the composition and pH of a buffer solution, using the equilibrium constant.

Include explanation of the effect of dilution of a buffer.	Reactivity 2.3 – How does Le Châtelier's principle enable us to interpret the behaviour of indicators and buffer solutions?

Reactivity 2.3 – How does Le Châtelier's principle enable us to interpret the behaviour of indicators and buffer solutions?

SKILLS

Weak acid–strong base titration with a pH-sensor – determination of the concentration of ethanoic acid in vinegar. Full details of how to carry out this experiment with a worksheet are available in the eBook.

Different buffers can be prepared for different pH values

The pH of a buffer solution will depend on the interactions among its components. We will consider here an acidic buffer made of the generic weak acid HA and its salt MA.

The equilibria that exist in the buffer will be:

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

$$MA(aq) \rightarrow M^+(aq) + A^-(aq)$$

We can make two approximations, based on the interpretation of these reactions:

1. The dissociation of the weak acid is so small that it can be considered to be negligible. So we can make the approximation

$$[HA]_{initial} \approx [HA]_{equilibrium}$$

2. The salt is considered to be fully dissociated into its ions. So we can approximate:

$$[MA]_{initial} \approx [A^-]_{equilibrium}$$

The equilibrium expression for the acid is:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Therefore

$$[H^+] = K_a \frac{[HA]}{[A^-]}$$

remembering that all values in this expression must be *equilibrium* concentrations.

From the approximations explained above, we know that $[HA]_{equilibrium} \approx [HA]_{initial}$ and $[A^-]_{equilibrium} \approx [MA]_{initial}$, so we can substitute these values as follows:

$$[H^+] = K_a \frac{[HA]_{initial}}{[MA]_{initial}}$$

which is usually given as:

$$[H^+] = K_a \frac{[acid]}{[salt]}$$

By taking the negative logarithms of both sides of the equation, we can derive:

$$pH = pK_a + \log_{10} \frac{[salt]}{[acid]}$$

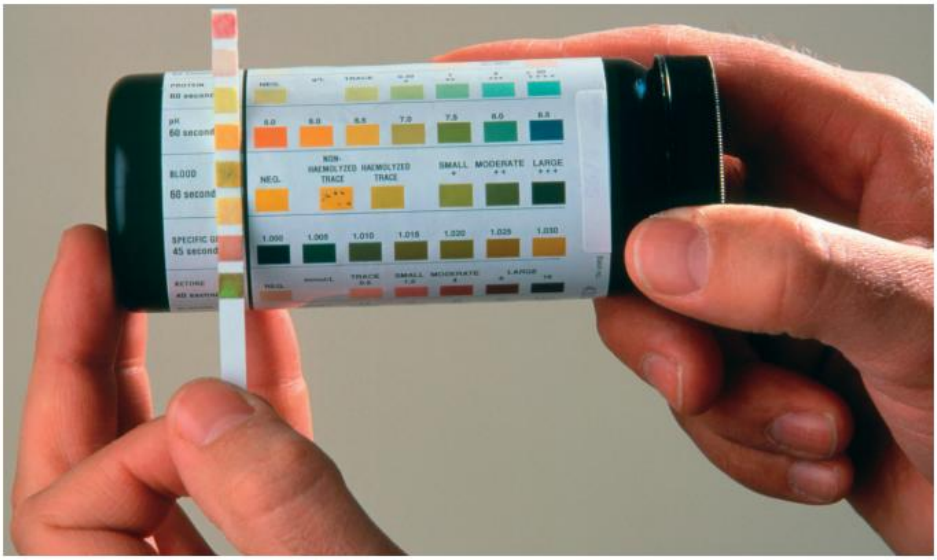
For basic buffer solutions the equivalent equations are:

$$[OH^-] = K_b \frac{[base]}{[salt]} \quad \text{and} \quad pOH = pK_b + \log_{10} \frac{[salt]}{[base]}$$

These expressions show that the pH of a buffer solution can be determined directly from:

- the pK_a or pK_b values of its component acid or base
- the ratio of initial concentrations of acid and salt used to prepare the buffer.

The expressions for the calculation of the pH of a buffer solution are often known as the Henderson–Hasselbalch equations. Joseph Henderson (1878–1942) was an American biochemist who developed equations showing that acid–base balance in the blood is regulated by buffers. Karl Hasselbalch (1874–1962), a Danish chemist and a pioneer in the use of pH measurement in medicine, converted the equations to logarithmic form in his work on studying acidosis in the blood. We now know that different buffers in the blood work together to keep the pH tightly controlled at 7.4. Any fluctuation in this value is so crucial that pH levels below 7.0 (acidosis) and above 7.8 (alkalosis) are, in the words of the medical profession, 'incompatible with life'.



Urine analysis using a multiple test stick against a reference chart. The pads test for pH as well as for various components of the urine. Body fluids such as urine are effectively buffered for pH, so alterations in the urine pH can provide insights into medical conditions and disease.

$$pH = pK_a + \log_{10} \frac{[salt]}{[acid]}$$

$$pOH = pK_b + \log_{10} \frac{[salt]}{[base]}$$

Worked example

Calculate the pH of a buffer solution at 298 K, prepared by mixing 25 cm^3 of 0.10 mol dm^{-3} ethanoic acid, CH_3COOH, with 25 mol dm^{-3} of 0.10 cm^3 sodium ethanoate, $Na^+CH_3COO^-$.

K_a of $CH_3COOH = 1.8 \times 10^{-5}$ at 298 K.

Solution

pK_a of $CH_3COOH = -\log_{10}(1.8 \times 10^{-5}) = 4.74$

As there are equal volumes and concentrations of CH_3COOH and $NaCH_3COO$, then [acid] = [salt].

$$pH = pK_a + \log_{10} \frac{[salt]}{[acid]} = 4.74 + \log_{10}(1) = 4.74 + 0 = 4.74$$

Note that $\log_{10}(1) = 0$

In a buffer solution, when [acid] = [salt], pH = pK_a
When [base] = [salt], pOH = pK_b

This example shows that when a buffer solution contains equimolar amounts of acid and salt (or base and salt), the ratio of [acid]:[salt] = 1, and $\log_{10}(1) = 0$, which means

pH = pK_a or pOH = pK_b.

This relationship is extremely useful when it comes to preparing buffers of a specified pH. All we have to do is choose an acid with a pK_a value close to the required pH and then, if necessary, adjust the concentrations of acid and salt accordingly.

Worked example

How would you prepare a buffer solution of pH 3.75 starting with methanoic acid (HCOOH) and NaOH?

Solution

pK_a(HCOOH) = 3.75, so a buffer with equal amounts in moles of this acid and its salt NaHCOO will have pH = 3.75.

This equimolar solution is prepared by reacting the acid with enough NaOH so that one half of it is converted into salt, and therefore [HCOOH] = [$HCOO^-$].

This is explained below.

An equimolar solution, one that contains equal amounts of acid or base and its salt, can be prepared by a neutralization reaction in which one half of the starting acid or base is converted into salt. After the reaction, the mixture will contain the unreacted acid or base and its salt in equimolar amounts. An example of this is illustrated below using simple mole ratios.

	$CH_3COOH(aq)$	+ $NaOH(aq)$	→ $NaCH_3COO(aq)$	+ $H_2O(l)$
initial amounts in moles	2	1	0	0
change during reaction	−1	−1	+1	+1
final amounts in moles	1	0	1	1

The final mixture, containing equal amounts of the weak acid CH_3COOH and its salt $NaCH_3COO$, is a buffer solution.

Alternatively, the buffer can be prepared by mixing the acid directly with an appropriate amount of its salt.

Worked example

How much 0.100 mol dm^{-3} butanoic acid solution and solid potassium butanoate should be used to make 1.00 dm^3 of pH 5.00 buffer solution? State the assumptions made in the calculation. M(potassium butanoate) = 126.12 g mol^{-1}.

Solution

pK_a (butanoic acid) = 4.83

$$pH = pK_a + \log_{10}\frac{[A^-]}{[HA]}$$

$$\therefore 5.00 - 4.83 = \log_{10} \frac{(\text{butanoate ion})}{0.100\ \text{mol dm}^{-3}}$$

taking antilogs of both sides gives:

$$10^{0.17} = \frac{(\text{butanoate ion})}{0.100\ \text{mol dm}^{-3}} = 1.479$$

$$\therefore [\text{butanoate ion}] = 0.1479\ \text{mol dm}^{-3}$$

The molar mass of potassium butanoate is $126.12\ \text{g mol}^{-1}$

$\therefore 1.00\ \text{dm}^3$ of $0.1479\ \text{mol dm}^{-3}$ solution $= 0.1479\ \text{mol} \times 126.12\ \text{g mol}^{-1} = 18.65\ \text{g}$

So 18.7 g potassium butanoate should be added to $1.00\ \text{dm}^3$ of $0.10\ \text{mol dm}^{-3}$ butanoic acid.

The following assumptions were made:

- $[\text{butanoate ion}]_{\text{equilibrium}} = [\text{potassium butanoate}]_{\text{initial}}$
- $[\text{butanoic acid}]_{\text{equilibrium}} = [\text{butanoic acid}]_{\text{initial}}$
- no volume change occurs on mixing the solution.

Factors that can influence buffers

Now that we know what determines the pH of a buffer, we can predict how it will respond in certain situations.

Dilution

K_a and K_b are equilibrium constants and so are not changed by dilution. Dilution also does not change the *ratio* of acid or base to salt concentration, as both components will be decreased by the same amount. Therefore diluting a buffer does not change its pH.

Nonetheless, diluting a buffer does alter the amount of acid or base it can absorb without significant changes in pH – the so-called **buffering capacity**. This depends on the molar concentrations of its components, so it decreases as the concentrations are decreased by dilution.

Dilution does not change the pH of a buffer, but it does lower its buffering capacity.

Challenge yourself

10. Contrast and explain how the pH of each of the following types of solution responds to dilution:

(a) strong acid

(b) weak acid

(c) buffer.

Temperature

As temperature affects the values of K_a and K_b, it accordingly affects the pH of the buffer. This is why a constant temperature should be maintained in all work involving buffers, such as calibration of pH meters. Temperature fluctuations must also be minimized in many medical procedures such as blood transfusions due to the effect on the buffers in the blood.

At high altitudes, where the air pressure and therefore the concentration of O_2 are significantly less than at sea level, some people suffer from altitude sickness. This is a potentially fatal condition that involves an increase in the pH of the blood (alkalosis). The causes are complex but stem from a decrease in CO_2 in the blood, resulting from hyperventilation. Drugs that can alleviate the symptoms lower the concentration of HCO_3^- through stimulating its excretion by the kidneys. This shifts the equilibrium

$$CO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

to the right and so acidifies the blood. Indigenous cultures in the Andes have used coca leaves for centuries to alleviate mild symptoms of altitude sickness, although the way in which this may be achieved is not fully understood.



Climbers in the Andes, Peru. At high altitudes like this, the lower concentration of oxygen in the air makes it more difficult to do vigorous exercise. The efficient buffering of blood can be disrupted by breathing changes due to the low level of available oxygen. Climbers need to acclimatize in order to avoid problems caused by alkalosis of the blood.

Worked example

State whether each of the following mixtures will form a buffer solution when dissolved in 1.00 dm^3 of water.

(a) 0.20 mol $NaHCO_3$ and 0.20 mol Na_2CO_3

(b) 0.20 mol CH_3COOH and 0.10 mol HCl

(c) 0.20 mol NH_3 and 0.10 mol HCl

(d) 0.10 mol H_3PO_4 and 0.20 mol NaOH

Solution

(a) Solution contains HCO_3^- and CO_3^{2-}, a conjugate pair, so it is a buffer.

(b) Solution contains two acids, so it is not a buffer.

(c) NH_3 and HCl react together to form 0.10 mol NH_4Cl, with 0.10 mol NH_3 unreacted, so it is a buffer.

(d) H_3PO_4 and NaOH react together to form 0.20 mol Na_2HPO_4

$$H_3PO_4(aq) + 2NaOH(aq) \rightarrow Na_2HPO_4 + 2H_2O(l)$$

so it is not a buffer.

We have seen that the action of both indicators and buffer solutions depends on equilibria which are able to respond to changing conditions. Specifically, the equilibria shift to the left or the right depending on the concentrations of H^+ and OH^- ions in the solution. These responses to changes in pH can be predicted by the application of Le Châtelier's principle – the response of the system to minimize the effects of the change.

Exercise

Q56. State and explain which of the following has the greater buffering capacity:

(i) 100 cm^3 0.30 mol dm^{-3} HNO_2 and 0.30 mol dm^{-3} $NaNO_2$ or

(ii) 100 cm^3 0.10 mol dm^{-3} HNO_2 and 0.10 mol dm^{-3} $NaNO_2$.

Q57. Given 100 cm^3 of 0.05 mol dm^{-3} methanoic acid, HCOOH, what volume of 0.05 mol dm^{-3} NaOH would you need to add to prepare a buffer of pH 4.23? pK_a of HCOOH = 1.77×10^{-4}.

HL end

Guiding Question revisited

What happens when protons are transferred?

In this chapter we have seen:

- A proton is $[H^+]$.
- Brønsted–Lowry acids are proton donors and Brønsted–Lowry bases are proton acceptors.
- A conjugate acid–base pair differs by a single proton.
- Amphiprotic species can act as both Brønsted–Lowry acids and bases.
- The pH scale is the negative base 10 logarithm of $[H^+]$.
- The ion product constant of water, K_w, is temperature dependent. It shows the inverse relationship between $[H^+]$ and $[OH^-]$.
- Strong acids and bases are fully ionized in solution, weak acids and bases are only partially ionized.
- Acids and bases react together in neutralization reactions to form salts. The overall reaction is $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ which is exothermic.
- The equivalence point in a titration is where the acid and base have exactly neutralized each other in a stoichiometric ratio.
- pH curves show the change in pH as an acid and base react together in titration.
- Neutralization involving a strong acid and strong base gives a characteristic pH curve. The pH at the equivalence point is 7.

HL

- The pOH scale is the negative base 10 logarithm of $[OH^-]$.
- Acid and base dissociation constants, K_a and K_b, quantify the equilibrium position of weak acids and bases. They are often expressed as their negative logarithms pK_a and pK_b.
- For a conjugate acid–base pair, $K_a \times K_b = K_w$.
- The pH of salt solutions depends on the extent of ion hydrolysis of its ions, which are the conjugates of the parent acid and base.
- Different combinations of strengths of acids and bases give characteristic pH curves.

- Acid–base indicators are weak acids that change colour according to the pH. The end point of an indicator occurs at the pH equal to its pK_a.
- An acid–base indicator in a titration is selected so that its end point occurs at the pH of the equivalence point.
- A buffer solution resists change in pH on the addition of small amounts of acid or alkali.
- The pH of a buffer solution depends on the pK_a or pK_b of its component acid or base and on the ratio of its conjugate acid–base components.

HL end

Practice questions

1. Which is a conjugate Brønsted–Lowry acid–base pair?

$$CH_3COOH(aq) + H_2O(l) \rightarrow CH_3COO^-(aq) + H_3O^+(aq)$$

A CH_3COO^- / H_3O^+ **B** H_2O / CH_3COO^-

C H_2O / H_3O^+ **D** CH_3COOH / H_2O

2. Which of the following can be described as amphiprotic?

A OH^- B NH_4^+ **C** $BeCl_2$ **D** SO_4^{2-}

3. CH_3OH is a very weak Brønsted–Lowry acid. What is true of the ion CH_3O^-?

A It is a good proton donor.

B It will be present in high concentration in CH_3OH at equilibrium.

C It is a strong Brønsted–Lowry base.

D It is a stronger Brønsted–Lowry acid than CH_3OH.

4. Two acids, X and Y, both of concentration 0.20 mol dm^{-3} have pH values of 2 and 4 respectively. Which of the following statements is true?

A X is a stronger acid than Y.

B Y is more dilute than X.

C X contains more undissociated molecules than Y.

D Y contains a higher concentration of H^+ ions than X.

5. Which of the following statements is the defining property of a Brønsted–Lowry base?

A donates protons **B** produces OH^- ions

C conducts electricity **D** accepts H^+ ions

6. The pH scale can be used to distinguish between different acids and bases in the laboratory.

(a) You are provided with five unlabelled bottles which are known to contain 0.10 mol dm^{-3} solutions of each of the following:

HCOOH(aq), KCl(aq), HNO_3(aq), NaOH(aq), NH_3(aq)

(i) Describe **two** ways in which you could measure the pH of the solutions. (2)

(ii) Suggest expected pH values for each solution. (3)

(b) **(i)** In the laboratory, some solid sodium hydrogencarbonate was added to an aqueous solution of hydrochloric acid. Formulate an equation for this reaction including state symbols, and predict what you would expect to observe during the reaction. (5)

(ii) The hydrogencarbonate can be described as amphiprotic. Explain this statement with reference to the Brønsted–Lowry theory of acids and bases. (4)

(c) Conductivity can be used to distinguish between strong and weak acids of the same concentration. Justify the claim that the use of a conductivity meter is a more scientifically acceptable approach than the use of an indicator. (2)

(Total 16 marks)

7. **(a)** Define the terms *acid* and *base* according to the Brønsted–Lowry theory. Distinguish between a weak base and a strong base. State **one** example of a weak base. (3)

(b) Weak acids in the environment may cause damage. Identify a weak acid in the environment *and* outline **one** of its effects. (2)

(Total 5 marks)

8. Water is an important substance that is abundant on the Earth's surface.

(a) State the expression for the ionic product constant of water, K_w. (1)

(b) Explain why even a very acidic aqueous solution still has some OH^- ions present in it. (1)

(c) State and explain the effect of increasing temperature on the value of K_w given that the ionization of water is an endothermic process. (3)

(d) State and explain the effect of increasing temperature on the pH of water. (2)

(Total 7 marks)

HL

9. The K_b value for a base is 5.0×10^{-2} mol dm^{-3} at 298 K. What is the K_a value for its conjugate acid at this temperature?

A 5.0×10^{-2} **B** 2.0×10^{-6} **C** 2.0×10^{-12} **D** 2.0×10^{-13}

10. Equal volumes and concentrations of hydrochloric acid and ethanoic acid are titrated with sodium hydroxide solutions of the same concentration. Which statement is correct?

A The initial pH values of both acids are equal.

B At the equivalence points, the solutions of both titrations have pH values of 7.

C The same volume of sodium hydroxide is needed to reach the equivalence point.

D The pH values of both acids increase equally until the equivalence points are reached.

11. Bromophenol blue changes from yellow to blue over the pH range of 3.0 to 4.6. Which statement is correct?

A Molecules of bromophenol blue, HInd, are blue.

B At pH < 3.0, a solution of bromophenol blue contains more ions, Ind^-, than molecules, HInd.

C The pK_a of bromophenol blue is between 3.0 and 4.6.

D Bromophenol blue is a suitable indicator to titrate ethanoic acid with potassium hydroxide solution.

12. What is the K_b expression for the reaction of ethylamine with water?

A $K_b = [CH_3CH_2NH_3^+][OH^-]$

B $K_b = \dfrac{[CH_3CH_2NH_3^+][OH^-]}{[CH_3CH_2NH_2]}$

C $K_b = \dfrac{[CH_3CH_2NH_3^+][H_2O]}{[CH_3CH_2NH_2]}$

D $K_b = [CH_3CH_2NH_2][H_2O]$

13. What is K_b for the aqueous fluoride ion given that K_w is 1.0×10^{-14} and K_a for HF is 6.8×10^{-4} at 298 K?

A $\dfrac{1}{6.8 \times 10^{-4}}$

B $(6.8 \times 10^{-4})(1.0 \times 10^{-14})$

C $\dfrac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}}$

D 6.8×10^{-4}

14. The indicator HInd is used in a titration between an acid and base. Which statement about the dissociation of the indicator, HInd, is correct?

$$\underset{\text{colour A}}{HInd(aq)} \rightleftharpoons \underset{\text{colour B}}{H^+(aq) + Ind^-(aq)}$$

A In a strongly alkaline solution, colour B would be observed.

B In a strongly acidic solution, colour B would be observed.

C $[Ind^-]$ is greater than [HInd] at the equivalence point.

D In a weakly acidic solution colour B would be observed.

15. Which salt dissolves in water to form an acidic solution?

A ammonium nitrate

B sodium ethanoate

C potassium chloride

D sodium hydrogencarbonate

16. Which of the following mixtures of equimolar solutions produces a buffer with pH < 7 at 298 K?

A 50 cm^3 HCl(aq) and 150 cm^3 NH_3(aq)

B 50 cm^3 CH_3COOH(aq) and 50 cm^3 HCl(aq)

C 100 cm^3 CH_3COOH(aq) and 50 cm^3 NaOH(aq)

D 50 cm^3 CH_3COOH(aq) and 50 cm^3 NH_3(aq)

17. Hypochlorous acid, HOCl(aq), is an example of a weak acid.

(a) State the expression for the ionic product constant of water, K_w. (1)

(b) A household bleach contains sodium hypochlorite, NaOCl(aq), at a concentration of 0.705 mol dm^{-3}. The hypochlorite ion, OCl^-(aq), is a weak base.

$$OCl^-(aq) + H_2O(l) \rightleftharpoons HOCl(aq) + OH^-(aq)$$

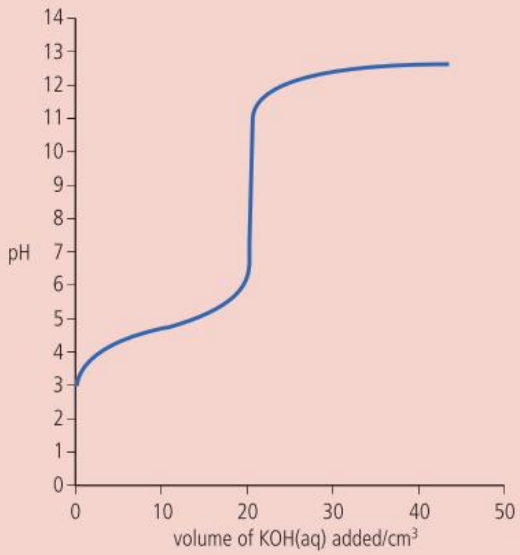
(i) The pK_a value of HOCl(aq) is 7.52. Determine the K_b value of OCl^-(aq) assuming a temperature of 298 K. (1)

(ii) Determine the concentration of OH^-(aq), in mol dm^{-3}, at equilibrium and state **one** assumption made in arriving at your answer other than a temperature of 298 K. (3)

(iii) Calculate the pH of the bleach. (2)

(Total 7 marks)

18. (a) (i) The graph below indicates the pH change during the titration of 20.0 cm^3 of 0.100 mol dm^{-3} of CH_3COOH(aq) with 0.100 mol dm^{-3} KOH(aq). From the graph, identify the volume of KOH(aq) and the pH at the equivalence point. (2)



(ii) Explain how the graph could be used to determine the pK_a of ethanoic acid *and* determine the pK_a value for these data. [2]

(iii) Sketch a graph, similar to the graph above, to indicate the change in pH during a titration of 25.0 cm^3 of 0.100 mol dm^{-3} HNO_3(aq) with 0.100 mol dm^{-3} OH^-(aq). On your graph, clearly indicate the starting pH value, the equivalence point, the pH at the equivalence point, and the final pH reached. (4)

(b) (i) Describe how an indicator works. (3)

(ii) Using Section 18 of the data booklet, identify the most appropriate indicator for the titration of ethanoic acid with potassium hydroxide. Explain your choice. (2)

(Total 13 marks)

19. Ammonia can be converted into nitric acid, $HNO_3(aq)$ and hydrocyanic acid, HCN(aq). The pK_a of hydrocyanic acid is 9.21.

(a) Distinguish between the terms *strong acid* and *weak acid* and state the equations used to show the dissociation of each acid in aqueous solution. (3)

(b) Deduce the expression for the ionization constant, K_a, of hydrocyanic acid and calculate its value from the pK_a value given. (2)

(c) Use your answer from part **(b)** to calculate the $[H^+]$ and the pH of an aqueous solution of hydrocyanic acid of concentration 0.108 mol dm^{-3}. State **one** assumption made in arriving at your answer. (4)

(Total 9 marks)

20. (a) Buffer solutions resist small changes in pH. A phosphate buffer can be made by dissolving NaH_2PO_4 and Na_2HPO_4 in water, in which NaH_2PO_4 produces the acidic ion and Na_2HPO_4 produces the conjugate base ion.

(i) Deduce the acid and conjugate base ions that make up the phosphate buffer and state the ionic equation that represents the phosphate buffer. (3)

(ii) Describe how the phosphate buffer minimizes the effect of the addition of a strong base, $OH^-(aq)$, to the buffer. Illustrate your answer with an ionic equation. (2)

(iii) Describe how the phosphate buffer minimizes the effect of the addition of a strong acid, $H^+(aq)$, to the buffer. Illustrate your answer with an ionic equation. (2)

(b) A 0.10 mol dm^{-3} ammonia solution is placed in a flask and titrated with a 0.10 mol dm^{-3} hydrochloric acid solution.

(i) Explain why the pH of the ammonia solution is less than 13. (2)

(ii) Estimate the pH at the equivalence point for the titration of hydrochloric acid with ammonia. Explain your reasoning. (2)

(iii) State the equation for the reaction of ammonia with water and write the K_b expression for $NH_3(aq)$. (2)

(iv) When half the ammonia has been neutralized (the half-equivalence point), the pH of the solution is 9.25. Deduce the relationship between $[NH_3]$ and $[NH_4^+]$ at the half-equivalence point. (1)

(v) Determine pK_b and K_b for ammonia based on the pH at the half-equivalence point. (3)

(vi) Describe the significance of the half-equivalence point in terms of its effectiveness as a buffer. (1)

(Total 18 marks)

21. Hydrazine, N_2H_4, reacts with water in a similar way to ammonia. (The association of a molecule of hydrazine with a second H^+ is so small it can be ignored.)

$$N_2H_4(aq) + H_2O(l) \rightarrow N_2H_5^+(aq) + OH^-(aq) \quad pK_b \text{ (hydrazine)} = 5.77$$

(a) Calculate the pH of a 0.0100 mol dm^{-3} solution of hydrazine. (3)

(b) Suggest a suitable indicator for the titration of hydrazine solution with dilute sulfuric acid using Section 18 of the data booklet. (1)

(Total 4 marks)

22. The concentration of a solution of a weak acid, such as ethanedioic acid, can be determined by titration with a standard solution of sodium hydroxide, NaOH(aq).

(a) Distinguish between a weak acid and a strong acid. (1)

(b) Suggest why it is more convenient to express acidity using the pH scale instead of using the concentration of hydrogen ions. (1)

(c) 5.00 g of an impure sample of hydrated ethanedioic acid, $(COOH)_2.2H_2O$, was dissolved in water to make 1.00 dm^3 of solution. 25.0 cm^3 samples of this solution were titrated against a 0.100 mol dm^{-3} solution of sodium hydroxide using a suitable indicator.

$$(COOH)_2(aq) + 2NaOH(aq) \rightarrow (COONa)_2(aq) + 2H_2O(l)$$

The mean value of the titre was 14.0 cm^3.

(i) Use the data booklet to suggest a suitable indicator for this titration. (1)

(ii) Calculate the amount, in mol, of NaOH in 14.0 cm^3 of 0.100 mol m^{-3} solution. (1)

(iii) Calculate the amount, in mol, of ethanedioic acid in each 25.0 cm^3 sample. (1)

(iv) Determine the percentage purity of the hydrated ethanedioic acid sample. (3)

(Total 8 marks)

23. Ammonia is a weak base.

(a) Calculate the pH of a 1.50 mol dm^{-3} solution of ammonia at 298 K to two decimal places using the data booklet. (2)

(b) A buffer solution is made using 25.0 cm^3 of 0.500 mol dm^{-3} hydrochloric acid, HCl(aq), and 20.0 cm^3 of 1.50 mol dm^{-3} ammonia solution, NH_3(aq).

(i) Describe the meaning of the term buffer solution. (2)

(ii) Determine the pH of the buffer solution at 298 K. (4)

(c) A 1.50 mol dm^{-3} solution of ammonia is added to 25.0 cm^3 of a 0.500 mol dm^{-3} hydrochloric acid solution in a titration experiment.

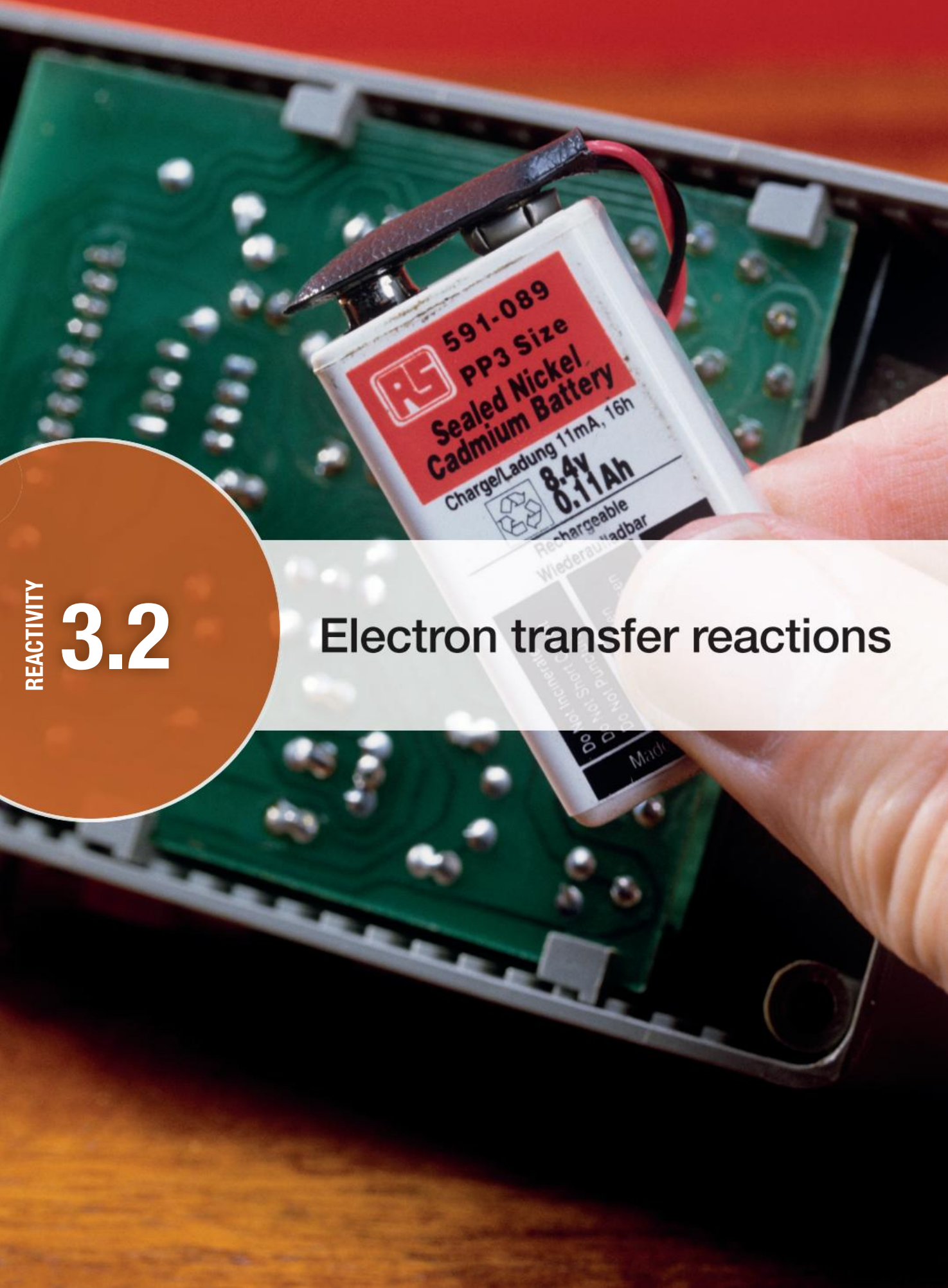
(i) Calculate the total volume of the solution at the equivalence point. (1)

(ii) Calculate the pH of the solution at the equivalence point using the data booklet. (4)

(iii) Identify a suitable indicator for this titration using the data booklet. (1)

(Total 14 marks)

HL end



REACTIVITY

3.2 Electron transfer reactions


A nickel–cadmium battery. This battery can be recharged by reversing a spontaneous reaction of electron transfer.

Guiding Question

What happens when electrons are transferred?

Oxygen makes up only about 20% by volume of the air, yet it is the essential component for many reactions. Without it, fuels would not burn, iron would not rust, and we would be unable to obtain energy from our food molecules through respiration. Indeed, animal life on the planet did not evolve until a certain concentration of oxygen had built up in the atmosphere over 600 million years ago. The term oxidation has been in use for a long time to describe these and other reactions where oxygen is involved in chemical change. Closer inspection of these reactions shows that species generally lose electrons when they react with oxygen and so the term oxidation has been broadened to include any reaction which involves the loss of electrons. Oxidation, though, can only be half of the story, as the electrons which are lost cannot disappear. They must be taken away by another species which we say is **reduced**. The transfer of electrons from one species to another is the basis for all **redox** reactions.

If a redox reaction is set up such that the electron transfer between the reactants can only occur through an external circuit, the electrons produce an electric current. A simple **voltaic cell** or **battery** works in this way and converts chemical energy to electrical energy. This energy change can be reversed if electrical energy is used to drive electrons to force redox reactions to take place against their spontaneous flow. This process of **electrolysis** can be used to break down stable compounds into their elements. These applications of redox reactions are collectively known as **electrochemical cells**.

Redox reactions have truly revolutionized our world. They form the basis of great industries, such as steel-making and aluminium extraction, and it would be hard to imagine life without the many battery-powered mobile devices we use every day. An understanding of oxidation and reduction is therefore at the heart of the study of a large branch of chemistry both in the laboratory and beyond.

Reactivity 3.2.1 – Redox reactions

Reactivity 3.2.1 – Oxidation and reduction can be described in terms of electron transfer, change in oxidation state, oxygen gain/loss or hydrogen loss/gain.	
Deduce oxidation states of an atom in a compound or an ion.	
Identify the oxidized and reduced species and the oxidizing and reducing agents in a chemical reaction.	
Include examples to illustrate the variable oxidation states of transition element ions and of most main group non-metals.	Structure 3.1 – What are the advantages and limitations of using oxidation states to track redox changes?
Include the use of oxidation numbers in the naming of compounds.	Structure 2.3 – The surface oxidation of metals is often known as corrosion. What are some of the consequences of this process?

Different definitions of oxidation and reduction

Oxidation is the loss of electrons

Oxygen is the most reactive gas in air and an essential component of many reactions. The term oxidation has been in use for a long time to describe reactions where oxygen is involved in chemical change. For example, magnesium metal combines with oxygen to form magnesium oxide which, as discussed in Structure 2.1, is an ionic solid consisting of Mg^{2+} ions and O^{2-} ions. The energy released in the reaction is emitted as light and heat.



Magnesium ribbon burning in air. The magnesium metal is oxidized to form magnesium oxide (MgO).

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

In this oxidation reaction each magnesium atom has lost two electrons and formed a doubly charged Mg^{2+} ion. Magnesium undergoes the same electron loss when it reacts with other non-metals such as chlorine:

$$Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$$



Magnesium reacting with chlorine.

The product, magnesium chloride, consists of Mg^{2+} ions and Cl^- ions. Each magnesium atom has again lost two electrons to become an Mg^{2+} ion. Although no oxygen is involved in the second reaction the magnesium has changed in the same way. This suggests that the meaning of the term oxidation can be extended to any reactions which involve *the loss of electrons*.

Reduction is the gain of electrons

Reduction traditionally referred to the extraction of a metal from its ore: the ore was *reduced* to the metal. Copper oxide can be reduced to copper by heating it with a more reactive metal.



Flames resulting from a reaction between magnesium metal and copper oxide. The more reactive magnesium reacts with the copper oxide to form magnesium oxide and copper metal.

$$Mg(s) + CuO(g) \rightarrow MgO(s) + Cu(s)$$

The magnesium has again been oxidized and lost electrons. The copper ions have been reduced and gained electrons to form Cu atoms. This suggests that reduction involves the gain of electrons. Electrons have been transferred from the Mg to the Cu^{2+} ions. More generally we can see that in all electron transfer reactions one species will lose electrons and another species will gain them. Oxidation and reduction must both occur together, so these reactions are also redox reactions.

Oxidation is the loss of electrons. Reduction is the gain of electrons.

It may help you to remember OILRIG: Oxidation Is Loss (of electrons), Reduction Is Gain (of electrons).

Oxidation is hydrogen loss and reduction is hydrogen gain

Hydrogen sulfide solution can react with oxygen to give different products.

$$H_2S(aq) + 2O_2(g) \rightarrow H_2SO_4(aq)$$

$$2H_2S(aq) + O_2(g) \rightarrow 2S(s) + H_2O(l)$$

It seems reasonable to say that the hydrogen sulfide has been oxidized in both cases, although it has lost hydrogen rather than gained oxygen in the second reaction. As the hydrogen is often removed to form water from compounds containing hydrogen, the term oxidation can also be applied to the removal of hydrogen.

Conversely, reduction refers to the addition of hydrogen. For example, chlorine is reduced when it reacts with hydrogen:

$$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$$

Oxidation is the removal of hydrogen. Reduction is the addition of hydrogen.

Oxidation is an increase in the oxidation state and reduction is a decrease in the oxidation state

In reactions involving ions it is easy to identify which elements have been oxidized and which reduced. In the earlier example, magnesium was oxidized as it changed from atoms to ions with a positive charge, and copper ions were reduced as their charge was decreased from 2+ to 0. This suggests that oxidation involves an increase in charge and reduction a decrease in charge.

But for some reactions, such as the reaction between hydrogen and chlorine, it is quite difficult to identify electron loss as the reactions do not involve ions. This is the idea behind the oxidation state introduced in Structure 3.1. The oxidation state is the charge an atom would have if the compound were composed of ions. Considering again the reaction between chlorine and hydrogen, both elements have an oxidation state of 0 as the bonds in H_2 and Cl_2 are both non-polar. The product HCl, by contrast, is polar, with the H possessing a partial positive charge and the chlorine a partial negative charge.

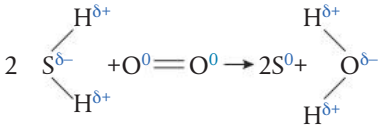
$$H^0{-}H^0 + Cl^0{-}Cl^0 \rightarrow 2H^{\delta+}{-}Cl^{\delta-}$$

Given the partial charges of the molecule, we assign H an oxidation state of +1 and chlorine an oxidation state of −1.

Chlorine is reduced as its oxidation state has decreased. Hydrogen has been oxidized as its oxidation state has increased. It is now recognized that oxidation and reduction occur during chemical change whenever there is a shift in electron density from one atom to another. Oxidation states are a very sensitive measure of electron distribution and so are an efficient tool to analyse all redox reactions.

Note that the charge on an ion X is written with the number first then the charge (as a superscript): e.g. X^{2+}. The oxidation state is written with the charge first then the number: e.g. +2.

Returning to the second reaction between hydrogen sulfide and oxygen:



Given the partial charges of the hydrogen sulfide and water molecule, we assign H an oxidation state of +1 and sulfur and oxygen an oxidation state of −2.

Oxidation occurs when there is an increase in the oxidation state of an element. Reduction occurs when there is a decrease in the oxidation state of an element.

Sulfur is oxidized as its oxidation state has increased and oxygen is reduced as its oxidation state has increased.

$$\underset{\substack{+1\\-2}}{H_2S} + \underset{0}{O_2} \rightarrow \underset{0}{S} + \underset{\substack{+1\\-2}}{H_2O}$$

Oxidation state

Oxidation and reduction are summarized below.

Oxidation is:	Reduction is:
• the addition of oxygen • the removal of hydrogen • electron loss • an increase in oxidation state	• the removal of oxygen • the addition of hydrogen • electron gain • a decrease in oxidation state

Nature of Science

The concepts of oxidation and reduction have evolved as they have been extended from their original meaning. A large number of what were thought to be diverse chemical reactions are now understood to be similar. This unification of diverse experience is a common feature of science and leads to a deeper understanding of nature.

Oxidation states enable us to analyse redox reactions

We have seen that the oxidation state of an atom in a compound is a measure of the electron possession it has relative to the atom in the pure element. Oxidation states allow us to keep track of the relative electron density of atoms in different compounds and how these change during a reaction.

Do we justify our knowledge of oxidation states and ionic charges in the same way?

So far in this chapter we have assigned oxidation states of elements in a compound as the charges an atom would have if the compound was ionic. We saw in Structure 3.1 that these charges could be formalized into a set of rules.

Worked example

Assign oxidation states to the metal ion in **(a)** $[Cu(NH_3)_6]^{2+}$ and **(b)** $[Cr(NH_3)_4Cl_2]^{+}$.

Solution

(a) NH_3 is a neutral ligand, so the charge on the complex is the same as the charge on the metal ion: $\therefore$ Cu = +2

(b) Cl has a 1− charge $\therefore$ Cr + (2 × −1) = +1 $\therefore$ Cr = +3

We can use these rules to deduce if an electron transfer has occurred during a reaction and to identify which species has been oxidized and which species has been reduced.

A redox reaction is a chemical reaction where changes in the oxidation states occur.

TOK Are oxidation states 'real' or are they artificial constructs invented by the chemist?

Worked example

Use oxidation states to deduce which species is oxidized and which is reduced in the following reactions:

(a) $Ca(s) + Sn^{2+}(aq) \rightarrow Ca^{2+}(aq) + Sn(s)$

(b) $4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$

(c) $2MnO_4^-(aq) + 6H^+(aq) + 5SO_3^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 3H_2O(l) + 5SO_4^{2-}(aq)$

(d) $4Fe(s) + 3O_2(g) + 6H_2O(l) \rightarrow 4Fe(OH)_3(s)$

(e) $Cl_2(g) + H_2O(l) \rightarrow HCl(aq) + HOCl(aq)$

Solution

Assign oxidation states to the elements in the reactants and products:

(a)	$Ca(s) + Sn^{2+}(aq) \rightarrow Ca^{2+}(aq) + Sn(s)$
Oxidation states	0 +2 +2 0

Ca is oxidized because its oxidation state increases from 0 to +2; Sn^{2+} is reduced because its oxidation state decreases from +2 to 0.

(b)	$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(l)$
Oxidation states	+1(H) 0 −2(O) +1(H) −3(N) +2(N) −2(O)

NH_3 is oxidized because the oxidation state of N increases from −3 to +2; O_2 is reduced because the oxidation state of O decreases from 0 to −2.

(c)	$2MnO_4^-(aq) + 6H^+(aq) + 5SO_3^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 3H_2O(l) + 5SO_4^{2-}(aq)$
Oxidation states	−2(O) +1(H) −2(O) +2(Mn) +1(H) +6(S) +7(Mn) +4(S) −2(O) −2(O)

$MnO_4^-(aq)$ is reduced because the oxidation state of Mn decreases from +7 to +2; $SO_3^{2-}(aq)$ is oxidized because the oxidation state of S increases from +4 to +6.

(d)	$4Fe(s) + 3O_2(g) + 6H_2O(l) \rightarrow 4Fe(OH)_3(s)$
Oxidation states	0 0 +1(H) +3(Fe) +1(H) −2(O) −2(O)

Fe(s) is oxidized because the oxidation state of Fe increases from 0 to +3; $O_2(g)$ is reduced because the oxidation state of O decreases from 0 to −2.

(e)	$Cl_2(g) + H_2O(l) \rightarrow HCl(aq) + HOCl(aq)$
Oxidation states	0 +1(H) +1(H) +1(H) +1(Cl) −2(O) −1(Cl) −2(O)

Cl_2 is oxidized because the oxidation state of one Cl increases from 0 to +1; but it is also reduced because the oxidation state of the other Cl increases from 0 to −1.

i A **disproportionation reaction** occurs when the oxidation state of the same element both increases and decreases.



Corrosion, or rust, on a painted cast iron figure. Rust forms when iron spontaneously oxidizes by water and the oxygen of the air, forming iron oxide. Rust flakes off the surface of the iron, causing it to be degraded and weakened. Several studies over the past 30 years have shown that the annual direct cost of corrosion to an industrial economy is approximately 3.1% of Gross National Product (GNP).

Structure 2.3 – The surface oxidation of metals is often known as corrosion. What are some of the consequences of this process?

The limitations of the oxidation concept

We have seen that oxidation states allow us to analyse redox reactions by identifying which atoms are involved in the electron transfer. Oxidation states do, however, have some limitations as, unlike ionic charge, they have little structural or physical significance. The oxidation number of carbon in carbon dioxide is +4 but the carbon is a covalently bonded atom. It should also be noted that the oxidation states calculated in molecules with more than one atom of an element is an average value and can be a non-integer.

Worked example

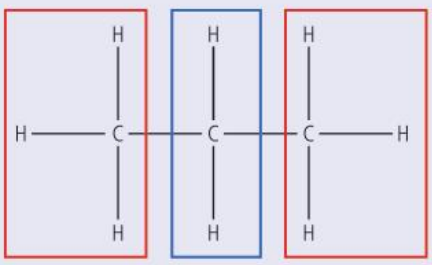
Assign oxidation states to carbon in C_3H_8 and comment on your answer.

Solution

We assign H = +1

Therefore, $8 \times (+1) + 3\,C = 0 \therefore C = -\frac{8}{3} = -2\frac{2}{3}$

This is a fractional value because it is an average for three non-equivalent carbon atoms.



We can divide the molecule into three regions, each with a zero charge.

For the carbon atoms in the red region $C + 3(+1) = 0 \therefore C = -3$

For the carbon atom in the blue region $C + 2(+1) = 0 \therefore C = -2$

The average oxidation state = $(2(-3) + (-2))/3 = -2\frac{2}{3}$ as expected.

HL Nature of Science

Oxidation state and formal charge (introduced in Structure 2.2) are both useful tools but they are based on very different models. Oxidation states are related to the ionic model and formal charge is assigned by assuming bonds are purely covalent. Models are simplifications of complex systems, and their limitations need to be considered in their application.

Structure 3.1 – What are the advantages and limitations of using oxidation states to track redox changes?

Challenge yourself

1. Assign oxidation states to the overall reactants and products of photosynthesis to show that it is a redox reaction. The reactants are CO_2 and H_2O. The products are $C_6H_{12}O_6$, and O_2.

Oxidizing and reducing agents

We have seen that redox reactions *always* involve the simultaneous oxidation of one reactant with the reduction of another as electrons are transferred between them. The reactant that accepts electrons is called the **oxidizing agent** because it brings about oxidation of the other reactant. In the process, it becomes reduced. Likewise, the reactant that supplies the electrons is known as the **reducing agent** because it brings about reduction and so is oxidized.

For example, in the reaction where iron (Fe) is extracted from its ore (Fe_2O_3):

	oxidizing agent		reducing agent				
	$Fe_2O_3(s)$	+	$3C(s)$	→	$2Fe(s)$	+	$3CO(g)$
	+3		0		0		+2

(The oxidation state of O is not shown as it does not change during the reaction.)

The reducing agent C brings about the reduction of Fe (+3 → 0), while C itself is oxidized to CO (0 → +2). The oxidizing agent Fe_2O_3 brings about the oxidation of C while itself being reduced to Fe.

In a redox equation the substance that is reduced is the oxidizing agent, the substance that is oxidized is the reducing agent.

Worked example

When an acidic solution of potassium dichromate(VI), $K_2Cr_2O_7(aq)$, is mixed with iron(II) chloride, $FeCl_2(aq)$, $Fe^{3+}(aq)$ and $Cr^{3+}(aq)$ are produced. Identify the oxidizing and reducing agents.

Solution

Oxidation of Fe: +2 → +3 so $FeCl_2(aq)$ is oxidized. It is the reducing agent.

Reduction of Cr: +6 → +3 so $K_2Cr_2O_7(aq)$ is reduced. It is the oxidizing agent.

Some examples of useful oxidizing and reducing agents are given below:

- oxidizing agent: O_2, O_3, H^+/MnO_4^-, $H^+/Cr_2O_7^{2-}$, F_2, Cl_2, conc. HNO_3, H_2O_2
- reducing agent: H_2, C, CO, SO_2, reactive metals

Note that some substances can act as an oxidizing agent in some reactions and as a reducing agent in others. Water, for example, can act as an oxidizing agent and be reduced to hydrogen with sodium, or act as a reducing agent and be oxidized to oxygen with fluorine.

- H_2O acting as an oxidizing agent:

$$\underset{+1}{2H_2O(l)} + 2Na(s) \rightarrow 2NaOH(aq) + \underset{0}{H_2(g)}$$

- H_2O acting as a reducing agent:

$$\underset{-2}{2H_2O(l)} + 2F_2(g) \rightarrow 4HF(aq) + \underset{0}{O_2(g)}$$

The ability of water to act as both an oxidizing and reducing agent makes it a useful solvent for many redox reactions.

Challenge yourself

2. Hydrogen peroxide, H_2O_2, can act as an oxidizing agent and as a reducing agent. With reference to the oxidation states of its atoms, suggest why this is so and which behaviour is more likely.

Systematic names of compounds use oxidation numbers

The use of oxidation numbers in the IUPAC nomenclature for naming compounds unambiguously is discussed in Structure 3.1. A Roman numeral, corresponding to the oxidation state, is inserted in brackets after the name of the relevant element.

The table shows some common examples.

Oxidation states are shown with a '+' or '–' sign and an Arabic numeral, e.g. +2. Oxidation numbers are shown by inserting a Roman numeral in brackets after the name or symbol of the element.

Formula of compound	Oxidation state	Name using oxidation number
FeO	Fe +2	iron(II) oxide
Fe_2O_3	Fe +3	iron(III) oxide
Cu_2O	Cu +1	copper(I) oxide
CuO	Cu +2	copper(II) oxide
MnO_2	Mn +4	manganese(IV) oxide
MnO_4^-	Mn +7	manganate(VII) ion
$K_2Cr_2O_7$	Cr +6	potassium dichromate(VI)

Worked example

Deduce the name of the following compounds using oxidation numbers.

(a) PbO_2 **(b)** $Cr(OH)_3$ **(c)** $KMnO_4$

Solution

1. First deduce the oxidation state:

(a) PbO_2
$O = -2$
$Pb = +4$

(b) $Cr(OH)_3$
$OH = -1$
$Cr = +3$

(c) $KMnO_4$
$K = +1$ and $O = -2$
$Mn = +7$

2. The corresponding Roman numeral is inserted after the name of the element. There is no space between the name and the number, and the number is placed in brackets.

(a) PbO_2
lead(IV) oxide

(b) $Cr(OH)_3$
chromium(III) hydroxide

(c) $KMnO_4$
potassium manganate(VII)

The IUPAC system aims to help chemists communicate more easily in all languages by introducing systematic names for compounds. However, its success in achieving this will be determined by how readily it is adopted. What do you think might prevent chemists using exclusively the 'new names'?

Exercise

Q1. Which equation represents a redox reaction?

A $NaOH(aq) + HNO_3(aq) \rightarrow NaNO_3(aq) + H_2O(l)$

B $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$

C $CuO(s) + 2HCl(aq) \rightarrow CuCl_2(aq) + H_2O(l)$

D $MgCO_3(s) + 2HNO_3(aq) \rightarrow Mg(NO_3)_2(aq) + H_2O(l) + CO_2(g)$

Q2. The oxidation state of iron is the same in all the following compounds except which one?

A $FeCl_3$ **B** Fe_2O_3 **C** $FeCO_3$ **D** $Fe_2(SO_4)_3$

Q3. Identify the correct descriptions of the redox reaction between manganese(IV) oxide and the chloride ions:

$$MnO_2(s) + 2Cl^-(aq) + 4H^+(aq) \rightarrow Mn^{2+}(aq) + Cl_2(g) + 2H_2O(l)$$

I. H^+ is the reducing agent.
II. MnO_2 undergoes reduction
III. $Cl^-(aq)$ is the reducing agent

A I and II only **B** I and III only
C II and III only **D** I, II and III

Q4. Assign oxidation states to all elements in the following compounds.

(a) CH_4 **(b)** $CuSO_4$ **(c)** C_2H_4 **(d)** CO

(e) $K_2Cr_2O_7$ **(f)** K_2CrO_4 **(g)** H_2O_2 **(h)** C_4H_{10}

Q5. Use oxidation states to deduce which species is oxidized and which is reduced in the following reactions.

(a) $Sn^{2+}(aq) + 2Fe^{3+}(aq) \rightarrow Sn^{4+}(aq) + 2Fe^{2+}(aq)$

(b) $2FeCl_2(aq) + Cl_2(aq) \rightarrow 2FeCl_3(aq)$

(c) $2H^+(aq) + S_2O_3^{2-}(aq) \rightarrow S(s) + SO_2(g) + H_2O(l)$

(d) $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

(e) $I_2(aq) + SO_3^{2-}(aq) + H_2O(l) \rightarrow 2I^-(aq) + SO_4^{2-}(aq) + 2H^+(aq)$

Q6. The combustion of ethanol is a redox reaction.

$$C_2H_5OH\,(g) + 3O_2\,(g) \rightarrow 2CO_2\,(g) + 3H_2O(l)$$

(a) Assign oxidation states to carbon in C_2H_5OH and comment on your answer.

(b) Discuss the application of the different definitions of oxidation and reduction in analysing the reaction.

Q7. Identify the oxidizing agents and the reducing agents in the following reactions.

(a) $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

(b) $2Al(s) + 3PbCl_2(s) \rightarrow 2AlCl_3(s) + 3Pb(s)$

(c) $Cl_2(aq) + 2KI(aq) \rightarrow 2KCl(aq) + I_2(aq)$

(d) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

Reactivity 3.2.2 – Half-equations

Reactivity 3.2.2 – Half-equations separate the processes of oxidation and reduction, showing the loss or gain of electrons.	
Deduce redox half-equations and equations in acidic or neutral solutions.	
	Tool 1, Inquiry 2 – Why are some redox titrations described as 'self-indicating'?

Writing half-equations for redox equations

Although oxidation and reduction always occur together, it can be useful to separate out the two processes in a redox equation and write separate equations for the oxidation and reduction processes. These **half-equations** emphasize the electron transfers that occur during the reaction. Electrons are included in both half-equations to balance the charges.

Worked example

Deduce the two half-equations for the following reaction:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

Solution

Assign oxidation states so you can see what is being oxidized and what is reduced.

$$\underset{0}{Zn(s)} + \underset{+2}{Cu^{2+}(aq)} \rightarrow \underset{+2}{Zn^{2+}(aq)} + \underset{0}{Cu(s)}$$

The Zn is oxidized and Cu^{2+} is reduced.

We write separate equations for oxidation and reduction adding electrons to balance the charges.

oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ electrons are lost by Zn(s)

reduction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ electrons are gained $Cu^{2+}(aq)$

Note there are equal numbers of electrons in the two half-equations, so that when they are added together the electrons cancel out.

Sometimes we may know the species involved in a redox reaction, but not the overall equation. We can work this out by making sure it is balanced for both atoms and charges. A good way to do this is to write half-equations for the oxidation and reduction processes separately and then add these two together to give the overall reaction. Many of these reactions take place in acidified solutions and we therefore use H_2O and/or H^+ ions to balance the half-equations. The process is best broken down into a series of steps, as shown in the example below.

Worked example

Deduce an equation for the reaction in which NO_3^- and Cu react together in acidic solution to produce NO and Cu^{2+}.

Solution

1. Write an unbalanced equation with the given reactants and products and assign oxidation states to determine which elements are being oxidized and which are being reduced:

$$\underset{+5\ -2}{NO_3^-(aq)} + \underset{0}{Cu(s)} \rightarrow \underset{+2\ -2}{NO(g)} + \underset{+2}{Cu^{2+}(aq)}$$

   In this example Cu is oxidized ($0 \rightarrow +2$) and N is reduced ($+5 \rightarrow +2$).

2. Write separate half-equations for oxidation and reduction including the electrons needed to account for the changes in oxidation state. Balance the atoms other than H and O. In this example the Cu and N are already balanced.

   oxidation: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ Cu 0 → +2, 2 electrons produced

   reduction: $NO_3^-(aq) + 3e^- \rightarrow NO(g)$ N +5 → +2, 3 electrons added

3. Balance each half-equation for O by adding H_2O as needed.

   In this example the reduction equation needs two more O atoms on the right-hand side. These are added as water molecules:

   reduction: $NO_3^-(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$

4. Balance each half-equation for H by adding H^+ as needed.

   Here the reduction equation needs four H atoms on the left-hand side:

   reduction: $NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$

5. Check that each half-equation is balanced for atoms and for charge.

6. Equalize the number of electrons in the two half-equations by finding a common factor and multiplying each appropriately.

   Here the common factor is 6. The equation for oxidation must be multiplied by 3, and the equation for reduction by 2. This gives six electrons in both equations:

   oxidation: $3Cu(s) \rightarrow 3Cu^{2+}(aq) + 6e^-$

   reduction: $2NO_3^-(aq) + 8H^+(aq) + 6e^- \rightarrow 2NO(g) + 4H_2O(l)$

7. Add the two half-equations together, cancelling out anything that is the same on both sides, which includes the electrons.

   $$3Cu(s) + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3Cu^{2+}(aq) + 2NO(g) + 4H_2O(l)$$

   Note the final equation is balanced for atoms and charge and has no electrons.

Summary of steps in writing redox equations.

1. **Assign oxidation states to determine which elements are oxidized and which are reduced.**
2. **Write separate half-equations for oxidation and reduction. Balance the atoms other than H and O and add electrons to account for the changes in oxidation states.**
3. **Balance each half-equation for O by adding H_2O as needed.**
4. **Balance each half-equation for H by adding H^+ as needed.**
5. **Check that each half-equation is balanced for atoms and for charge.**
6. **Equalize the number of electrons in the two half-equations by multiplying each appropriately.**
7. **Add the two half-equations together, cancelling out anything that is the same on both sides.**

Challenge yourself

3. Reactions in which the same element is simultaneously oxidized and reduced are known as **disproportionation reactions**. Deduce the equation for the reaction when $I_2(aq)$ reacts with KOH(aq) to produce KI, KIO_3, and H_2O, and show that this is a disproportionation reaction.

Redox titrations are used to determine the unknown concentrations in redox reactions

As discussed in Structure 1.3, titrations are used to determine the unknown concentration of a substance in solution. In redox titrations the technique is based on a redox reaction between the two reactants and finds the equivalence point where

they have reacted stoichiometrically by transferring electrons. Redox titrations are carried out in much the same way as acid–base titrations, using a burette and pipette to measure volumes accurately and a standard solution of one reactant. An indicator is often used to signal the equivalence point, although some redox changes are accompanied by a colour change and may not need an external indicator. From the volume of the solution added from the burette to reach equivalence, which is known as the **titre**, the concentration of the other reactant can be determined. The calculations are based on the equation for redox reactions, which can be deduced from the half-equations.

Examples of redox titrations

Iodine–thiosulfate reaction

Several different redox titrations use an oxidizing agent to convert excess iodide ions to iodine.

$$2I^-(aq) + \text{oxidizing agent} \rightarrow I_2(aq) + \text{other products}$$

Examples of oxidizing agents used in this way include $KMnO_4(aq)$, $KIO_3(aq)$, $K_2Cr_2O_7(aq)$, and $NaOCl(aq)$.

The liberated iodine, $I_2(aq)$, is then titrated with sodium thiosulfate, $Na_2S_2O_3(aq)$.

Redox equations:

oxidation: $2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2e^-$

reduction: $I_2(aq) + 2e^- \rightarrow 2I^-(aq)$

Adding the half-reactions:

$$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

deep blue in presence of starch

Starch can be added as an indicator just before the equivalence point is reached. It forms a deep blue colour by forming a complex with free I_2. As the I_2 is reduced to I^- during the reaction, the blue colour disappears, making the equivalence point very distinct.



At the start of an iodine titration the solution is brown in colour. A standard sodium thiosulfate solution of known concentration is added to the iodine solution until it becomes a pale yellow. A few drops of starch solution are added to turn it a very dark blue to sharpen the visibility of the end point. The end point occurs when the last trace of blue disappears and the final solution is colourless.

'Iodine solution' is made by dissolving I_2 in a solution of iodide ions. A complex ion, $I_3^-(aq)$, is formed which is more soluble in water than iodine, I_2, which has a very low solubility.

It is valid to use I_2 in equations, as the $I^-(aq)$ ions are spectator ions.

Worked example

Household bleach is an oxidizing agent that contains sodium hypochlorite, NaOCl(aq), as the active ingredient. It reacts with iodide ions in acidic solution as follows:

$$OCl^-(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow I_2(aq) + Cl^-(aq) + H_2O(l)$$

A 10.00 cm^3 sample of bleach was reacted with a solution of excess iodide ions, and the liberated iodine was then titrated with $Na_2S_2O_3$. The titration required 38.65 cm^3 of 0.0200 mol dm^{-3} $Na_2S_2O_3(aq)$. Determine the concentration of $OCl^-(aq)$ in the bleach.

Solution

First we need the balanced equation for the titration, which can be solved by the half-equation method above.

Next we calculate the number of moles of $Na_2S_2O_3$ as we know both its concentration and its volume.

$$n = cV$$

$$n(S_2O_3^{2-}) = 0.0200 \text{ mol dm}^{-3} \times \frac{38.65}{1000} \text{ dm}^3 = 7.73 \times 10^{-4} \text{ mol } S_2O_3^{2-}$$

From the equation on the previous page we know the reacting ratio $S_2O_3^{2-} : I_2 = 2 : 1$

$\therefore\ n(I_2) = 7.73 \times 10^{-4} \times 0.5 = 3.865 \times 10^{-4}$

This is a back-titration as the I_2 was liberated by the reaction of I^- with OCl^-, as given in the question. The reacting ratio is $OCl^-(aq) : I_2(aq) = 1 : 1$

$\therefore\ n(OCl^-) = n(I_2) = 3.865 \times 10^{-4}$

The concentration of the OCl^- in the bleach can now be calculated.

$n(OCl^-) = cV$

$$\therefore\ 3.865 \times 10^{-4} \text{ mol} = c \times \frac{10}{1000} \text{ dm}^3$$

$[OCl^-] = 0.0387 \text{ mol dm}^{-3}$

Analysis of iron with manganate(VII)

Determination of the level of rust in a rusted nail. Full details of how to carry out this experiment with a worksheet are available in the eBook.

SKILLS

This redox titration uses $KMnO_4$ in an acidic solution to oxidize Fe^{2+} ions to Fe^{3+}. During the reaction MnO_4^- is reduced to Mn^{2+}. This is accompanied by a colour change from deep purple to colourless, so the reaction mixture acts as its own indicator, and the equivalence point is determined.

Redox equations:

oxidation: $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$

reduction: $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

So the overall equation is

$$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$$

Worked example

All the iron in a 2.000 g tablet was dissolved in an acidic solution. The resulting solution of $Fe^{2+}(aq)$ ions was then titrated with $KMnO_4$. The titration required 27.50 cm^3 of 0.100 mol dm^{-3} $KMnO_4(aq)$. Calculate the percentage by mass of iron in the tablet. Describe what would be observed during the reaction and how the equivalence point can be detected.

Solution

The balanced equation for the reaction can be deduced by the half-equation method above.

The O and H are balanced by adding H_2O as a product and $H^+(aq)$ as a reactant.

$$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$$

Next we need to know the amounts of reactants used to reach equivalence. We start with $KMnO_4(aq)$ as we know both its concentration and its volume.

$$n = cV$$

$$n(MnO_4^-) = 0.100 \text{ mol dm}^{-3} \times \frac{27.50}{1000} \text{ dm}^3 = 0.00275 \text{ mol } MnO_4^-$$

From the equation for the reaction, we know the reacting ratio:

$MnO_4^- : Fe^{2+} = 1 : 5$

$\therefore\ n(Fe^{2+}) = n(MnO_4^-) \times 5 = 0.00275 \text{ mol} \times 5 = 0.01375 \text{ mol}$

$M(Fe) = 55.85 \text{ g mol}^{-1}$

$$n = \frac{m}{M}$$

$\therefore\ m(Fe) = n \times M = 0.01375 \text{ mol} \times 55.85 \text{ g mol}^{-1} = 0.7679 \text{ g}$

$$\% \text{ Fe in tablet} = \frac{0.768 \text{ g}}{2.000 \text{ g}} \times 100 = 38.39\%$$

MnO_4^- in the burette is purple, but a nearly colourless solution in the flask is formed as it reacts to form Mn^{2+}. When the reducing agent Fe^{2+} in the flask has been used up at equivalence, MnO_4^- ions will not react when added after the equivalence point, and the purple colour persists.



The browning of fruit when it is exposed to the air is an oxidation reaction. It occurs when phenols released in damaged cells are oxidized with molecular oxygen at alkaline pH. The brown products are tannins.

Tool 1, Inquiry 2 – Why are some redox titrations described as 'self-indicating'?

SKILLS

Redox titrations can be used to analyse many household chemicals such as food and drinks. Wines, for example, can be analysed for the presence of sulfur dioxide, and foods for vitamin C.

In titration calculations, always look first for the reactant where you know both its reacting volume ***and*** its concentration. Start by using this data to calculate the number of moles. Then use the reacting ratio in the equation to deduce the moles of the other reactant.

Exercise

Q8. Consider the following unbalanced equation:

$$MnO_4^-(aq) + SO_3^{2-}(aq) + H^+(aq) \rightarrow Mn^{2+}(aq) + SO_4^{2-}(aq) + H_2O(l)$$

Deduce the amount of MnO_4^- which reacts with 1 mol of SO_3^{2-} ions.

A 0.40 mol **B** 3 mol **C** 1.50 mol **D** 7 moles

Q9. Consider the following unbalanced equation:

$$MnO_4^-(aq) + H_2O_2(aq) + H^+(aq) \rightarrow Mn^{2+}(aq) + H_2O(l) + O_2(g)$$

Deduce the amount of $H_2O_2(aq)$ which reacts with 1 mol of $MnO_4^-(aq)$.

A 0.40 mol **B** 1.25 mol **C** 2.50 mol **D** 5 moles

Q10. Deduce the half-equations of oxidation and reduction for the following reactions.

(a) $Ca(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2(g)$

(b) $2Fe^{2+}(aq) + Cl_2(aq) \rightarrow 2Fe^{3+}(aq) + 2Cl^-(aq)$

(c) $Sn^{2+}(aq) + 2Fe^{3+}(aq) \rightarrow Sn^{4+}(aq) + Fe^{2+}(aq)$

(d) $Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$

Q11. Write balanced equations for the following reactions that occur in acidic solutions.

(a) $I^-(aq) + HSO_4^-(aq) \rightarrow I_2(aq) + SO_2(g)$

(b) $I_2(aq) + OCl^-(aq) \rightarrow IO_3^-(aq) + Cl^-(aq)$

(c) $MnO_4^-(aq) + H_2SO_3(aq) \rightarrow SO_4^{2-}(aq) + Mn^{2+}(aq)$

Q12. A bag of 'road salt', used to melt ice and snow from roads, contains a mixture of calcium chloride, $CaCl_2$, and sodium chloride, NaCl. A 2.765 g sample of the mixture was analysed by first converting all the calcium into calcium oxalate, CaC_2O_4. This was then dissolved in H_2SO_4 and titrated with 0.100 mol dm^{-3} $KMnO_4$ solution. The titration required 24.65 cm^3 of $KMnO_4(aq)$ and produced $Mn^{2+}(aq)$, $CO_2(g)$, and $H_2O(l)$.

(a) What would be observed at the equivalence point of the titration?

(b) Write the half-equation for the oxidation reaction, starting with $C_2O_4^{2-}$.

(c) Write the half-equation for the reduction reaction, starting with MnO_4^-.

(d) Write the overall equation for the redox reaction.

(e) Determine the number of moles of $C_2O_4^{2-}$.

(f) Deduce the number of moles of Ca^{2+} in the original sample.

(g) What was the percentage by mass of $CaCl_2$ in the road salt?

Q13. Alcohol levels in blood can be determined by a redox titration with potassium dichromate, $K_2Cr_2O_7$, according to the following equation:

$$C_2H_5OH(aq) + 2Cr_2O_7^{2-}(aq) + 16H^+(aq) \rightarrow 2CO_2(g) + 4Cr^{3+}(aq) + 11H_2O(l)$$

(a) Determine the alcohol percentage in the blood by mass if a 10.000 g sample of blood requires 9.25 cm^3 of 0.0550 mol dm^{-3} $K_2Cr_2O_7$ solution to reach equivalence.

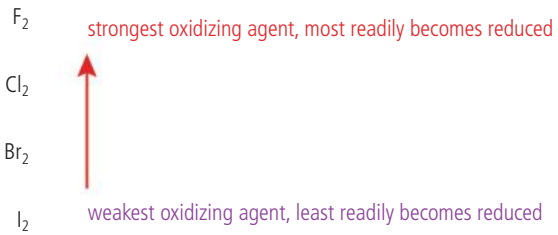
(b) Describe the change in colour that would be observed during the titration.

Reactivity 3.2.3 – Trends in ease of oxidation and reduction of elements

Reactivity 3.2.3 – The relative ease of oxidation and reduction of an element in a group can be predicted from its position in the periodic table. **The reactions between metals and aqueous metal ions demonstrate the relative ease of oxidation of different metals.** Predict the relative ease of oxidation of metals. Predict the relative ease of reduction of halogens. Interpret data regarding metal and metal ion reactions.	
The relative reactivity of metals observed in metal/metal ion displacement reactions does not need to be learned; appropriate data will be supplied in examination questions.	Structure 3.1 – Why does metal reactivity increase, and non-metal reactivity decrease, down the main groups of the periodic table? Tool 1, Inquiry 2 – What observations can be made when metals are mixed with aqueous metal ions and solutions of halogens are mixed with aqueous halide ions?

More reactive non-metals are stronger oxidizing agents

Some oxidizing and reducing agents are stronger than others, depending on their relative tendencies to lose or gain electrons. We saw in Structure 3.1 that the halogens (group 17 elements) react by gaining electrons and forming negative ions, so act as oxidizing agents by removing electrons from other substances. We also learned that this tendency to gain electrons decreases down the group. This gives the following trend:



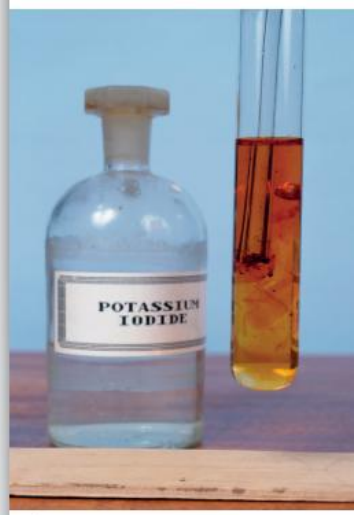
For example, adding a more reactive halogen to a solution containing the ions of a less reactive halogen (known as halide ions) leads to a reaction. For example:

$$Cl_2(aq) + 2KI(aq) \rightarrow 2KCl(aq) + I_2(aq)$$

Species which do not change during a reaction, like $K^+(aq)$ here, are called **spectator ions** and can be cancelled out in the equation. This gives the ionic equation:

$$Cl_2(aq) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$$

As discussed in Structure 3.1, a reaction occurs because Cl atoms attract electrons more strongly than I atoms due to their smaller atomic radius. You can think of it as a competition for electrons where the stronger oxidizing agent, in this case chlorine, 'wins'.



Chlorine gas bubbling through a clear solution of potassium iodide KI(aq). The solution turns brown due to the formation of iodine in solution, as chlorine oxidizes the iodide ions and forms chloride ions.

Adding a less reactive halogen to the ions of a more reactive halogen results in no reaction.

$$I_2(aq) + 2Cl^-(aq) \rightarrow \text{no reaction}$$

More reactive non-metals oxidize the ions of a less reactive non-metal.

As non-metals generally react by gaining electrons this pattern can be summarized: more reactive non-metals are stronger oxidizing agents than less reactive non-metals.

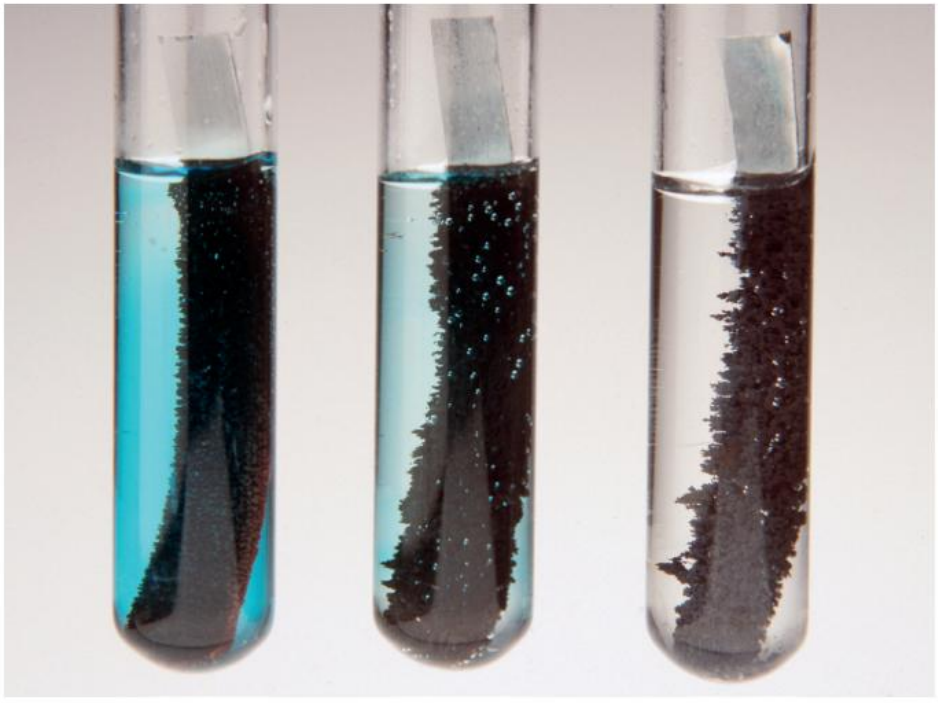
More reactive metals are stronger reducing agents

Structure 3.1 – Why does metal reactivity increase, and non-metal reactivity decrease, down the main groups of the periodic table?

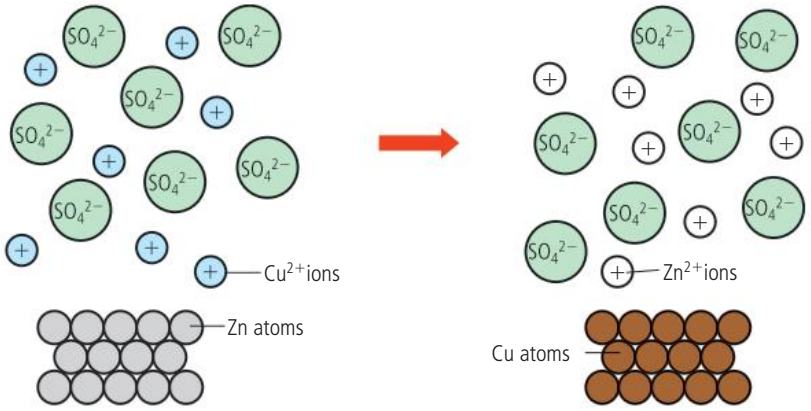
The different strengths of metals as reducing agents can be compared in a similar way. We saw in Structure 2.3 that metals have a tendency to lose electrons and form positive ions. They act as reducing agents – they give their electrons to another substance. More reactive metals lose their electrons more readily and are stronger reducing agents than less reactive metals. We saw in Structure 3.1 that the reactivity of the group 1 metals increases down the group, so potassium is a stronger reducing agent than sodium. More generally we can compare the reactivity of the metals in displacements similar to those discussed earlier between the halogens and the halide ions.

If we add zinc metal, for example, to an aqueous solution of copper sulfate, we would see a reaction (Figure 1). The blue colour of the solution fades, the pink/brown colour of the copper metal appears, and there is a rise in temperature. The $Cu^{2+}(aq)$ ions are displaced from solution as they are reduced by the more reactive $Zn(s)$, which simultaneously dissolves as it is oxidized to $Zn^{2+}(aq)$.

$$Zn(s) + CuSO_4(aq) \rightarrow ZnSO_4(aq) + Cu(s)$$



A strip of zinc metal half submerged in a solution of $CuSO_4(aq)$. Solid copper that appears as a pink/brown solid is precipitated and the blue colour of the solution fades as the copper ions are reduced by the zinc. Zinc is a stronger reducing agent than copper.



R3.2 Figure 1 The reaction of zinc with copper(II) sulfate solution.

Again we can write this as an ionic equation. The sulfate ions are not included because they act as spectator ions and are not changed during the reaction.

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

Zinc is acting as the reducing agent – it is therefore the more reactive metal. We can think of it as having the reducing strength to 'force' copper ions to accept the electrons. This can be confirmed by trying the reaction the other way round by adding copper metal to a solution of zinc ions. There is no reaction because copper is not a strong enough reducing agent to force electrons to reduce $Zn^{2+}(aq)$ ions. This is another way of saying that Cu(s) is a less reactive metal, less able to push the electrons onto $Zn^{2+}(aq)$.

More reactive metals are stronger reducing agents than less reactive metals. A more reactive metal is able to reduce the ions of a less reactive metal.

By repeating displacement reactions like these between different combinations of metals and their ions, we can build up a list of relative strengths of the metals as reducing agents. This is called the **activity series** and it enables us to predict whether a particular redox reaction between a metal and the ions of another metal will be feasible. Later in this chapter we will learn how to quantify these differences in metal reactivity, which is of great importance in many industrial processes. For example, the extraction of a metal from its ore often involves choosing a suitable reducing agent by reference to this data.

The activity series is not something that needs to be learned. The key point is that you are able to interpret it to deduce the order of reactivity from given data.

Here is a small part of the activity series of metals:

Mg — strongest reducing agent, most readily becomes oxidized
Al
Zn
Fe
Pb
Cu
Ag — weakest oxidizing agent, least readily becomes oxidized



The thermite reaction between powdered aluminium and iron oxide to produce aluminium oxide and iron. Aluminium is a stronger reducing agent than iron.

Worked example

Refer to the activity series given on the previous page to predict whether the following reactions will occur:

(a) $ZnCl_2(aq) + 2Ag(s) \rightarrow 2AgCl(s) + Zn(s)$

(b) $2FeCl_3(aq) + 3Mg(s) \rightarrow 3MgCl_2(aq) + 2Fe(s)$

Solution

(a) This reaction would involve Ag(s) reducing $Zn^{2+}(aq)$ in $ZnCl_2(aq)$. Ag(s) is a weaker reducing agent than Zn, so this will not occur.

(b) This reaction involves Mg(s) reducing $Fe^{3+}(aq)$ in $FeCl_3(aq)$. Mg(s) is a stronger reducing agent than Fe, so this will occur.

Tool 1, Inquiry 2 – What observations can be made when metals are mixed with aqueous metal ions, and solutions of halogens are mixed with aqueous halide ions?

We can investigate how some non-metals such as carbon and hydrogen would fit into this activity series of metals by similar types of displacement reactions. Carbon is able to reduce the oxides of iron and metals below it in the series, which provides one of the most effective means for the extraction of these metals. The position of hydrogen relative to the metals is discussed on page 760.

Investigating the activity series. Full details of how to carry out this experiment with a worksheet are available in the eBook.

SKILLS

Challenge yourself

4. Carbon can be used as the reducing agent in the extraction of iron and zinc. Lead salts are produced when lead is added to dilute acids. Suggest where you place the non-metals carbon and hydrogen in the activity series on page 757.

Exercise

Q14. Use the activity series on the previous page to predict what happens when zinc powder is added to an aqueous solution of sodium chloride.

A $Cl_2(g)$ is produced **B** Na(s) is produced

C $ZnCl_2(aq)$ is produced **D** No reaction

Q15. Consider the following reactions of three unidentified metals P, Q and R.

1. $PCl_2(aq) + 2Q(s) \rightarrow P(s) + 2QCl(aq)$

2. $RCl_2(aq) + 2Q(s) \rightarrow R(s) + 2QCl(aq)$

3. $RCl_2(aq) + 2P(s) \rightarrow$ no reaction

Deduce the order of **increasing** reactivity of the metals.

A P < Q < R **B** P < R < Q **C** R < P < Q **D** Q < R < P

Q16. Use the activity series given to predict if a reaction occurs between the following reactants, and write equations where relevant.

(a) $CuCl_2 + Ag$ **(b)** $Fe(NO_3)_2 + Al$

(c) $NaI + Br_2$ **(d)** $KCl + I_2$

Q17. An activity series can be deduced from observing displacement reactions.

(a) Use the following reactions to deduce the order of reactivity of the elements W, X, Y and Z, putting the most reactive first.

$W + X^+ \rightarrow W^+ + X$ $\quad\quad$ $Y^+ + Z \rightarrow$ no reaction

$X + Z^+ \rightarrow X^+ + Z$ $\quad\quad$ $X + Y^+ \rightarrow X^+ + Y$

(b) Which of the following reactions would you expect to occur according to the activity series you established in part **(a)**?

(i) $W^+ + Y \rightarrow W + Y^+$ $\quad\quad$ **(ii)** $W^+ + Z \rightarrow W + Z^+$

Reactivity 3.2.4 – Oxidation of metals by acids

Reactivity 3.2.4 – Acids react with reactive metals to release hydrogen.

Deduce equations for reactions of reactive metals with dilute HCl and H_2SO_4.

Acids react with metals to form salts and release hydrogen

As discussed in Reactivity 3.1 the term **salt** refers to an ionic compound formed when the hydrogen of an acid is replaced by a metal or another positive ion.

For example:

$$HCl(aq) + Zn(s) \rightarrow ZnCl_2(aq) + H_2(g)$$

$$H_2SO_4(aq) + Fe(s) \rightarrow FeSO_4(aq) + H_2(g)$$

$$2CH_3COOH(aq) + Mg(s) \rightarrow Mg(CH_3COO)_2(aq) + H_2(g)$$

$ZnCl_2$, $FeSO_4$, and $Mg(CH_3COO)_2$ are all salts.

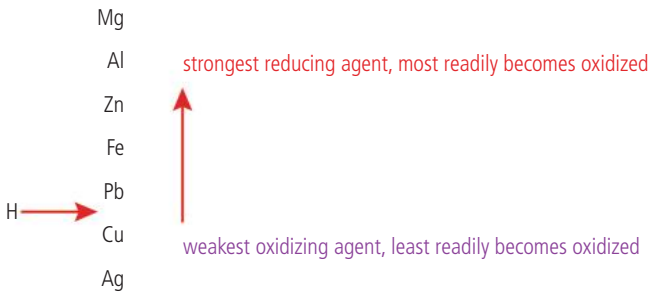


Magnesium reacting with dilute hydrochloric acid. $Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$ The tiny bubbles are hydrogen gas being produced.

We can also write these as ionic equations, showing only the species that change during the reaction. For example:

$$2H^+(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + H_2(g)$$

As zinc is oxidized from 0 to +2 during the reaction it is acting as the reducing agent. We can think of it as having the reducing strength to 'force' hydrogen ions to accept the electrons. As there is no reaction between copper and dilute acids we can deduce that hydrogen is more reactive than copper. These results show that hydrogen is below zinc and above copper in the activity series. You can demonstrate the release of hydrogen from acids in simple experiments by adding a small piece of metal to a dilute solution of the acid. There is a big range, however, in the reactivity of metals in these reactions. More reactive metals such as sodium and potassium in group 1 would react so violently that it would not be safe to perform the experiment, while copper and other less reactive metals such as silver and gold will usually not react at all. These results show that we can insert hydrogen between copper and lead in the activity series above.



These reactions of metals with acids illustrate why acids are so corrosive and why, for example, it is important to keep car battery acid well away from the metal bodywork of a car. This also explains why the less reactive metals such as silver and gold are so valuable – they are resistant to corrosion.

Exercise

Q18. Identify the metals which will react with 0.1 mol dm^{-3} hydrochloric acid.

I. Ag II. Fe III. Zn

A I and II only **B** I and III only

C II and III only **D** I, II and III

Q19. Identify the products formed when a metal reacts with a dilute acid.

I. a salt II. water III. hydrogen gas

A I and II **B** I and III

C II and III **D** I, II and III

Q20. Write complete and ionic equations for the following reactions.

(a) hydrochloric acid reacting with aluminium

(b) sulfuric acid reacting with magnesium

(c) ethanoic acid reacting with zinc

Q21. Write balanced equations for the following reactions that occur in acidic solutions.

(a) $Zn(s) + SO_4^{2-}(conc) \rightarrow Zn^{2+}(aq) + SO_2(g)$

(b) $NO_3^-(conc) + Zn(s) \rightarrow NH_4^+(aq) + Zn^{2+}(aq)$

(c) $NO_3^-(aq) + Cu(s) \rightarrow NO(g) + Zn^{2+}(aq)$

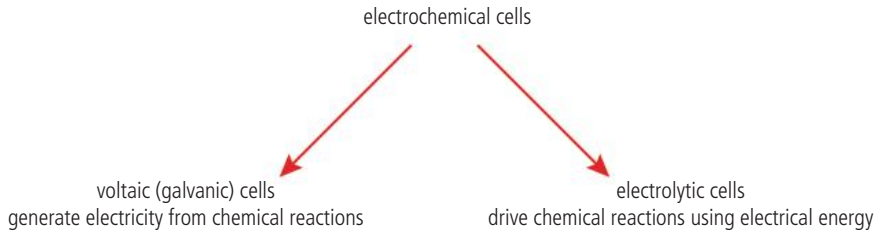
(d) $NO_3^-(conc) + Cu(s) \rightarrow NO_2(g) + Zn^{2+}(aq)$

Reactivity 3.2.5 – Comparing voltaic and electrochemical cells

Reactivity 3.2.5 – Oxidation occurs at the anode and reduction occurs at the cathode in electrochemical cells.

Label electrodes as anode and cathode, and identify their signs/polarities in voltaic cells and electrolytic cells, based on the type of reaction occurring at the electrode.

Voltaic and electrolytic cells are collectively known as electrochemical cells.



A voltaic cell converts chemical energy to electrical energy: a spontaneous chemical reaction drives electrons around a circuit. An electrolytic cell converts electrical energy to chemical energy. An electric current reverses the normal directions of chemical change, and non-spontaneous reactions occur. Stable compounds like sodium chloride can be broken down into their reactive constituent elements.

The anode and cathode in electrochemical cells are defined by the chemical changes that take place. Oxidation occurs at the anode and reduction occurs at the cathode in both types of cell. The polarity of the cell, however, changes. The anode is the negative terminal in a voltaic cell but the positive terminal in an electrolytic cell. The cathode is the positive terminal in a voltaic cell but the negative in an electrolytic cell.

'An Ox and a Red Cat' may help you remember the reaction at the electrodes of an electrochemical cell (**ox**idation occurs at the **an**ode, **red**uction occurs at the cathode.

	Type of cell	
	Voltaic	**Electrolytic**
Type of reaction	spontaneous	non-spontaneous
Electrode of oxidation	anode	anode
Electrode of reduction	cathode	cathode
Polarity of anode	negative	positive
Polarity of cathode	positive	negative

Voltaic and electrolytic cells are explored in more detail in the sections that follow.

Exercise

Q22. Identify the processes that occur at the positive electrode in voltaic and electrolytic cells.

	Electrolytic cell	Voltaic cell
A	oxidation	reduction
B	reduction	oxidation
C	oxidation	oxidation
D	reduction	reduction

Q23. Identify the best description of the reaction that occurs at the negative electrode of an electrolytic cell.

	Type of reaction	Voltaic cell
A	spontaneous	reduction
B	not spontaneous	reduction
C	spontaneous	oxidation
D	not spontaneous	oxidation

Reactivity 3.2.6 – Primary (voltaic) cells

Reactivity 3.2.6 – A primary (voltaic) cell is an electrochemical cell that converts energy from spontaneous redox reactions to electrical energy.

Explain the direction of electron flow from anode to cathode in the external circuit, and ion movement across the salt bridge.

Construction of primary cells should include: half-cells containing metal/metal ion, anode, cathode, electric circuit, salt bridge.	Reactivity 1.3 – Electrical energy can be derived from the combustion of fossil fuels or from electrochemical reactions. What are the similarities and differences in these reactions?

Voltaic cells generate electricity from spontaneous redox reactions

We have seen that in oxidation reactions electrons are lost and that in reduction reactions they are gained. If the half-reactions occur at spatially separated electrodes, the electrons need to pass through an external circuit between the electrodes and an electric current is produced. Let us consider again the reaction we discussed on page 756 in which zinc reduced copper ions. Remember that here zinc was the reducing agent and became oxidized while copper ions were reduced. When the reaction is carried out in a single test tube, as shown in the photo on page 756, the electrons flow spontaneously from the zinc atoms to the copper ions in the solution and, as we noted, energy is released in the form of heat. It is an exothermic reaction. Alternatively, we can separate the two half-reactions:

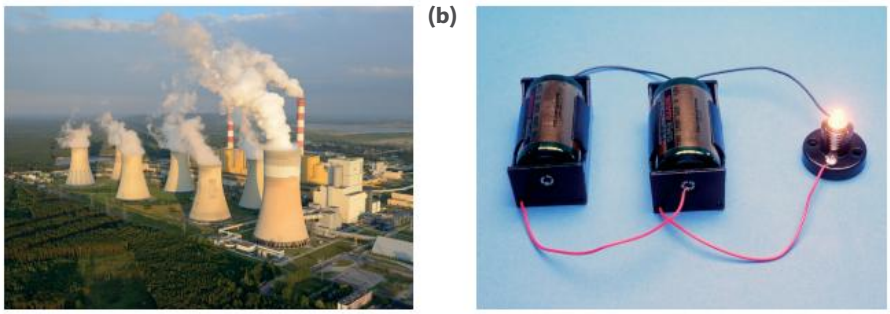
oxidation $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

reduction $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Electrons pass from the zinc to the copper ions through the external circuit.

This is known as a voltaic or a **galvanic cell**, and we will see how it is constructed in the next section. The half-cells connected in this way are often called **electrodes.** As the chemicals are not renewed during the process it is also known as a **primary cell.** A battery normally consists of several cells connected together.

(a) **(b)**

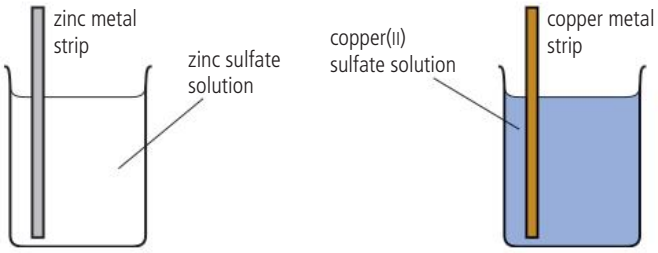


Electrical energy can be produced from chemical energy **(a)** indirectly by the combustion of fuels or **(b)** directly in a battery. Both involve redox reactions. Electrical energy is produced directly from the oxidation of a fuel in a fuel cell. These are discussed on page 772

Reactivity 1.3 – Electrical energy can be derived from the combustion of fossil fuels or from electrochemical reactions. What are the similarities and differences in these reactions?

Half-cells generate electrode potentials

There are many types of half-cell but probably the simplest is made by putting a strip of metal into a solution of its ions (Figure 2).



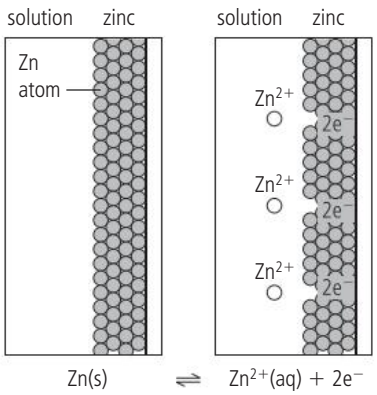
R3.2 Figure 2 Copper and zinc half-cells.



A copper half-cell consisting of a piece of copper metal dipped into a solution of a copper salt. An equilibrium is set up between the Cu metal and its ions:
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$

In the zinc half-cell, zinc atoms form ions by releasing electrons that will make the surface of the metal negatively charged with respect to the solution (Figure 3).

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \text{ (electrons give the electrode a negative charge)}$$



R3.2 Figure 3 Zinc atoms form zinc ions by releasing electrons. An equilibrium is set up between the metal and its solution of ions.

The negative charge on the electrode attracts zinc ions which can gain electrons in the reverse process:

$$Zn(s) \leftarrow Zn^{2+}(aq) + 2e^-$$

At a particular charge separation the rates of both processes will be the same and equilibrium is reached:

$$Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$$

The position of this equilibrium depends on the reactivity of the metal. The more reactive the metal, the more the equilibrium favours the formation of ions, and the greater the negative charge on the electrode. As copper is a less reactive metal, the equilibrium position favours the formation of metal in its half-cell:

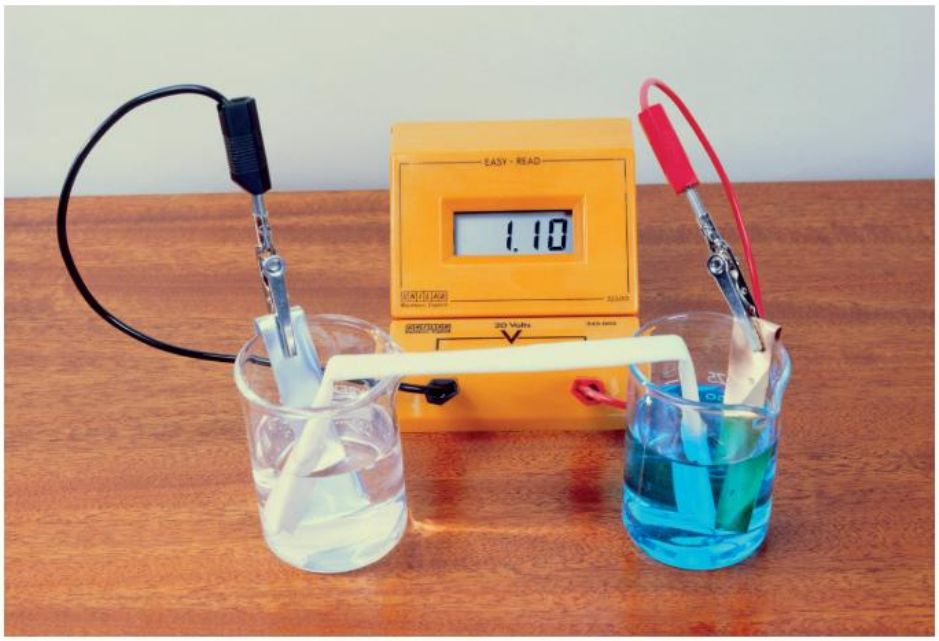
$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$$

Investigation of voltaic cells. Full details of how to carry out this experiment with a worksheet are available in the eBook.

SKILLS

The copper metal strip will have fewer electrons and be less negative than the zinc metal strip.

When these two half-cells are connected by an external wire and a salt bridge, electrons will have a tendency to flow spontaneously through the external circuit from the more negative zinc half-cell to the less negative copper half-cell. The tendency for the electrons to flow can be quantified by measuring the potential difference between the two electrodes with a voltmeter.



Zinc–copper voltaic cell showing a copper half-cell and a zinc half-cell connected by a salt bridge. Electrons flow from the zinc electrode to the copper electrode through the electrical wires, while ions flow through the salt bridge to complete the circuit. The voltmeter is showing 1.10 V, the potential difference of this cell.

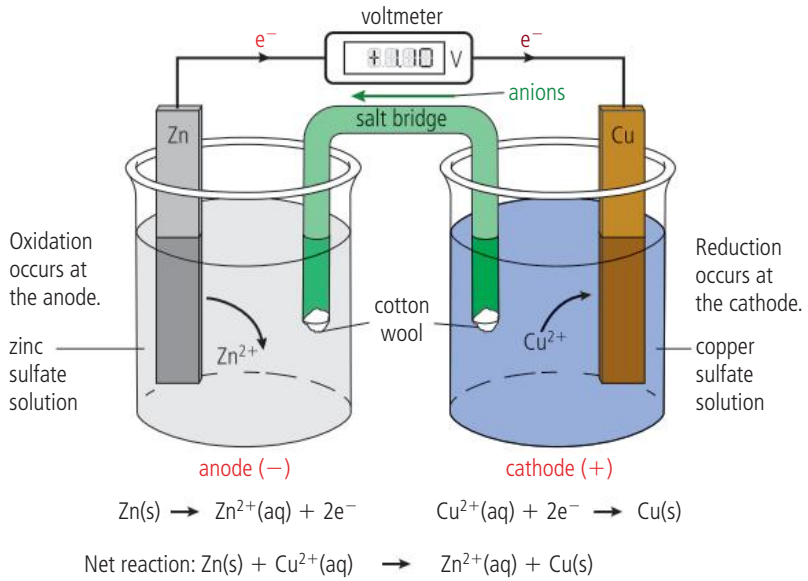
Oxidation always occurs at the anode; reduction always occurs at the cathode. In the voltaic cell, the anode has a negative charge and the cathode has a positive charge.

The electrode where oxidation occurs is called the **anode**, in this case it is the zinc electrode, and it has a negative charge:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

The electrode where reduction occurs is called the **cathode**, in this case it is the copper electrode and it has a positive charge:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$



R3.2 Figure 4 A copper–zinc voltaic cell.

The voltaic cell (Figure 4) must therefore have the following connections between the half-cells.

- An external electronic circuit, connected to the metal electrode in each half-cell. A voltmeter can also be attached to this external circuit to record the voltage generated. Electrons will flow from the negative terminal, the anode, to the positive terminal, the cathode, through the wire.
- A salt bridge completes the circuit. The salt bridge is a glass tube or strip of absorptive paper that contains an aqueous solution of ions. Movement of these ions neutralizes any build up of charge and maintains the potential difference. Anions move in the salt bridge from the cathode to the anode. Anions move in the opposite direction to the electrons in the external circuit. Cations move in the opposite direction to anions in the salt bridge from the anode to the cathode. The solution chosen is often aqueous $NaNO_3$ or KNO_3 as these ions will not interfere with the reactions at the electrodes. Without a salt bridge, the circuit is incomplete and no voltage is generated.

SKILLS

Building voltaic cells with different combinations of metals/metal ion electrodes will help in the understanding of this topic.

In general, the more reactive the metal, the greater the build-up of electrons and the more negative the electrode potential in its half-cell.

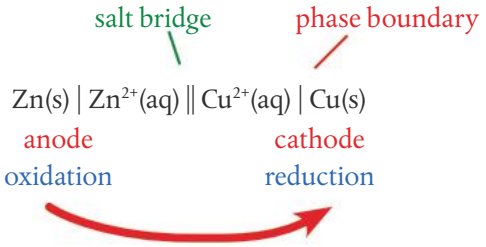
Cell diagram convention

The arrangements of electrodes in a voltaic cell can be summarized in a **cell diagram.** This has the following features:

- a single vertical line represents a phase boundary such as that between a solid electrode and an aqueous solution within a half-cell
- a double vertical line represents the salt bridge
- the aqueous solutions of each electrode are placed next to the salt bridge

- the anode is generally put on the left and the cathode on the right, so electrons flow from left to right
- spectator ions are usually omitted from the diagram
- if a half-cell includes two ions, they are separated by a comma because they are in the same phase.

The cell diagram for the copper–zinc cell discussed earlier is:



$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $\quad$ $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Note that the cell diagram is set out to show the direction of the two half-reactions.

Anode	Cathode
$Zn(s) \mid Zn^{2+}(aq) : Zn(s) \rightarrow Zn^{2+}(aq)$	$Cu^{2+}(aq) \mid Cu(s) : Cu^{2+}(aq) \rightarrow Cu(s)$

Different half-cells make voltaic cells with different voltages

Any two half-cells can be connected together to make a voltaic cell. For any such cell, the direction of electron flow and the voltage generated will be determined by the *difference* in reducing strength of the two metals. In most cases this can be judged by the relative position of the metals in the activity series. For example, if we connect a zinc half-cell to a silver half-cell the corresponding cell reaction is:

$$Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2\,Ag(s)$$

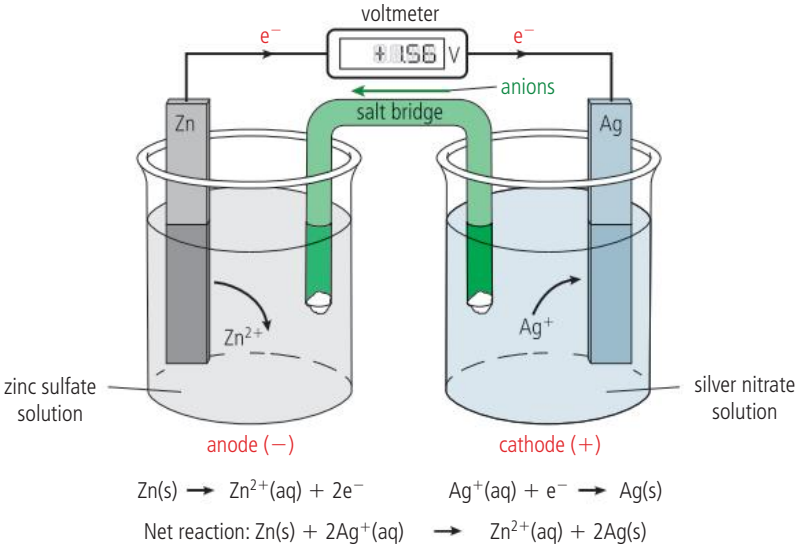
A larger voltage would be produced than with the copper half-cell discussed earlier because the difference in electrode potentials of zinc and silver is greater than that between zinc and copper.

The two half-reactions are:

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

$$2Ag^{2+}(aq) + 2e^- \rightarrow 2Ag(s)$$

Electrons would flow from zinc (anode), where electrons are produced, to silver (cathode), where they are accepted as shown in Figure 5.



R3.2 Figure 5 A silver–zinc voltaic cell.

If we now make a voltaic cell with one copper electrode and one silver electrode (Figure 6), the cell reaction is:

$$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

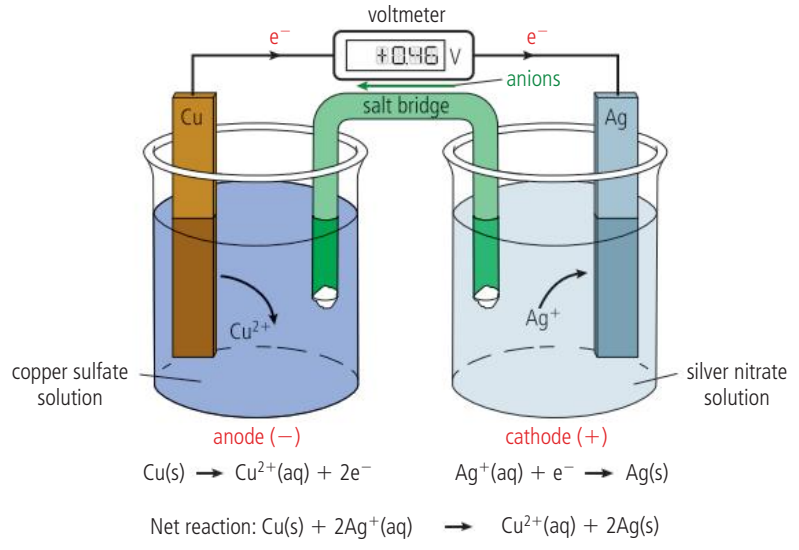
and the half-reactions are:

$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$$

$$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$$

The direction of electron flow is now *away* from copper and towards silver due to the greater reducing power of copper. The copper electrode is the negative electrode of the cell as it has the lower electrode potential.

In a voltaic cell, electrons always flow in the external circuit from anode to cathode. The anode is the negative electrode, and the cathode is the positive electrode.



R3.2 Figure 6 A silver–copper voltaic cell.

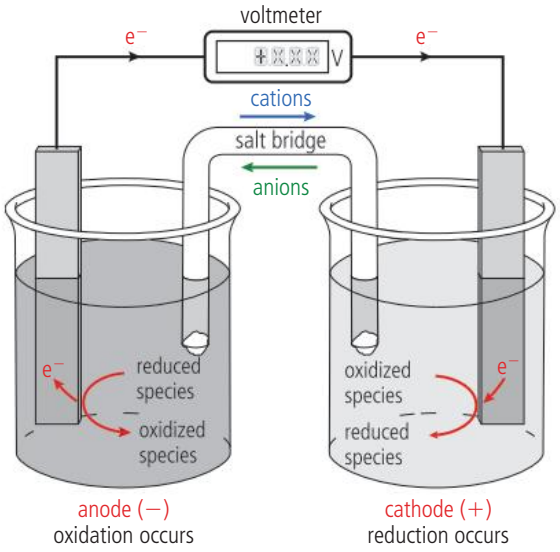


Used batteries awaiting recycling. Batteries contain metals that can be recycled.

Batteries are an application of a voltaic cell, making electrical energy available as a source of power. Our reliance on batteries increases as global demand for mobile electronic devices such as smartphones, laptops and tablets continues to grow. While demand for batteries looks set to continue, there is concern over toxicity and environmental damage from battery disposal. Batteries should be recycled as they contain metals such as zinc, cobalt, manganese, copper, cadmium and iron.

We can now summarize the parts of a voltaic cell and the direction of movement of electrons and ions (Figure 7):

- the anode is the negative electrode and the cathode is the positive electrode
- electrons flow from anode to cathode through the external circuit
- anions migrate from cathode to anode through the salt bridge
- cations migrate from anode to cathode through the salt bridge.



R3.2 Figure 7 Summary of the components of a voltaic cell showing the ion and electron movements.

Nature of Science

The Italian scientist Luigi Galvani noticed the leg muscles of a dead frog twitched when they were in contact with two different metals. After many experiments, he concluded that the contractions were caused by an electrical fluid that was carried to the muscles in the nerves. His contemporary and fellow countryman Alessandro Volta had an intuition that the source of the electricity was not biological but originated instead from the interaction between the two metals. He confirmed his hypothesis by building a 'voltaic pile' from pairs of metals separated by a conducting solution and demonstrated that this generated an electric current. The terms galvanic cell and voltaic cell are used in recognition of both men's contribution to their discovery. The role of chance observations or serendipity is often a feature of scientific discovery. Scientific progress is not, however, down to luck, as the significance of these observations needs to be recognized. As Louis Pasteur said, 'Chance favours only the prepared mind'.



Italian physicist Count Alessandro Volta (1745–1827) demonstrates his newly invented battery or 'voltaic pile' to Napoleon Bonaparte in 1801. Constructed from alternating discs of zinc and copper with pieces of cardboard soaked in brine between the metals, his voltaic pile was the first battery that produced a reliable, steady current of electricity.

Exercise

Q24. Use the metal activity series on page 760 to predict which electrode will be the anode and which will be the cathode when the following half-cells are connected. Write half-equations for the reactions occurring at each electrode.

(a) Zn/Zn^{2+} and Fe/Fe^{2+}

(b) Fe/Fe^{2+} and Mg/Mg^{2+}

(c) Mg/Mg^{2+} and Cu/Cu^{2+}

Q25. A voltaic cell can be constructed with one half-cell consisting of Mg and a solution of Mg^{2+} ions and the other of Zn and a solution of Zn^{2+} ions.

(a) Draw a diagram of the cell and label the electrodes with name and polarity, and the direction of electron and ion movement, and write equations for the reactions occurring at each electrode.

(b) Write the cell diagram to represent the above voltaic cell.

Q26. Predict what would be observed if an iron spatula was left in a solution of copper sulfate overnight.

Reactivity 3.2.7 – Secondary (rechargeable) cells

Reactivity 3.2.7 – Secondary (rechargeable) cells involve redox reactions that can be reversed using electrical energy.	
Deduce the reactions of the charging process from given electrode reactions for discharge, and vice versa.	
Include discussion of advantages and disadvantages of fuel cells, primary cells and secondary cells.	Reactivity 2.3 – Secondary cells rely on electrode reactions that are reversible. What are the common features of these reactions?

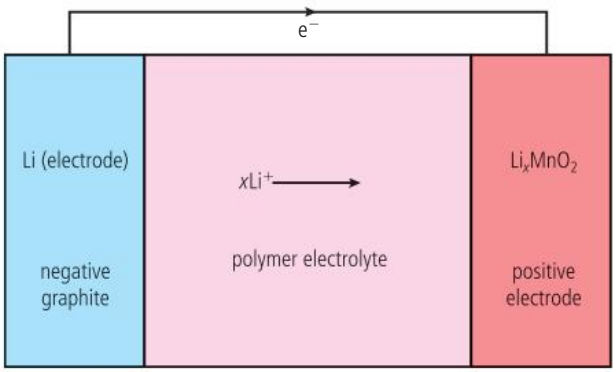
Secondary (rechargeable) cells involve redox reactions that can be reversed

A primary cell or battery is one that cannot be recharged. A secondary cell or battery is one that can be recharged.

We have so far discussed primary cells where the electrochemical reaction is irreversible. The cell reactions involve the production of aqueous ions or gas molecules which become dispersed during the reaction. In this section we will discuss secondary cells which involve redox reactions that can be reversed using electrical energy. As they can be recharged, they have a longer life than primary cells. Rechargeable batteries, which contain many rechargeable cells connected together, are more expensive to buy but they become more economical with use.

The lithium-ion battery

One of the most promising reusable batteries is the lithium-ion battery, which benefits from lithium's low density and high reactivity (Figure 8). It can store a lot of electrical energy per unit mass. As lithium metal is reactive, steps must be taken to prevent it from forming an oxide layer which would decrease contact with the electrolyte. The lithium cathode is placed in the lattice of a metal oxide (MnO_2) and the lithium anode is mixed with graphite. A non-aqueous polymer-based electrolyte is used. As discussed in Reactivity 1.8, an electrolyte is a substance which does not conduct electricity in the solid state, but does conduct electricity when molten or in aqueous solution as it has ions which are free to move.



R3.2 Figure 8 The lithium-ion battery.

Discharging a lithium-ion battery

At the negative electrode, lithium is oxidized:

$$Li(polymer) \rightarrow Li^+(polymer) + e^-$$

At the positive electrode, the Li^+ ion and MnO_2 are reduced:

$$Li^+(polymer) + MnO_2(s) + e^- \rightarrow LiMnO_2(s)$$

The two half-reactions are reversed when the battery is recharged.

Lithium-ion batteries are used in cell (mobile) phones, laptops, computers and cameras.



Lithium-ion battery. This is a rechargeable battery often used in electrical equipment. The energy is stored in the battery through the movement of lithium ions. The first commercial lithium-ion battery was produced in 1991.

Worked example

Rechargeable nickel–cadmium batteries are used in electronics and toys. When the battery is discharged, the positive electrode is nickel hydroxide and the negative electrode is cadmium hydroxide. The electrolyte is aqueous potassium hydroxide.

During the charging process a cadmium(II) hydroxide electrode is reduced to the element and a nickel(II) hydroxide electrode is oxidized to NiO(OH).

(a) Deduce the reduction half-reaction during charging.

(b) Deduce the oxidation half-reaction during charging.

(c) Deduce the chemical equation for the charging process.

(d) State the chemical equation for the discharging process and explain why the process can be reversed.

Solution

(a) $Cd(OH)_2(s) + 2e^- \rightarrow Cd(s)$: 2 electrons are needed as Cd is reduced from $+2 \rightarrow 0$

$Cd(OH)_2(s) + 2e^- \rightarrow Cd(s) + 2OH^-(aq)$: 2 $OH^-(aq)$ are needed to balance the charges and the atoms.

(b) $Ni(OH)_2(s) \rightarrow NiO(OH)(s) + e^-$: 1 electron is produced as Ni is oxidized from $+2 \rightarrow +3$

$Ni(OH)_2(s) + OH^-(aq) \rightarrow NiO(OH)(s) + e^-$: 1 $OH^-(aq)$ is needed to balance the charges

$Ni(OH)_2(s) + OH^-(aq) \rightarrow NiO(OH)(s) + H_2O(l) + e^-$: 1 $H_2O(aq)$ is added to balance the atoms

(c) State the half-reactions for 2 electrons:

$Cd(OH)_2(s) + 2e^- \rightarrow Cd(s) + 2OH^-(aq)$

$2Ni(OH)_2(s) + 2OH^-(aq) \rightarrow 2NiO(OH)(s) + 2H_2O(l) + 2e^-$

Add the half-reactions:

$$2Ni(OH)_2(s) + \cancel{2OH^-(aq)} + Cd(OH)_2(s) + \cancel{2e^-} \rightarrow 2NiO(OH)(s) + 2H_2O(l) + \cancel{2e^-} + Cd(s) + \cancel{2OH^-(aq)}$$

which gives

$$2Ni(OH)_2(s) + Cd(OH)_2(s) \rightarrow 2NiO(OH)(s) + 2H_2O(l) + Cd(s)$$

(d) $2NiO(OH)(s) + Cd(s) + 2H_2O(l) \rightarrow 2Ni(OH)_2(s) + Cd(OH)_2(s)$

This reaction can be reversed as both metal hydroxides are insoluble and so cannot be dispersed. A common feature of secondary cells is that the products cannot be dispersed away from the electrodes.

A fuel cell converts chemical energy directly to electrical energy

As combustion reactions are redox reactions, they can be used to produce an electric current if the reactants are physically separated. This is the basis of a fuel cell which, unlike primary voltaic cells, requires a constant supply of fuel and oxygen to the electrodes to produce electricity continuously as they are consumed in the process.

Reactivity 2.3 – Secondary cells rely on electrode reactions that are reversible. What are the common features of these reactions?

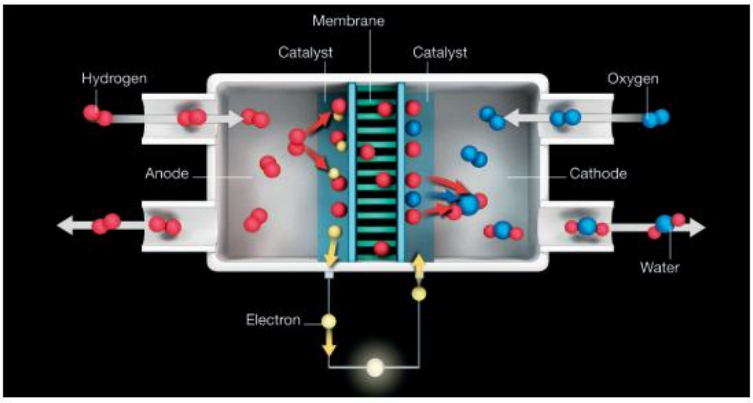
The hydrogen fuel cell

The use of the hydrogen fuel cell could reduce our dependence on fossil fuels. One mole of hydrogen can release 286 kJ of heat energy when it combines directly with oxygen:

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta H_f^{\ominus}\ (\text{kJ mol}^{-1}) = -285.8\ \text{kJ mol}^{-1}$$

HL The Gibbs energy, introduced in Reactivity 3.4, gives the maximum energy available for electrical output.

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta G^{\ominus} = -228.6\ \text{kJ mol}^{-1}$$



The hydrogen fuel cell is a clean and efficient power source. Hydrogen (red) is pumped into the cell, where protons (the hydrogen nuclei) are separated from their electrons (yellow). The electrons flow around a conducting loop as an electric current, which can be harnessed. The hydrogen nuclei (H^+) pass through a membrane and then combine with the electrons and oxygen from the air to form steam, and water is the only waste product.

Worked example

Deduce the two half-reactions that occur at the anode and the cathode in the hydrogen–oxygen fuel cell in acid conditions.

Solution

At the negative electrode (anode), $H_2(g)$ is oxidized:

$$2H_2(g) \rightarrow 4H^+(aq) + 4e^-$$

At the positive electrode (cathode), $O_2(g)$ is reduced:

$$4H^+(aq) + O_2(g) + 4e^- \rightarrow 4H_2O(l)$$

Challenge yourself

5. Deduce the two half-reactions that occur at the anode and the cathode in the hydrogen–oxygen fuel cell with aqueous sodium hydroxide as the electrolyte.

HL

6. **(a)** Show that the maximum efficiency of the hydrogen fuel cell with water as the product is about 83%.

(b) Calculate the maximum efficiency of the hydrogen cell when steam is produced instead of water.

(c) Explain the increased efficiency of a hydrogen–oxygen fuel cell which produces steam compared to water.

HL end

Advantages and disadvantages of fuel cells, primary cells and secondary cells

Some advantages and disadvantages of the different systems are summarized below.

Type of cell/battery		Advantages	Disadvantages
Primary	general	• inexpensive • convenient • lightweight • good shelf life	• can only be used once • leads to a large amount of waste as batteries need to be recycled • batteries put into landfill sites have severe environmental impact • can only deliver small currents
	fuel cell	• more efficient than direct combustion as more chemical energy is converted to useful electrical energy • no pollution if hydrogen is the fuel • low density of hydrogen	• hydrogen is a potentially explosive gas • hydrogen must be stored and transported in large/heavy containers • very expensive • technical problems due to catalytic failures, leaks and corrosion • can deliver only small currents • low reaction rates and therefore low power output
Rechargeable / secondary	general	• materials can be regenerated • can deliver high current	
	lead–acid	• can deliver large amounts of energy over short periods	• heavy mass • lead and sulfuric acid could cause pollution
	cadmium–nickel	• longer life than lead-acid batteries	• cadmium is very toxic • produces a low voltage • very expensive
	lithium ion	• low density of lithium • high voltage • does not contain a toxic heavy metal	• expensive • limited life span

Exercise

Q27. The reaction taking place when a lead–acid storage battery discharges is:

$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$$

(a) Use oxidation numbers to explain what happens to the Pb(s) in terms of oxidation and reduction during this reaction.

(b) Write a balanced half-equation for the reactions taking place at the negative terminal during this discharge process.

(c) Identify the property of $PbSO_4$ which allows this process to be reversed.

(d) State **one** advantage and **one** disadvantage of using a lead–acid battery.

Q28. One type of fuel cell uses methanol as the fuel with an acid electrolyte. The overall equation for the process is:

$$2CH_3OH\,(aq) + 3O_2\,(g) \rightarrow 2CO_2\,(g) + 4H_2O\,(l)$$

(a) State the half-equations for the reactions at the negative electrode.

(b) State the half-equations for the reactions at the positive electrode.

(c) Suggest **one** advantage and **one** disadvantage of a methanol fuel cell over a lead–acid battery as an energy source in a car.

Q29. One type of fuel cell uses hydrogen as the fuel with hot aqueous potassium hydroxide as the electrolyte. The overall equation for the process is:

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

(a) State the two half-equations for the reactions involving each reactant.

(b) Hydrogen is a more expensive source of chemical energy than gasoline (petrol). Explain why fuel cells are considered to be more economical than gasoline engines.

(c) State one common feature of primary, fuel and rechargeable cells.

Reactivity 3.2.8 – Electrolytic cells

Reactivity 3.2.8 – An electrolytic cell is an electrochemical cell that converts electrical energy to chemical energy by bringing about non-spontaneous reactions.	
Explain how current is conducted in an electrolytic cell. Deduce the products of the electrolysis of a molten salt.	
Construction of electrolytic cells to include DC power source connected to anode and cathode, electrolyte.	Structure 2.1 – Under what conditions can ionic compounds act as electrolytes?

An external source of electricity can drive non-spontaneous redox reactions

As we have seen, a voltaic cell takes the energy of a spontaneous redox reaction and harnesses it to generate electrical energy. An **electrolytic cell** reverses this process: it uses an external source of electrical energy to bring about a non-spontaneous

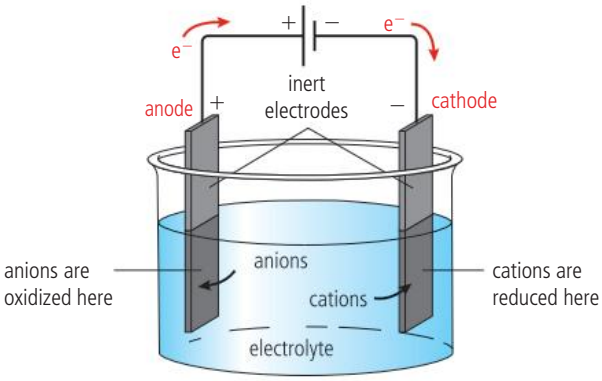
redox reaction that would otherwise not take place. You can think of it in terms of an external power supply pumping electrons into the electrolytic cell, driving reactions of oxidation and reduction. As the word *electro-lysis* suggests, it is the process where electricity is used to bring about chemical reactions which break down substances.

The reactant in the process of electrolysis must contain mobile ions which allow the current to pass between the electrodes. It is an **electrolyte**, which is a liquid, usually a molten ionic compound or an aqueous solution of an ionic compound. As the electric current passes through the electrolyte, redox reactions occur at the electrodes, removing the charges on the ions and forming products that are electrically neutral. The ions are therefore said to be **discharged** during this process.

An electrolyte is a substance which does not conduct electricity in the solid state but does conduct electricity when molten or in aqueous solution as it has ions which are free to move.

An electrolytic cell

The components of an electrolytic cell are shown in Figure 9 and described below.



R3.2 Figure 9 Components of an electrolytic cell.

SKILLS

Investigating electrolytic cells. Full details of how to carry out this experiment with a worksheet are available in the eBook.

- The source of electric energy is a battery or a DC power source. This is shown in the diagram as ||– where the longer line represents the positive terminal and the shorter line the negative terminal.
- The electrodes are placed in the electrolyte and connected to the power supply. Electrodes are made from a conducting substance – generally a metal or graphite. They are described as **inert** when they do not take part in the redox reactions. They must not touch each other as this would 'short' the circuit, and the current would bypass the electrolytic cell.
- Electric wires connect the electrodes to the power supply.

Electricity can reverse the natural direction of change

In Structure 2.1 we discussed the spontaneous reaction between sodium and chlorine to produce sodium chloride.

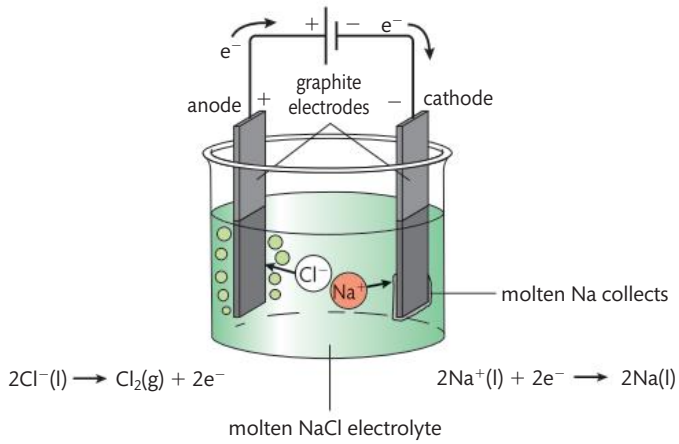
$$Na(s) + \tfrac{1}{2}Cl_2(g) \rightarrow NaCl(s)$$

Electrons are transferred from the sodium to the chlorine. Sodium and chloride ions are formed which then bond to form a sodium chloride lattice.

This process can be reversed if solid sodium chloride is first converted into the molten state:

$$NaCl(s) \rightarrow Na^+(l) + Cl^-(l)$$

The ions are now mobile so the molten state conducts electricity and the ions act as an electrolyte if placed in an electrochemical cell (Figure 10).



R3.2 Figure 10 Electrolysis of molten sodium chloride. Chloride ions are oxidized at the anode and sodium ions are reduced at the cathode.

Reactive metals, including aluminium, lithium, magnesium, sodium and potassium, are found naturally in compounds such as Al_2O_3 and NaCl where they exist as positive ions. Extraction of the metal therefore involves reduction of these ions. This is best done using electrolysis.

The battery or DC power source pushes electrons towards the negative electrode, or cathode, where they are accepted as Na^+ ions are reduced in the electrolyte.

$$Na^+(l) + e^- \rightarrow Na(l)$$

Electrons are released at the positive terminal, the anode, as chloride ions are oxidized to chlorine atoms which then form chlorine molecules.

$$2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$$

Electrodes are electrically conducting, electrolytes are ionically conducting. Ionic compounds can act as electrolytes in the molten state or in solution.

The released electrons then move towards the positive terminal of the DC power source.

Balancing the two half-reactions at the electrodes we have the overall reaction:

$$2Na^+(l) + \cancel{2e^-} + Cl^-(l) \rightarrow 2Na(l) + \cancel{2e^-} + Cl_2(g)$$

$$2Na^+(l) + Cl^-(l) \rightarrow 2Na(l) + Cl_2(g)$$

The chemical reactions occurring at each electrode remove the ions from the electrolyte. The compound has been split into its constituent elements and electrolysis has occurred.

Note the current is passed through the electrolyte not by electrons but by the mobile ions as they migrate to the electrodes.

Ionic compounds can also conduct electricity in aqueous solution. This is discussed later in the chapter.

Structure 2.1 – Under what conditions can ionic compounds act as electrolytes?

The electrolysis of molten salts

We can generalize the results for the electrolysis of sodium chloride to other molten compounds. When the electrolyte is a molten salt, the only ions present are those from the compound itself, so one ion migrates to each electrode. Positive ions are reduced and gain electrons at the cathode – the negative electrode – and negative ions are oxidized and lose electrons at the anode – the positive electrode.

Worked example

Describe the reactions that occur at the two electrodes during the electrolysis of molten lead(II) bromide. Write an equation for the overall reaction and comment on any likely changes that would be observed.

Solution

1. Identify the ions present in the electrolyte and to which electrode they will be attracted:

$$PbBr_2(l) \rightarrow Pb^{2+}(l) + 2Br^-(l)$$

to cathode to anode

2. Deduce the half-reactions at each electrode:

anode: Br^- is oxidized: $2Br^-(l) \rightarrow Br_2(l) + 2e^-$

cathode: Pb^{2+} is reduced: $Pb^{2+}(l) + 2e^- \rightarrow Pb(l)$

3. Add the half-equations to obtain overall reaction:

$$Pb^{2+}(l) + 2Br^-(l) \rightarrow Pb(l) + Br_2(l)$$

4. $Br_2(g)$, a brown vapour with a strong smell, is produced at the anode and Pb(l), a molten grey metal, is produced at the cathode.

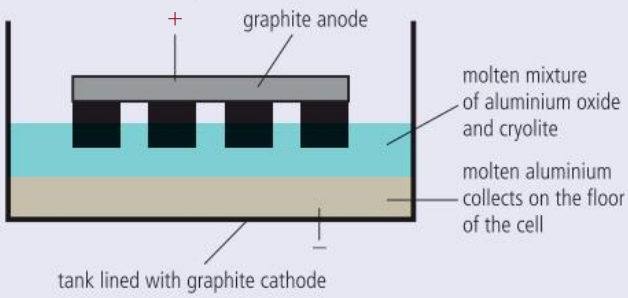
This can be set out in a table.

	Cathode	Anode
Ions present	$Pb^{2+}(l)$	$2Br^-(g)$
Reaction at electrode	$Pb^{2+}(l) + 2e^- \rightarrow Pb(l)$ lead is a liquid at the temperatures used	$2Br^-(l) \rightarrow Br_2(g) + 2e^-$ bromine is a gas at the temperatures used
Observations	a molten grey metal is produced	a brown vapour with a strong smell is produced

Lead(II) bromide has a relatively low melting point of 373 °C, but most other ionic compounds have very high melting points, so electrolysis of molten compounds generally involves working at high temperatures.

Worked example

Molten aluminium oxide is electrolyzed in the cell shown in the figure below. The graphite-lined steel on the outside acts as the cathode and graphite anodes are dipped into the molten electrolyte.



Describe and explain what happens at the cathode and anode. Explain your answer in terms of the redox reactions occurring at the electrodes, including equations in your answer.

The electrolytic extraction of aluminium was developed almost simultaneously by Charles Martin Hall and Paul Héroult, who worked independently on different sides of the Atlantic. They both discovered the process in the same year, 1886. Both were born in the same year (1863) and died in the same year (1914).

Napoleon III, the Emperor of France from 1848 to 1870, owned an aluminium dinner service which was said to be more precious than gold. The high value reflects the difficulty of extracting the metal at the time.



Worker siphoning off molten aluminium in an aluminium processing plant. Electrolysis of a solution of alumina (Al_2O_3) dissolved in cryolite is used to reduce the Al^{3+} ions at the cathode. The molten aluminium is siphoned off and cooled before any further processing.

Solution

Aluminium ions are attracted towards the negative electrode where they are reduced to aluminium atoms:

$$Al^{3+}(l) + 3e^- \rightarrow Al(l)$$

Oxygen is produced at the anode from the oxide ions:

$$2O^{2-}(l) \rightarrow O_2(g) + 4e^-$$

Challenge yourself

7. Explain with chemical equations why the carbon anodes used in the electrolysis of aluminium oxide need to be replaced at regular intervals.
8. Cryolite is added to molten aluminium oxide to increase its conductivity. Explain the low conductivity of aluminium oxide.

Exercise

Q30. Identify the electrodes to which potassium ions are attracted during the electrolysis of molten potassium bromide.

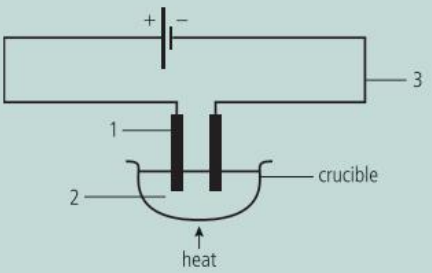
A The anode which has a positive charge.

B The anode which has a negative charge.

C The cathode which has a positive charge.

D The cathode which has a negative charge.

Q31. Identify the processes that occur in an electrical circuit with an electrolytic cell with a lithium iodide electrolyte.



	1	2	3
A	electrode where reduction occurs	ions migrating	electrons moving anticlockwise
B	electrode where oxidation occurs	ions migrating	electrons moving clockwise
C	electrode where reduction occurs	electrons moving anticlockwise	ions migrating
D	electrode where oxidation occurs	electrons moving clockwise	ions migrating

Q32. Which statement is *not* correct for the electrolysis of copper(II) chloride?

A Copper ions and chloride ions move through the electrolyte.

B Oxidation of chloride takes place at the anode.

C Electrons move through the external circuit.

D Oxidation of chlorine takes place at the cathode.

Q33. Write half-equations for the electrode reactions occurring during the electrolysis of the following molten salts using graphite electrodes.

(a) KBr **(b)** MgF_2 **(c)** ZnS **(d)** $CaCl_2$

Q34. Magnesium metal is produced by the electrolysis of molten magnesium chloride using inert electrodes.

(a) Draw a fully labelled diagram of the electrolytic cell, including the polarity on the electrodes and the direction of electron and ion migration.

(b) Write equations for the reactions occurring at each electrode and the overall cell reaction.

In industrial processes, another compound is often added to lower the melting point of the compound to be electrolyzed. This makes the process more economical. Molten cryolite – a mineral form of Na_3AlF_6 is added to reduce the melting point of aluminium oxide and so reduces the energy requirements of the process. Pure aluminium oxide would not be a suitable electrolyte because it has a very high melting point, and it is a poor electrical conductor even when molten.

Reactivity 3.2.9 – Oxidation of functional groups in organic compounds

Reactivity 3.2.9 – Functional groups in organic compounds may undergo oxidation.

Deduce equations to show changes in the functional groups during oxidation of primary and secondary alcohols, including the two-step reaction in the oxidation of primary alcohols.

Include explanation of the experimental set-up for distillation and reflux. Include the fact that tertiary alcohols are not oxidized under similar conditions. Names and formulas of specific oxidizing agents and the mechanism will not be assessed.	Structure 3.2 – How does the nature of the functional group in a molecule affect its physical properties, such as boiling point? Reactivity 1.3 – What is the difference between combustion and oxidation of an alcohol? HL Structure 3.1 – Why is there a colour change when an alcohol is oxidized by a transition element compound?

Oxidation of alcohols

As discussed in Reactivity 1.3, the combustion of organic compounds breaks the carbon chain.

Worked example

Use oxidation numbers to show the difference in the extent of oxidation of complete and incomplete combustion of propane.

Solution

In C_3H_8 the average oxidation state of C is $-\frac{8}{3}$

Complete combustion produces CO_2 in which the carbon has an oxidation state of +4.

Incomplete oxidation produces CO, in which the carbon has an oxidation state of +2, and C, in which the carbon has an oxidation state of 0.

Challenge yourself

9. Use oxidation numbers to show the differences in the extent of oxidation in the complete combustion of propane, $CH_3CH_2CH_3$, and propene, CH_3CHCH_2.

More subtle oxidation can occur when an oxidizing agent selectively oxidizes only the carbon atom of a functional group. Alcohols can be oxidized into other important organic compounds when oxidizing agents selectively oxidize the carbon atom attached to the −OH group, keeping the carbon skeleton of the molecule intact. The products of these reactions are determined by whether the alcohol is a primary, secondary or tertiary alcohol. The distinction between the different alcohols is described in Structure 3.2.

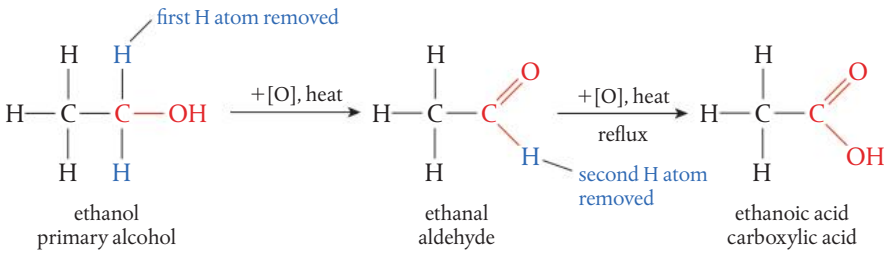
Various oxidizing agents can be used for these reactions, but commonly the laboratory process uses acidified potassium dichromate(VI). This is a bright orange solution, which is reduced to green $Cr^{3+}(aq)$ as the alcohol is oxidized on heating. The colour of a transition metal depends on the oxidation state of the metal.

HL Structure 3.1 – Why is there a colour change when an alcohol is oxidized by a transition element compound?

When writing equations for these reactions it is sometimes convenient to show the oxidizing agent simply as '+ [O]'.

The degree of oxidation can be related to the number of H atoms attached to the carbon with the hydroxyl group. Primary alcohols have two H atoms attached to the carbon with the hydroxyl group and can be oxidized in a two-step reaction. The removal of the first H atom leads to the formation of the aldehyde. The second H atom is removed under prolonged reaction, and a carboxylic acid is formed.

For example: ethanol is oxidized to ethanal in one step and to ethanoic acid in two steps:



When a bottle of wine is exposed to the air, bacteria slowly oxidize the ethanol to ethanoic acid, giving the smell of vinegar – *'vin aigre'* means 'bitter wine' in French.

And acidified dichromate $Cr_2O_7^{2-}$ is reduced to $Cr^{3+}(aq)$:

$$Cr_2O_7^{2-} \xrightarrow{\text{reduction}} Cr^{3+}(aq)$$

It is possible to remove the aldehyde product as it is formed by distillation because it has a lower boiling point than the primary alcohol or the carboxylic acid. Aldehydes do not have hydrogen bonding between their molecules, unlike the alcohol or the acid.

Distillation is discussed in more detail in Structure 1.1.



Distillation apparatus is used to separate liquids with different boiling points. In the oxidation of primary alcohols, the aldehyde has a lower boiling point than the alcohol or the acid, and so is collected as a gas and passes into the condensing tube, which is surrounded by cold flowing water. The gas condenses back to a liquid which is collected in the beaker at the bottom.

If we want to produce the carboxylic acid, the aldehyde needs to react with the oxidizing agent for a prolonged period of time. The reaction mixture is heated under **reflux** which means the aldehyde condenses back into the reaction mixture when it evaporates. The apparatus for reflux is shown below.

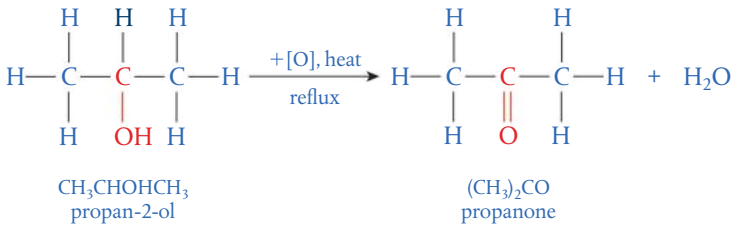


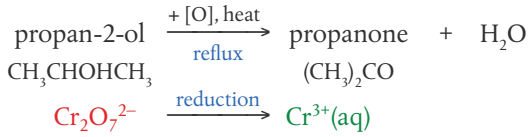
Reflux heating using an electric mantle. The heat boils the liquid, allowing the reaction to proceed at the boiling point of the solvent. The tubes bring cooling water to the condenser. Any vapour condenses back into the reaction vessel. This arrangement is used to oxidize primary alcohols to carboxylic acids.

Structure 3.2 – How does the nature of the functional group in a molecule affect its physical properties, such as boiling point?

When you are asked for the conditions for the oxidation reactions for primary alcohols, make sure that you specify the aldehyde is produced by distillation and the carboxylic acid by reflux.

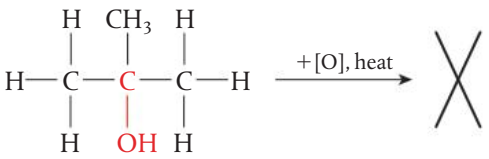
Secondary alcohols are oxidized to **ketones** by a similar process of oxidation. As there is only one H attached to the carbon bonded to the hydroxyl group, this is a one-step reaction.





SKILLS
Reactions of alcohols. Full details of how to carry out this experiment with a worksheet are available in the eBook.

Tertiary alcohols have no H atoms attached to the carbon bonded to the hydroxyl group and so are not readily oxidized without breaking the carbon chain. The carbon skeleton of the molecule is broken in combustion.



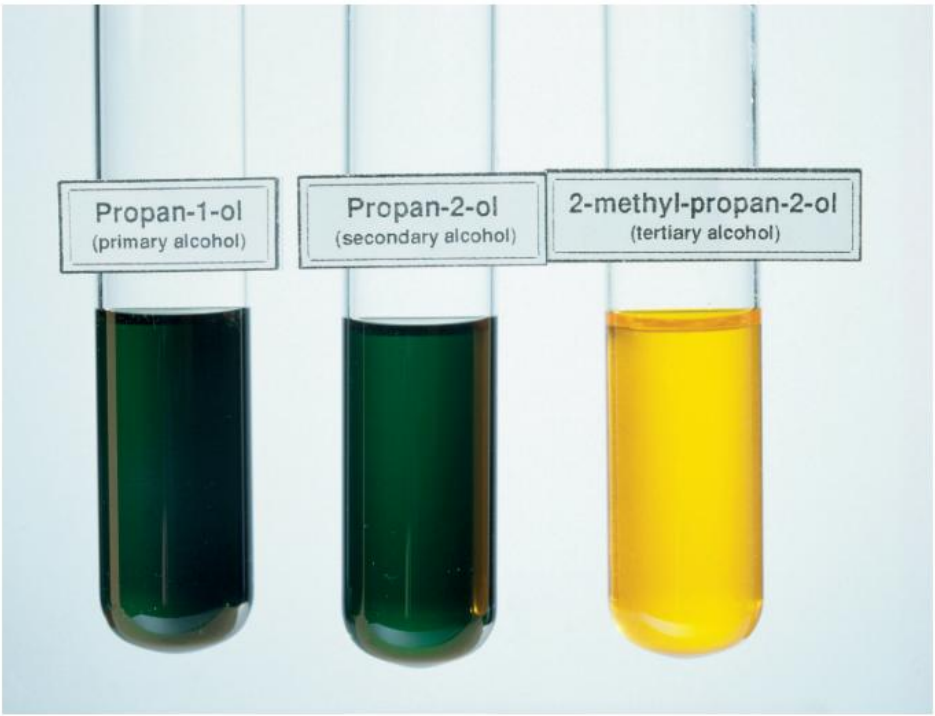
2-methylpropan-2-ol no reaction

2-methylpropan-2-ol $\xrightarrow{+[O],\ heat}$ no reaction

$H^+/Cr(VI)$ $\longrightarrow$ no change in colour

The colour change observed with potassium dichromate(VI), when it acts as an oxidizing agent from orange to green, is used to distinguish primary and secondary alcohols from tertiary alcohols. As there is no reaction with the tertiary alcohols, there is no colour change.

Reactivity 1.3 – What is the difference between combustion and oxidation of an alcohol?



The colour of the alcohol solutions after oxidation with potassium dichromate(VI) solution, $K_2Cr_2O_7$, which is orange. Primary and secondary alcohols are oxidized to carboxylic acids and ketones respectively, and the $Cr_2O_7^{2-}$ is reduced to green Cr^{3+}. Tertiary alcohols are not oxidized.

Alcohol	Oxidation product	Colour change with acidified $K_2Cr_2O_7$(aq)
primary alcohol	aldehyde → carboxylic acid	orange → green
secondary alcohol	ketone	orange → green
tertiary alcohol	not oxidized	no colour change

Alcoholic drinks are widely consumed globally. However, as blood alcohol levels rise, a person's balance and judgement could be impaired. Most countries have set legal limits of alcohol consumption for activities such as driving. Analysis of ethanol concentration is based on samples of breath, blood or urine. Common techniques use the oxidation reactions of ethanol in fuel cells or photocells (in which orange $Cr_2O_7^{2-}$ is reduced to green Cr^{3+}). Alcohol abuse can be a major contributor to social and economic problems in society.

Worked example

(a) Deduce the half-equations of oxidation and reduction for the reaction between ethanol and acidified potassium dichromate(VI) to produce ethanoic acid.

(b) Deduce the overall reaction.

Solution

(a) Consider first the oxidation: ethanol → ethanoic acid

We need to calculate the average oxidation state of carbon in each molecule.

The average oxidation state of C in ethanol = $\frac{(-6+2)}{2} = -2$

The average oxidation state of C in ethanoic acid = $\frac{(-4+4)}{2} = 0$

As both carbon atoms increase their oxidation state by +2, 4 electrons are released.

$$C_2H_5OH(aq) \rightarrow CH_3COOH(aq) + 4e^-$$

We add $4H^+$ to balance the charges:

$$C_2H_5OH(aq) \rightarrow CH_3COOH(aq) + 4e^- + 4H^+(aq)$$

We add H_2O to balance the H and the O atoms:

$$C_2H_5OH(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + 4e^- + 4H^+(aq)$$

Now consider the reduction: $Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq)$

The oxidation state of Cr in $Cr_2O_7^{2-}$ = +6 and the oxidation state of Cr in Cr^{3+} = +3

As both chromium atoms decrease their oxidation state by 3, 6 electrons are released.

$$Cr_2O_7^{2-}(aq) + 6e^- \rightarrow 2Cr^{3+}(aq)$$

Add $14H^+(aq)$ to balance the charges:

$$Cr_2O_7^{2-}(aq) + 6e^- + 14H^+(aq) \rightarrow 2Cr^{3+}(aq)$$

Add $7H_2O(l)$ to balance the H and O atoms:

$$Cr_2O_7^{2-}(aq) + 6e^- + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

(b) To deduce the overall reaction, balance the number of electrons in the half-reactions:

$$Cr_2O_7^{2-}(aq) + 6e^- + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

$$C_2H_5OH(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + 4e^- + 4H^+$$

12 is a common multiple

$$2Cr_2O_7^{2-}(aq) + 12e^- + 28H^+(aq) \rightarrow 4Cr^{3+}(aq) + 14H_2O(l)$$

$$3C_2H_5OH(aq) + 3H_2O(l) \rightarrow 3CH_3COOH(aq) + 12e^- + 12H^+(aq)$$

Adding the half-reactions and simplifying:

$$2Cr_2O_7^{2-}(aq) + \cancel{12e^-} + 28H^+(aq) + 3C_2H_5OH(aq) + 3H_2O(l) \rightarrow 4Cr^{3+}(aq) + 14H_2O(l) + 3CH_3COOH(aq) + \cancel{12e^-} + 12H^+(aq)$$

$$2Cr_2O_7^{2-}(aq) + 16H^+(aq) + 3C_2H_5OH(l) \rightarrow 4Cr^{3+}(aq) + 11H_2O(l) + 3CH_3COOH(aq)$$

Challenge yourself

10. Deduce the half-equations of oxidation and reduction for oxidation of ethanol to produce ethanal with acidified potassium dichromate(VI) and state the overall reaction.

Exercise

Q35. Identify the product when $CH_3CH_2CH(OH)CH_3$ is reacted with acidified potassium dichromate(VI).

A $CH_3CH_2COOCH_3$

B $CH_3CH_2CH_2CHO$

C $CH_3CH_2COCH_3$

D $CH_3CH_2CH_2COOH$

Q36. Identify the compound produced when propan-1-ol is oxidized using acidified potassium dichromate(VI), $K_2Cr_2O_7(aq)$, under two different conditions.

	Reaction mixture heated the under reflux	Product distilled as the oxidizing agent is added
A	propanone	propanal
B	propanone	propanoic acid
C	propanoic acid	propanal
D	propanal	propanoic acid

Q37. Identify the compound with the highest boiling point.

A $CH_3CH_2\,CH_2CH_3$

B $CH_3CH_2CH_2OH$

C $CH_3OCH_2CH_3$

D CH_3CH_2CHO

Q38. Write equations for the complete combustion of butanol and pentanol.

Q39. Predict the products of heating the following alcohols with acidified potassium dichromate(VI) solution, and the colour changes that would be observed in the reaction mixture.

(a) butan-2-ol

(b) methanol (product collected by distillation)

(c) 2-methylbutan-2-ol

Reactivity 3.2.10 – Reduction of functional groups in organic compounds

Reactivity 3.2.10 – Functional groups in organic compounds may undergo reduction. Deduce equations to show reduction of carboxylic acids to primary alcohols via the aldehyde, and reduction of ketones to secondary alcohols.	
Include the role of hydride ions in the reduction reaction. Names and formulas of specific reducing agents and the mechanisms will not be assessed.	Structure 3.1 – How can oxidation states be used to show that the following molecules are given in increasing order of oxidation: CH_4, CH_3OH, HCHO, HCOOH, CO_2?

Reduction of carbonyl compounds

It is often convenient in organic chemistry to analyse redox reactions in terms of gain and loss of oxygen or hydrogen, rather than in terms of electrons. As we saw in the last section, the oxidation of secondary alcohols to ketones involves the removal of 2 H atoms. We can reverse this process: ketones can be reduced to secondary alcohols by adding two H atoms. The reducing agent used provides the hydrogens in the form of H^- and H^+ ions. The carbonyl group is polar with a partial positive charge on the carbon atom and so can be attacked by species with a lone pair of electrons. As discussed in Reactivity 3.4, the hydride ion, H^- is acting as a **nucleophile** on the electron-deficient carbonyl carbon.

Aldehydes can be reduced to primary alcohols in a similar reaction.

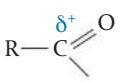
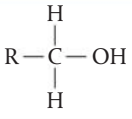
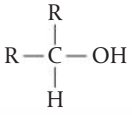
Carboxylic acids can also be reduced to aldehydes. We can show these reactions using '[+ H]' to represent reduction, in the same way as we used '[+O]' to represent oxidation of alcohols. Some examples are given below.

$$\underset{\substack{\text{ethanoic acid}\\\text{carboxylic acid}}}{CH_3COOH} \xrightarrow{[+H]} \underset{\substack{\text{ethanal}\\\text{aldehyde}}}{CH_3CHO} \xrightarrow{[+H]} \underset{\substack{\text{ethanol}\\\text{primary alcohol}}}{CH_3CH_2OH}$$

Conditions: heat with $LiAlH_4$ in dry ether. The reaction cannot be stopped at the aldehyde as it reacts too readily with $LiAlH_4$.

$$\underset{\substack{\text{propanone}\\\text{ketone}}}{(CH_3)_2CO} \xrightarrow{[+H]} \underset{\substack{\text{propan-2-ol}\\\text{secondary alcohol}}}{(CH_3)_2CHOH}$$

The reduction reactions are summarized in the table.

Attacking species	Reactive site	Functional group attacked	Functional group formed
H^- (hydride ion)		carboxylic acid aldehyde	primary alcohol 
		ketone	secondary alcohol 

Worked example

(a) Predict the product when pentan-2-one is reduced.

(b) Predict the product when butanoic acid is reduced.

Solution

(a) Draw the condensed formula with carbonyl group: $CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3$	Add H atoms to the carbonyl group: $CH_3CH_2CH_2\overset{\overset{OH}{\|}}{C}HCH_3$ Pentan-2-ol
(b) Draw the condensed formula with carbonyl group: $CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}OH$	Replace OH group by H: $CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}H$ Butanal
Aldehydes are further reduced by $LiAlH_4$ with H atoms added to carbonyl group.	$CH_3CH_2CH_2\overset{\overset{OH}{\|}}{C}H_2$ Butan-1-ol

Worked example

Deduce the half-equations for the reduction of methanoic acid to methanol.

Solution

$$HCOOH \rightarrow CH_3OH$$

The oxidation state of C in methanoic acid = −2 + 4 = +2

The oxidation state of C in methanol = −4 + 2 = −2

The carbon atom decreases its oxidation state by 4, so 4 electrons are needed:

$$HCOOH + 4e^- \rightarrow CH_3OH$$

Add $4H^+$ to balance the charges:

$$HCOOH + 4H^+ + 4e^- \rightarrow CH_3OH$$

Add H_2O to balance the H and the O atoms:

$$HCOOH + +4e^- + 4H^+ \rightarrow CH_3OH + H_2O$$

Challenge yourself

11. Deduce the half-equations for the reduction of methanal.

In the previous sections we have seen how alcohols, aldehydes, ketones and carboxylic acid can be interconverted by redox reactions. The degree of oxidation can be indicated by the oxidation state of the carbon atom as shown in the previous Worked example.

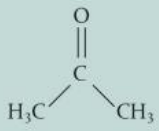


Structure 3.1 – How can oxidation states be used to show that the following molecules are given in increasing order of oxidation: CH_4, CH_3OH, HCHO, HCOOH, CO_2?

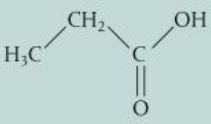
Exercise

Q40. Identify the compound which can be reduced to an aldehyde.

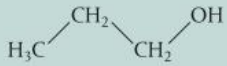
A



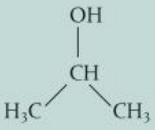
B



C



D



Q41. Identify the class of compound which are produced when RCOR' are reduced.

A ROR' **B** RCOOR' **C** RCH(OH)R' **D** RCOOH

Q42. Explain how the following reduction reactions are carried out in the laboratory:

(a) propanoic acid to propanol

(b) ethanal to ethanol

Q43. Deduce the half-equations for the reduction of ethanal with sodium borohydride.

Reactivity 3.2.11 – Reduction of unsaturated compounds

Reactivity 3.2.11 – Reduction of unsaturated compounds by the addition of hydrogen lowers the degree of unsaturation.	
Deduce the products of the reactions of hydrogen with alkenes and alkynes.	
	Reactivity 3.4 – Why are some reactions of alkenes classified as reduction reactions while others are classified as electrophilic addition reactions?

Alkenes and alkynes are unsaturated hydrocarbons.

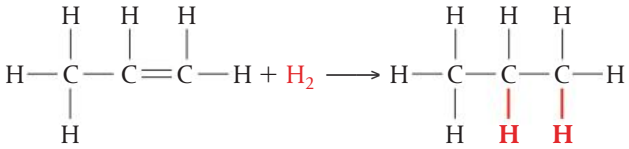
HL As discussed in Structure 2.2, alkenes contain a carbon–carbon double bond with a reactive π bond and alkynes have two reactive π bonds.

This enables both alkenes and alkynes to undergo **addition reactions** and so form a range of different saturated products. The alkenes generally react by electrophilic addition as discussed in Reactivity 3.4.

Alkenes can be reduced to alkanes by reacting with hydrogen:

$$C_nH_{2n} + H_2 \rightarrow C_nH_{2n+2}$$

Propene, for example, reacts with hydrogen in the presence of a nickel catalyst at about 150 °C:



$$\underset{\text{propene}}{CH_3CHCH_2} + H_2 \xrightarrow[150\,^\circ C]{\text{Ni catalyst}} \underset{\text{propane}}{CH_3CH_2CH_3}$$

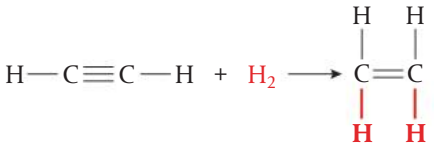
The nickel catalyst provides a surface for the reactant molecules to come together with the correct orientation. The hydrogen atoms add to the two carbon atoms simultaneously and the products leave the surface once the reaction is complete.

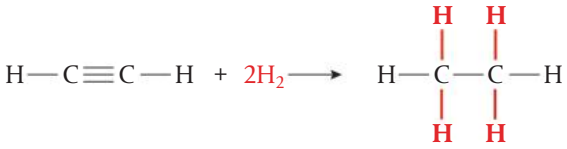
Reactivity 3.4 – Why are some reactions of alkenes classified as reduction reactions while others are classified as electrophilic addition reactions?

The hydrogenation of ethenes should be contrasted with halogenation which is an electrophilic addition where the chlorine atoms are added in two separate steps.

Unsaturated fatty acids have one or more carbon–carbon double bonds. As double bonds cannot rotate, the unsaturated carbon chains have kinks which make it more difficult for the molecules to pack closely together. The intermolecular forces are weaker, and the melting points are lower. Unsaturated fats are liquid oils under normal conditions. Hydrogenation is used in the margarine industry to convert oils containing many unsaturated hydrocarbon chains into more saturated compounds which have higher melting points. This is done so that margarine will be a solid at room temperature. However, there are widespread concerns about the health effects of so-called ***trans*** fats, produced by partial hydrogenation.

Similarly, alkynes can be reduced to alkenes and alkanes.





Be careful not to confuse the terms *hydrogenation* (addition of hydrogen) with *hydration* (addition of water).

The number of molecules of H_2 needed to convert the organic molecule to the corresponding saturated molecule is related to the number of multiple bonds in the molecule. The alkenes have the general molecular formula C_nH_{2n} so one molecule of hydrogen reacts with the carbon–carbon double bond of the alkenes to form alkanes with the general formula C_nH_{2n+2}. Similarly, alkynes with a triple bond have the general molecular formula C_nH_{2n-2} and react with two molecules of hydrogen to form the saturated alkanes.

HL Challenge yourself

12. Show that the number of hydrogen molecules needed to saturate a molecule with the molecular formula $C_nH_pO_qN_rX_s$, is given by the general formula:

$$n_{H_2} = \frac{1}{2} \times [2n + 2 - p - s + t]$$

Exercise

Q44. Outline how vegetable oils are converted to margarine and explain the difference in their melting points.

Q45. Deduce the molecular structure of the reduction products of the following.

(a) CH_3COCH_3 **(b)** CH_3CO_2H **(c)** CH_2CHCl **(d)** C_3H_4

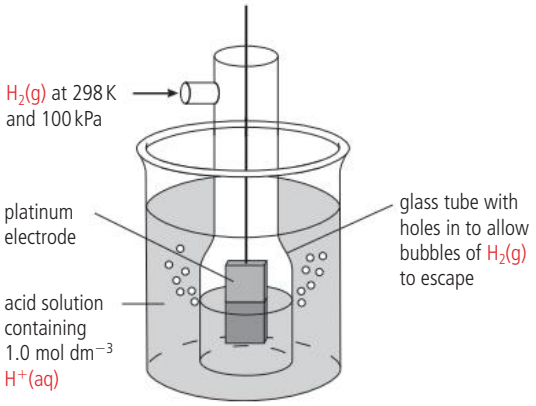
HL

Reactivity 3.2.12 – The standard hydrogen electrode

Reactivity 3.2.12 – The hydrogen half-cell $H_2(g) \rightleftharpoons 2H^+(aq) + 2e^-$ is assigned a standard electrode potential of zero by convention. It is used in the measurement of standard electrode potential, $E^\ominus$.	
Interpret standard electrode potential data in terms of ease of oxidation/reduction.	
Standard electrode potentials are given in the data booklet.	

A voltaic cell generates a potential difference known as the **electromotive force** (**emf**). As electrons tend to flow from the half-cell with the more negative potential to the half-cell with the more positive potential, the potential generated is called the **cell potential** or **electrode potential** and is given the symbol ***E***. This potential difference is measured by a voltmeter and depends on the *difference* in the tendencies of these two half-cells to undergo reduction. Clearly, a voltmeter cannot measure the electrode potential of a single half-cell in isolation, but only when electrons flow when it is linked to another half-cell. In order to compare the relative reducing power of different half-cells, it is convenient to compare them with the same fixed reference point. This is similar to the way in which we compare mountain heights using the same agreed zero point of sea level.

In electrochemistry, the reference standard that gives the baseline for measuring and comparing the electrode potentials of other half-cells is the **standard hydrogen electrode (SHE)**. The standard hydrogen electrode (sometimes called the standard hydrogen half-cell) is a modified form of the pH electrode encountered in Reactivity 3.1 and is shown in Figure 11.



R3.2 Figure 11 The standard hydrogen electrode (SHE).

Do not confuse *absorption* with *adsorption*. Absorption occurs when something is taken up through the *volume* of another substance, such as a sponge taking up water; adsorption occurs only at the *surface*, and so depends on the surface area.

Platinum is used as the conducting metal in the electrode because it is inert and will not ionize, and catalyses the reduction of $H^+(aq)$ ions. The surface of the metal is coated with very finely divided platinum (sometimes known as platinum black or 'platinized platinum') which increases the large surface area and helps in the adsorption of hydrogen gas. This increases the rate of reaction of both the forward and backward reactions. Note that the concentration of $H^+(aq)$ is 1.0 mol dm^{-3} (pH = 0) and the pressure of $H_2(g)$ is 100 kPa at 298 K.

As the electrode is immersed in the acidic solution, an equilibrium is set up between the adsorbed layer of $H_2(g)$ and aqueous H^+ ions.

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$$

The standard hydrogen electrode is assigned an electrode potential value of 0 V.

$H^+(aq)$ ions are reduced in the forward reactions and $H_2(g)$ molecules are oxidized in the backward reaction. We will see later that the position of the equilibrium depends on the electrode potential of the other half-cell to which the SHE is connected in a circuit.

The hydrogen half-cell is arbitrarily assigned an electrode potential of zero volts, 0 V. This gives us a means to measure and compare electrode potentials of any other half-cell to which it is connected.

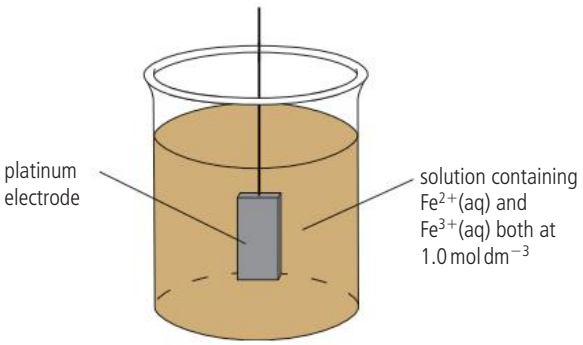
Nature of Science

The standard electrode potential concept brings a quantitative approach to the study of reactivity which is more objective than qualitative observations. Quantitative data obtained by measurements can be analysed using mathematical tools which help scientists to recognize patterns, trends and discrepancies.

Measuring standard electrode potentials

As electrode potentials depend on the concentrations of ions, gas pressures, purity of substance and temperature, these must all be controlled in order to make valid comparisons between different half-cells.
The **standard conditions** used in the measurement of electrode potential are:

- all solutions must have a concentration of 1.0 mol dm^{-3}
- all gases must be at a pressure of 100 kPa
- all substances used must be pure
- temperature is 298 K
- if the half-cell does not include a solid metal, platinum is used as the electrode (Figure 12).

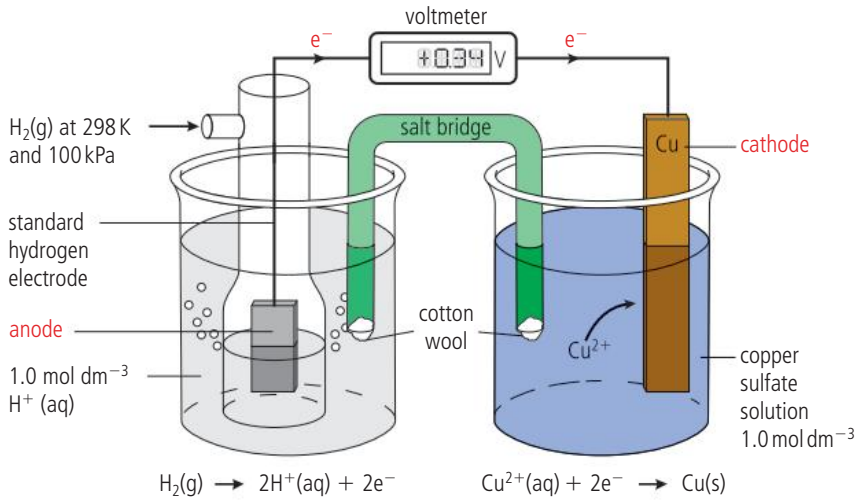


R3.2 Figure 12 As the $Fe^{2+}(aq)/Fe^{3+}(aq)$ half-reaction does not include a metal, a platinum electrode is used as the site of electron transfer. The platinum does not take part in the redox reaction. The standard hydrogen electrode also uses platinum for the same reason.

Half-cells under these conditions are known as **standard half-cells**.

When the standard hydrogen electrode is connected to another standard half-cell by an external circuit with a high-resistance voltmeter and a salt bridge, the emf generated is the **standard electrode potential** of that half-cell. It is given the symbol $\boldsymbol{E^{\ominus}}$.

For example, as shown in Figure 13, $E^{\ominus}$ for the $Cu^{2+}(aq)/Cu(s)$ half-cell is +0.34 V.



R3.2 Figure 13 Measuring the standard electrode potential for $Cu^{2+}(aq)/Cu(s)$.

The positive value for $E^{\ominus}$ shows that electrons tend to flow from the hydrogen half-cell to the copper half-cell. This indicates that electrons are produced by the oxidation of $H_2(g)$:

$$H_2(g) \rightarrow 2H^+(aq) + 2e^-$$

and used to reduce $Cu^{2+}(aq)$ ions:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

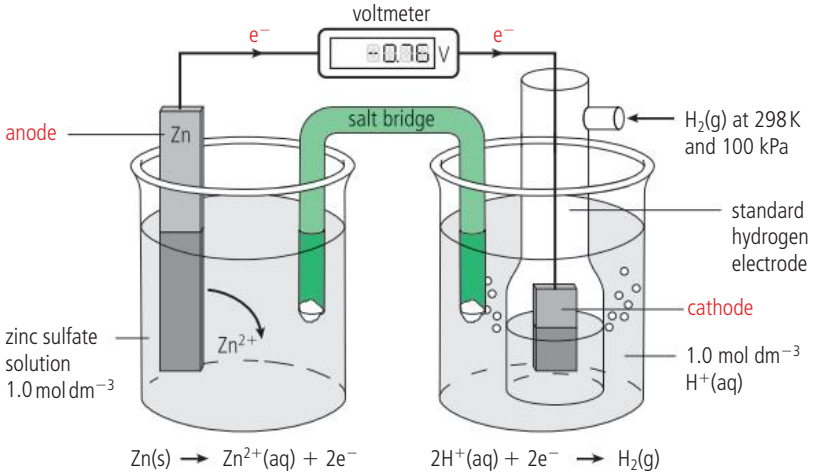
Because oxidation occurs at the hydrogen half-cell, it is designated the anode and because reduction occurs at the copper half-cell, it is the cathode.

The overall reaction is therefore:

$$Cu^{2+}(aq) + H_2(g) \rightarrow 2H^+(aq) + Cu(s) \qquad E_{cell} = +0.34\ V$$

The positive cell potential shows that Cu^{2+} ions have a higher tendency to be reduced than H^+ ions. This can be related to the low reactivity of copper. As discussed earlier, copper does not produce hydrogen gas when added to dilute acids. More reactive metals lose their electrons readily and so bring about the reduction of H^+ and produce hydrogen gas when added to dilute acids. In these cases, the electrons flow towards the standard hydrogen electrode and the $E^{\ominus}_{cell}$ of the metal half-cell is negative.

Consider the $Zn^{2+}(aq)/Zn(s)$ half-cell shown in Figure 14.



R3.2 Figure 14 Measuring the standard electrode potential for $Zn^{2+}(aq)/Zn(s)$.

$E^{\ominus}$ for the $Zn^{2+}(aq)/Zn(s)$ half-cell is −0.76 V. The negative value for $E^{\ominus}$ indicates electrons move from the zinc half-cell, in the external circuit, to the hydrogen half-cell.

$Zn(s)$ is oxidized: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

and $H^+(aq)$ is reduced: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

The zinc half-cell is the anode and the hydrogen half-cell is the cathode and the overall reaction is:

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g) \qquad E^{\ominus}_{cell} = -0.76\ V$$

The standard electrode potential, $E_{cell}^{\ominus}$ of a half-cell is the emf generated when it is connected to the standard hydrogen electrode by an external circuit and a salt bridge, measured under standard conditions.

The negative cell potential of the zinc half-cell can be related to the high reactivity of zinc and the observation that it produces hydrogen gas when added to dilute acids. More generally, metals with a negative electrode potential react with dilute acids and form salts with the production of hydrogen gas, but metals with a positive electrode potential do not react generally react with dilute acids in this way.

We can represent the zinc–hydrogen cell using the cell diagram convention we introduced earlier.

$Zn(s) \mid Zn^{2+}(aq) \quad \| \quad H^+(aq) \mid H_2(g) \mid Pt(s)$

anode half-cell oxidation — cathode half-cell reduction

Is the choice of the hydrogen half-cell as a standard reference an arbitrary or random decision? Has the decision helped the pursuit of chemical knowledge? Have similar decisions had an impact of other areas of knowledge?

As stated earlier, the overall reactions can be deduced from the cell diagram:

Anode	Cathode
$Zn(s) \mid Zn^{2+}(aq)$ $Zn(s) \rightarrow Zn^{2+}(aq)$	$H^+(aq) \mid H_2(g) \mid Pt(s)$ $2H^+(aq) + 2e^- \rightarrow H_2(g)$

Standard electrode potentials are given for the reduction reaction

For purposes of standardization, the standard hydrogen electrode is connected to the negative terminal of the voltmeter and other cells connected to the positive terminal. This explains the positive reading on the voltmeter for copper and the negative reading for zinc. It follows that the standard electrode potential is always given for the *reduction* reaction. For this reason, standard electrode potential values, $E^{\ominus}_{cell}$, are sometimes known as **standard reduction potentials**.

A selection of standard electrode potential values is given in Section 19 in the data booklet. Data from this table corresponding to the half-cells discussed so far in this chapter are given here.

	Oxidized species		Reduced species	$E^{\ominus}$/ V, at 298 K
increasing tendency to occur as reduction ↓	$Zn^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Zn(s)$	−0.76
	$H^+(aq) + e^-$	$\rightleftharpoons$	$\frac{1}{2}H_2(g)$	0.00
	$Cu^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Cu(s)$	+0.34
	$Ag^+(aq) + e^-$	$\rightleftharpoons$	$Ag(s)$	+0.80

The following points should be noted:

- All $E^{\ominus}$ values refer to the reduction reaction.
- The $E^{\ominus}$ values do not depend on the total number of electrons, so do not have to be scaled up or down with the stoichiometry of the equation for a reaction.
- The more positive the $E^{\ominus}$ value for a half-cell, the more readily it is reduced.
- Electrons always flow through the external circuit in a voltaic cell from the half-cell with the more negative standard electrode potential to the half-cell with the more positive electrode potential.

Electrons are produced by an oxidation reaction at the half-cell with the more negative electrode potential, the anode. Reduction occurs at the half-cell with the more positive electrode as electrons are accepted, the cathode.

In a voltaic cell, the half-cell with the higher (more positive) electrode potential is the cathode (+), and the half-cell with the lower (more negative) electrode potential is the anode (−).

Electrons always flow towards the half-cell with the highest $E^{\ominus}$ value.

Exercise

Q46. Identify the conditions of a standard hydrogen electrode.

I. temperature of 298 K
II. 1.0 mol dm^{-3} $H_2SO_4(aq)$
III. hydrogen gas at 1.00×10^5 Pa

A I and II only
B I and III only
C II and III only
D I, II and III

Q47. The overall equation for the reaction occurring in a voltaic the cell is:

$$Mg(s) + ZnSO_4(aq) \rightarrow MgSO_4(aq) + Zn(s)$$

Which statement is correct when the cell produces electricity?

I. Magnesium atoms lose electrons.

II. The mass of the zinc electrode increases.

III. SO_4^{2-} ions migrate from the magnesium to the zinc electrode.

A I and II only **B** I and III only **C** II and III only **D** I, II and III

Q48. Metal Q(s) is more reactive than metal R(s). A voltaic cell is made with the cell diagram: $Q(s)|Q^{2+}(aq) \,||\, R^{2+}(aq)|R(s)$

Identify the correct description.

I. Positive ions flow through the salt bridge from Q to R.

II. Electrons flow through the salt bridge from R to Q.

III. Electrons flow in the external circuit from Q to R.

A I and II only **B** I and III only **C** II and III only **D** I, II and III

Q49. Metal W(s) is more reactive than metal X(s). A voltaic cell is made with the cell diagram:

$$W(s)|W^{2+}(aq) \,||\, X^{2+}(aq)|X(s)$$

Identify the correct description of electron flow and the element oxidized.

	Electron flow	Element oxidized
A	W to X	X
B	X to W	X
C	W to X	W
D	X to W	W

Q50. Calculate the cell potential for the reaction:

$$2Cr(s) + 3Cd^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Cd(s)$$

The following data are available.

$$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s) \qquad E^\ominus = -0.75\ V$$

$$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s) \qquad E^\ominus = -0.40\ V$$

Reactivity 3.2.13 – Standard electrode potentials

Reactivity 3.2.13 – Standard cell potential, $E^\ominus_{cell}$, can be calculated from standard electrode potentials. $E^\ominus_{cell}$ has a positive value for a spontaneous reaction.

Predict whether a reaction is spontaneous in the forward or reverse direction from $E^\ominus$ data.

Calculating the cell potential, $E^{\ominus}_{cell}$

As standard electrode potential data are all referenced to the standard hydrogen electrode we can make predictions about redox reactions and the direction of electron flow. We will look at two applications of **standard cell potentials.**

We can calculate the emf for a voltaic cell made from any two half-cells and deduce the direction of electron flow.

As the cell potential is the difference in the tendencies of these two half-cells to be reduced, we can calculate it by substituting the appropriate values into the following expression:

$$E^{\ominus}_{cell} = E^{\ominus}_{\text{half-cell where reduction occurs}} - E^{\ominus}_{\text{half-cell where oxidation occurs}}$$

Note the following:

- The $E^{\ominus}$ values used in this expression must be the *reduction* potentials as supplied in data tables. The subtraction in the equation reverses its sign for the half-cell undergoing oxidation.

Worked example

Calculate the emf for a voltaic cell constructed from a zinc half-cell and a copper half-cell and identify the anode and cathode. Write the equation for the overall cell reaction.

Solution

Standard electrode potential data for these half-cells at 298 K are:

$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $\quad E^{\ominus} = -0.76$ V

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $\quad E^{\ominus} = +0.34$ V

As the copper half-cell has the higher value for $E^{\ominus}$ it accepts electrons when the half-cells are connected.

$Cu^{2+}(aq)$ ions are reduced: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Electrons are produced at the zinc half-cell as $Zn(s)$ is oxidized: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Electrons flow from zinc to copper.

$$E^{\ominus}_{cell} = E^{\ominus}_{\text{half-cell where reduction occurs}} - E^{\ominus}_{\text{half-cell where oxidation occurs}}$$

$$E^{\ominus}_{cell} = E^{\ominus}_{\text{half-cell where } Cu^{2+} \text{ reduced}} - E^{\ominus}_{\text{half-cell where Zn oxidized}} = +0.34 - (-0.76)\text{ V} = +1.10\text{ V}$$

The zinc half-cell is the anode and the copper half-cell is the cathode.

Adding the two half-equations: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

This confirms the value shown on the photograph on page 764.

$E^{\ominus}_{cell} = E^{\ominus}_{\text{half-cell where reduction occurs}} - E^{\ominus}_{\text{half-cell where oxidation occurs}}$



Sacrificial anode on a ship's rudder. The zinc plate at the center protects the rudder from erosion. Zinc is more reactive than the metal the rudder is made out of, and so corrodes in preference to the rudder. This sacrificial anode is on an abandoned fishing boat in Applecross, Scotland, UK.

Worked example

Determine $E^{\ominus}_{cell}$ for the voltaic cell based on the following two half-cells, for which $E^{\ominus}$ values are given. Write the equation for the overall reaction and represent the cell with a cell diagram.

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l) \qquad E^{\ominus} = +1.51\ V$$

$$IO_4^-(aq) + 2H^+(aq) + 2e^- \rightleftharpoons IO_3^-(aq) + H_2O(l) \qquad E^{\ominus} = +1.60\ V$$

Solution

$IO_4^-(aq)$ ions gain electrons and are reduced, as they have the higher $E^{\ominus}$ value, and $Mn^{2+}(aq)$ ions are oxidized.

$$E^{\ominus}_{cell} = E^{\ominus}_{\text{half-cell where reduction occurs}} - E^{\ominus}_{\text{half-cell where oxidation occurs}}$$
$$= +1.60\ V - (+1.51\ V)$$
$$= +0.09\ V$$

To balance the half-equations for electrons, find a common multiple of 2 and 5:

$$2Mn^{2+}(aq) + 8H_2O(l) \rightarrow 2MnO_4^-(aq) + 16H^+(aq) + 10e^-$$

$$5IO_4^-(aq) + 10H^+(aq) + 10e^- \rightarrow 5IO_3^-(aq) + 5H_2O(l)$$

Adding the two half-equations together, cancelling out terms on both sides:

$$5IO_4^-(aq) + 2Mn^{2+}(aq) + 3H_2O(l) \rightarrow 5IO_3^-(aq) + 2MnO_4^-(aq) + 6H^+(aq)$$

$Pt(s) \mid Mn^{2+}(aq), 2MnO_4^-(aq) \parallel IO_4^-(aq), IO_3^-(aq) \mid Pt(s)$

anode half-cell oxidation | cathode half-cell reduction

Note that Pt is used in both half-cells since it is stable in these conditions, and the half-cells do not contain a metal to conduct.

When substituting $E^{\ominus}$ values into the equation for $E^{\ominus}_{cell}$ used here, make sure you use the values with the sign given for the *reduction* reaction, i.e. exactly as in the data table. The subtraction in the equation reverses the sign for the half-cell undergoing oxidation.

Determining the direction of reaction spontaneity

As $E^{\ominus}$ values can be used to predict the redox change that will occur among a mixture of reactants, it follows that we can use them to determine whether a particular reaction will occur spontaneously. This is based on the fact that electrons move from the half-cell with the more negative potential.

Worked example

Use $E^{\ominus}$ values to determine whether the reaction

$Ni(s) + Mn^{2+}(aq) \rightarrow Ni^{2+}(aq) + Mn(s)$

will occur spontaneously under standard conditions.

Solution

The relative electrode potentials are as follows:

$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ $\quad E^{\ominus} = -0.26\ V$

$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$ $\quad E^{\ominus} = -1.18\ V$

From electrode potentials we see that electrons will move from the half-cell with the more negative electrode potential to the half-cell with the more positive/less negative value. Mn(s) is oxidized and $Ni^{2+}(aq)$ is reduced.

The direction of the reaction is:

$$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$$

$$Mn(s) \rightarrow Mn^{2+}(aq) + 2e^-$$

Adding the half-equations: $Ni^{2+}(aq) + Mn(s) \rightarrow Ni(s) + Mn^{2+}(aq)$

The proposed reaction in the question is the reverse of the spontaneous reaction and so does not occur.

Considering again the worked example.

Proposed reaction:

$Ni(s) + Mn^{2+}(aq) \rightarrow Ni^{2+}(aq) + Mn(s)$

Ni(s) is oxidized and $Mn^{2+}(aq)$ is reduced

$E^{\ominus}_{cell} = E^{\ominus}_{\text{half-cell where reduction occurs}} - E^{\ominus}_{\text{half-cell where oxidation occurs}}$

$= -1.18\ V - (-0.26\ V)$

$= -0.92\ V$

The negative sign for $E^{\ominus}_{cell}$ tells us that the cell is not set up correctly and the spontaneous reaction does not happen in this direction.

Spontaneous reaction:

$Ni^{2+}(aq) + Mn(s) \rightarrow Ni(s) + Mn^{2+}(aq)$

Mn(s) is oxidized and $Ni^{2+}(aq)$ is reduced

$E^{\ominus}_{cell} = E^{\ominus}_{\text{half-cell where reduction occurs}} - E^{\ominus}_{\text{half-cell where oxidation occurs}}$

$= -0.26\ V - (-1.18\ V)$

$= +0.92\ V$

The positive sign for $E^{\ominus}_{cell}$ tells us that the cell is set up correctly and the spontaneous reaction happens in this direction.

This result can be generalized: *the voltaic cell will always run in the direction that gives a positive value for the* $E^{\ominus}_{cell}$.

- If $E^{\ominus}_{cell}$ is positive, the reaction is spontaneous as written.
- If $E^{\ominus}_{cell}$ is negative, the reaction is non-spontaneous and the reverse reaction is spontaneous.



$E^{\ominus}_{cell}$ is positive for all spontaneous reactions.

Comparing relative oxidizing and reducing power of half-cells

The $E^{\ominus}$ values for half-reactions confirm the activity series discussed earlier in the chapter. Metals with the most negative $E^{\ominus}$ values are the strongest reducing agents and non-metals with the more positive $E^{\ominus}$ values are the strongest oxidizing agents.

These trends are summarized below.

	Oxidized species		Reduced species	$E^{\ominus}$ / V	
increasing strength as oxidizing agent ↓	$Zn^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Zn(s)$	−0.76	↑ increasing strength as reducing agent
	$H^+(aq) + e^-$	$\rightleftharpoons$	$\frac{1}{2}H_2(g)$	0.00	
	$Cu^{2+}(aq) + 2e^-$	$\rightleftharpoons$	$Cu(s)$	+0.34	
	$\frac{1}{2}I_2(s) + e^-$	$\rightleftharpoons$	$I^-(aq)$	+0.54	
	$\frac{1}{2}Cl_2(g) + e^-$	$\rightleftharpoons$	$Cl^-(aq)$	+1.36	

Worked example

A solution containing potassium manganate(VII) and concentrated hydrochloric acid reacts to form chlorine gas. Identify the strongest oxidizing agent in the solution and calculate the standard potential of the corresponding cell.

Solution

First extract the relevant half-equations from Section 19 in the data booklet.

$MnO_4^-(aq)$ is reduced in the presence of $H^+(aq)$:

$$MnO_4^-(aq) + 8H^+ + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l) \qquad E^{\ominus} = +1.51\ V$$

and Cl^- is oxidized to $Cl_2(g)$:

$$\tfrac{1}{2}Cl_2(g) + e^- \rightarrow Cl^-(aq) \qquad E^{\ominus} = +1.36\ V$$

$MnO_4^-(aq)$ is the stronger oxidizing agent as it has the higher value for $E^{\ominus}$ so it will be reduced.

$$E^{\ominus}_{cell} = E^{\ominus}_{\text{half-cell where reduction occurs}} - E^{\ominus}_{\text{half-cell where oxidation occurs}}$$

$$E^{\ominus}_{cell} = E^{\ominus}_{MnO4-(aq)} - E^{\ominus}_{Cl2(g)} = +1.51 - (+1.36) = +0.15\ V$$

The higher the value of $E^{\ominus}$ for a half-cell, the stronger the oxidizing agent; the lower the value of $E^{\ominus}$, the stronger the reducing agent.

Exercise

Q51. Consider the following table of standard electrode potentials.

Reaction	$E^{\ominus}$ / V
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	−0.76
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	−0.14

Identify the strongest oxidizing agent.

A Sn^{2+} **B** Sn **C** Zn^{2+} **D** Zn

Q52. From the half-equations below, determine the cell reaction and standard cell potential.

$BrO_3^-(aq) + 6H^+(aq) + 6e^- \rightarrow Br^-(aq) + 3H_2O$ $\quad E^\ominus = +1.44\ V$

$I_2(s) + 2e^- \rightarrow 2I^-(aq)$ $\quad E^\ominus = +0.54\ V$

Q53. Identify the strongest oxidizing agent and the strongest reducing agent from the following data.

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $\quad E^\ominus = +0.34\ V$

$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$ $\quad E^\ominus = -2.37\ V$

$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $\quad E^\ominus = -0.76\ V$

Q54. Use the standard electrode potentials given below to predict whether a reaction will be spontaneous between the following pairs. State equations and calculate the cell potentials for the proposed reactions.

$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$ $\quad E^\ominus = -0.75\ V$

$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$ $\quad E^\ominus = -0.40\ V$

$BrO_3^-(aq) + 6H^+(aq) + 6e^- \rightarrow Br^-(aq) + 3H_2O$ $\quad E^\ominus = +1.44\ V$

$I_2(s) + 2e^- \rightarrow 2I^-(aq)$ $\quad E^\ominus = +0.54\ V$

$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $\quad E^\ominus = +0.34\ V$

$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$ $\quad E^\ominus = -2.37\ V$

$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $\quad E^\ominus = -0.76\ V$

(a) $Cu^{2+}(aq)$ and $I_2(s)$

(b) $Cd(s)$ and $BrO_3^-(aq)$ in acidic solution

(c) $Cr(s)$ and $Mg^{2+}(aq)$

Reactivity 3.2.14 – Electrode potentials and Gibbs energy changes

Reactivity 3.2.14 – The equation $\Delta G^\ominus = -nFE^\ominus_{cell}$ shows the relationship between standard change in Gibbs energy and standard electrode potential for a reaction. Determine the value for $\Delta G^\ominus$ from $\Delta E^\ominus$ data.	
The equation and the value of F in C mol^{-1} are given in the data booklet.	Reactivity 1.4 – How can thermodynamic data also be used to predict the spontaneity of a reaction?

Electrode potentials and Gibbs energy changes both predict the directions of change

In Reactivity 1.4 we saw that $-\Delta G$ gives the useful energy that can be obtained from a chemical reaction. The $E^\ominus_{cell}$ is related to the electrical energy when 1 C of charge passes through a circuit.

Consider a reaction where n moles of electrons are transferred:

Total charge (Q) transferred = n × charge of 1 electron (e) × Avogadro's constant (N_A)

Electrical energy = $E^{\ominus}_{cell} \times \mathbf{Q} = E^{\ominus}_{cell} \times n \times e \times N_A = -\Delta G^{\ominus}$

This equation can be simplified as F is the charge of one mole of electrons: $F = n \times e$

This gives $\Delta G^{\ominus} = -n\mathbf{F}E^{\ominus}_{cell}$

- n = number of moles of electrons transferred in the reaction
- F = the charge carried by 1 mol of electrons, known as the Faraday constant (it has a value of approximately 96 500 C mol^{-1}).

The equation $\Delta G^{\ominus} = -nFE^{\ominus}$ and the value of F are given in the data booklet. You are not expected to derive the equation.

The units of the terms in this equation are consistent with the relationship:

$\Delta G^{\ominus}$ (J) = $-n$ (mol) F (C mol^{-1}) $E^{\ominus}$ (V = J/C)

Challenge yourself

13. Determine a more precise value of the Faraday constant using information in the data booklet.

We also have seen that a reaction is spontaneous when:

- $E^{\ominus}_{cell}$ is positive
- $\Delta G^{\ominus}$ is negative

which is consistent with the negative sign in the equation.

Reactivity 1.4 – How can thermodynamic data also be used to predict the spontaneity of a reaction?

This equation shows that the more positive the value of $E^{\ominus}_{cell}$, the more energetically favourable the reaction. This implies that a voltmeter can be considered as an indirect measure of Gibbs energy change as well as of electrode potential.

Worked example

Calculate the standard Gibbs energy change at 298 K for the zinc–copper voltaic cell, which has a standard cell potential of +1.10 V.

Solution

First write the equation for the overall cell reaction, to determine the number of electrons transferred:

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

As shown above, 2 electrons are transferred: $n = 2$

$$\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$$
$$= -2 \text{ (mol)} \times 96\,500 \text{ (C mol}^{-1}) \times 1.10 \text{ (V)}$$
$$= 212\,000 \text{ J}$$
$$\therefore \Delta G^{\ominus} = -212 \text{ kJ}$$

Challenge yourself

14. An equation that relates the Gibbs energy change of a reaction to its equilibrium constant is covered in Reactivity 1.4. Here we have used an equation that relates the Gibbs energy change to the electrode potential. Formulate an equation to show how the potential of a cell depends on the equilibrium constant.

A little caution about interpreting $E^{\ominus}$ data

$E^{\ominus}_{cell}$ and $\Delta G^{\ominus}$ both give information on the energetic feasibility of a reaction. They do not, however, give any information on the rate of reaction. So a reaction that is predicted to be spontaneous may not actually happen at an observable rate if the activation energy is too high as discussed in Reactivity 2.2. 'How far?' – the *feasibility* of a reaction and 'How fast?' – the *rate* of a reaction are different questions which are affected by different factors.

In addition, the $E^{\ominus}$ values that we have used throughout these examples strictly apply only to standard conditions, and any changes in temperature, concentration or pressure will alter the values, possibly even changing whether a reaction is spontaneous or not.

In summary, the interpretation of electrode potential data involves recognizing one fundamental fact: *electrons always tend to flow towards the half-cell with the highest $E^{\ominus}$ value*. All other deductions and interpretations follow from this.

Challenge yourself

15. Identify a metal in Section 19 of the data booklet which has a more negative electrode potential than expected from its reactivity with water and suggest an explanation for the discrepancy between its reactivity and its electrode potential.

Exercise

Q55. Identify the correct description for a redox reaction with a positive standard electrode potential: $\Delta G^{\ominus} = -nFE^{\ominus}$ and $\Delta G^{\ominus} = -RT \ln K$

A $\Delta G^{\ominus}$ is negative and K is less than 1.

B $\Delta G^{\ominus}$ is negative and K is greater than 1.

C $\Delta G^{\ominus}$ is positive and K is less than 1.

D $\Delta G^{\ominus}$ is positive and K is greater than 1.

Q56. Aluminium displaces $Cr^{3+}(aq)$ from aqueous solution.

$$Al(s) + Cr^{3+}(aq) \rightarrow Al^{3+}(aq) + Cr(s)$$

The standard electrode potential for the reaction is 0.92 V at 298 K. Determine the standard Gibbs energy change for this reaction.

Reactivity 3.2.15 – Electrolysis of aqueous solutions

Reactivity 3.2.15 – During electrolysis of aqueous solutions, competing reactions can occur at the anode and cathode, including the oxidation and reduction of water. Deduce from standard electrode potentials the products of the electrolysis of aqueous solutions.	
Electrolytic processes should include the electrolysis of water and of aqueous solutions. The effects of concentration and the nature of the electrode are limited to the electrolysis of NaCl(aq) and $CuSO_4$(aq).	

Competing reactions can occur during electrolysis of aqueous solutions

When electrolysis is carried out on an aqueous solution, predicting the products at the electrodes is more difficult than with molten compounds because the water present can also be oxidized or reduced. On page 776 we considered the electrolysis of molten sodium chloride and saw that sodium is produced at the cathode and chlorine at the anode. When the same experiment is carried out in the presence of water, sodium cannot be produced at the cathode as it would react immediately with water to produce hydrogen.

The reaction at the cathode can be understood in terms of a sequence of two hypothetical steps:

$$Na^+ + e^- \rightarrow Na$$

$$Na + H_2O \rightarrow Na^+ + OH^- + \tfrac{1}{2}H_2$$

These two steps lead to the overall reaction:

$$\cancel{Na^+} + e^- + \cancel{Na} + H_2O \rightarrow \cancel{Na} + \cancel{Na^+} + OH^- + \tfrac{1}{2}H_2$$

$$H_2O + e^- \rightarrow OH^- + \tfrac{1}{2}H_2$$

Water is preferentially reduced to hydrogen.

Similarly, under certain conditions water can be oxidized to oxygen at the anode:

$$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$$

These results can be generalized. When a solute M^+A^- is in an aqueous solution, there is more than one redox reaction possible at each electrode. Specifically:

- at the anode: either A^- or H_2O can be oxidized
- at the cathode: either M^+ or H_2O can be reduced.

The discharge of an ion at the electrode in these cases is known as **selective discharge**. In the example of aqueous sodium chloride, water is reduced in preference to sodium due to the high reactivity of sodium, which in turn can be related to its

negative electrode potential. More generally the outcome can be determined by the following factors:

- the relative $E^{\ominus}$ values of the ions compared to water
- the relative concentrations of the ions in the electrolyte
- the nature of the electrodes.

Competing reactions can occur during electrolysis of aqueous solutions

The following steps are a useful summary.

1 Identify all the ions present in the electrolyte and determine which will migrate to which electrode: anions (negative ions) to anode (positive electrode), and cations (positive ions) to cathode (negative electrode).

↓

2 Where there is more than one possible reaction at each electrode, write the half-equation for the reaction at each electrode as in the data booklet.

↓

3 The half-reaction with the higher electrode potential is the oxidation reaction at the cathode. The higher electrode potential indicates the half-cell that gains electrons most readily.

↓

4 The half-reaction with the lower electrode potential is the reduction reaction at the anode. The lower electrode potential indicates the half-cell that loses electrons most readily.

↓

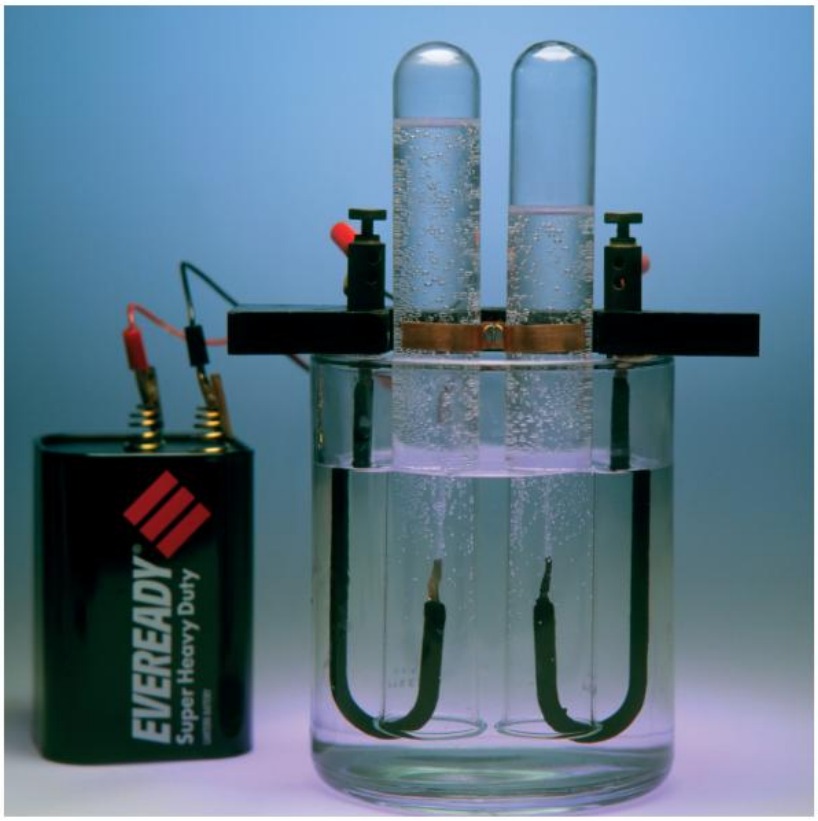
5 To deduce the overall reaction, balance the electrons lost and gained at the anode and the cathode, then add the two half-equations to write the equation for the net reaction.

↓

6 Consider what changes would be observed in the cell as a result of the redox reactions. These may include colour changes in the electrolyte, precipitation of solid, gas discharge, or pH changes.

We will now explore this in more detail with reference to specific examples.

Electrolysis of water



The electrolysis of water. The battery on the left is the source of electrical energy that drives the reactions at the electrodes. Hydrogen is produced by the reduction of H_2O at the cathode (on the right), and oxygen is produced by the oxidation of H_2O at the anode (on the left). The ratio of volumes of hydrogen : oxygen is 2 : 1, which confirms the formula of water.

As pure water is not a good conductor of electricity, some sulfuric acid or sodium hydroxide is usually added. As we will see, this does not interfere with the electrolysis of the water.

When sodium hydroxide is added, the ions present are $Na^+(aq)$ and $OH^-(aq)$.

	Cathode	Anode
Ions present	$Na^+(aq)$	$OH^-(aq)$
Relevant half-reactions	$Na^+(aq) + e^- \rightleftharpoons Na(s)$ $E^\ominus = -2.71$ V $2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$ $E^\ominus = -0.83$ V H_2O gains electrons most readily as it has a higher $E^\ominus$ and so is preferentially reduced; $H_2(g)$ is produced	$2H_2O(l) + O_2(g) + 4e^- \rightleftharpoons 4OH^-(aq)$ $E^\ominus = +0.40$ V $4H^+(aq) + O_2(g) + 4e^- \rightleftharpoons 2H_2O(l)$ $E^\ominus = +1.23$ V $OH^-(aq)$ loses electrons most readily as it has a lower $E^\ominus$ and so is preferentially oxidized; $O_2(g)$ is produced
Reaction at electrode	$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$
Observations	colourless gas evolved (H_2) pH increases as OH^- produced	colourless gas evolved (O_2) pH decreases as H^+ is produced

The overall balanced equation is:

$$\cancel{4H_2O(l)} + 2H_2O(l) + \cancel{4e^-} \rightarrow 2H_2(g) + \cancel{4OH^-(aq)} + \cancel{4H^+(aq)} + O_2(g) + \cancel{4e^-}$$

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$$

From the equation, the ratio by volumes of the gases is 2 H_2 : 1 O_2 (by application of Avogadro's law on gas volumes).

The electrolysis of water, sometimes known as the 'splitting of water', is of great interest because of the demand for a cheap source of hydrogen to drive the so-called **hydrogen economy**. Hydrogen can be used as a store of energy as it can be produced with electricity and then used as a possible replacement to fossil fuels, for example in cars and airplanes. This is currently an area of active research.



A hydrogen bus in Reykjavik, Iceland. The bus was part of a project to help Iceland move away from imported oil, to powering its vehicles with hydrogen. Iceland is committed to moving to a hydrogen economy by 2050. Iceland is ideally suited to a hydrogen economy as it has plentiful supplies of renewable generated electricity that can be used to split water, to create hydrogen.

Electrolysis of NaCl(aq)

A concentrated aqueous solution of sodium chloride is sometimes known as brine. Electrolysis of this solution leads to the production of $H_2(g)$, $Cl_2(g)$, and NaOH(aq), all of which are of commercial importance. When the solution is more dilute, oxygen can be produced at the anode instead of chlorine.

For NaCl(aq) the ions present are $Na^+(aq)$ and $Cl^-(aq)$.

	Cathode	Anode
Ions present	$Na^+(aq)$	$Cl^-(aq)$
Relevant half-reactions	$Na^+(aq) + e^- \rightleftharpoons Na(s)$ $E^\ominus = -2.71$ V $2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$ $E^\ominus = -0.83$ V H_2O gains electrons most readily as it has a higher $E^\ominus$ and so is preferentially reduced; $H_2(g)$ is produced	$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ $E^\ominus = +1.36$ V $4H^+(aq) + O_2(g) + 4e^- \rightleftharpoons 2H_2O(l)$ $E^\ominus = +1.23$ V In dilute solution: $H_2O(l)$ loses electrons most readily as it has a lower $E^\ominus$ and so is preferentially oxidized; $O_2(g)$ is produced For brine with high concentrations of $Cl^-(aq)$: $Cl^-(aq)$ loses electrons most readily and so is preferentially oxidized; $Cl_2(g)$ is produced
Reaction at electrode	$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	Dilute solution: $2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$ Brine/concentrated solution: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$
Observations	colourless gas evolved (H_2) pH increases as $OH^-(aq)$ produced	Dilute solution: colourless gas evolved (O_2) pH decreases as H^+ is produced Brine/concentrated solution: $Cl_2(g)$ identified at the anode as it has a strong smell and bleaches damp blue litmus paper

When a question asks you to describe the electrolysis of NaCl, be clear on whether it is asking about NaCl(l) or dilute or concentrated NaCl(aq). As you have seen here, they are different processes leading to distinct products and applications.

The overall balanced equation for brine:

$$2H_2O(l) + \cancel{2e^-} + 2Cl^-(aq) \rightarrow H_2(g) + 2OH^-(aq) + Cl_2(g) + \cancel{2e^-}$$

$$2H_2O(l) + 2Cl^-(aq) \rightarrow 2H_2(g) + 2OH^-(aq) + Cl_2(g)$$

The commercial electrolysis of aqueous sodium chloride, known as the **chlor-alkali** industry, is of major significance economically because of the simultaneous yield of H_2, Cl_2 and NaOH. It is important that chlorine and sodium hydroxide are prevented from reacting with each other during the process. Older processes used mercury cells to accomplish this, but the United Nations Environment Programme agreed in 2013 to a deadline for the phase-out their use. This was accepted by more than 140 countries and membrane cells, which selectively act as a barrier to all gas and liquid flow and only allow sodium ions to pass, are now in general use in most countries.

The preferential discharge of Cl^- occurs at high concentration. $E^\ominus$ values depend on the concentration.

Electrolysis of $CuSO_4$(aq) with carbon (graphite) or other 'inert' electrodes

$CuSO_4$(aq) is a bright blue colour, due to the presence of hydrated Cu^{2+} ions. Electrolysis of this solution yields different products depending on the nature of the electrodes. We will consider first the reaction with graphite electrodes. The ions present are Cu^{2+}(aq) and SO_4^{2-}(aq).

	Cathode	Anode
Ions present	$Cu^{2+}(aq)$	$SO_4^{2-}(aq)$
Relevant half-reactions	$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ $E^\ominus = +0.34$ V $2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$ $E^\ominus = -0.83$ V $Cu^{2+}(aq)$ gains electrons most readily as it has a higher $E^\ominus$ and so is preferentially reduced; Cu(s) is produced	$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons H_2SO_3(aq) + H_2O(l)$ $E^\ominus = +0.17$ V $4H^+(aq) + O_2(g) + 4e^- \rightleftharpoons 2H_2O(l)$ $E^\ominus = +1.23$ V $H_2O(l)$) loses electrons most readily as it has a lower $E^\ominus$ and so is preferentially oxidized; $O_2(g)$ is produced
Reaction at electrode	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$
Observations	pinky brown colour of copper deposited loss of intensity of blue colour (due to discharge of Cu^{2+}(aq)) which spreads throughout the solution	colourless gas evolved (O_2) pH decreases as H^+ is produced

The overall balanced equation is:

$$2Cu^{2+}(aq) + 2H_2O(l) \rightarrow 2Cu(s) + O_2(g) + 4H^+(aq)$$

Electrolysis of $CuSO_4$(aq) with copper electrodes

The reaction at the cathode is the same as with graphite electrodes, but the reaction is different at the anode. The Cu electrode itself is oxidized, supplying electrons for the reaction and dissolving as Cu^{2+}(aq):

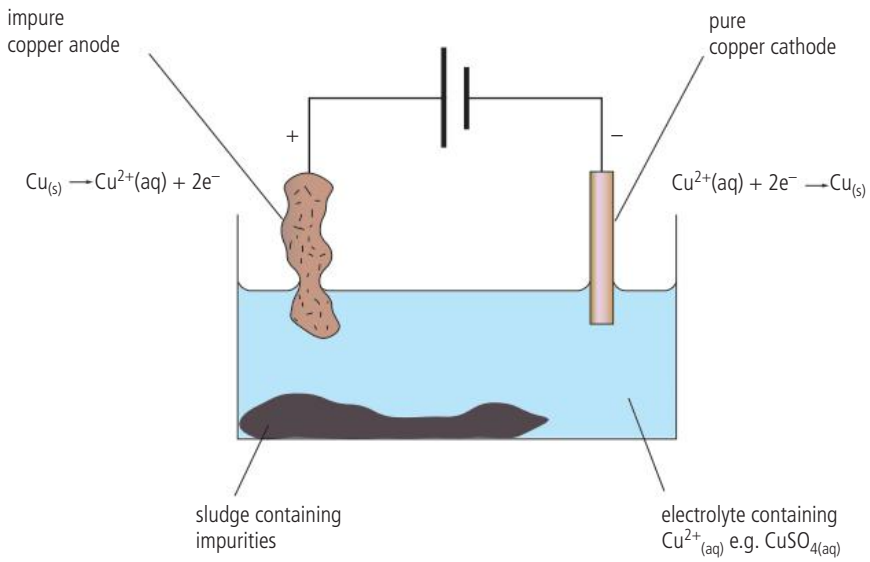
$$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$$

As this reaction is the reverse of the cathode, the net reaction is the movement of $Cu^{2+}(aq)$ from where they are produced at the anode to the cathode where they are discharged as Cu(s). The process is summarized in the table:

	Cathode	Anode
Ions present	$Cu^{2+}(aq)$	$SO_4^{2-}(aq)$
Reaction at electrode	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
Observations	pink/brown colour of copper deposited mass increases	copper lost mass decreases

There is no change in the intensity of the blue colour of the solution as Cu^{2+} ions are both formed and removed from the solution simultaneously, so the concentration remains constant.

This process can be used to purify copper. The process uses electrolysis of a solution containing $Cu^{2+}(aq)$ with an impure copper anode and a small pure copper cathode (Figure 15). As the current runs, the anode erodes as copper ions are formed and transferred to the cathode, which therefore increases in mass. Only copper atoms are formed at the cathode but impurities leave the anode as copper ions are formed and fall to the bottom of the cell.



R3.2 Figure 15 The purification of copper using electrolysis. Reactions at the electrodes result in a net transfer of copper from the anode to the cathode.

The electrolytic processes involving copper are respectively called 'electro-winning' (with the inert C anode) and 'electro-refining' (with a reactive Cu anode). In industry, the electro-winning anode is usually an inert lead/antimony alloy.

Exercise

Q57. Identify the products when a concentrated aqueous solution of copper(II) chloride is electrolyzed using inert electrodes.

	Negative electrode (cathode)	Positive electrode (anode)
A	$O_2(g)$	$Cl_2(g)$
B	Cu(s)	$O_2(g)$
C	Cu(s)	$Cl_2(g)$
D	$H_2(g)$	$O_2(g)$

Selective discharge of an ion during electrolysis depends on relative $E^{\ominus}$ values, the ion concentration, and the nature of the electrode.

Q58. Compare the products at each electrode when a concentrated aqueous solution and molten magnesium iodide are separately electrolyzed.

	$E^{\ominus}$ / V
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	−2.37
$H_2O(l) + e^- \rightleftharpoons \frac{1}{2}H_2(g) + OH^-(aq)$	+1.23
$\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O(l)$	−0.83
$\frac{1}{2}I_2(s) + e^- \rightleftharpoons I^-(aq)$	+0.54

	Negative electrode (cathode)		Positive electrode (anode)	
	$MgI_2(l)$	$MgI_2(aq)$	$MgI_2(l)$	$MgI_2(aq)$
A	$I_2(g)$	$H_2(g)$	$Mg(s)$	$O_2(aq)$
B	$Mg(s)$	$H_2(g)$	$I_2(g)$	$I_2(g)$
C	$Mg(s)$	$Mg(s)$	$I_2(g)$	$I_2(g)$
D	$I_2(g)$	$Mg(s)$	$O_2(aq)$	$H_2(g)$

Q59. Deduce the products formed during the electrolysis of an aqueous solution of potassium fluoride. Write an equation for the reaction at the anode and explain your reasoning.

Q60. $CuCl_2(aq)$ can be electrolyzed with carbon or copper electrodes.

(a) Describe the changes you would expect to see using carbon electrodes. Write equations to support your predicted observations.

(b) How would your answer to part **(a)** change if Cu electrodes were used instead?

Q61. Write an equation for a reaction that occurs during the electrolysis of NaCl(aq) that does not occur during the electrolysis of NaCl(l).

Reactivity 3.2.16 – Electroplating

Reactivity 3.2.16 – Electroplating involves the electrolytic coating of an object with a metallic thin layer.	
Deduce equations for the electrode reactions during electroplating.	
	Tool 1 – How is an electrolytic cell used for electroplating?

Electroplating is a widely used application of electrolysis

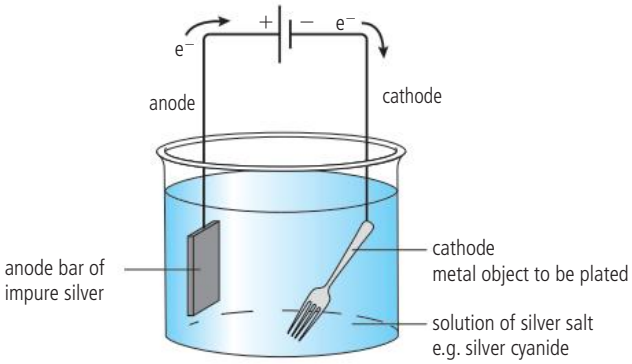
We saw that copper is deposited on the cathode during the electrolysis of $CuSO_4(aq)$. This is one example of **electroplating**, the process of using electrolysis to deposit a layer of a metal on top of another metal or other conductive object.

SKILLS

Electroplating. Full details of how to carry out this experiment with a worksheet are available in the eBook.

As Figure 16 shows, an electrolytic cell used for electroplating has the following features:

- the object to be plated forms the cathode
- the electrolyte contains the metal ions which are to coat the object
- the anode is sometimes made of the same plating metal. As it is oxidized it replenishes the ions in the electrolyte which are discharged at the cathode.



R3.2 Figure 16 Apparatus for electroplating silver.

Reduction of the metal ions at the cathode leads to their deposition on its surface. The process can be controlled by altering the current and the time according to how thick a layer of metal is desired.

Electroplating serves many different purposes, some of which are outlined here.

- Decorative purposes: for example, covering a metal with a layer of a more expensive or decorative metal, such as silver- and nickel-plating of cutlery.
- Corrosion control: for example, iron with a layer of zinc deposited on its surface, known as **galvanized iron**, is protected from corrosion as the zinc will be preferentially oxidized. This is sometimes called **sacrificial protection**.
- Improvement of function: for example electroplating with chromium improves the wear on steel parts such as crankshafts and hand tools.



The Guggenheim museum, Bilbao, Spain, which opened in 1997, is sheathed in panels of titanium. Although the metal is very resistant to corrosion, when it is anodized using electrolysis, the layer of titanium oxide deposited on its surface changes its optical properties, causing it to have different colours in different lights.

Tool 1 – How is an electrolytic cell used for electroplating?

Anodizing is an electrolytic process in which a metal anode is oxidized to deposit a metal oxide coat on the surface of the metal. This surface coat protects the underlying metal from corrosion. It is commonly applied to aluminium and chromium and enables these metals to be used much more extensively than would be possible with the uncoated metal. For example, anodized aluminium is commonly used in cooking utensils and does not react even when heated despite its relatively high position in the activity series.

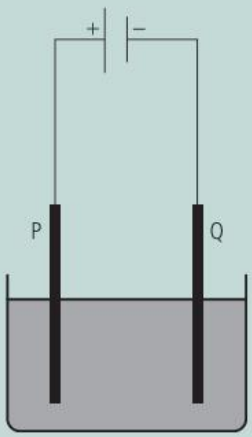
Summary of voltaic and electrolytic cells

We have seen that voltaic and electrolytic cells are the reverse of each other. A voltaic cell converts chemical energy to electrical energy when a reaction with a positive value for E proceeds towards equilibrium. An electrolytic cell converts electrical energy to chemical energy when an electric current drives a reaction with a negative value for E away from equilibrium. These relationships, together with the Gibbs energy change, ΔG, for the different cells are summarized below.

Type of cell	E_{cell}	ΔG	Type of reaction
voltaic	> 0	< 0	spontaneous
electrolytic	< 0	> 0	non-spontaneous
equilibrium	0	0	dead battery

Exercise

Q62. Identify an arrangement which can be used to electroplate an object with copper.



	P	Q
A	plastic object	Cu(s)
B	Cu(s)	plastic object
C	metallic object	Cu(s)
D	Cu(s)	metallic object

Q63. A metal spoon is plated with silver using an aqueous solution of $AgNO_3$ and an impure silver anode. Predict how the masses of the two electrodes will change with time and what other changes might be visible.

HL end

Guiding Question revisited

What happens when electrons are transferred?

In this chapter we have explored electron transfer or redox reactions.

- Oxidation is electron loss and reduction is electron gain. The two processes can be shown in terms of half-reactions.
- Oxidation and reduction can be identified by changes in oxidation state. A species with an element whose oxidation state is increased is oxidized. A species with an element with a decreased oxidation state is reduced.
- The oxidizing agent is the species that is reduced, and the reducing agent is the species that is oxidized.
- When the electron transfer in a spontaneous reaction occurs via an outside circuit, it can be used to produce an electric current. Electrons flow from anode to cathode in the external circuit and ions move between the electrodes in the electrolyte.
- HL The standard electrode potential is defined relative to the standard hydrogen electrode.
- Only reactive metals with negative electrode potentials produce hydrogen gas when added to dilute acids.
- A primary cell produces electricity from reagents which are used up in an irreversible chemical reaction. A secondary cell can be recharged as the cell reaction is reversible. In a fuel cell the reagents are supplied as it operates.
- HL A positive cell potential shows that the reducing agent at the anode has a natural tendency to reduce the oxidizing agent at the anode. $\Delta G^{\ominus} = -nFE^{\ominus}_{cell}$
- Electricity can be used to drive non-spontaneous reactions.
- Electrolysis can be used to break down stable compounds in the molten state. It is used to extract reactive metals and non-metals and for electroplating.
- Reduction occurs at the cathode and oxidation occurs at the anode in both voltaic and electrolytic cells.
- Oxidation reactions in organic chemistry involve the addition of oxygen or the removal of hydrogen. Alcohols and aldehydes are oxidized by oxidizing agents. When oxidizing agents contain a transition metal, there is a colour change as the oxidation state changes.
- Reduction reactions in organic chemistry involve the addition of hydrogen or the removal of oxygen. The alkenes and alkynes are reduced by H_2 adding across a C=C bond. The aldehydes, ketones and carboxylic acids are reduced by reducing agents with the H^- ion, which react with the partially positive charge of the carbon atom in the carbonyl group.

Practice questions

1. Which conditions are required to obtain a good yield of a carboxylic acid when ethanol is oxidized using potassium dichromate(VI), $K_2Cr_2O_7(aq)$?

I. add sulfuric acid

II. heat the reaction mixture under reflux

III. distil the product as the oxidizing agent is added

A I and II only

B I and III only

C II and III only

D I, II and III

2. Which species could be reduced to form NO_2?

A N_2O

B NO_3^-

C HNO_2

D NO

3. Consider the following reaction.

$$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$$

Which statement is correct?

A MnO_4^- is the oxidizing agent and it loses electrons.

B MnO_4^- is the reducing agent and it loses electrons.

C MnO_4^- is the oxidizing agent and it gains electrons.

D MnO_4^- is the reducing agent and it gains electrons.

4. What is the reducing agent in the reaction below?

$$2MnO_4^-(aq) + Br^-(aq) + H_2O(l) \rightarrow 2MnO_2(s) + BrO_3^-(aq) + 2OH^-(aq)$$

A Br^-

B BrO_3^-

C MnO_4^-

D MnO_2

5. Which changes could take place at the positive electrode (cathode) in a voltaic cell?

I. $Zn^{2+}(aq)$ to $Zn(s)$ II. $Cl_2(g)$ to $Cl^-(aq)$ III. $Mg(s)$ to $Mg^{2+}(aq)$

A I and II only

B I and III only

C II and III only

D I, II and III

6. What happens at the negative electrode in a voltaic cell and in an electrolytic cell?

	Voltaic cell	Electrolytic cell
A	oxidation	reduction
B	reduction	oxidation
C	oxidation	oxidation
D	reduction	reduction

7. **(a)** Outline two differences between an electrolytic cell and a voltaic cell. (2)

(b) Explain why solid sodium chloride does not conduct electricity but molten sodium chloride does. (2)

(c) Molten sodium chloride undergoes electrolysis in an electrolytic cell. For each electrode deduce the half-equation and state whether oxidation or reduction takes place. Deduce the equation of the overall cell reaction including state symbols. (5)

(d) Electrolysis has made it possible to obtain reactive metals such as aluminium from their ores, which has resulted in significant developments in engineering and technology. State one reason why aluminium is preferred to iron in many uses. (1)

(e) HL Electroplating is an important application of electrolysis. State the composition of the electrodes and the electrolyte used in the silver electroplating process. (3)

(Total 13 marks)

8. Fuel cells may be twice as efficient as the internal combustion engine. Although fuel cells are not yet in widespread use, NASA has used a basic hydrogen–oxygen fuel cell as the energy source for space vehicles.

(a) State the half-equations occurring at each electrode in the hydrogen-oxygen fuel cell in an alkaline medium. (2)

(b) Describe the composition of the electrodes and state the overall cell equation of a nickel–cadmium battery. (3)

(Total 5 marks)

9. The high activity of lithium metal leads to the formation of an oxide layer on the metal which decreases the contact with the electrolyte in a battery.

(a) Suggest how this is overcome in the lithium-ion battery. (2)

(b) Describe the migration of ions taking place at the two electrodes in the lithium-ion battery when it produces electricity. (2)

(c) Discuss one similarity and one difference between fuel cells and rechargeable batteries. (2)

(Total 6 marks)

10. Aluminium and its alloys are widely used in industry.

(a) Aluminium metal is obtained by the electrolysis of alumina dissolved in molten cryolite.

(i) Suggest the function of the molten cryolite. (1)

(ii) State the half-equations for the reactions that take place at each electrode. (2)

(b) Outline **two** different ways that carbon dioxide may be produced during the production of aluminium. (2)

(Total 5 marks)

11. **(a)** Explain why iron is obtained from its ores using chemical reducing agents but aluminium is obtained from its ores using electrolysis. (2)

(b) Both carbon monoxide and hydrogen can be used to reduce iron ores. State the equations for the reduction of magnetite, Fe_3O_4, with

(i) carbon monoxide

(ii) hydrogen. (2)

(Total 4 marks)

12. Aluminium is the most abundant metal in the Earth's crust.

(a) State the materials used for the positive and negative electrodes in the production of aluminium by electrolysis. (2)

(b) Discuss why it is important to recycle aluminium. (2)

(Total 4 marks)

13. Brass is a copper-containing alloy with many uses. An analysis is carried out to determine the percentage of copper present in three identical samples of brass. The reactions involved in this analysis are shown below.

Step 1: $Cu(s) + 2HNO_3(aq) + 2H^+(aq) \rightarrow Cu^{2+}(aq) + 2NO_2(g) + 2H_2O(l)$

Step 2: $4I^-(aq) + 2Cu^{2+}(aq) \rightarrow 2CuI(s) + I_2(aq)$

Step 3: $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

(a) **(i)** Deduce the change in the oxidation numbers of copper and nitrogen in step 1. (2)

(ii) Identify the oxidizing agent in step 1. (1)

(b) A student carried out this experiment three times with three identical small brass nails and obtained the following results.

mass of brass = 0.456 g ± 0.001 g

Titre	1	2	3
Initial volume of 0.100 mol dm^{-3} $S_2O_3^{2-}$ (±0.05 cm^3)	0.00	0.00	0.00
Final volume of 0.100 mol dm^{-3} $S_2O_3^{2-}$ (±0.05 cm^3)	28.50	28.60	28.40
Volume added of 0.100 mol dm^{-3} $S_2O_3^{2-}$ (±0.10 cm^3)	28.50	28.60	28.40
Average volume added of 0.100 mol dm^{-3} $S_2O_3^{2-}$ (±0.10 cm^3)	28.50		

(i) Calculate the average amount, in mol, of $S_2O_3^{2-}$ added in step 3. (2)

(ii) Calculate the amount, in mol, of copper present in the brass. (1)

(iii) Calculate the mass of copper in the brass. (1)

(iv) Calculate the percentage by mass of copper in the brass. (1)

(v) The manufacturers claim that the sample of brass contains 44.2% copper by mass. Determine the percentage error in the result. (1)

(Total 9 marks)

HL

14. The standard electrode potentials for two metals are given below.

$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$ $\quad E^\ominus = -1.66\ V$

$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$ $\quad E^\ominus = -0.23\ V$

What is the equation and cell potential for the spontaneous reaction that occurs?

A $2Al^{3+}(aq) + 3Ni(s) \rightarrow 2Al(s) + 3Ni^{2+}(aq)$ $\quad E^\ominus = -1.89\ V$

B $2Al(s) + 3Ni^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Ni(s)$ $\quad E^\ominus = -1.89\ V$

C $2Al^{3+}(aq) + 3Ni(s) \rightarrow 2Al(s) + 3Ni^{2+}(aq)$ $\quad E^\ominus = -1.43\ V$

D $2Al(s) + 3Ni^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Ni(s)$ $\quad E^\ominus = -1.43\ V$

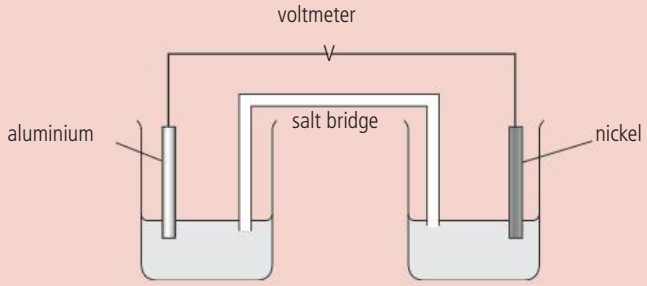
15. Consider the following half-cell reactions and their standard electrode potentials.

	$E^\ominus$ / V
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	−0.26
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	−1.66

(a) Deduce a balanced equation for the overall reaction which will occur spontaneously when these two half-cells are connected. (2)

(b) Determine the cell potential when the two half-cells are connected. (1)

(c) On the cell diagram below, label the negative electrode (anode), the positive electrode (cathode), and the directions of the movement of electrons and ion flow. (4)



(Total 7 marks)

16. For the electrolysis of aqueous copper(II) sulfate, which of the following statements is correct?

A Cu and O_2 are produced in a mol ratio of 1 : 1

B H_2 and O_2 are produced in a mol ratio of 1 : 1

C Cu and O_2 are produced in a mol ratio of 2 : 1

D H_2 and O_2 are produced in a mol ratio of 2 : 1

17. What condition is necessary for the electroplating of silver, Ag, onto a steel spoon?

A The spoon must be the positive electrode.

B The silver electrode must be the negative electrode.

C The spoon must be the negative electrode.

D The electrolyte must be acidified.

18. How do the products compare at each electrode when aqueous 1 mol dm^{-3} magnesium bromide and molten magnesium bromide are electrolyzed?

	$E^{\ominus}$ / V
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	−2.37
$\frac{1}{2}Br_2(l) + e^- \rightleftharpoons Br^-(aq)$	+1.07
$\frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O(l)$	+1.23

	Positive electrode (anode)	Negative electrode (cathode)
A	same	same
B	same	different
C	different	same
D	different	different

19. What is the cell potential, in V, for the reaction that occurs when the following two half-cells are connected?

	$E^{\ominus}$ / V
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.44
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33

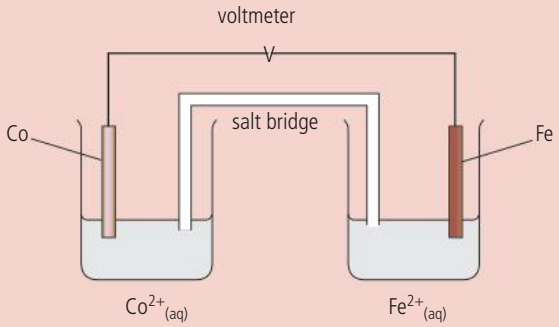
A +0.01

B +0.89

C +1.77

D +2.65

20. (a) An electrochemical cell is made from an iron half-cell connected to a cobalt half-cell:



The standard electrode potential for $Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$ is −0.45 V. The total cell potential obtained when the cell is operating under standard conditions is 0.17 V. Cobalt is produced during the spontaneous reaction.

(i) Define the term *standard electrode potential* and state the meaning of the minus sign in the value of −0.45 V. (3)

(ii) Calculate the value for the standard electrode potential for the cobalt half-cell. (1)

(iii) Deduce which species acts as the oxidizing agent when the cell is operating. (1)

(iv) Deduce the equation for the spontaneous reaction taking place when the iron half-cell is connected instead to an aluminium half-cell. (2)

(v) Explain the function of the salt bridge in the electrochemical cell. (2)

(b) Deduce the oxidation number of cobalt in the following species.

(i) $[Co(H_2O)_6]^{2+}$ **(ii)** $Co_2(SO_4)_3$ **(iii)** $[CoCl_4]^{2-}$ (3)

(c) An electrolytic cell is made using a very dilute solution of sodium chloride.

(i) Draw a labelled diagram of the cell. Use an arrow to show the direction of the electron flow and identify the positive and negative electrodes. (3)

(ii) Give the formulas of all the ions present in the solution. (2)

(iii) Predict the products obtained at each electrode and state the half-equation for the formation of each product. (3)

(iv) Deduce the molar ratios of the products obtained at the two electrodes. (1)

(d) Predict the products by giving the relevant half-equation for the reaction occurring at each electrode if the electrolyte of the cell described in part **(c)** was changed to:

(i) concentrated sodium chloride (2)

(ii) molten sodium bromide. (2)

(Total 25 marks)

HL end



REACTIVITY

3.3 Electron sharing reactions

The kayaker's clothing and equipment, including the kayak, paddle and personal flotation device, are made almost entirely of organic compounds that have been artificially synthesized. Organic chemists use knowledge of the functional groups in organic molecules to design compounds with the required properties such as waterproofing, breathability, strength, density, flexibility and insulation. Addition polymers such as polyethene, which the kayak is made of, are synthesized using electron sharing reactions involving reactive species called radicals.

Guiding Question

What happens when a species possesses an unpaired electron?

Radicals are highly reactive species that contain an unpaired electron. This unpaired electron makes radicals energetically unstable so they readily react with other species to form products that are energetically more stable. These reactions can involve radicals breaking bonds in other compounds or reacting with each other by combining their unpaired electrons and forming a covalent bond.

The high reactivity of radicals means they are capable of breaking down compounds which would otherwise be stable. This can be beneficial when used in applications such as wastewater treatment and the breakdown of persistent pollutants, as well as in the industrial production of additional polymers. However the high reactivity of radicals can also result in environmentally harmful processes such as smog formation and atmospheric ozone depletion. Beneficial reactions involving radicals occur within our bodies, including various enzyme reactions and the destruction of pathogens. However, radicals can also cause cell damage and have been associated with various illnesses such as cancers, strokes and heart disease as well as being identified as a possible cause of the ageing process.

Radical reactions occur via a mechanism involving three stages: initiation, propagation and termination. In this chapter we will use the substitution of alkanes by halogens as a case study to illustrate how stable compounds can react with radicals through this mechanism.

Nature of Science

The development of scientific knowledge relies on the ability of scientists to obtain empirical evidence that either supports or discredits proposed theories. Early chemists, relying on personal observations and/or simple measurements, were often only able to postulate or make inferences about the nature of reactions being studied and the presence of reactive intermediates. Progressive developments in technologies and instrumentation have allowed chemists to obtain increasingly detailed empirical evidence, including the detection and measurement of previously undetectable species such as radicals. This has led to many breakthroughs in our understanding of chemical reactivity.

Reactivity 3.3.1 – Radicals

Reactivity 3.3.1 – A radical is a chemical entity that has an unpaired electron. Radicals are highly reactive. Identify and represent radicals, e.g. $\bullet CH_3$ and $Cl\bullet$.	
	Structure 2.1 – How is it possible for a radical to be an atom, a molecule, a cation or an anion? Consider examples of each type.

Radicals have unpaired electrons and are highly reactive

A **radical** is a chemical species that contains an unpaired electron. The presence of an unpaired electron results in radicals having a high enthalpy. This makes radicals very reactive as it is energetically favourable for them to take an electron from other species or to combine with other radicals to form a covalent bond, as both can result in products with a lower enthalpy.

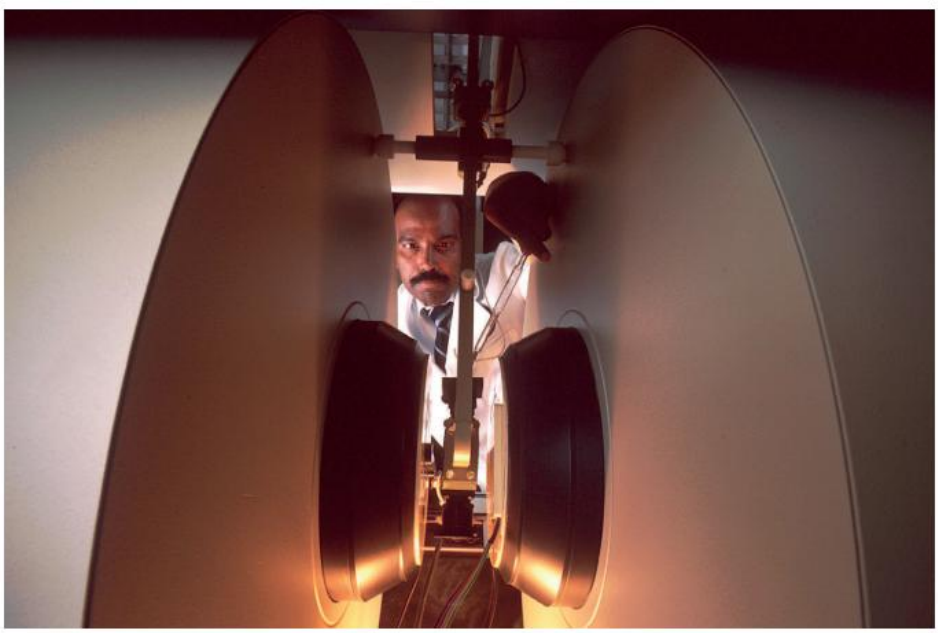


Fresh fruits and vegetables are good sources of antioxidants, which may help prevent damaging oxidative reactions from occurring in cells.

i The radical theory of ageing suggests that the physiological changes associated with ageing are the result of oxidative reactions in cells causing damage to membranes and large molecules such as DNA. These changes accumulate with time and may explain the increase in degenerative diseases, such as cancer, with age. The theory suggests that supplying cells with antioxidants will help to slow down the damaging oxidative reactions. Antioxidants are particularly abundant in fresh fruit and vegetables, as well as in tea and cocoa. Although there is strong evidence that antioxidant supplementation may help protect against certain diseases, it has not yet been shown to produce a demonstrated increase in the human life span.

Because they are highly reactive, radicals tend to have short lifetimes and do not exist for very long. One notable exception is when radicals are formed in the upper atmosphere where they can persist for a significant length of time as there is a low probability of them colliding and reacting with other chemical species.

TOK The free-radical theory of ageing is a hypothesis that is not universally supported. Will the explanation of certain natural processes ever go beyond hypotheses?



A researcher using electron resonance spectroscopy to examine the role of radicals in anticancer drug activity.

i The presence of radicals in specific chemical reactions was first postulated by chemists in the 1900s but these radicals could not be isolated or observed directly. The development of Electron Spin Resonance (ESR) spectroscopy in the 1940s enabled radicals to be detected due to the unique magnetic properties associated with unpaired electrons. Further advancements in ESR and other spectroscopic techniques combined with increased computer processing power, have demonstrated the importance of radical reactions in many areas of chemistry.

The only formal requirement of a radical is the presence of an unpaired electron. It is therefore possible for radicals to be atoms, molecules or ions. Examples of the different types of radicals include:

- atomic: chlorine (Cl•), bromine (Br•), hydrogen (H•)
- molecular: neutral molecules with an odd number of electrons will be radicals, e.g. nitric oxide (NO•), hydroxyl radical (OH•), methyl radical ($•CH_3$)
- anionic: molecules that gain electrons can become radical anions, e.g. superoxide radical ($O_2•^-$), benzene radical anion ($C_6H_6•^-$)

- cationic: molecules that lose electrons can become radical cations. For example, in the mass spectrometry of organic compounds (Structure 3.2), the molecular ions formed ($M^{\bullet+}$) are radical cations, e.g. propane cation ($C_3H_8^{\bullet+}$), ethanol cation ($C_2H_5OH^{\bullet+}$).

The different species given in the above list are all identified as radicals by including a dot (•) in their chemical formulas. This dot represents an unpaired electron and is usually aligned vertically with the middle of the chemical formula.

Nature of Science

As chemistry has progressed, the term radical has been applied in different contexts. In earlier definitions a radical was described as a group of atoms that could exist on its own, or as part of a larger molecule. If the group was to exist *free* of the other atoms in the molecule, this would require the homolytic breaking of a covalent bond so a *free* radical would have an unpaired electron.

In modern contexts, the term functional group (see Structure 3.2) is now used instead of radical to describe a specific group of atoms within a molecule, with 'radical' specifically referring to a chemical species that contains an unpaired electron. However the term 'free radical' is still commonly used.

Nature of Science

Classification of reactions can be approached in many different ways. For example, combustion reactions can be defined as a redox reaction, because carbon atoms in the fuel are oxidized to give CO_2, or as an electron sharing (radical) reaction, because they proceed via a chain reaction involving various radical species.

It is estimated that around 50% of the world's polymers are addition polymers which have been made via radical reactions. Two examples of addition polymers are polypropene and acrylonitrile butadiene styrene (ABS), which can be used in 3D printers to create custom shapes and designs. Addition polymers are covered in more detail in Structure 2.4.



3D printing can use addition polymers to make custom shapes and designs.

Structure 2.1 – How is it possible for a radical to be an atom, a molecule, a cation or an anion? Consider examples of each type.

An unpaired electron is represented in a chemical formula by a dot (•).

Make sure that you understand the difference between a radical and an ion. A radical has an unpaired electron but no net charge; an ion carries a charge. Species that are radicals ***and*** carry a charge are known as radical cations or radical anions.



A beach campfire at sunset. Combustion reactions, such as the burning of wood, occur via chain reactions of many steps, with radical species progressively breaking the fuel down into smaller compounds, eventually forming carbon dioxide, water and other simple oxides.

Exercise

Q1. Which of the following species is a radical?

A F **B** Cl^- **C** Ne **D** Li^+

Q2. Which of the following molecules is a radical?

A CO_2 **B** NO_2 **C** CH_4 **D** NH_3

Q3. Which of the following ions is a radical?

A Cl^- **B** NO_3^- **C** Mg^{2+} **D** CH_4^+

Reactivity 3.3.2 – Homolytic fission

Reactivity 3.3.2 – Radicals are produced by homolytic fission, e.g. of halogens, in the presence of ultraviolet (UV) light or heat.

Explain, including with equations, the homolytic fission of halogens, known as the initiation step in a chain reaction.

The use of a single-barbed arrow (fish hook) to show the movement of a single electron should be covered.	Reactivity 1.2 – Why do chlorofluorocarbons (CFCs) in the atmosphere break down to release chlorine radicals but not fluorine radicals? Structure 2.2 – What is the reverse process of homolytic fission? Structure 2.2 – Chlorine radicals released from CFCs are able to break down ozone, O_3, but not oxygen, O_2, in the stratosphere. What does this suggest about the relative bond strengths of bonds in the two allotropes?

Radicals can be made through the breaking of covalent bonds

When **homolytic fission** occurs, a covalent bond breaks to form two radicals. 'Homo' means 'the same' and refers to the fact that the two products have an equal assignment of electrons from the bond.

As shown in Reactivity 1.2, breaking bonds is an endothermic process, so homolytic fission requires energy for it to happen. The amount of energy required depends on the strength of the covalent bond. For weaker bonds, sufficient energy can come from heating the compound and the process is known as **thermolytic fission**. The breaking of stronger bonds requires the absorption of high-energy UV light and is known as **photolytic fission**.

Thermolytic fission

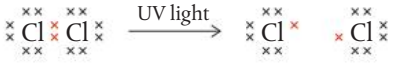
$$X{:}X \xrightarrow{\text{Heat}} X^{\bullet} + X^{\bullet}$$

Photolytic fission

$$X{:}X \xrightarrow{\text{UV}} X^{\bullet} + X^{\bullet}$$

The Cl–Cl bond in chlorine, Cl_2, can be broken through photolytic fission. The molecule splits into two chlorine atoms, each has an unpaired electron and both atoms are therefore radicals.

$$Cl_2 \xrightarrow{\text{UV light}} 2Cl\bullet \text{ radicals}$$



2 chlorine radicals

This process can also be shown using single-headed curly arrows, sometimes known as 'fish hooks', to show the movement of a single electron.



As we will see later in this chapter, termination reactions occur when two radicals combine, sharing their unpaired electrons and forming a covalent bond. This is effectively the reverse process of homolytic fission and can also be represented using single-headed curly arrows. For example, the termination reaction between $CH_3\bullet$ and $Cl\bullet$ radicals to form CH_3Cl can be represented by:



Homolytic fission occurs when a bond breaks by splitting the shared pair of electrons between the two products. It produces two radicals, each with an unpaired electron:

$$X:X \rightarrow X\bullet + X\bullet$$

Structure 2.2 – What is the reverse process of homolytic fission?

Chlorine radicals can cause ozone depletion

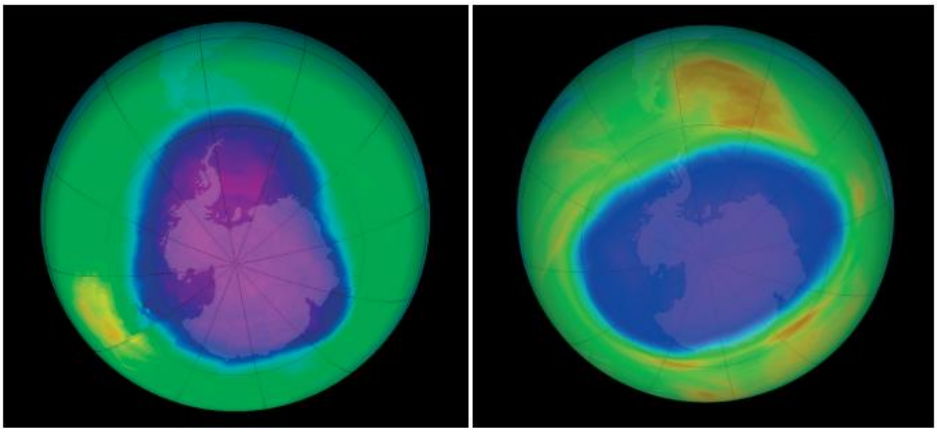
Chlorofluorocarbons (CFCs) were widely used in aerosols, refrigerants, solvents and plastics due to their low reactivity and low toxicity in the troposphere. But when CFCs enter the stratosphere, the higher energy UV radiation breaks them down, releasing chlorine atoms, which are reactive radicals.

In 1985 measurements showed unusually low levels of atmospheric ozone over Antarctica and the Southern Ocean. The main culprit for ozone depletion, chlorofluorocarbons (CFCs), had been identified as far back as 1974, but efforts to ban CFCs had proved controversial due to economic concerns and difficulties in finding alternative substances. The levels of depletion observed in 1985 led to urgent action with the Montreal Protocol, which banned ozone depleting substances, being adopted in 1987. Global cooperation in adhering to this Protocol has stopped the decline in atmospheric ozone levels, with measurements in recent years showing signs of a recovery.

The level observed in 2000 was one of the lowest measured, as shown by the large purple region in the figure on the left below. The greater amount of blue present in 2020 provides evidence that atmospheric ozone levels are now recovering.



Used spray paint cans. Before being banned under the Montreal Protocol, chlorofluorocarbons (CFCs) were used as refrigerants and propellants for spray paints, deodorant and hair sprays, along with other applications.



Minimum annual ozone levels measured over Antarctica in September 2000 (left) and October 2020 (right). The colours represent ozone concentrations and follow the progression: purple (lowest), blue, green yellow (highest).

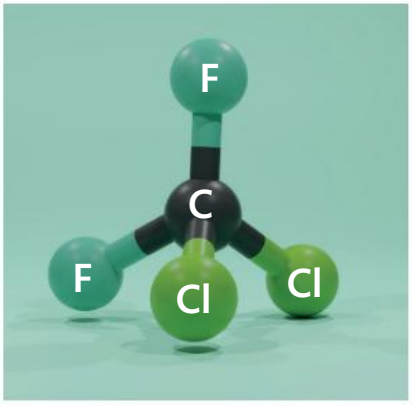
Reactivity 1.2 – Why do chlorofluorocarbons (CFCs) in the atmosphere break down to release chlorine radicals but not fluorine radicals?

Although CFCs contain both C–Cl and C–F bonds, the C–Cl bond has a much lower bond enthalpy (324 kJ mol^{-1}) compared to the C–F bond (492 kJ mol^{-1}). When UV radiation is absorbed, the weaker C–Cl bond breaks in preference to the C–F bond.

For example, the CFC dichlorodifluoromethane, commonly known as Freon-12, undergoes photochemical decomposition as follows:

$$CCl_2F_2(g) \xrightarrow{UV} CClF_2\bullet(g) + Cl\bullet(g)$$

$$CCl_2F_2(g) \not\xrightarrow{UV} CCl_2F\bullet(g) + F\bullet(g)$$



▲ A molecular model of dichlorodifluoromethane (Freon-12), a chemical that was commonly used as a refrigerant and aerosol propellant before being banned under the Montreal Protocol.

TOK

The success of the Montreal Protocol in banning CFCs in order to avoid serious environmental consequences is often compared to the current global heating crisis. The scientific evidence is now unequivocal that the Earth is warming due to human activities, and that this will have major environmental and societal impacts. However, this is proving to be a much more controversial issue due to the significant political, economic, technological and social challenges that governments, industry and individuals all face in making the significant reductions in greenhouse gas emissions required. How might developments in scientific knowledge trigger political controversies or controversies in other areas of knowledge?

Challenge yourself

1. The average bond enthalpies for the C–Cl and C–F bonds are 324 kJ mol^{-1} and 492 kJ mol^{-1} respectively. Calculate the wavelengths of UV radiation required to break C–Cl and C–F bonds.

The chlorine radicals released then catalyse the decomposition of ozone, O_3.

$$Cl\bullet(g) + O_3(g) \rightarrow O_2(g) + ClO\bullet(g)$$

$$ClO\bullet(g) + O\bullet(g) \rightarrow O_2(g) + Cl\bullet(g)$$

Here $Cl\bullet(g)$ has acted as a catalyst and the net reaction is:

$$O_3(g) + O\bullet(g) \rightarrow 2O_2(g)$$

Because it acts as a catalyst and is regenerated in the reaction, one chlorine radical is capable of catalysing the decomposition of many thousands of ozone molecules.

Structure 2.2 – Chlorine radicals released from CFCs are able to break down ozone, O_3, but not oxygen, O_2, in the stratosphere. What does this suggest about the relative bond strengths of bonds in the two allotropes?

Although they can break down ozone, the chlorine radicals do not readily react with oxygen, O_2, present in the stratosphere. In Structure 2.2 we see that the ozone molecule can undergo resonance, with the O–O bonds in ozone having a bond strength somewhere between a single bond and a double bond. The O=O double bond in oxygen is therefore a stronger bond, and this makes O_2 more resistant to reactions with chlorine radicals.

Nature of Science

Sometimes the unintended consequences of scientific innovation are not known until problems have developed on a large scale and are difficult to reverse. Many ozone-depleting chemicals are expected to persist in the atmosphere for a long time. Other chemicals such as hydrofluorocarbons (HFCs), which replaced CFCs as refrigerants and have high global warming potentials, are now being detected in increasing amounts in the atmosphere. As a result, the use of HFCs is now also being phased out under the Kigali amendment to the Montreal Protocol.

TOK

F. Sherwood Rowland and Mario Molina were the two scientists who first identified that CFCs were capable of seriously depleting atmospheric ozone if their industrial use continued unabated. Abstracts of scientific papers summarize the results and conclusions, often using highly specific language aimed at other scientists active in the field of study. The abstract of Rowland and Molina's 1974 paper in the prestigious journal *Nature* is a good example of clarity and ability to convey the seriousness of their results, even to non-scientists.

'Chlorofluoromethanes are being added to the environment in steadily increasing amounts. These compounds are chemically inert and may remain in the atmosphere for 40–150 years, and concentrations can be expected to reach 10 to 30 times present levels. Photodissociation of the chlorofluoromethanes in the stratosphere produces significant amounts of chlorine atoms, and leads to the destruction of atmospheric ozone.'

Does scientific language have a primarily descriptive, explanatory or interpretive function? Does the precision of the language used in the natural sciences successfully eliminate all ambiguity?

Exercise

Q4. Which of the following reactions involves homolytic fission?

A $CH_4 + Br_2 \rightarrow CH_3Br + HBr$

B $Br_2 \rightarrow Br^+ + Br^-$

C $C + O_2 \rightarrow CO_2$

D $HBr \rightarrow H + Br$

Q5. The homolytic fission of a Cl–Cl bond:

A is exothermic

B forms two ions

C always requires heat

D is endothermic

Q6. Use curly arrows to illustrate the homolytic fission of the covalent bond in iodine, I_2.

Q7. Explain the difference between homolytic fission that occurs thermolytically or photolytically.

Reactivity 3.3.3 – Radical substitution reactions of alkanes

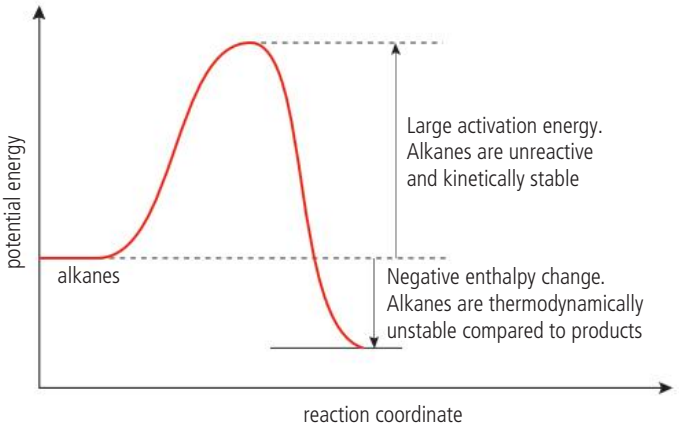
Reactivity 3.3.3 – Radicals take part in substitution reactions with alkanes, producing a mixture of products.	
Explain, using equations, the propagation and termination steps in the reactions between alkanes and halogens.	
Reference should be made to the stability of alkanes due to the strengths of the C–C and C–H bonds and their essentially non-polar nature.	Reactivity 2.2 – Why are alkanes described as kinetically stable but thermodynamically unstable?

Substitution reactions of alkanes with halogens occur via a radical mechanism

Alkanes contain strong C–C and C–H bonds which take a lot of energy to break. Because alkanes are non-polar compounds, they do not attract reactive species such as electrophiles and nucleophiles. These two factors contribute to alkanes being relatively unreactive compounds.

The low reactivity of alkanes is also explained by the high activation energies that are associated with their reactions. At regular temperatures, the reactant molecules lack sufficient kinetic energy to overcome the activation energy, and alkanes are therefore regarded as being **kinetically stable**.

The high kinetic stability of alkanes is one reason that they have become the world's predominant fuel source as they can be safely compressed, transported and stored before use.



Reactivity 2.2 – Why are alkanes described as kinetically stable but thermodynamically unstable?

However, as covered in Reactivity 1.2, alkanes do undergo highly exothermic combustion reactions. Because the reaction is exothermic, this means that the alkane reactants have a higher enthalpy and are **thermodynamically unstable** compared to the products.



▲ A Liquefied Natural Gas (LNG) tanker at sea. LNG is natural gas (mainly methane) that has been purified and cooled to below –162 °C, which condenses it into a liquid. In liquefied form it only requires 1/600th the volume of the gas so larger amounts can be transported in special, highly-insulated tanks.

Radical substitution reactions occur via three stages

As alkanes are saturated molecules, the main type of reaction that they can undergo is **substitution**. This occurs when another reactant, such as a halogen, takes the place of a hydrogen atom in the alkane. The products of a substitution reaction between an alkane and a halogen will be a halogenoalkane and the hydrogen halide. For example, methane, CH_4, reacts with chlorine, Cl_2, to produce chloromethane, CH_3Cl, and hydrogen chloride, HCl.

$$CH_4(g) + Cl_2(g) \xrightarrow{\text{UV light}} CH_3Cl(g) + HCl(g)$$

The reaction does not take place in the dark as the energy of UV light is necessary to break the covalent bond in the chlorine molecule and form chlorine radicals.

Once formed, these radicals will start a **chain reaction** in which a mixture of products including the halogenoalkane is formed. We can describe the reaction as a sequence of steps, known as the **reaction mechanism**, and it occurs via three stages; initiation, propagation and termination.

Bromination of hydrocarbons. Full details of how to carry out this experiment with a worksheet are available in the eBook.

Initiation

The initiation stage involves the formation of the radical species, which can then react with the alkane. For the substitution reaction of methane with chlorine, the initiation step is the photolytic fission of chlorine:

$$Cl_2 \xrightarrow{\text{UV light}} 2Cl\bullet$$

Propagation

In the propagation stage, the radicals formed in the initiation stage react with other species present to form new radicals. There are many possible propagation steps, which all allow the reaction to continue. This is why this type of reaction is often called a chain reaction.

For example:

$$Cl\bullet + CH_4 \rightarrow CH_3\bullet + HCl$$

$$CH_3\bullet + Cl_2 \rightarrow CH_3Cl + Cl\bullet$$

$$CH_3Cl + Cl\bullet \rightarrow CH_2Cl\bullet + HCl$$

$$CH_2Cl\bullet + Cl_2 \rightarrow CH_2Cl_2 + Cl\bullet$$

Termination

Termination reactions remove radicals from the mixture when they react with each other and pair up their electrons to form a covalent bond. Again there are many possible termination steps.

For example:

$$Cl\bullet + Cl\bullet \rightarrow Cl_2$$

$$CH_3\bullet + Cl\bullet \rightarrow CH_3Cl$$

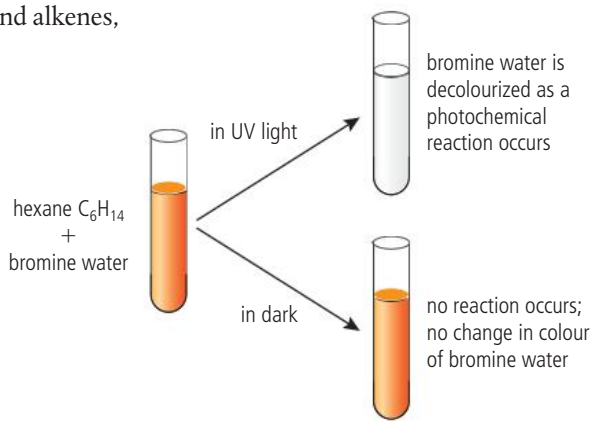
$$CH_3\bullet + CH_3\bullet \rightarrow C_2H_6$$

$$CH_2Cl\bullet + Cl\bullet \rightarrow CH_2Cl_2$$

So the reaction mixture may contain mono- and disubstituted halogenoalkanes, as well as HCl and larger alkanes.

As a termination step involves two unpaired electrons combining to form a covalent bond, this is, in effect, the reverse process of homolytic fission where a bond is broken to give two radicals.

A similar reaction to the example given above, for methane and chlorine, also occurs with other alkanes and bromine, Br_2. The change in colour from brown to colourless of bromine water when it reacts with an alkane occurs only in the presence of UV light, as shown in Figure 1. This reaction is sometimes used to distinguish between alkanes and alkenes, as will be discussed in more detail in the following chapter.



R3.3 Figure 1 The reaction between hexane, C_6H_{14}, and bromine water takes place only in the presence of UV light.

The reaction of methane, CH_4, with chlorine, Cl_2, via a free radical mechanism involves a number of different possible propagation and termination steps resulting in a mixture of products. The primary product of interest is chloromethane, CH_3Cl. Focusing on the steps that result in the formation of this product gives a simplified version of the mechanism;

Initiation:

$$Cl_2 \xrightarrow{UV} 2Cl\bullet$$

Propagation:

$$Cl\bullet + CH_4 \rightarrow CH_3\bullet + HCl$$

Termination:

$$CH_3\bullet + Cl\bullet \rightarrow CH_3Cl$$

Overall:

$$CH_4(g) + Cl_2(g) \xrightarrow{UV} CH_3Cl(g) + HCl(g)$$

Alkanes are saturated hydrocarbons and undergo substitution reactions.

Exercise

Q8. What are the three stages of a radical mechanism? Use the reaction of methane, CH_4, with bromine, Br_2, to explain your answer, giving relevant equations for each stage.

Q9. Alkanes react with halogens in the presence of UV light to form halogenoalkanes.

(a) Write equations showing the possible steps leading to the formation of bromoethane, C_2H_5Br, when bromine, Br_2, and ethane, C_2H_6, react together in UV light.

(b) Explain, using equations, how this reaction also leads to the formation of trace amounts of butane, C_4H_{10}.

(c) If the reaction is allowed to proceed for a sufficient length of time, large amounts of dibromoethane products can be formed. Draw and name the structures of possible dibromoethane products in this reaction.

Q10. State and explain what would be observed during the following experiments carried out at room temperature.

(a) Bromine water is added to hexane in a test tube exposed to UV light.

(b) Bromine water is added to hexane in a test tube that is covered in foil.

Q11. Chlorofluorocarbons (CFCs) such as trichlorofluoromethane, $CFCl_3$, are ozone-depleting substances.

(a) Explain, using curly arrows, how trichlorofluoromethane reacts with UV light to produce chlorine radicals.

(b) Provide chemical equations showing how chlorine radicals catalyse the decomposition of ozone, O_3.

Guiding Question revisited

What happens when a species possesses an unpaired electron?

In this chapter we have learnt that:

- Radicals are chemical species that contain an unpaired electron and are highly reactive.
- Radicals are formed through homolytic fission of covalent bonds.
- Alkanes are kinetically stable but react with halogens, in the presence of UV light, through a radical mechanism.
- Radical mechanisms have three stages: initiation, propagation and termination.
- Ozone depletion due to chlorofluorocarbons (CFCs) also occurs through a radical mechanism.

Practice questions

1. Which reaction occurs via a radical mechanism?

A $C_2H_6 + Br_2 \rightarrow C_2H_5Br + HBr$

B $C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$

C $C_4H_9I + OH^- \rightarrow C_4H_9OH + I^-$

D $(CH_3)_3CI + H_2O \rightarrow (CH_3)_3COH + HI$

2. Which statement is true about radical mechanisms?

A Radical mechanisms involve four stages.

B Radicals form spontaneously in the initiation stage.

C Radicals react with non-radical species in the termination stage.

D Radicals react with other radicals in the termination stage.

3. Under the correct conditions, pentane reacts with bromine to form a number of different products. The reaction can be represented by the equation

$$C_5H_{12} + Br_2 \rightarrow C_5H_{11}Br + Y$$

(a) Identify the product Y. (1)

(b) State the essential condition for this reaction. (1)

(c) The reaction takes place through a stepwise mechanism with three stages. Give the names of these stages along with one equation for each stage. (3)

(d) The reaction can form three different products with the formula $C_5H_{11}Br$.

(i) State the relationship between these products. (1)

(ii) Draw and name the structures of the three products. (3)

(Total 9 marks)

4. Propane, C_3H_8, reacts with chlorine, Cl_2, in the presence of UV light.

(a) State the type of reaction that occurs. (1)

(b) Give equations to explain how this reaction occurs through a stepwise mechanism. (3)

(c) Draw and name two possible monosubstituted products of the reaction. (2)

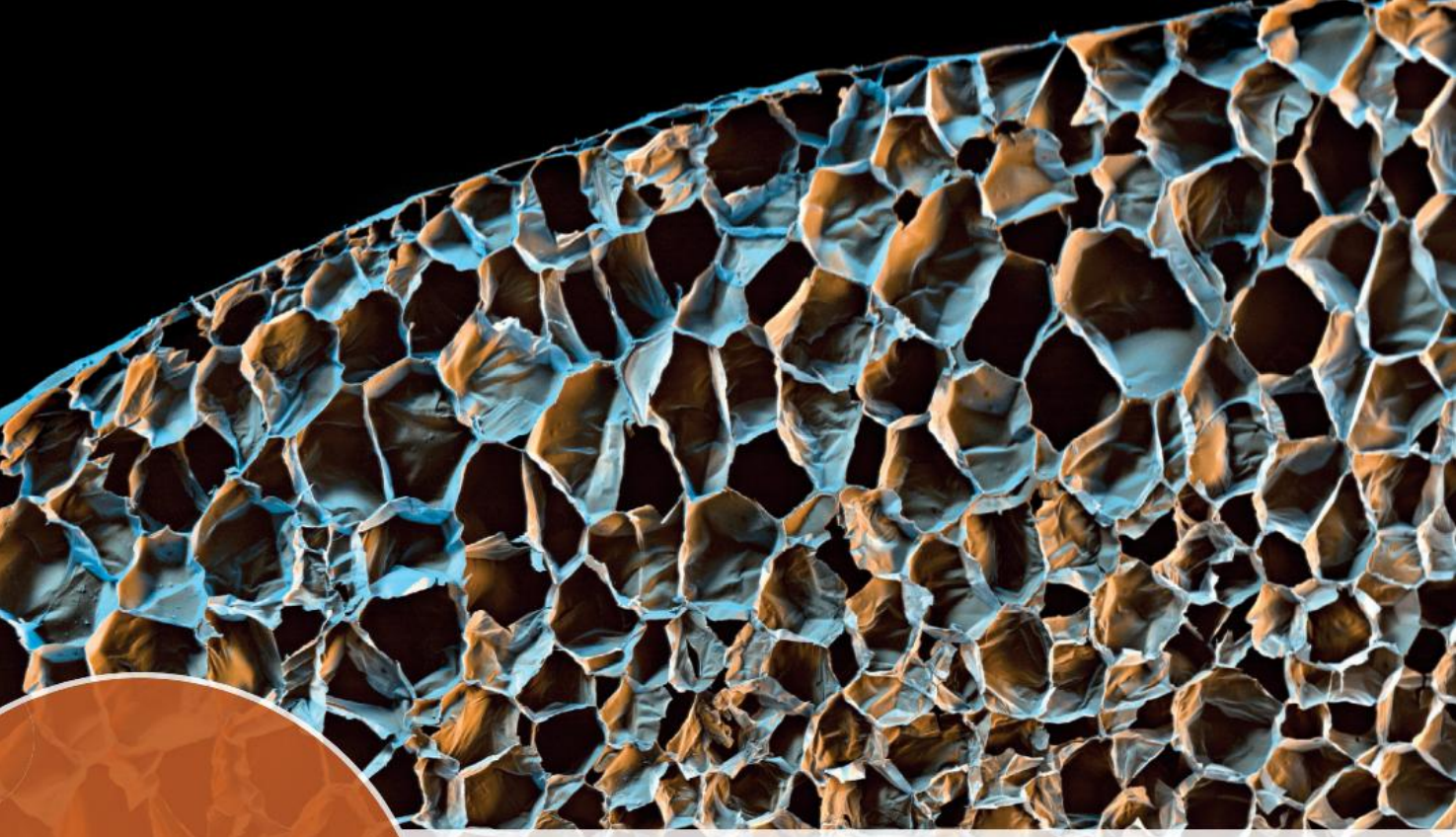
(d) Explain why propane is regarded as kinetically stable but thermodynamically unstable. (2)

(Total 8 marks)

5. **(a)** Explain, using equations, how ethane can be converted to chloroethane. (4)

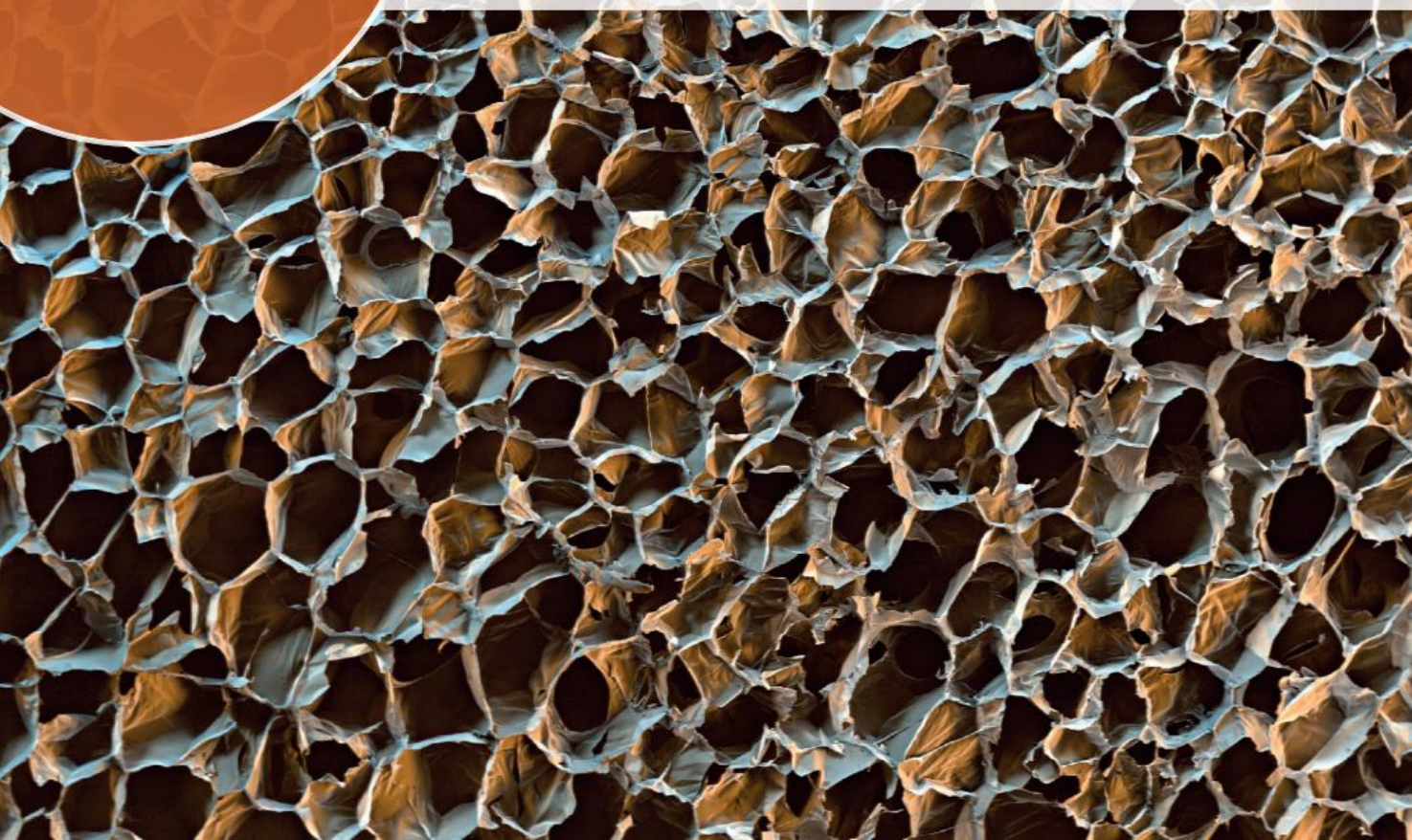
(b) Identify a possible alkane, other than ethane, that can be found in the product mixture. Give an equation that explains the formation of this alkane. (2)

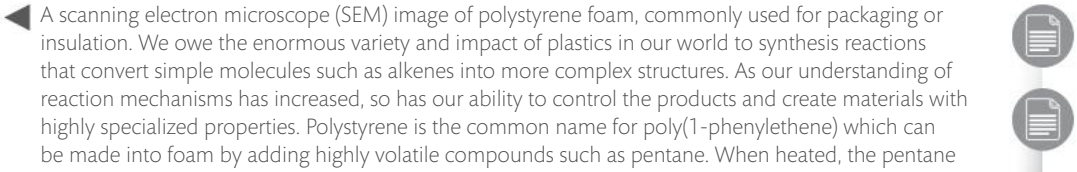
(Total 6 marks)



REACTIVITY

3.4 Electron-pair sharing reactions





A scanning electron microscope (SEM) image of polystyrene foam, commonly used for packaging or insulation. We owe the enormous variety and impact of plastics in our world to synthesis reactions that convert simple molecules such as alkenes into more complex structures. As our understanding of reaction mechanisms has increased, so has our ability to control the products and create materials with highly specialized properties. Polystyrene is the common name for poly(1-phenylethene) which can be made into foam by adding highly volatile compounds such as pentane. When heated, the pentane becomes gaseous and expands, forming air spaces, clearly visible in the image above, that make up 95% of polystyrene foam. It is the presence of these air spaces that gives polystyrene foam its insulating properties. Its low density also makes it a useful material for applications such as flotation devices.

Guiding Question

What happens when reactants share their electron pairs with others?

When one reactant shares an electron pair with another reactant, this results in the formation of a coordination bond. This is a common theme in many areas of chemistry, including the reactions of acids and bases, transition metal ions and many organic compounds. Specific examples of these different reactions, highlighting how each involves the movement of electron pairs, will be presented in this chapter. In particular we will examine how:

- organic compounds react with electrophiles and nucleophiles, donating or accepting electron pairs to form new covalent bonds
- HL Lewis bases can react by donating electron pairs to Lewis acids
- HL ligands donate electron pairs to transition metal ions and form complex ions.

We will also look at how the use of curly arrows, that represent the movement of electron pairs, provides an effective way of explaining the mechanisms of electron-pair sharing reactions. This is of particular relevance to the reactions of organic compounds, such as the substitution reactions of halogenoalkanes and the addition reactions of alkenes, as we will see in this chapter.

Reactivity 3.4.1 – Nucleophiles

Reactivity 3.4.1 – A nucleophile is a reactant that forms a bond to its reaction partner (the electrophile) by donating both electrons.	
Recognize nucleophiles in chemical reactions.	
Both neutral and negatively charged species should be included.	

Nucleophiles form bonds by donating electron pairs

A **nucleophile** is a reactant that forms a covalent bond to its reaction partner (the **electrophile**) by donating both bonding electrons. Nucleophiles themselves tend to be electron rich, having one or more lone pairs of electrons and they may also carry a negative charge. Examples of nucleophiles include;

Neutral: H_2O, NH_3, ROH (alcohols), RNH_2 (amines)

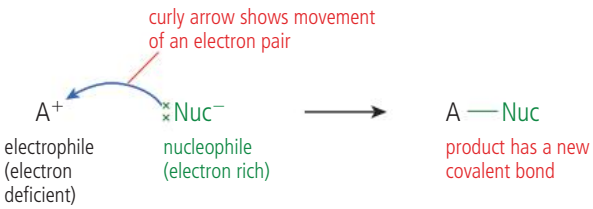
Anions: OH^-, F^-, Cl^-, Br^-, I^-, CN^-, R^- (carbanions)

The names nucleophile and electrophile reflect earlier definitions for these species that were based on their attraction to charges on other species. The suffix *-phile* implies 'a strong liking for' and refers to the fact that:

- *nucleophiles*, typically being electron rich, are attracted to positive charges such as that of a *nucleus*
- *electrophiles*, typically being electron deficient, are attracted to negative charges such as that of an *electron*.

Nucleophiles donate electron pairs to form coordination bonds

When nucleophiles donate a pair of electrons to other species (electrophiles), a new covalent bond is formed. This is illustrated in the diagram below, with the green colouring of the new bond formed in the product showing that both bonding electrons came from the nucleophile.



Because the nucleophile donated both electrons in forming the new covalent bond, this is a **coordination bond** which is introduced in Structure 2.2.

Exercise

Q1. What is the essential feature of a nucleophile?

A a lone pair of electrons
B a negative charge
C a pi bond
D a positive charge

Q2. Which of the following species can act as a nucleophile?

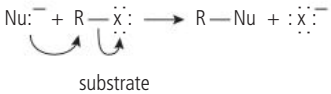
I. NH_3 II. CH_4 III. H_2O

A I, II and III
B II and III
C I and III
D I and II

Reactivity 3.4.2 – Nucleophilic substitution reactions

Reactivity 3.4.2 – In a nucleophilic substitution reaction, a nucleophile donates an electron pair to form a new bond, as another bond breaks producing a leaving group.

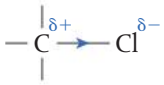
Deduce equations with descriptions and explanations of the movement of electron pairs in nucleophilic substitution reactions.



Further details of the mechanisms are not required at SL.

Halogenoalkanes react via nucleophilic substitution

Halogenoalkanes are polar compounds due to the fact that the halogen atom is more electronegative than carbon and so exerts a stronger pull on the shared electrons in the carbon–halogen bond. As a result, the halogen gains a partial negative charge ($\delta-$), and the carbon gains a partial positive charge ($\delta+$) and is said to be **electron deficient**.



Nucleophiles, such as OH^-, are attracted to the electron-deficient carbon in a halogenoalkane. This leads to reactions in which substitution of the halogen occurs, known as **nucleophilic substitution** reactions.

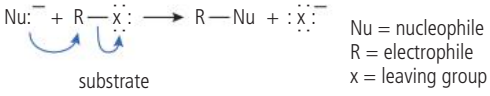
$$\underset{\text{chloromethane}}{CH_3Cl} + OH^- \rightarrow \underset{\text{methanol}}{CH_3OH} + Cl^-$$

$$\underset{\text{1-bromopropane}}{C_3H_7Br} + OH^- \rightarrow \underset{\text{propan-1-ol}}{C_3H_7OH} + Br^-$$

The halogen atom can be substituted by a variety of nucleophiles, and this means that halogenoalkanes can be converted into many different classes of compounds. This makes them very useful intermediates in organic synthesis pathways.

HL The mechanism for these reactions is discussed in more detail on page 848.

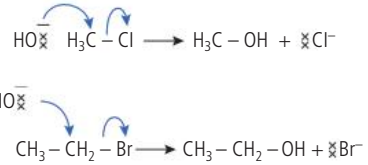
The overall reaction that occurs between a nucleophile and an electron-deficient substrate molecule such as a halogenoalkane, can be illustrated using curly arrows;



For the nucleophile to donate an electron pair to the substrate molecule and form a new bond, another bond must break. This causes a species, known as a **leaving group,** to break away from the substrate molecule. The leaving group is represented by an x in the figure above.

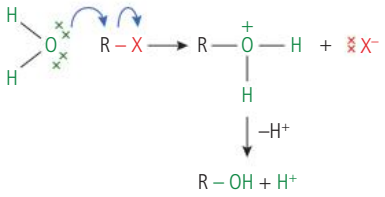
Halogens, in general, make good leaving groups as they form relatively weak bonds with carbon. Their higher electronegativity also means the bonded electrons are drawn towards the halogen atom, making the carbon atom electron deficient and susceptible to nucleophilic attack.

The nucleophilic substitution reactions of hydroxide ions with chloromethane and 1-bromopropane are illustrated below using curly arrows. Note that the bond that forms and the bond that breaks must both involve the carbon atom that is bonded to the leaving group.



The curly arrows shown in the mechanism represent the movement of electron pairs and this is explained further on page 835. You should be able to explain how these arrows relate to the formation and breaking of covalent bonds in nucleophilic substitution reactions.

If the nucleophile is a neutral species, such as water, then the initial product formed from the substrate molecule will be positively charged. However, this subsequently deprotonates and loses an H^+ to give a neutral product. If the leaving group was a halide ion, this could combine with the H^+ ion to form a hydrogen halide.



Overall Equation: $H_2O + RX \rightarrow ROH + HX$

Exercise

Q3. In the reaction R–X + OH^- → R-OH + X^-

X^- acts as a:

A nucleophile **B** electrophile

C reducing agent **D** leaving group

Q4. Explain what is meant by nucleophilic substitution, using the reaction between NaOH and chloroethane to illustrate your answer.

Q5. Use curly arrows to show how hydroxide ions react with bromomethane to form methanol.

Q6. Use Section 12 in the data booklet to predict which halide ion will be the best leaving group in a nucleophilic substitution reaction.

Reactivity 3.4.3 – Heterolytic fission

Reactivity 3.4.3 – Heterolytic fission is the breakage of a covalent bond when both bonding electrons remain with one of the two fragments formed. Explain, with equations, the formation of ions by heterolytic fission.	
Curly arrows should be used to show the movement of electron pairs during reactions.	Reactivity 3.3 – What is the difference between the bond-breaking that forms a radical and the bond-breaking that occurs in nucleophilic substitution reactions?

Heterolytic fission creates oppositely charged ions

The bond-breaking that occurs in nucleophilic substitution reactions to generate the leaving group involves **heterolytic fission.** This occurs when a covalent bond breaks such that one of the products gains both of the shared electrons. *Hetero-* means 'different' and refers to the fact that the two products have an unequal assignment of electrons from the bond.



In Reactivity 3.3 we learn that homolytic fission produces two radicals as products. Here we see that heterolytic fission results in the formation of oppositely charged ions. When the bond contains two different atoms, the more electronegative atom will gain the negative charge.

Reactivity 3.3 – What is the difference between the bond-breaking that forms a radical and the bond-breaking that occurs in nucleophilic substitution reactions?

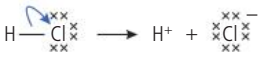
Examples of heterolytic fission:

$$Cl–Cl \rightarrow Cl^+ + Cl^-$$

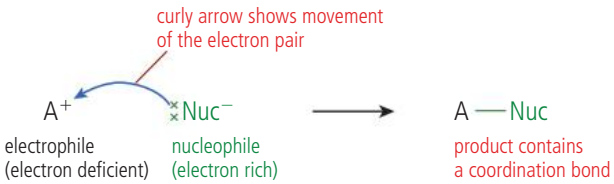
$$H–Cl \rightarrow H^+ + Cl^-$$

In Reactivity 3.3 we also learnt that the movement of single electrons in homolytic fission could be represented by single-headed curly arrows. Heterolytic fission can also be illustrated by curly arrows but it is important to distinguish the important fact that this type of bond breakage occurs through the movement of an electron *pair*. The distinction is made by using a *double-headed* arrow ( ) to show the movement of an electron pair. The tail shows where the electron pair comes from, and the head of the arrow shows where it is moving to.

For example, the heterolytic fission of a H–Cl bond would be represented as:



The opposite process to heterolytic fission occurs when a nucleophile donates a pair of electrons to an electrophile, forming a coordination bond. This bond formation can also be represented using curly arrows.



Exercise

Q7. Which of the following reactions best represents heterolytic fission?

A $C + O_2 \rightarrow CO_2$

B $HF \rightarrow H^+ + F^-$

C $BF_3 + F^- \rightarrow BF_4^-$

D $Br_2 \rightarrow Br\bullet + Br\bullet$

Q8. Use curly arrows to explain the difference between the homolytic and heterolytic fission of a H–Br bond.

Reactivity 3.4.4 – Electrophiles

Reactivity 3.4.4 – An electrophile is a reactant that forms a bond with its reaction partner (the nucleophile) by accepting both bonding electrons from that reaction partner.	
Recognize electrophiles in chemical reactions.	
Both neutral and positively-charged species should be included.	

Electrophiles form bonds by accepting electron pairs

An electrophile is a reactant that forms a covalent bond to its reaction partner (the nucleophile) by accepting both electrons. Electrophiles tend to be electron deficient, or contain an electron-deficient region, so they often have a positive charge or partial positive charge. Examples of electrophiles include:

Neutral: HX (hydrogen halides), X_2 (halogens), H_2O, halogenoalkanes (RX)

Cations: H^+, NO_2^+, NO^+, CH_3^+, R^+ (carbocations)

Nature of Science

Definitions in science need to be broad enough to be inclusive. For example, electrophiles are often described as 'electron deficient', but this definition would exclude molecules such as bromine, Br_2, that are not electron deficient but can act as electrophiles in addition reactions.

Exercise

Q9. What is the essential feature of an electrophile?

A It has a lone pair of electrons.
B It can accept a pair of electrons.
C It has a negative charge.
D It has a positive charge.

Q10. Which of the following species can act as an electrophile?

I. HBr II. Br_2 III. NH_3

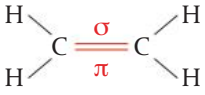
A I, II and III
B II and III
C I and III
D I and II

Reactivity 3.4.5 – Electrophilic addition of alkenes

Reactivity 3.4.5 – Alkenes are susceptible to electrophilic attack because of the high electron density of the carbon–carbon double bond. These reactions lead to electrophilic addition.	
Deduce equations for the reactions of alkenes with water, halogens and hydrogen halides.	
The mechanisms of these reactions will not be assessed at SL.	Reactivity 3.3 – Why is bromine water decolourized in the dark by alkenes but not by alkanes? Structure 2.4 – Why are alkenes sometimes known as 'starting molecules' in industry?

Addition reactions of alkenes give saturated products

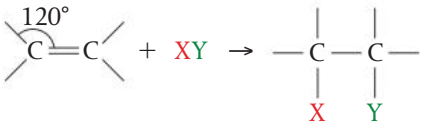
Alkenes have the general formula C_nH_{2n} and are **unsaturated hydrocarbons** containing a carbon–carbon double bond.



HL As we learn in Structure 2.2, the double bond is made of two different bonds, one sigma, σ, and one pi, π. The carbon atoms are sp^2 hybridized, forming a trigonal planar shape with angles of 120°.

Alkenes are more reactive than alkanes because the double bond has a high electron density which makes it attractive to electrophiles. The reaction occurs at the site of the double bond, as the pi bond is selectively broken, which creates two new bonding positions on the carbon atoms. This enables alkenes to undergo **addition reactions** with electrophiles and form a range of different saturated products.

Alkenes are unsaturated hydrocarbons and undergo addition reactions.



Common addition reactions of alkenes are described below.

HL The mechanism of these reactions will be discussed in more detail in Reactivity 3.4.11.

Addition of water

The reaction with water is known as **hydration**, and converts the alkene into an alcohol. Water is actually a poor electrophile and this addition reaction requires the use of a strong acid catalyst. In the laboratory, it can be achieved using concentrated sulfuric acid as a catalyst.

Ethanol is an important component of many hand sanitizers. Health agencies recommend a minimum concentration of 60% ethanol to ensure it is effective in killing bacteria and viruses.



The modern industrial process for ethanol synthesis is by direct catalytic hydration of ethane over a phosphoric acid catalyst absorbed onto silica (SiO_2).

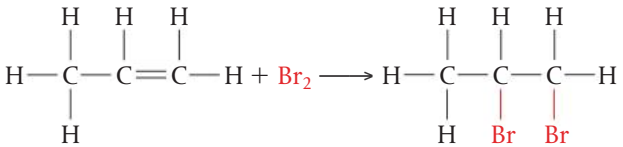
The overall equation for the hydration of ethene is:

$$\underset{\text{ethene}}{CH_2CH_2} \xrightarrow[H_2O]{H_2SO_4(\text{conc.})} \underset{\text{ethanol}}{CH_3CH_2OH}$$

The hydration reaction of ethene is of industrial significance because ethanol is a very important solvent and is manufactured on a large scale.

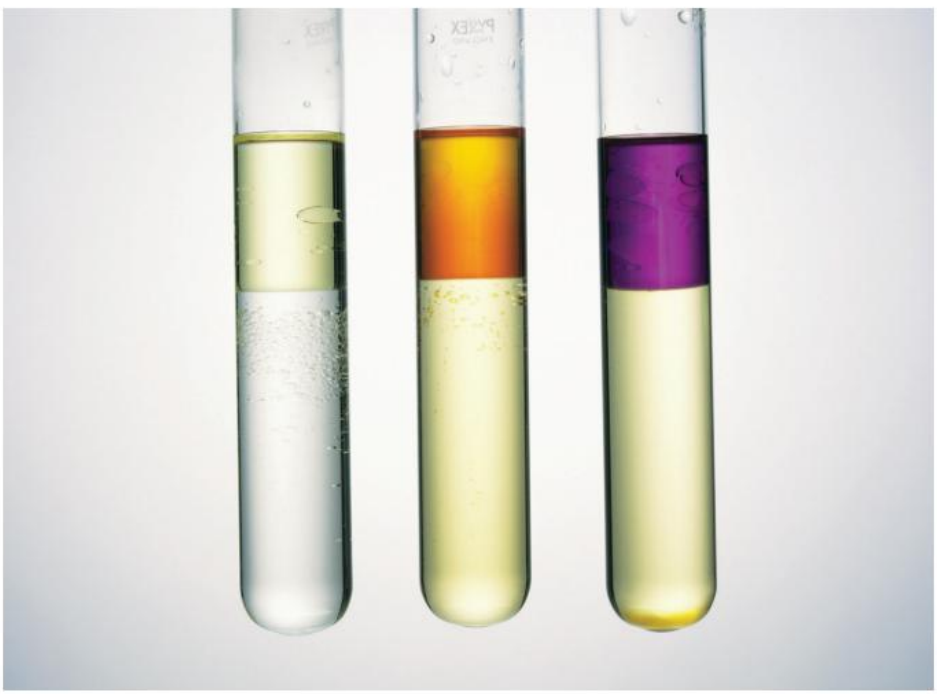
Addition of halogens

Halogens react with alkenes to produce dihalogeno compounds. These reactions happen quickly at room temperature and are accompanied by the loss of colour of the reacting halogen. Note that the name and structure of the product indicate that a halogen atom attaches to each of the two carbon atoms of the double bond.



propene 1,2-dibromopropane

Solutions of halogens have distinct colours: Cl_2 is green, Br_2 is orange/brown and I_2 is purple. When dissolved in organic solvents, these colours are particularly vivid.



Test tubes containing solutions of chlorine, Cl_2 (left), bromine, Br_2 (middle) and iodine, I_2 (right) in water (lower layer) and cyclohexane (top layer). Being non-polar, the halogens are more soluble in cyclohexane where they produce vivid colours.

As mentioned on page 827, bromine water is often used to distinguish between alkanes and alkenes. Alkanes react with bromine water through a radical mechanism which requires the presence of ultraviolet (UV) light to initiate the reaction. However, the pi bonds in alkenes readily react with Br_2 and do not require UV light, so this reaction will happen in the dark.

Reactivity 3.3 – Why is bromine water decolourized in the dark by alkenes but not by alkanes?

Nature of Science

A simple chemical test to distinguish between alkanes and alkenes using bromine water has been outlined in this section.

Alkenes decolourize bromine water rapidly at room temperature, whereas alkanes will only do this in the presence of UV light.

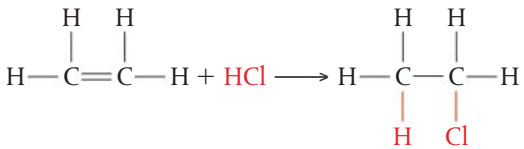
This test might be considered as an appropriate way to distinguish between the two classes of compound, but it relies on qualitative data and is subjective, based on the eye of the observer. Wherever possible, experiments are designed to produce quantitative data that is more objective and able to be analysed. Consider what instrumentation and sensors could be used to develop these observations into more rigorous tests to distinguish between saturated and unsaturated hydrocarbons.



Use of bromine water to distinguish between an alkane (hexane) and an alkene (hex-1-ene). Without UV light, the brown colour is decolourized by the alkene but not by the alkane. This is due to the addition reaction that occurs with the unsaturated alkene but does not occur with the saturated alkane.

Addition of halogen halides

Hydrogen halides, such as HCl and HBr, react with alkenes to produce halogenoalkanes. These reactions take place rapidly in solution at room temperature.



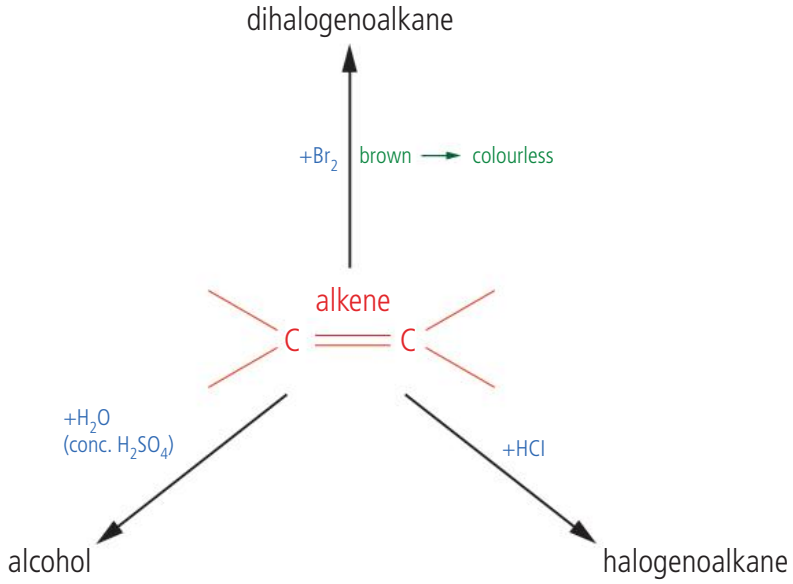
$CH_2CH_2 + HCl \longrightarrow CH_3CH_2Cl$
ethene chloroethane

All the hydrogen halides are able to react in this way, but the reactivity is in the order HI > HBr > HCl due to the decreasing strength of the hydrogen halide bond down group 17. So HI, with the weakest bond, reacts the most readily.

The examples of addition reactions provided above show that alkenes can react with specific electrophiles to make different classes of organic compounds such as alcohols, halogenoalkanes and dihalogenoalkanes. These products can be further converted into many other classes of compounds so this makes alkenes very useful starting molecules in organic synthetic pathways.

Structure 2.4 – Why are alkenes sometimes known as 'starting molecules' in industry?

The following diagram summarizes the important addition reactions covered in this chapter and shows the different classes of compounds formed along with a specific example of the reactants required for each conversion.



Nature of Science

It is hard to assess the vastness of the scale of the impact that alkanes and alkenes have had on society. As fuels, alkanes have made energy widely available, and as chemical feedstock, alkenes have led to the synthesis of diverse plastics. Yet these innovations have come at significant cost to the environment, and the long-term consequences are still being determined. While scientific progress is responsible for both the intended and unintended consequences, it is scientists who must respond to the problems. The issues of climate change, air pollution, and plastic disposal are currently pressing areas of research and development.

Exercise

Q11. In the reaction between ethene and hydrogen chloride, $CH_2CH_2 + HCl$, the product is:

A CH_2ClCH_2Cl

B CH_3CH_3

C no reaction occurs

D CH_3CH_2Cl

Q12. Give the condensed formulas and names of the products for the following reactions:

(a) $CH_3CH{=}CHCH_3 + HBr$

(b) $CH_2{=}CH_2 + \text{conc. } H_2SO_4$

(c) $CH_3CH{=}CH_2 + Br_2$

Q13. Explain how bromine water, $Br_2(aq)$, can be used to distinguish between an alkane and an alkene.

HL

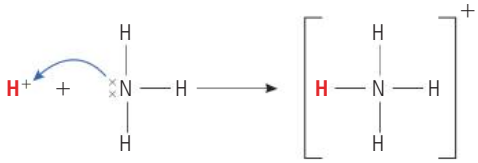
Reactivity 3.4.6 and 3.4.7 – Lewis acids and Lewis bases

Reactivity 3.4.6 – A Lewis acid is an electron-pair acceptor and a Lewis base is an electron-pair donor. Apply Lewis acid–base theory to inorganic and organic chemistry to identify the role of the reacting species.	
	Reactivity 3.1 – What is the relationship between Brønsted–Lowry acids and bases and Lewis acids and bases?

Reactivity 3.4.7 – When a Lewis base reacts with a Lewis acid, a coordination bond is formed. Nucleophiles are Lewis bases and electrophiles are Lewis acids. Draw and interpret Lewis formulas of reactants and products to show coordination bond formation in Lewis acid–base reactions.	
	Structure 2.2 – Do coordination bonds have any different properties from other covalent bonds?

Lewis acid–base theory focuses on lone pairs

Gilbert Lewis, whose name famously belongs to electron dot structures for representing covalent bonding (Structure 2.2), used such structures in interpreting Brønsted–Lowry theory. Realizing that the base must have a lone pair of electrons, he reasoned that the entire reaction could be viewed in terms of the electron pair rather than in terms of proton transfer. For example, the reaction in which ammonia acts as a base can be represented as follows:



H^+ is acting as an electron-pair acceptor and the nitrogen atom in ammonia is acting as an electron-pair donor. From such thinking, Lewis developed a new, broader definition of acids and bases.

- A Lewis acid is a lone pair acceptor.
- A Lewis base is a lone pair donor.

Lewis bases and Brønsted–Lowry bases (Reactivity 3.1) are therefore the same group of compounds: by either definition, they are species that must have a lone pair of electrons.

Gilbert N. Lewis is most well-known for his contributions to the modern understanding of covalent bonding and molecular structure along with identifying acids and bases as electron pair acceptors and donors. However he was accomplished in many areas of chemistry and physics including thermodynamics, photochemistry, quantum physics and relativity. Lewis' contributions were so significant that he was nominated for the Nobel Prize in Chemistry an incredible 41 times. However none of these nominations were successful, making Lewis arguably one of the most esteemed chemists to *not* be awarded a Nobel Prize.

Brønsted–Lowry acids are proton (H^+) donors. Brønsted–Lowry bases are proton (H^+) acceptors.

A Lewis acid is a lone pair acceptor. A Lewis base is a lone pair donor.

TOK

Although Lewis never won the Nobel Prize he was an effective teacher and mentor to many students. A number of Lewis' students went on to become distinguished scientists themselves, including a number of Nobel Prize winners.
In what way have influential individuals contributed to the development of the natural sciences as an area of knowledge?

Nature of Science

Different theories to explain a phenomenon can sometimes supplement rather than contradict each other. Brønsted–Lowry and Lewis theories each contribute to our understanding of acid–base behaviour.

Nature of Science

Brønsted, Lowry and Lewis independently developed the acid–base theories that are named for them. They worked in an era before mass communication and would only have become aware of each other's results through written correspondence and/or publication in printed journals. Scientists today have the ability to communicate and share data almost instantaneously through digital communications and are therefore able to more readily engage in collaborative research.

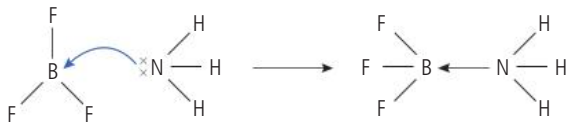
Reactivity 3.1 – What is the relationship between Brønsted–Lowry acids and bases and Lewis acids and bases?

In the case of acids, however, the Lewis definition is broader than the Brønsted–Lowry theory which is restricted to H^+. An acid, by Lewis definition, is any species capable of accepting a lone pair of electrons. Of course, this *includes* H^+ with its vacant orbital (so all Brønsted–Lowry acids *are* Lewis acids) – but it will also include molecules that have an incomplete valence shell.

Double-headed curly arrows were previously used to show the movement of electron pairs in organic substitution reactions. They can also be used to show the donation of a pair of electrons from a Lewis base to a Lewis acid.

Lewis acid–base reactions result in the formation of a covalent bond, which will always be a coordination bond because both the electrons come from the base.

Here is another example:



BF_3 has an incomplete octet, so is able to act as a Lewis acid and accept a pair of electrons. NH_3 acts as a Lewis base, donating its lone pair of electrons. The arrow on the covalent bond in the product denotes the fact that it is a coordination bond with both electrons donated from the nitrogen.

Structure 2.2 – Do coordination bonds have any different properties from other covalent bonds?

Once a coordination bond is formed it is no different from a covalent bond that is formed by the same atoms donating one electron each. The final outcome is the same: a pair of electrons being shared between these two atoms. Coordination bonds therefore have the same properties as other covalent bonds including bond length, bond strength and chemical reactivity.

Make sure that when you are describing Lewis acid–base behaviour, you refer to donation and acceptance of an electron *pair*. If you omit the word pair, you would be describing a redox reaction (Reactivity 3.2), which is entirely different.

Lewis acids are electrophiles and Lewis bases are nucleophiles

In previous sections, we introduced substitution reactions (page 833) and addition reactions (page 837) which both involve the formation of covalent bonds due to the actions of electrophiles or nucleophiles. The definitions presented earlier for electrophiles and nucleophiles were also defined in terms of bond formation.

A nucleophile ('likes nucleus') is an electron-rich species that donates a lone pair to another reactant to form a new covalent bond.

An electrophile ('likes electrons') is an electron-deficient species that accepts a lone pair from another reactant to form a new covalent bond.

Clearly these definitions are consistent with those derived by Lewis. In other words, a nucleophile is a Lewis base and an electrophile is a Lewis acid.

TOK

Different approaches and vocabulary can sometimes be used to explain the same phenomenon. Does the precision of the language used in natural sciences successfully eliminate all ambiguity?

A nucleophile is a Lewis base and an electrophile is a Lewis acid.

Exercise

Q14. Which of the following is **not** a Lewis base?

A Cl^- **B** NH_3 **C** H_2O **D** CH_4

Q15. Which of the following is a Lewis acid?

A BCl_3 **B** NH_3 **C** H_2O **D** BF_4^-

Q16. Which of the following reactions represents an acid–base reaction according to Lewis theory but not according to Brønsted–Lowry theory?

A $NH_3(aq) + HCl(aq) \rightarrow NH_4Cl(aq)$

B $2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

C $BH_3(aq) + F^-(aq) \rightarrow BH_3F^-(aq)$

D $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4OH(aq)$

Q17. Trifluoroborate, BF_3, reacts with the F^- ion to form the tetrafluoroborate ion, BF_4^-.

(a) (i) Use Lewis diagrams to explain how this reaction is a Lewis acid–base reaction.

(ii) State the type of bond formed in this reaction.

(b) State a reason why this reaction is not a Brønsted–Lowry acid–base reaction.

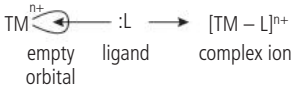
Reactivity 3.4.8 – Complex ions

Reactivity 3.4.8 – Coordination bonds are formed when ligands donate an electron pair to transition element cations, forming complex ions.

Deduce the charge on a complex ion, given the formula of the ion and ligands present.

Transition metal ions act as Lewis acids with ligands as Lewis bases

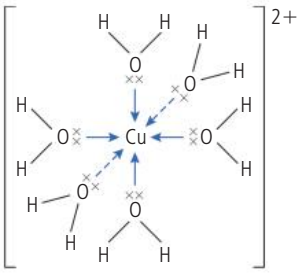
Another good example of Lewis acid–base reactions is found in the chemistry of the transition elements. As we learn in Structure 3.1, these metals in the middle of the periodic table often form ions with vacant orbitals in their d subshell. So they are able to act as Lewis acids and accept lone pairs of electrons when they bond with ligands to form **complex ions,** as shown in the simplified figure below. Because the ligand donates both electrons, a coordination bond is formed.



Ligands, as donors of lone pairs, are therefore acting as Lewis bases. For example, Cu^{2+} in aqueous solution reacts with water ligands as follows:

$$Cu^{2+}(aq) + 6H_2O(l) \rightarrow [Cu(H_2O)_6]^{2+}(aq)$$

In the reaction above, Cu^{2+} is a Lewis acid and H_2O is a Lewis base.



In the complex ion $[Cu(H_2O)_6]^{2+}$, Cu^{2+} has acted as a Lewis acid and the H_2O ligands as Lewis bases. The bonds within the complex ion are coordination bonds, as indicated by the arrows.

A coordination bond uses a lone pair of electrons to form a covalent bond.

The chemical formulas for complex ions are always written inside square brackets with the charge given at the top right. For example, $[Fe(H_2O)_6]^{3+}$.



The colours of many gemstones are due to the presence of complex ions formed by transition metal ions present in the mineral structure.

Nature of Science

Different descriptions can be used to describe the same reaction. Transition metal complexes are examples of: coordination bonding, Lewis acid–base reactions, and electrophilic /nucleophilic behaviour.

Complex ions are coloured due to the absorption of light when an electron is promoted between the orbitals of the split d-orbital sublevels in the transition metal ion (see Structure 3.1).



The light blue solution on the right contains the complex ion $[Cu(H_2O)_6]^{2+}$ which is formed when water acts as a ligand and bonds to dissolved Cu^{2+} ions. Different coloured solutions are produced when other ligands displace the coordinated water molecules to make new complex ions. The examples shown are due to the addition of: chloride ions (yellow), 1,2-diaminoethane (purple), and ammonia (dark blue).

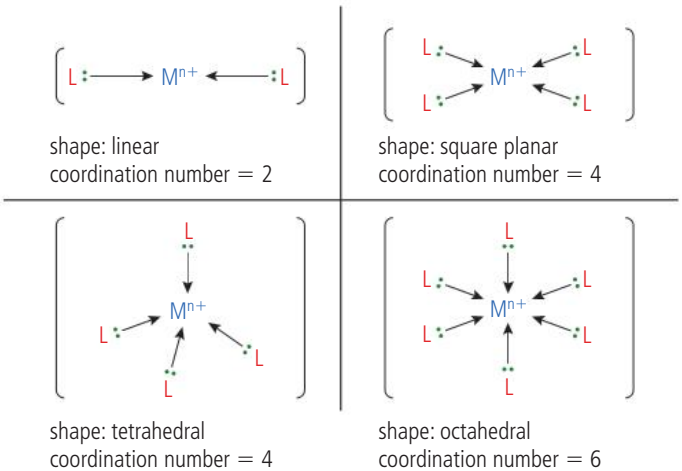
A ligand is a species that uses a lone pair of electrons to form a coordination bond with a metal ion.

Ligands can be neutral molecules or anions but they must always contain at least one lone pair of electrons. Common ligands include:

Neutral: H_2O, NH_3, CO

Anions: I^-, Br^-, Cl^-, F^-, OH^-, SCN^-, CN^-

Transition metal ions typically bond to more than one ligand when they form complex ions. The number of coordination bonds between the ligands and the central ion in the complex ion is called the **coordination number**. The shapes of some complex ions and their coordination numbers are shown in Figure 1.



R3.4 Figure 1 Shapes and coordination numbers of some complex ions.

From the information presented above, we can see that the charge on a complex ion depends on three factors:

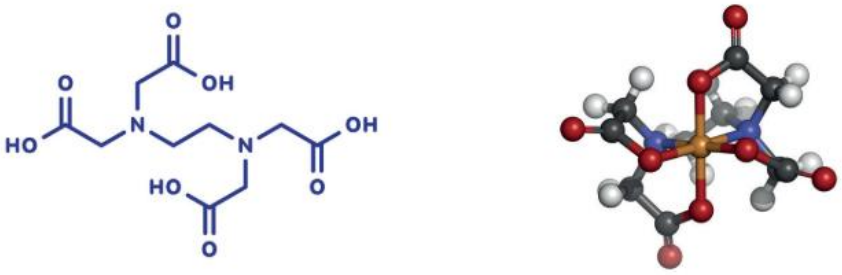
- the charge on the central transition metal ion;
- the charge on the ligands;
- the coordination number.

If these factors are known, then we can deduce the charge on the complex ion by adding the charge of the central ion to the charge of each ligand present. Examples of this are given in the following table.

Central ion	Ligand	Coordination number	Charge on complex ion	Formula of complex ion
Fe^{3+}	H_2O	6	$3^+ + (6 \times 0) = 3^+$	$[Fe(H_2O)_6]^{3+}$
Cr^{3+}	CN^-	6	$3^+ + (6 \times 1^-) = 3^-$	$[Cr(CN)_6]^{3-}$
Cu^{2+}	Cl^-	4	$2^+ + (4 \times 1^-) = 2^-$	$[CuCl_4]^{2-}$
Ag^+	NH_3	2	$1^+ + (2 \times 0) = 1^+$	$[Ag(NH_3)_2]^+$
Cr^{3+}	NH_3	4	$3^+ + (4 \times 0) + (2 \times 1^-) = 1^+$	$[Cr(NH_3)_4F_2]^+$
	F^-	2		

Similarly we can work backwards and deduce the charge on the central transition metal ion in a complex ion if presented with the ligands and the charge of the complex ion.

Ethylenediaminetetraacetic acid (EDTA) is a hexadentate ligand that can form six coordination bonds to a metal ion. Its ability to strongly coordinate to metal ions makes it useful in many commercial and medical applications. Examples include water treatment where EDTA is used to remove transition metal ions and chelation therapy where it is used to remove excess iron or toxic metals, such as mercury and lead, from the bloodstream of affected patients.



Ethylenediaminetetraacetic acid (EDTA), shown on the left, is a hexadentate ligand that can form six coordination bonds to a metal ion. Shown on the right is a molecular model of EDTA coordinated to a metal ion, forming an octahedral complex.

Worked example

Determine the charge and give the formula for the complex ion formed when Fe^{2+} coordinates with two water and four chloride ligands.

Solution

Water, H_2O, is a neutral ligand and each chloride ion, Cl^-, has a 1^- charge. The total charge on the complex ion will be: $2^+ + (2 \times 0) + (4 \times 1^-) = 2^-$.

The formula for the complex ion is $[Fe(H_2O)_2Cl_4]^{2-}$.

Worked example

Determine the charge on the central chromium ion in the complex ion $[Cr(NH_3)_2(SCN)_4]^-$.

Solution

From the list of ligands given on page 845, we can confirm that NH_3 is a neutral ligand and SCN^- is negatively charged. We can use this to determine the charge of the chromium ion (x) as:

$x + (2 \times 0) + 4 \times 1^- = 1^-$

Solving this equation, we find that $x = 3^+$.

Therefore, the central ion is Cr^{3+}.

Challenge yourself

1. Complex ions can have stereoisomers, similar to those encountered for organic compounds. The complex ion $[Cr(NH_3)_4F_2]^+$, included in the table, can exist as *cis*- and *trans*-isomers. See if you can deduce the difference between these two stereoisomers by drawing possible 3D structures of $[Cr(NH_3)_4F_2]^+$.

Exercise

Q18. A coordination bond is formed from the reaction between:

I. an electrophile and a nucleophile
II. a ligand and a transition metal ion
III. a Lewis base and a Lewis acid

A III only **B** II and III **C** I, II and III **D** I and II

Q19. Which of these complex ions contains a transition metal ion with a 3^+ charge?

A $[Fe(H_2O)_6]^{2+}$ **B** $[Cr(H_2O)_6]^{3+}$ **C** $[NiCl_4]^{2-}$ **D** $[Cu(H_2O)_6]^{2+}$

Q20. Determine the charge, and give the formula, for the complex ions formed in the following reactions.

(a) Fe^{3+} coordinates with six cyanide ligands.
(b) Cu^{2+} coordinates with six bromide ligands.
(c) Cr^{3+} coordinates with four water and two chloride ligands.

Reactivity 3.4.9 and 3.4.10 – S_N1 and S_N2 nucleophilic substitution mechanisms

Reactivity 3.4.9 – Nucleophilic substitution reactions include the reactions between halogenoalkanes and nucleophiles. Describe and explain the mechanisms of the reactions of primary and tertiary halogenoalkanes with nucleophiles.	
Distinguish between the concerted one-step S_N2 reaction of primary halogenoalkanes and the two-step S_N1 reaction of tertiary halogenoalkanes. Both mechanisms occur for secondary halogenoalkanes. The stereospecific nature of S_N2 reactions should be covered.	Reactivity 2.2 – What differences would be expected between the energy profiles for S_N1 and S_N2 reactions? Reactivity 2.2 – What are the rate equations for these S_N1 and S_N2 reactions? Nature of Science, Reactivity 2.2 – How useful are mechanistic models such as S_N1 and S_N2?

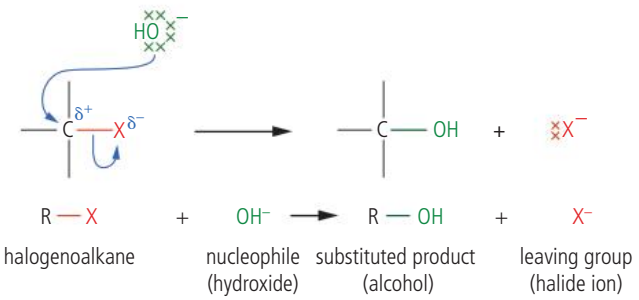
Reactivity 3.4.10 – The rate of the substitution reactions is influenced by the identity of the leaving group.	
Predict and explain the relative rates of the substitution reactions for different halogenoalkanes.	
Different halogenoalkanes should include RCl, RBr, RI. The roles of the solvent and the reaction mechanism on the rate will not be assessed.	Structure 3.1 – Why is the iodide ion a better leaving group than the chloride ion?

The reactions of nucleophiles with primary and tertiary halogenoalkanes have different mechanisms

A nucleophile is a reactant that forms a bond by donating both bonding electrons to another reactant.

The shorthand notation $\mathbf{S_N}$ – **s**ubstitution **n**ucleophilic – is used to describe this type of reaction. As we saw on page 833, the polar carbon–halogen bond in halogenoalkanes means that the carbon atom is electron deficient, and it is attacked by nucleophiles such as OH^-. During these reactions, the carbon–halogen bond breaks and the halogen atom is released as a negative ion (the halide).

Heterolytic fission is when a bond breaks and both the shared electrons go to one of the products. It produces two oppositely charged ions.

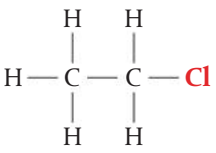


Heterolytic fission of the carbon–halogen bond occurs during the substitution reaction. Note that X represents any halogen atom.

The exact mechanism of these reactions depends on whether the halogenoalkane is primary, secondary or tertiary – as described in Structure 3.2. We will discuss examples of two different mechanisms here when halogenoalkanes react with aqueous sodium hydroxide, NaOH, to produce alcohols. Similar reactions take place with water as the nucleophile, but they occur more slowly. Because H_2O lacks a negative charge, it is a weaker nucleophile than OH^-.

Primary halogenoalkanes react via S_N2

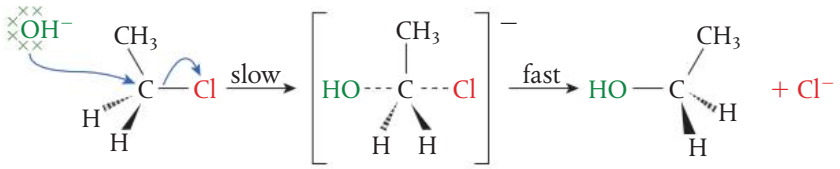
Primary halogenoalkanes have at least two hydrogen atoms attached to the carbon of the carbon–halogen bond. For example, chloroethane:



The overall reaction that occurs with NaOH is:

$$C_2H_5Cl + OH^- \rightarrow C_2H_5OH + Cl^-$$

As the hydrogen atoms are so small, the carbon atom is relatively open to attack by the nucleophile. An unstable **transition state** is formed in which the carbon is weakly bonded to both the halogen and the nucleophile. The carbon–halogen bond then breaks heterolytically, releasing Cl^- and forming the alcohol product.

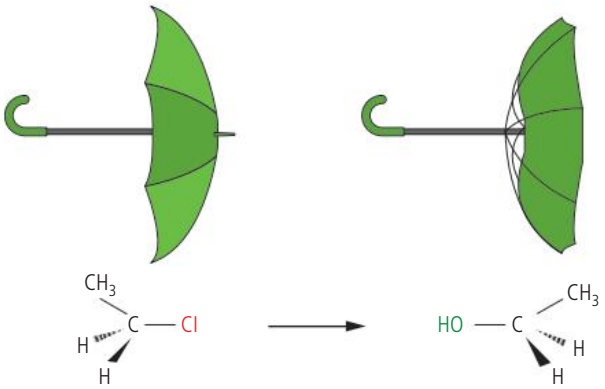


unstable transition state

Effectively this is a one-step concerted reaction with an unstable transition state. Because the mechanism is dependent on the concentration of *both* the halogenoalkane *and* the hydroxide ion, it is a **bimolecular** reaction and will be second order overall (see Reactivity 2.2).

Therefore, this mechanism is fully described as **S_N2**: **s**ubstitution **n**ucleophilic **2**nd order (or bimolecular).

Note that the nucleophile attacks the electrophilic carbon atom on the *opposite side* from the leaving group, which causes an **inversion** of the arrangement of the atoms around the carbon atom. The process can be likened to an umbrella blowing inside out, as shown in Figure 2.



R3.4 Figure 2 An umbrella blowing inside out is somewhat similar to the inversion of the configuration at the electrophilic carbon atom in the S_N2 mechanism.

These configurations are a result of different spatial arrangements around tetrahedrally bonded carbon atoms. The S_N2 mechanism is described as **stereospecific** because the three-dimensional arrangement of the reactants determines the three-dimensional configuration of the products. This happens because bond formation comes before bond cleavage (breaking) in the transition state, so the stereochemistry of the carbon attacked is not lost. Because the reaction is stereospecific, this means that optically active reactants will react via S_N2 to give optically active products.

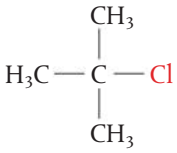
Stereospecific reactions are important in the synthesis of compounds that have optical isomers such as biological molecules, for example, amino acids, and in many drug syntheses. The topics of stereochemistry and optical isomers are introduced in Structure 3.2.

Note that dotted lines are used to show the weak bonds that exist between the carbon atom and both the leaving group and the incoming nucleophile in the transition state. Note also that the transition state is shown in a square bracket with the negative charge shown at the top right.

The order of reaction with respect to a reactant is the power to which it is raised in the rate equation. The overall order for the reaction is the sum of the individual orders for all reactants (page 602).

Tertiary halogenoalkanes react via S_N1

Tertiary halogenoalkanes have three alkyl groups attached to the carbon of the carbon–halogen bond. 2-Chloro-2-methylpropane is an example:

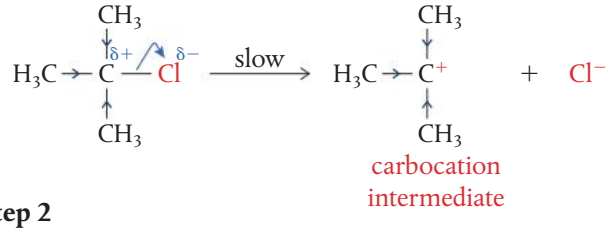


The overall reaction that occurs with NaOH is:

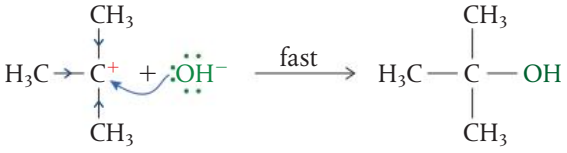
$$\underset{\text{2-chloro-2-methylpropane}}{(CH_3)_3CCl} + OH^- \rightarrow \underset{\text{2-methylpropan-2-ol}}{(CH_3)_3COH} + Cl^-$$

Here, the presence of the three alkyl groups around the carbon of the carbon–halogen bond causes what is called **steric hindrance**, meaning that these bulky groups make it difficult for an incoming group to attack this carbon atom. Rather than the nucleophile attacking the electron-deficient carbon, as in S_N2, the first step of an S_N1 reaction instead involves heterolytic fission of the carbon–halogen bond and the halide ion leaving. This creates a **carbocation intermediate**, with a positive charge centred on the carbon. This intermediate is then attacked by the nucleophilic Cl^- in the second step of the reaction, leading to the formation of a new bond.

Step 1



Step 2



A carbocation is a positive ion with the charge centred on a carbon atom.

Because the slow step of this reaction, the rate-determining step, is determined by the concentration only of the halogenoalkane, it is described as a **unimolecular** reaction and will be first order overall (see Reactivity 2.2.10).

$$\text{rate} = k\,[\text{halogenoalkane}]$$

Therefore, this reaction mechanism is fully described as **S_N1**: **s**ubstitution **n**ucleophilic **1**st order (or unimolecular).

The carbocation intermediate has a planar shape, which means the nucleophile can attack from any position in the second step. This means that the S_N1 reaction is not stereospecific, and optically active reactants react via S_N1 to give products that are racemic mixtures. Racemic mixtures are introduced in Structure 3.2.

This mechanism is favoured in tertiary halogenoalkanes because the carbocation is stabilized by the presence of the three alkyl groups, as each of these has an electron-donating or **positive inductive effect**, shown by the blue arrows in the diagram on the previous page. This stabilizing effect helps the carbocation to persist long enough for the second step to occur.

Secondary halogenoalkanes

It is not possible to be precise about the mechanism of nucleophilic substitution in secondary halogenoalkanes, as data shows that they usually undergo a mixture of both S_N1 and S_N2 mechanisms.

The influence of the leaving group (halogen)

Experimental data shows that the rate of nucleophilic reactions for halogenoalkanes, with the same carbon chain length and branching, follows the order:

iodoalkanes > bromoalkanes > chloroalkanes > fluoroalkanes

Bond enthalpies for the different carbon–halogen bond enthalpies are given in the following table.

Bond	C–F	C–Cl	C–Br	C–I
Bond enthalpy / kJ mol^{-1}	492	324	285	228

Comparing the bond enthalpies with the observed rates of reaction for different halogenoalkanes it is apparent that the rate of reaction depends on the strength of the C–X bond. The weaker the bond, the easier it is to break and the better the halide ion is as a leaving group.

Ranking the halide ions in order of best leaving group to worst gives:

$I^- > Br^- > Cl^- > F^-$

S_N1 and S_N2 mechanisms have different rate expressions and reaction profiles

As we have seen, the S_N2 mechanism is favoured by primary halogenoalkanes and occurs through a concerted one-step mechanism. It is a second order reaction with the rate depending on the concentrations of both the halogenoalkane and nucleophile: rate = k[halogenoalkane][nucleophile].

The S_N1 mechanism is favoured by tertiary halogenoalkanes and is a two-step mechanism. The rate depends on the slow first step and it is first order with the rate only depending on the concentration of the halogenoalkane: rate = k[halogenoalkane].

Because the S_N2 mechanism only has one step, it proceeds from reactants to products via a single transition state as shown in the reaction profile provided in the summary table on the next page.

The S_N1 mechanism has two steps so it proceeds from reactants to products via an intermediate, which is shown as a local minimum in the reaction profile also on the next page. Because it involves two steps, the S_N1 reaction profile has two activation energies and each step proceeds through independent transition states.

Structure 3.1 – Why is the iodide ion a better leaving group than the chloride ion?

The rate of nucleophilic substitution reactions in halogenoalkanes increases down group 17 from the fluoroalkane to the iodoalkane.

Reactivity 2.2 – What are the rate equations for these S_N1 and S_N2 reactions?

Reactivity 2.2 – What differences would be expected between the energy profiles for S_N1 and S_N2 reactions?

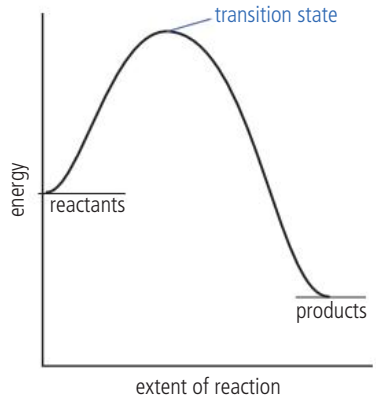
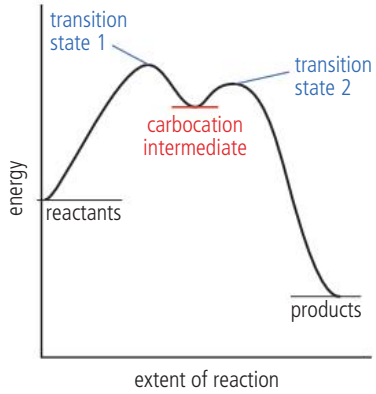
Nature of Science, Reactivity 2.2 – How useful are mechanistic models such as S_N1 and S_N2?

S_N1 and S_N2 reaction mechanisms are mechanistic models that, as demonstrated above, are effective in explaining the nature of the products and reaction kinetics observed in nucleophilic substitution reactions. This includes the stereochemistry of products formed in the nucleophilic substitution reactions of optical isomers. Optical isomers are introduced in S3.2.

Challenge yourself

2. Use 3D stereochemical formulas and curly arrows to draw the S_N2 reaction of hydroxide ions with 2-bromobutane. Use this mechanism to explain why only one product optical isomer is formed in S_N2 reactions of a reactant that is an optical isomer.
3. Use 3D stereochemical formulas and curly arrows to draw the S_N1 reaction of hydroxide ions with 2-bromo-2-methylpentane. Use this mechanism to explain why a racemic mixture is formed in S_N1 reactions of reactants that are optical isomers.
4. Determine the relative amounts of the two optical isomers in the product mixture if an optically pure compound undergoes nucleophilic substitution via both S_N1 (30%) and S_N2 (70%) reactions.

Summary of S_N1 and S_N2 mechanisms

	S_N2	S_N1
Favoured by	primary halogenoalkanes	tertiary halogenoalkanes
Nature of mechanism	concerted one-step mechanism with unstable transition state	two-step reaction via carbocation intermediate and two unstable transition states
Order of reaction	second order, bimolecular	first order, unimolecular
Reaction profile		

Exercise

Q21. Which compound reacts most readily by an S_N1 mechanism?

A $(CH_3)_3CCl$ **B** $CH_3CH_2CH_2CH_2Cl$

C $(CH_3)_3CI$ **D** $CH_3CH_2CH_2CH_2I$

Q22. Which compound will undergo nucleophilic substitution most quickly with hydroxide ions?

A $CH_3CH_2CH_2CH_2Cl$ **B** $CH_3CH_2CH_2CH_2F$

C $CH_3CH_2CH_2CH_2Br$ **D** $CH_3CH_2CH_2CH_2I$

Q23. Which statement is true of S_N2 reactions?

A They occur via a carbocation intermediate.

B They involve a single-step mechanism.

C They require electrophilic attack.

D They convert alkenes into alcohols.

Q24. Suggest an explanation for why iodo- and bromo- compounds are more useful than chloro- compounds as intermediates in synthesis pathways.

Q25. **(a)** C_4H_9Cl has a number of structural isomers. Draw and name the structural formulas of an isomer of C_4H_9Cl that is:

(i) a primary isomer

(ii) a secondary isomer

(iii) a tertiary isomer.

(b) (i) Identify which of these isomers will react with aqueous sodium hydroxide almost exclusively by an S_N1 mechanism. Explain the symbols in the term S_N1.

(ii) Draw the mechanism for this reaction using curly arrows to represent the movement of electron pairs.

(c) (i) Identify which of these isomers will react with aqueous sodium hydroxide almost exclusively by an S_N2 mechanism.

(ii) Draw the mechanism for this reaction using curly arrows to represent the movement of electron pairs.

Q26. **(a)** 2-Bromobutane is a chiral compound. Draw the two optical isomers of this compound.

(b) Based on <u>one</u> of the structures in part **(a)**, draw the product(s) that occur when this optical isomer reacts with hydroxide ions via an S_N1 mechanism.

(c) Using the same structures, draw the product(s) that occur when this optical isomer reacts with hydroxide ions via an S_N2 mechanism.

(d) Use your answers to parts **(b)** and **(c)** to explain how a polarimeter could be used to determine if the optical isomer reacts via an S_N1 or S_N2 mechanism.

Q27. The generic equation $R–X + OH^- \rightarrow R\text{-}OH + X^-$ can be used to describe nucleophilic substitution reactions.

(a) Give the rate expressions that would be obtained if:

(i) the reaction occurs via an S_N1 mechanism

(ii) the reaction occurs via an S_N2 mechanism.

(b) Draw the reaction profiles that would be observed for the two different mechanisms. Clearly label any transition states or intermediates that occur during the reaction.

Reactivity 3.4.11 – Electrophilic addition reaction mechanism

Reactivity 3.4.11 – Alkenes readily undergo electrophilic addition reactions.

Describe and explain the mechanisms of the reactions between symmetrical alkenes and halogens, water and hydrogen halides.

Electrophilic addition reactions of alkenes require the breaking of a pi bond

Alkenes are unsaturated molecules and, as we saw on page 837, are important compounds in many synthesis pathways because of their ability to undergo addition reactions.

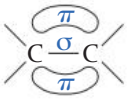
To understand the mechanism of these reactions, it is useful to focus in more detail on some key features of the carbon–carbon double bond.

The carbon atoms of the double bond are sp^2 hybridized, forming a planar triangular shape, with bond angle 120°. This is a fairly open structure that makes it relatively easy for incoming groups to attack.

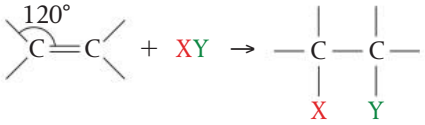
The pi (π) bond represents an area of electron density above and below the plane of the bond axis. Because it is an area of electron density, the π bond is attractive to electrophiles, species that either are electron deficient or that become electron deficient in the presence of the π bond.

Because electrons in the π bond are less closely associated with the nuclei, it is a weaker bond than the sigma (σ) bond and so breaks more easily during the addition reactions.

The nature of the double bond in alkenes is:



When the π bond breaks, reactants attach at each carbon atom through the formation of two σ bonds:



An addition reaction occurs when two reactants combine to form a single product. It is characteristic of unsaturated compounds containing double or triple bonds.

An electrophile is an electron-deficient species that forms a bond by accepting an electron pair. Electrophiles are positive ions or have a partial positive charge.

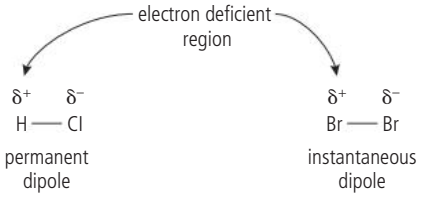


A molecular model of ethene, C_2H_4, showing the double bond between the two carbon atoms. This bond is the site of reactivity of alkenes and enables them to undergo addition reactions, producing a wide range of products.

Reactions between these reagents and alkenes are therefore known as **electrophilic addition reactions**. Good examples include the addition of halogens and hydrogen halides to alkenes, which happen readily under mild conditions. In these reactions, the electrophile is produced through heterolytic fission, as described in the mechanisms presented below.

Addition reactions of alkenes involve a two-step mechanism

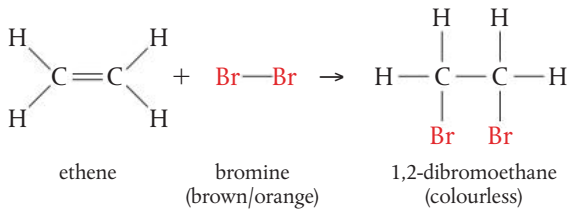
On page 836 we learnt that electrophiles are reactants that form a bond by accepting both bonding electrons from other reactants. They tend to be electron-deficient species such as positive ions or molecules containing partial positive charges. Neutral molecules such as halogens and hydrogen halides can act as electrophiles as they contain electron-deficient areas that result from instantaneous dipoles or permanent dipoles.



The addition reaction of halogens and hydrogen halides with alkenes occurs via a two-step mechanism as described in more detail below.

Addition reaction of halogens

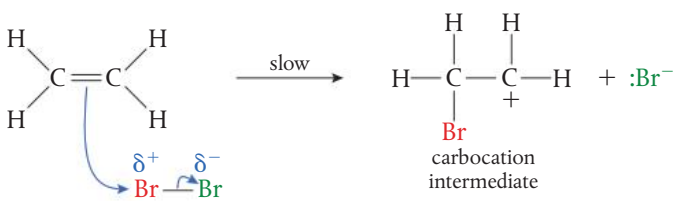
When ethene gas is bubbled through bromine at room temperature, the brown colour of the bromine fades as it reacts to form the saturated product 1,2-dibromoethane.



We saw on pages 827 and 839 that colour changes of this type are often used to show the presence of unsaturation.

The mechanism of the reaction is as follows:

Step 1:



The addition reactions of alkenes with halogens occur with specific colour changes. Alkynes contain pi bonds so they also undergo addition reactions and will give the same colour changes.

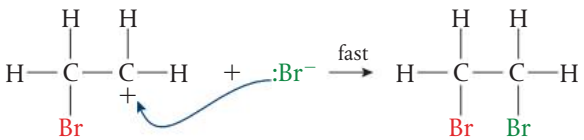
The compound 1,2-dichloroethane is synthesized by the addition of chlorine to ethene. It is one of the most widely used chemicals in the world, mostly as a starting material for the manufacture of the plastic PVC, poly(vinyl chloride).

Bromine is a non-polar molecule, but as it approaches the electron-rich region of the alkene it becomes polarized, due to electron repulsion, and this creates a dipole. The electron-deficient bromine (δ^+) then acts as the electrophile in the reaction.

The electrons in the pi bond of the alkene are attracted to the electrophilic bromine and this causes the Br–Br bond to break heterolytically.

This step is slow, resulting in the formation of an unstable carbocation intermediate.

Step 2:



The unstable carbocation reacts rapidly with the negative bromide ion, Br^-, acting as a nucleophile and attacking the positively charged carbon in the carbocation, forming a covalent bond. The final product is 1,2-dibromoethane.

Overall the equation for the reaction is:

$$C_2H_4 + Br_2 \rightarrow CH_2BrCH_2Br$$

Similar reactions take place with other alkenes such as propene. For example:

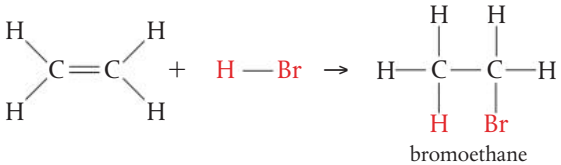
$$C_3H_6 + Br_2 \rightarrow CH_3CH_2BrCH_2Br$$

1,2-dibromopropane

Evidence for this reaction mechanism can be gained by carrying out the same reaction, C_2H_4 and Br_2, with the additional presence of chloride ions, Cl^-. It is found that the products are BrH_2CCH_2Br and BrH_2CCH_2Cl. This is consistent with the mechanism described, as the carbocation formed in the first step is equally ready to combine with Br^- or Cl^-. The fact that no dichloro compound is ever formed in this reaction confirms that the initial attack was by the electrophile Br^+ formed from Br_2.

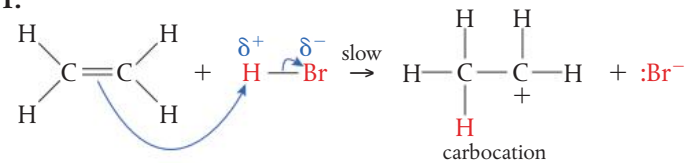
Addition reaction of hydrogen halides

When ethene gas is bubbled through a concentrated aqueous solution of hydrogen bromide, HBr, an addition reaction occurs fairly readily at room temperature, forming bromoethane.

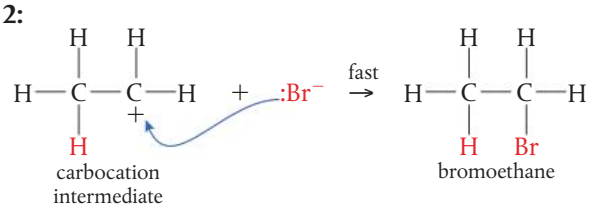


The reaction occurs by a similar two-step mechanism to that described above.

Step 1:



Step 2:



The electrons in the pi bond of the alkene are attracted to the electrophilic hydrogen and this causes the H-Br bond to break heterolytically. The unstable carbocation intermediate that forms from this step then reacts quickly with Br^- to form the addition product, bromoethane.

One piece of evidence that supports this mechanism is that the reaction is favoured by a polar solvent that facilitates the production of ions from heterolytic fission.

The other hydrogen halides react similarly with alkenes. HI reacts more readily than HBr due to its weaker bond, and HCl reacts less readily due to its stronger bond.

Nature of Science

The growth of chemistry as a field of study has resulted in the isolation and synthesis of millions of compounds. Systems have been developed for the naming of these compounds as well as classification according to their chemical features, physical properties and reactivity. As the use of chemicals in industry and research increased, classification systems also expanded to include toxicity, flammability and other environmental hazards. The Globally Harmonized System of Classification and Labelling of Chemicals (GHS), managed by the United Nations, was established to ensure consistency in the way that different national, international and industrial agencies label chemicals and catalogue their relevant properties and hazards in highly detailed Safety Data Sheets (SDS).



A selection of internationally accepted labels warning of various chemical hazards.

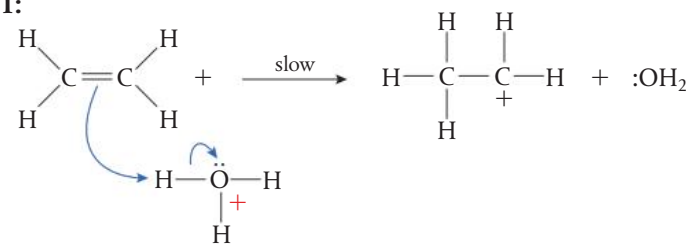
TOK

The physical and chemical properties of halogenated compounds make them suitable for use in a number of applications and have led to many innovations. Halogenated compounds have been used as solvents, refrigerants, aerosols, pesticides, herbicides and polymers. Many pharmaceutical drugs contain fluorine atoms. However scientific evidence now shows that many halogenated compounds released into the environment persist for a long time and can have serious impacts on animal and plant life, as well as the physical environment. As a result, many halogenated compounds are now classified as Persistent Organic Pollutants, with the Stockholm Convention, first signed in 2001, seeking to eliminate or restrict their production and use. How can it be that scientific knowledge changes over time?

Addition reaction of water

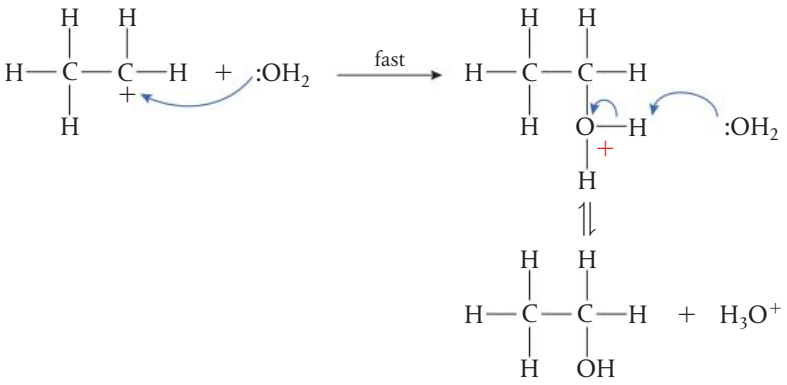
Water is actually a weak electrophile and does not directly undergo addition reactions with alkenes. However, the presence of strong acids can catalyse the reaction with H_3O^+ acting as the electrophile. The reaction proceeds via the following mechanism:

Step 1:



In the first step, the pi electrons in the alkene are attracted to an electrophilic hydrogen on H_3O^+. Heterolytic fission of the H_3O^+ results in the formation of a carbocation intermediate and a water molecule.

Step 2:



In the second step, water acts as a nucleophile, donating a lone pair of electrons to the positively charged carbon and forming a C–O bond. The product initially formed is positively charged but an equilibrium reaction involving deprotonation occurs. Another water molecule acts as a base and the alcohol product is formed. The H_3O^+ that was used up in the first step is regenerated in the final step, hence its role as a catalyst in the reaction.

Hydrogen, H_2, will react with alkenes in the presence of metal catalysts (Ni, Pt, Pd) and at elevated temperature, 150 °C. One important global application of this hydrogenation reaction is in the margarine industry where unsaturated oils are converted into more saturated compounds, which have higher melting points. This is done so that the margarine will be a soft solid at room temperature. However there are now concerns about the health effects of ***trans***-fats which are formed if any of the remaining double bonds are converted from ***cis***- to ***trans***- isomers in the hydrogenation process.



Margarine is formed from the hydrogenation of vegetable oils. This raises the melting point and results in margarine being a soft, spreadable solid at room temperature.

Challenge yourself

5. Explain why hydrogen (H_2) is a very weak nucleophile and the addition reaction of alkenes with hydrogen (hydrogenation) requires metal catalysts such as Ni, Pt or Pd and the reaction occurs at the surface of the catalyst. Provide a general outline of the mechanism of this reaction and how it differs from the typical electrophilic substitution mechanism presented in this chapter.

6. Use your knowledge of molecular geometries, intermolecular forces and melting points to explain why the hydrogenation of liquid vegetable oils can result in a solid product at room temperature.

Exercise

Q28. Which statement is true for an addition reaction?

A It involves the breaking of a sigma bond in an alkene.
B It involves the breaking of a sigma bond and a pi bond in an alkene.
C It involves the breaking of a pi bond in an alkene.
D It occurs via a one-step mechanism.

Q29. Which of the following compounds would be the product in the addition reaction of but-2-ene with HCl?

A 2-chlorobutane
B butane
C 2,3-dichlorobutane
D 2,2-dichlorobutane

Q30. Which statement is true for when bromine water is added to pent-1-yne?

A A reaction occurs but no colour change is observed.
B A colour change occurs but only if the reaction happens under UV light
C A colour change occurs even if the reaction happens in the dark
D No reaction occurs

Q31. Which of the following compounds would be the product in the addition reaction of propene with Br_2?

A 1-bromopropane
B propane
C 2-bromopropane
D 1,2-dibromopropane

Q32. Explain carefully why alkenes undergo electrophilic addition reactions. Using curly arrows, draw the mechanism of the reaction between but-2-ene and bromine. Give the name of the product.

Q33. Predict the product for the reaction of but-2-ene with water. Give the name of the product and state the conditions required for the reaction.

Reactivity 3.4.12 – Addition of hydrogen halides to asymmetrical alkenes

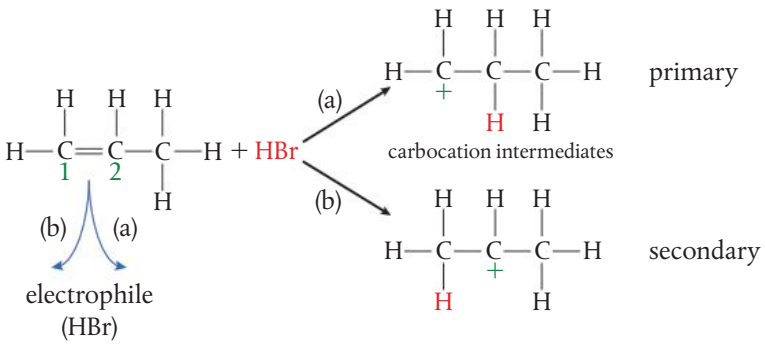
Reactivity 3.4.12 – The relative stability of carbocations in the addition reactions between hydrogen halides and unsymmetrical alkenes can be used to explain the reaction mechanism.

Predict and explain the major product of a reaction between an unsymmetrical alkene and a hydrogen halide or water.

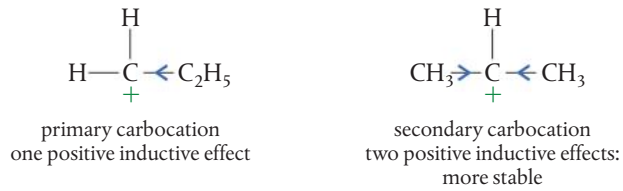
Addition reactions of unsymmetrical alkenes follow Markovnikov's rule

The addition reactions examined to date have all involved symmetrical alkenes where only a single addition product is possible. The addition reaction of an unsymmetrical alkene has two potential products but only one is formed exclusively. The specificity of this reaction can be explained by looking at the example of the addition reaction of propene, C_3H_6, with hydrogen bromide, HBr.

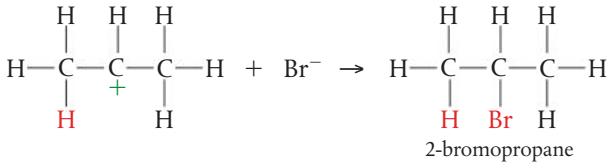
In the first step, the pi bond is attracted to the electrophile and it can open up in two different ways, (a) and (b), resulting in two different carbocation intermediates. One of these is a primary carbocation, (a), and the other is a secondary carbocation, (b).



We saw on page 851 that alkyl groups around a carbocation stabilize it somewhat due to their positive inductive effects, meaning that they push electron density away from themselves and so lessen the density of the positive charge. In (a) above, the carbocation is a **primary carbocation** and is stabilized by *only one* such positive inductive effect, whereas in (b), a **secondary carbocation** forms in which there are *two* such effects and the stabilization is greater.

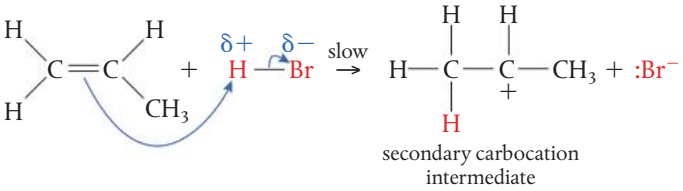


Consequently, in the reaction of propene with HBr shown on the previous page, the more stable carbocation in (b) will be more likely to persist and react with Br^-, leading to 2-bromopropane as the main product of the reaction.

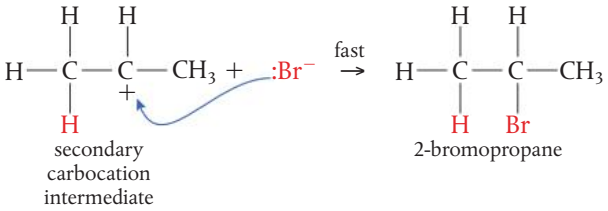


Therefore, the correct mechanism for the reaction is:

Step: 1



Step: 2



We can predict such an outcome for any reaction involving the addition of a hydrogen halide to asymmetric alkenes by using what is known as **Markovnikov's rule**. This states: *the hydrogen will attach to the carbon that is already bonded to the greater number of hydrogens*. As we have seen, this is based on the fact that the mechanism that proceeds via the most stable carbocation will be favoured.

In more general terms, Markovnikov's rule can be stated as *the more electropositive part of the reacting species bonds to the least highly substituted carbon atom in the alkene* (the one with the smaller number of carbons attached). Applying this rule enables us to predict the outcomes from any reactions involving asymmetric reagents undergoing addition reactions with asymmetric alkenes.

Markovnikov's rule can be remembered as 'the rich get richer', but rather than money the currency is hydrogen atoms. The carbon with the most hydrogen atoms attached gets the incoming hydrogen. Note that the currency can also be substituents: the carbon with the most substituents gets another substituent.

Worked example

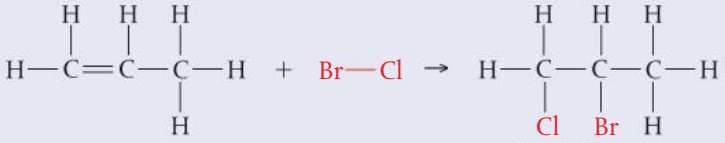
Write names and structures for the two possible products of the addition of the interhalogen compound BrCl to propene. Consider which is likely to be the major product and explain why.

When an unsymmetrical reagent adds to an unsymmetrical alkene, the electrophilic portion of the reagent adds to the carbon that is bonded to the greater number of hydrogen atoms.

Solution

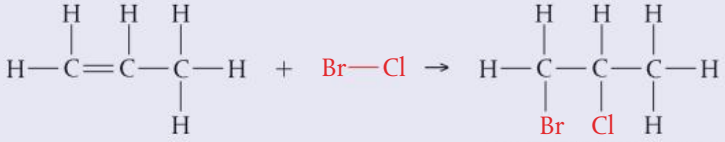
The two possible reactions are:

(i)



1-chloro-2-bromopropane

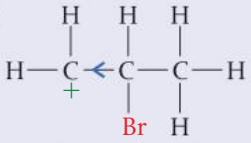
(ii)



1-bromo-2-chloropropane

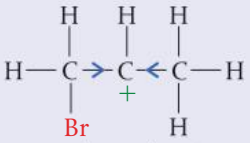
Chlorine is more electronegative than bromine, so Br–Cl is polarized with Br $\delta+$ and Cl $\delta-$. Consider the carbocation that would be produced on the way to each of these products by addition of the electrophile Br^+.

(i)



primary carbocation

(ii)



secondary carbocation

We can see that the secondary carbocation in (ii) is more stable than the primary carbocation in (i) owing to the greater number of positive inductive effects to spread the density of the positive charge. So this mechanism is favoured, leading to the synthesis of 1-bromo-2-chloropropane as the major product.

Vladimir Markovnikov (1838–1904) was a Russian chemist who also studied in Germany under Erlenmeyer and Kolbe. He developed his famous rule in 1869 but as he refused to publish in a foreign language, these findings were unknown outside of Russia until 1899. It has been observed that his published work was not based on much of his own experimental work and may have been more of an inspired guess. 1869 was also the year that Mendeleev, another Russian chemist, published his periodic table.

Nature of Science

Markovnikov's rule explains why the addition reactions of asymmetrical alkenes result in the formation of one product, known as the Markovnikov product. Focused research has led to the development of specialized catalysts and reactions which preferentially form non-Markovnikov's products. This is one example of how science can expand on the understandings developed for processes with predictable outcomes to develop methods that can instead produce alternative results.

Exercise

Q34. Predict the major product of the reaction between but-1-ene and hydrogen bromide. Explain the basis of your prediction and draw the mechanism for the formation of the product using curly arrows.

Q35. By considering the polarity within the molecule ICl, determine how it would react with propene. Draw the structure and name the main product, explaining your reasoning for its formation.

Reactivity 3.4.13 – Electrophilic substitution of benzene

Reactivity 3.4.13 – Electrophilic substitution reactions include the reactions of benzene with electrophiles. Describe and explain the mechanism of the reaction between benzene and a charged electrophile, E^+.	
The formation of the electrophile will not be assessed.	Structure 2.2 – What are the features of benzene, C_6H_6, that make it not prone to undergo addition reactions, despite being highly unsaturated? Reactivity 3.1 – Nitration of benzene uses a mixture of concentrated nitric and sulfuric acids to generate a strong electrophile, NO_2^+. How can the acid/base behaviour of HNO_3 in this mixture be described?

Benzene undergoes electrophilic substitution reactions

The benzene molecule is resonance stabilized

In Structure 2.2 we see that a benzene molecule contains three pi bonds, and the pi electrons are delocalized due to resonance. This minimizes the repulsion between the pi electrons, so the benzene molecule is stabilized compared to regular alkenes. Despite its high unsaturation, benzene does not behave like alkenes in its characteristic reactions. Its unusual and highly stable aromatic ring determines that substitution, not addition, is its favoured reaction.



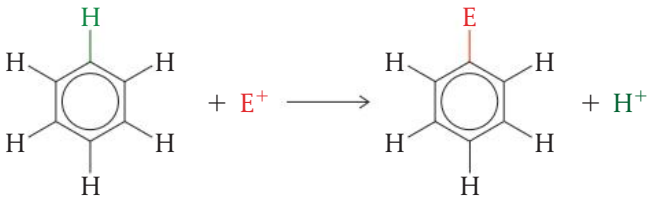
Bromine water decolourizes when it is added to alkenes but not when added to alkanes. In the test tube on the right, bromine water has decolourized after being added to cyclohexene. In the test tube on the left, bromine water has been added to cyclohexane and no colour change has occurred. The test tube in the middle contains benzene. No colour change has occurred which confirms that benzene does not undergo addition reactions.

Structure 2.2 – What are the features of benzene, C_6H_6, that make it not prone to undergo addition reactions, despite being highly unsaturated?

Benzene has two resonance structures and exists as the resonance hybrid of these structures.

Electrophilic substitution reactions of benzene

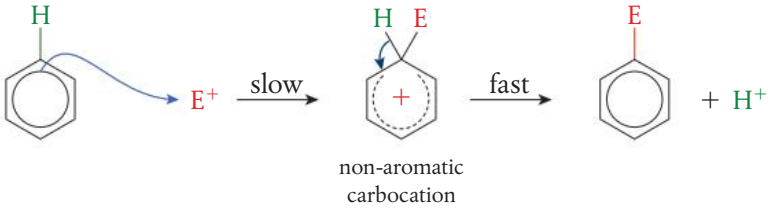
Although it does not undergo addition reactions, benzene is attractive to electrophiles because its ring is a region of high electron density. The delocalized cloud of π electrons attracts electron-deficient species and can form a new bond as a hydrogen atom is lost. The reactions are therefore **electrophilic substitution**.



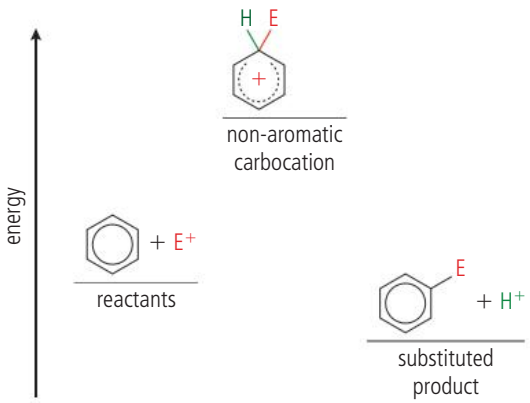
Electrophilic substitution reaction of benzene with a generic electrophile E^+. Note that the product has the arene ring conserved.

The mechanism of the electrophilic substitution reactions of benzene follows a similar path with different electrophiles. The reaction has a high activation energy so proceeds rather slowly. This is because the first step in the mechanism, in which an electron pair from benzene is attracted to the electrophile, leads to a disruption of the delocalized π system. The unstable carbocation intermediate that forms has both the entering atom or group and the leaving hydrogen temporarily bonded to the ring.

Using E^+ to represent an electrophile, we can show the reaction as follows.



The incomplete circle inside the ring shows the delocalized pi system has been disrupted, with the positive charge distributed over the carbon atoms in the ring. Heterolytic breaking of the C–H bond results in the two electrons from the C–H bond moving to regenerate the aromatic ring and the formation of a neutral substitution product. This product is more stable, as shown in Figure 3.



R3.4 Figure 3 The energy profile of an electrophilic substitution reaction in benzene.

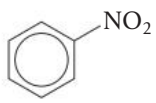
These reactions can be used with different electrophiles to introduce different functional groups into the ring. We will illustrate the process with nitration.

Nature of Science

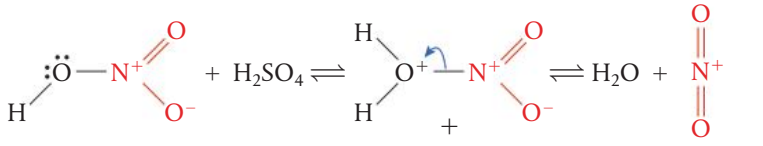
The analysis of reaction mechanisms gives a molecular level understanding to organic reactions. This has helped research and industrial chemists to devise the most efficient conditions for synthesis reactions, leading to developments of new materials with novel properties. Innovative products such as breathable fabrics, strong and biodegradable plastics, and new superconducting materials are all the results of such research. But organic chemistry involves working with some toxic reactants, and can be associated with products and by-products that have significant impact on the environment. This makes it all the more urgent to incorporate aspects of Green Chemistry into modern organic synthesis. Examples of this include the use of more selective catalysts and safer solvents, in addition to maximizing the atom economy of a process to limit waste.

Nitration of benzene

The nitration of benzene is the substitution of –H by $–NO_2$ to form nitrobenzene, $C_6H_5NO_2$.



The electrophile for the reaction is NO_2^+, the nitronium ion. This is generated by using a **nitrating mixture**, a mixture of concentrated nitric acid and concentrated sulfuric acid at 50 °C. As the stronger of the two acids, sulfuric acid protonates the nitric acid, which means that nitric acid is actually behaving as a Brønsted–Lowry base. The initial product formed then loses a molecule of water to produce the electrophile NO_2^+.

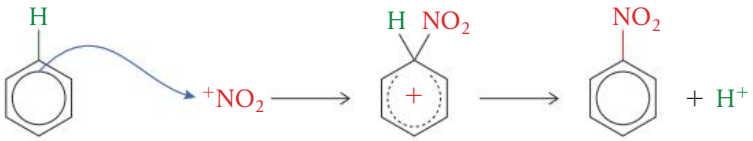


HNO_3
nitric acid

HSO_4^-

NO_2^+
nitronium ion

NO_2^+ is a strong electrophile and it attracts the π electrons of the benzene ring to form the carbocation intermediate. Loss of a proton from this intermediate leads to reformation of the arene ring in the product nitrobenzene, which appears as a yellow oil. The hydrogen ion released reacts with the base HSO_4^- to reform sulfuric acid, H_2SO_4.

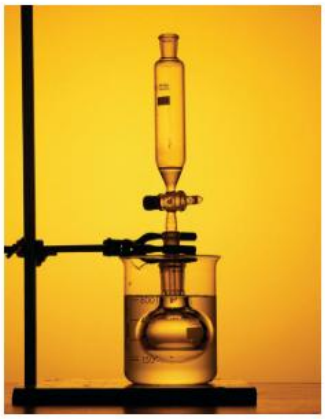


Reactivity 3.1 – Nitration of benzene uses a mixture of concentrated nitric and sulfuric acids to generate a strong electrophile, NO_2^+. How can the acid/base behaviour of HNO_3 in this mixture be described?

The overall reaction is:

$$C_6H_6 + HNO_3 \xrightarrow[50\,^\circ C]{\text{conc. } H_2SO_4} C_6H_5NO_2 + H_2O$$

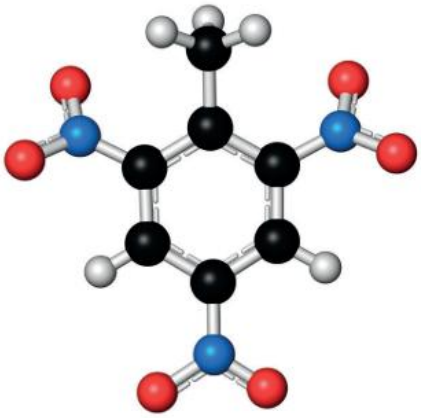




Apparatus used to make nitrobenzene from benzene in the laboratory. The round-bottomed reaction flask is held in a beaker of cold water by a clamp. The dropping funnel above this contains benzene, which is added slowly to the nitrating mixture in the flask. The mixture of concentrated nitric and sulfuric acids reacts and gives out heat, which is why the cold water and controlled addition of benzene are necessary.

Most of the nitrobenzene produced by this reaction is converted to phenylamine, $C_6H_5NH_2$. Smaller quantities of nitrobenzene are used in flavourings or perfume additives, but its use is limited due to its high toxicity.

The explosive substance trinitrotoluene (TNT) is synthesized through electrophilic substitution reactions of toluene (methylbenzene) with the nitronium ion, NO_2^+. TNT was first synthesized in 1863 and was initially valued for its yellow colour and used as a dye. Because it was chemically stable under normal conditions, TNT's explosive potential was not realized until many years later. TNT's ability to be safely transported and stored before use then made it a popular explosive for commercial uses. Ultimately these same properties also made it attractive for military applications and its use in warfare.

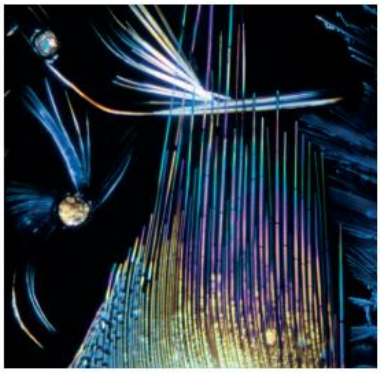


A ball and stick model of trinitrotoluene (TNT). Note the dashed lines representing the delocalization of pi electrons between the carbon atoms in the ring as well as between the nitrogen and oxygen atoms. This extensive delocalization contributes to TNT's stability.

The preferred IUPAC name for trinitrotoluene is 2-methyl-1,3,5-trinitrobenzene.

Challenge yourself

7. Relative to benzene, phenylamine, $C_6H_5NH_2$, is more reactive towards electrophilic substitution, whereas nitrobenzene, $C_6H_5NO_2$, is less reactive. Consider what this might suggest about the electron density in the ring for these three compounds, and why this might be the case.



Crystals from an explosive mixture containing TNT viewed under polarized light. This technique can be used on residues found at explosion sites to determine if TNT was present in the explosive mixture used.

TOK

Ongoing research has led to the development of substances that are even more explosive and destructive than TNT, along with more effective methods for harnessing and directing the energy released in explosive reactions. Should scientific research be subject to ethical constraints or is the pursuit of all scientific knowledge intrinsically worthwhile?

i

Another commonly known explosive is dynamite, a stable mixture of compounds that includes highly explosive nitroglycerin, invented by Swedish chemist Alfred Nobel in 1867. After false reports of his death, Nobel was horrified to read that he was primarily associated with the military use of dynamite, along with the death and destruction caused, rather than the beneficial, commercial uses he had intended it for. As a result, upon his actual death, in 1896, he bequeathed his fortune to the establishment of the Nobel Prizes recognizing scientific advancements in physics, chemistry and medical science along with prizes for literature and the promotion of peace and fellowship among nations.



A gold medal displaying the likeness of Alfred Nobel, founder of the Nobel Prizes. Each winner of a Nobel Prize receives one of these medals.

TOK

Over 125 years after his death, Nobel's legacy, and his desire to contribute to the development of science and improvement of society, continues to be recognized through the annual awarding of the Nobel Prizes. In what ways have influential individuals contributed to the development of the natural sciences as an area of knowledge?

Exercise

Q36. Benzene will react with a mixture of nitric and sulfuric acids by which of the following reaction mechanisms?

- **A** nucleophilic substitution
- **B** electrophilic substitution
- **C** electrophilic addition
- **D** radical substitution

Q37. Which statement is true for when benzene is added to a solution of bromine water?

- **A** A reaction occurs but no colour change is observed.
- **B** A colour change occurs but only if the reaction happens under UV light.
- **C** A colour change occurs even if the reaction happens in the dark.
- **D** No reaction occurs.

Q38. State the reactants used in converting benzene to nitrobenzene. Explain how they enable the nitration reaction to occur.

Q39. Chlorobenzene, C_6H_5Cl, can be made from the reaction of benzene, C_6H_6, with chlorine, Cl_2, when $FeCl_3$ is used as a catalyst.

$$C_6H_6 + Cl_2 \xrightarrow{FeCl_3} C_6H_5Cl + HCl$$

(a) State the name of the mechanism for this reaction.

(b) Using Cl^+ as the electrophile, draw the mechanism for this reaction using curly arrows to show the movement of electron pairs.

HL end

Guiding Question revisited

What happens when reactants share their electron pairs with others?

In this chapter we have seen that the donation of an electron pair from an electron-rich species to an electron-deficient species results in the formation of a coordination bond. Curly arrows are used to show the movement of electron pairs in these electron sharing reactions.

- A nucleophile forms a coordination bond by donating a pair of electrons to its reaction partner, the electrophile.
- In a nucleophilic substitution reaction;
  - the nucleophile donates an electron pair to form a coordination bond
  - a leaving group forms as another bond breaks heterolytically.Heterolytic fission of a covalent bond produces two oppositely charged ions.
- An electrophile forms a bond by accepting a pair of electrons from its reaction partner, the nucleophile.
- Alkenes undergo electrophilic addition reactions in which the carbon–carbon double bond breaks and two single bonds are added.

HL

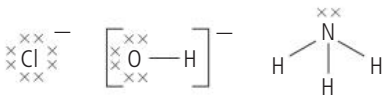
- Lewis bases donate electron pairs to Lewis acids.
- Nucleophiles are Lewis bases, electrophiles are Lewis acids.
- Ligands donate an electron pair to transition metal cations to form complex ions.
  - ligands are Lewis bases, transition metal cations are Lewis acids.
  - the overall charge on a complex ion depends on the charge of the transition metal ion, the charge on the ligand(s) and the coordination number.
- Nucleophilic substitution reactions of halogenoalkanes occur through two possible mechanisms:
  - primary halogenoalkanes react via the stereospecific S_N1 mechanism
  - tertiary halogenoalkanes react via the non-stereospecific S_N2 mechanism
  - secondary halogenoalkanes can react via both $S_N1$or S_N2.
- Electrophilic addition reactions of alkenes occur via a two-step mechanism:
  - electrophilic attack selectively breaks the carbon-carbon pi bond
  - the reaction proceeds through a carbocation intermediate.
- For asymmetrical alkenes the product of electrophilic addition reactions depends upon the relative stability of the carbocation intermediates. (Markovnikov's rule).
- Benzene undergoes electrophilic substitution reactions · via a two-step mechanism;
  - the reaction proceeds through a non-aromatic carbocation
  - the products formed retain the resonance-stabilized benzene ring.

HL end

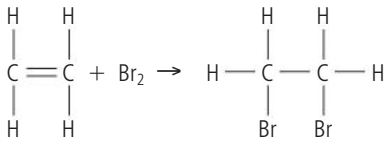
The following tables should prove a useful summary of the various conventions and definitions that have been introduced for these reactions, along with the radical substitution mechanism introduced in Reactivity 3.3.

Types of reactant

Saturated	Unsaturated
• compounds which contain only single bonds • for example: alkanes	• compounds which contain double or triple bonds • for example: alkenes, arenes

Electrophile (electron-seeking)	Nucleophile (nucleus-seeking)
• a reactant that forms a covalent bond by accepting both bonding electrons from another reactant • electrophiles are typically positive ions or have a partial positive charge and are therefore attracted to parts of molecules which are electron rich • for example: NO_2^+, H^+, Br^+	• a reactant that forms a covalent bond by donating both bonding electrons to another reactant • nucleophiles have a lone pair of electrons and may also have a negative charge; they are therefore electron rich and are attracted to parts of molecules which are electron deficient • for example: Cl^-, OH^-, NH_3 

Types of reaction

Addition	• occurs when two reactants combine to form a single product • characteristic of unsaturated compounds • for example: $C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$ 
Substitution	• occurs when one atom or group of atoms in a compound is replaced by a different atom or group • characteristic of saturated compounds and aromatic compounds • for example: $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

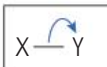
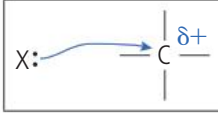
Types of bond-breaking (bond fission)

Homolytic fission	Heterolytic fission
• is when a covalent bond breaks by splitting the shared pair of electrons between the two products • produces two radicals, each with an unpaired electron 	• is when a covalent bond breaks with both the shared electrons going to one of the products • produces two oppositely charged ions 

Convention for depicting organic reaction mechanisms

Describing organic reaction mechanisms often involves showing the movement of electrons within bonds and between reactants. The convention adopted for this is a **curly arrow**, drawn from the site of electron availability, such as a pair of non-bonding electrons, to the site of electron deficiency, such as an atom with a partial positive charge.

For example:

	represents the electron pair being pulled towards Y so Y becomes $\delta-$ and X becomes $\delta+$
	the nucleophile X: is attracted to the electron-deficient C ($\delta+$)

A 'normal' double-barbed arrow () represents the motion of an electron pair (as above). Often the mechanism involves several steps. The electrons are transferred ultimately to an atom or group of atoms that then detaches itself and is known as the leaving group. We used blue throughout this chapter to show curly arrows and the pull of electrons.

Note that a single-barbed arrow (), known as a **fish hook**, represents the movement of a single electron. These single arrows are often used in reactions involving radicals (Reactivity 3.3).

Practice questions

1. Which compound will decolourize bromine water in the dark?

A pentane **B** cyclopentane

C pent-1-ene **D** methane

2. What is the product in the reaction of ethene with bromine, Br_2?

A bromoethane **B** 1,2-dibromoethane

C 1,1-dibromoethane **D** ethane

3. What is the product in the reaction of ethene with HI?

A 1,2-diiodoethane **B** 1,1-diiodoethane

C 1-iodoethane **D** ethane

4. The conversion of C_4H_9Cl to C_4H_9OH involves what type of reaction?

A electrophilic addition **B** radical substitution

C electrophilic substitution **D** nucleophilic substitution

HL

5. Which species is a Lewis acid but **not** a Brønsted–Lowry acid?

A Fe^{3+} **B** CH_3OH

C Fe **D** NH_3

6. Which species is **not** a Lewis base?

A H_2O **B** NH_4^+

C OH^- **D** NH_3

7. Which of the following will **not** result in the formation of a coordination bond?

A the reaction between an electrophile and a nucleophile

B the reaction between a ligand and a transition metal ion

C the reaction between a Lewis base and a Lewis acid

D the reaction between two radicals

8. Which of these complex ions contains a transition metal ion with a 3+ charge?

A $[Fe(H_2O)_6]^{2+}$ **B** $[Cr(H_2O)_6]^{3+}$

C $[CuBr_4]^{3-}$ **D** $[Co(NH_3)_6]^{2+}$

9. Determine the charge and give the formula for the complex ions formed in the following reactions:

(a) Fe^{3+} coordinates with six thiocyanate ligands

(b) Co^{2+} coordinates with five water and one chloride ligands

(c) Cr^{3+} coordinates with two ammonia and four fluoride ligands

10. Which reaction type is typical for halogenoalkanes?

A electrophilic substitution

B electrophilic addition

C nucleophilic substitution

D nucleophilic addition

11. Which statement about the reactions of halogenoalkanes with potassium hydroxide is correct?

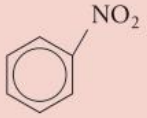
A Primary halogenoalkanes react mainly by an S_N2 mechanism.

B Bromoalkanes react faster than iodoalkanes.

C Hydroxide ions act as electrophiles.

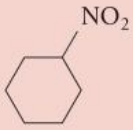
D The primary product of the reaction is an aldehyde.

12. Which of the following molecules can react by an electrophilic substitution mechanism?

A 

B 

C 

D 

13. In the nitration of benzene, which of the following species acts as the electrophile?

A NO_2^+ **B** NO^+ **C** HNO_3 **D** NH_3

14. Consider the following two reactions of the hydroxide ion, OH^-.

(i) $OH^-(aq) + CO_2(g) \rightarrow HCO_3^-(aq)$

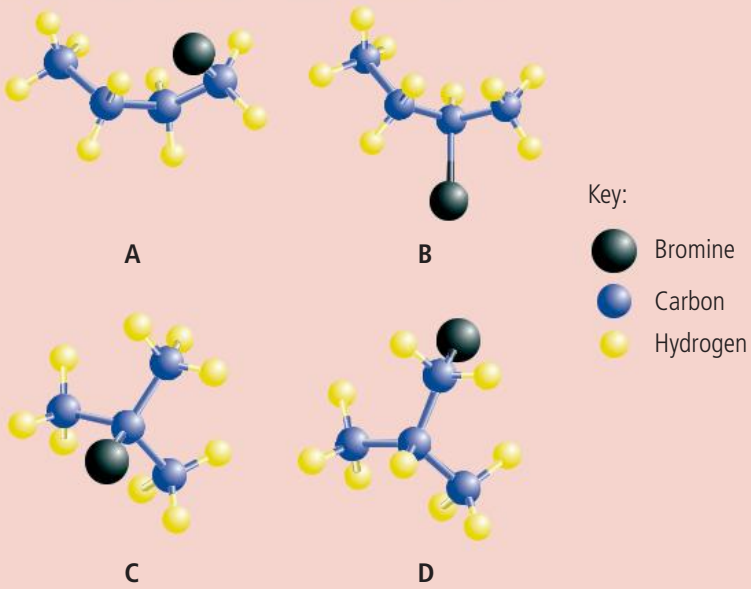
(ii) $OH^-(aq) + H_2CO_3(aq) \rightarrow HCO_3^-(aq) + H_2O(l)$

(a) Use these two reactions to explain the difference between a Lewis base and a Brønsted–Lowry base. (2)

(b) Using $Fe[OH_2]_6^{3+}$ as an example, explain how the formation of a complex ion is also an example of a Lewis acid–base reaction. (2)

(Total 4 marks)

15. (a) Below are four structural isomers with molecular formula C_4H_9Br. State the name of each of the isomers A, B, C and D.



(4)

(b) (i) Identify the isomer(s) which will react with aqueous sodium hydroxide almost exclusively by an S_N1 mechanism. State the meaning of the symbols in the term S_N1 mechanism. (2)

(ii) Using the formula RBr to represent a bromoalkane, state an equation for the rate-determining step of this S_N1 reaction. (1)

(iii) Identify one isomer that will react with aqueous sodium hydroxide almost exclusively by an S_N2 mechanism. Draw the mechanism for this reaction using curly arrows to represent the movement of electron pairs. Include the structural formulas of the transition state and the organic product. (4)

(c) State and explain how the rates of the reactions in parts **(b) (i)** and **(b) (iii)** are affected when the concentration of the sodium hydroxide is doubled. (2)

(d) State and explain how the rate of reaction of 1-bromobutane with sodium hydroxide compares with that of 1-chlorobutane with sodium hydroxide. (2)

(Total 15 marks)

16. Alkenes are useful starting materials in organic synthetic reaction pathways. Consider the bromination of propene:

$$C_3H_6 + HBr \rightarrow C_3H_7Br$$

(a) State the type of reaction that occurs. (1)

(b) Draw the mechanism for the reaction using curly arrows to show the movement of electron pairs. (4)

(c) Explain why only one major product is formed and give the IUPAC name of this product. (2)

(Total 7 marks)

17. Bromobutane, C_4H_9Br, has a number of isomers. The reaction of one of these isomers with aqueous sodium hydroxide gave the following results:

Trial	$[C_4H_9Br]$ / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	Initial rate / mol dm^{-3} s^{-1}
1	0.10	0.10	2.1×10^{-3}
2	0.10	0.20	2.1×10^{-3}
3	0.20	0.10	4.3×10^{-3}

(a) Determine the rate expression from the results, explaining your reasoning. (2)

(b) Deduce the type of mechanism that the reaction occurs by and name the isomer of C_4H_9Br that is reacting. (2)

(c) Draw the mechanism for the reaction using curly arrows to represent the movement of electron pairs. (4)

(Total 8 marks)

18. Nitrobenzene, $C_6H_5NO_2$, can be made from benzene, C_6H_6, by an electrophilic substitution reaction.

(a) State what other reactants are required and give the formula of the electrophile. (2)

(b) Draw the mechanism for the reaction using curly arrows to represent the movement of electron pairs. (4)

(c) Draw a reaction profile for the reaction, clearly labelling any intermediates or transition states present. (3)

(Total 9 marks)

HL end

Green Chemistry

'Green chemistry is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products.'

Green Chemistry: Theory and Practice, P. T. Anastas and J. C. Warner, Oxford University Press, Oxford, 1998

Green Chemistry is also known as sustainable chemistry and applies across the life cycle of a chemical product, from design to ultimate disposal.

The 12 principles of Green Chemistry are:

1. Pollution prevention

It is better to prevent waste than to treat or clean up waste after it has been created.

2. Atom economy

Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3. Less hazardous chemical synthesis

Whenever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to people or the environment.

4. Design safer chemicals

Chemical products should be designed to effect their desired function while minimizing their toxicity.

5. Safer solvents and auxiliaries

The use of auxiliary substances (e.g. solvents or separation agents) should be made unnecessary whenever possible and not harmful when used.

6. Design for energy efficiency

Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

7. Use of renewable feedstocks

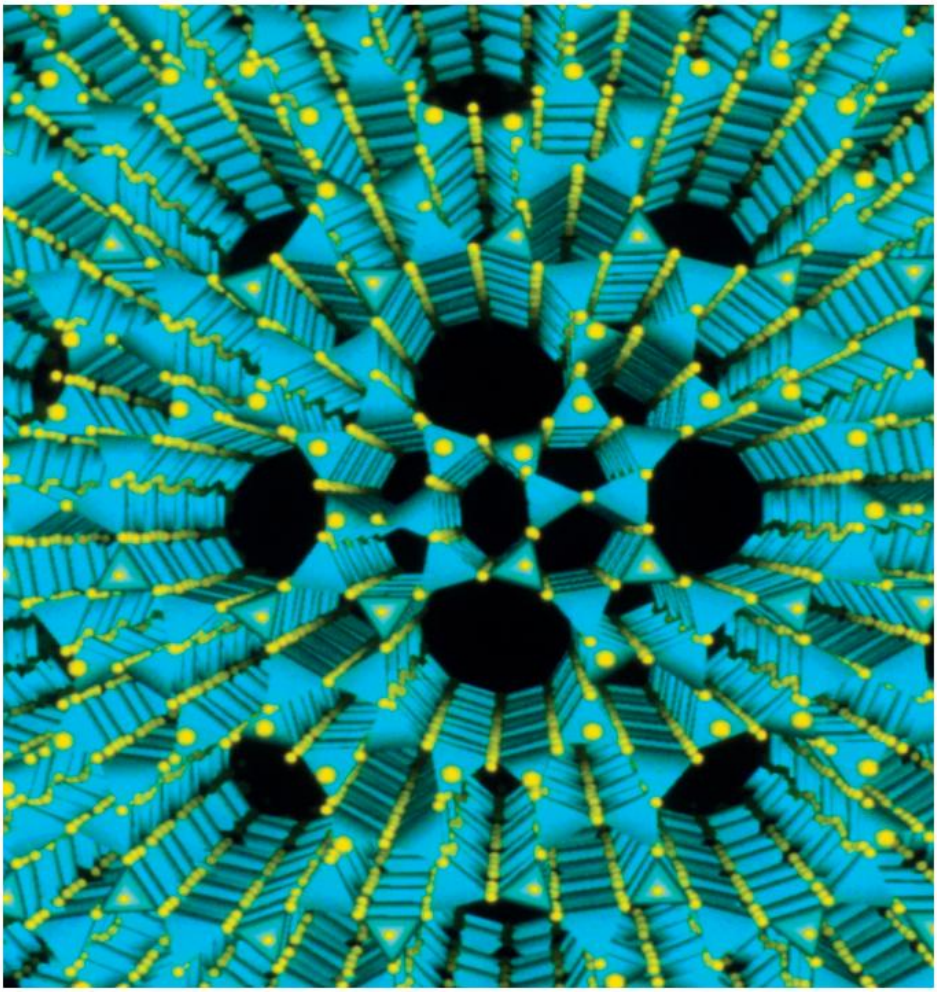
A raw material or feedstock should be renewable rather than being used up whenever technically and economically practicable.

8. Reduce derivatives

Unnecessary derivatization (use of blocking groups, protection/de-protection, and temporary modification of physical/chemical processes) should be minimized or avoided if possible because such steps require additional reagents and can generate waste.

9. Catalysis

Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.



Molecular graphic of the structure of a synthetic zeolite catalyst showing its microchannel architecture. Zeolites, often called molecular sieves, contain a silica–alumina crystalline structure and are used as catalysts in the petroleum industry. They are becoming increasingly important in processes such as biomass conversion, fuel cells and air and water purification.

10. Design for degradation

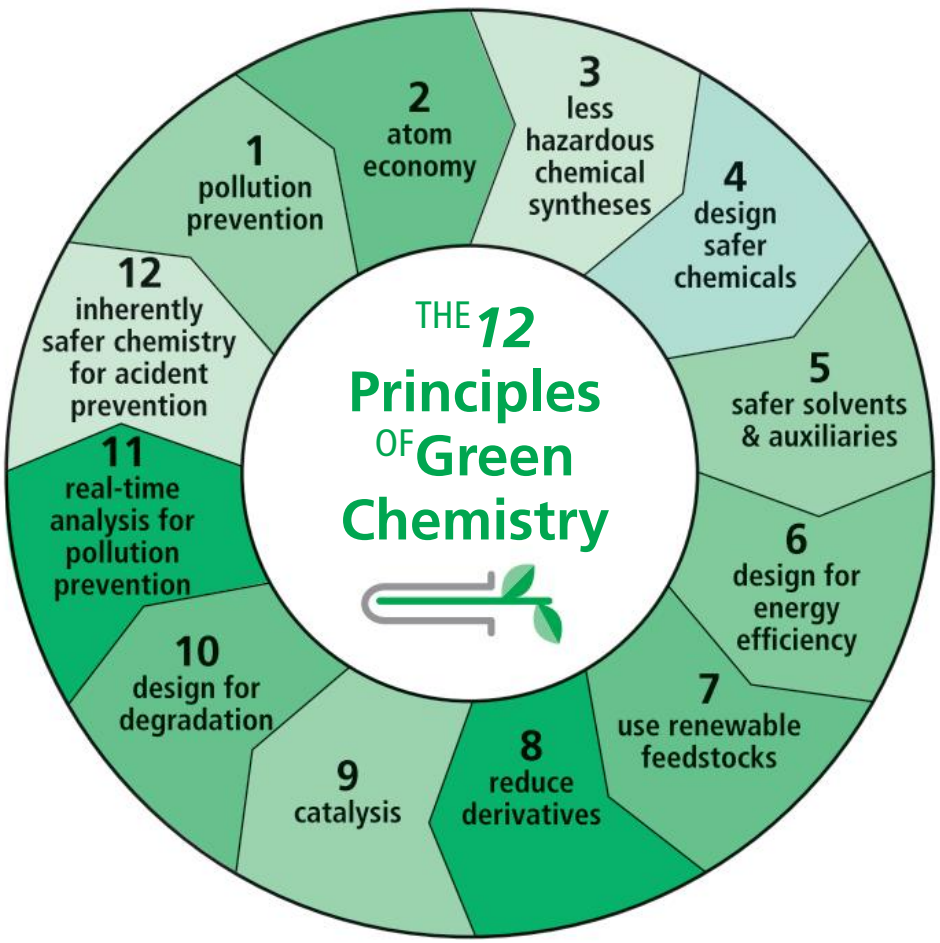
Chemical products should be designed so that at the end of their function they break down into harmless degradation products and do not remain in the environment.

11. Real-time analysis for pollution prevention

Analytical methods need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

12. Inherently safer chemistry for accident prevention

Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions and fires.



The 12 principles of Green Chemistry.

Application of these principles in research and industry is beneficial to human health and the environment in many ways. With an emphasis on *prevention* of waste and pollution rather than on treatment of the problems, Green Chemistry helps reduce both the negative impacts and the cost of chemical products and processes.

Applications of Green Chemistry in IB chemistry

During the IB chemistry course, there are many ways in which the principles of Green Chemistry can be considered and applied. For example:

- In all laboratory work, consideration can be given to reducing the volumes and/or concentrations of reagents used.
- Micro-scale experimentation can be an effective alternative to full-scale laboratory work to reduce waste.
- Disposal of chemicals should be carried out on a case-by-case basis, and where possible, excess reactants and products should be reused.
- The choice of solvent for a reaction should be carefully considered, and where possible aqueous solutions or simple alcohols or alkanes should be used.
- In the research design phase of the investigation, knowledge and assessment of risk should be made before developing a chemical procedure.
- In Reactivity 2.2, the study of catalysts can include consideration of how waste is minimized and energy costs of a process reduced.
- In Reactivity 2.1 and Structure 2.4, determination of the atom economy of a reaction helps to assess the efficiency of the process in terms of the incorporation of reactants into the final product.

Green Chemistry is a rapidly growing and interdisciplinary area of study. You can find out more about this field on the two websites below:







Passengers are warned to mind the gap as they leave an underground train in London. We often make a 'jump' when we accept knowledge claims and should always be aware of the gap that we have crossed. When we see bubbles in a test tube and infer that hydrogen is produced, or draw a best fit line through a series of points, we are 'leaping' across such a gap. When we go from the specific to the general we cross a precarious gap, as discussed later in the chapter.

Theory of Knowledge in chemistry

Chemistry ⇌ TOK

Introduction

In Theory of Knowledge (TOK) you are encouraged to think critically about the production and the application of knowledge in the subjects that you study. You are asked to reflect on the nature of the different subjects, looking for similarities and differences. You are also asked to reflect on the impact of the learning experience on you as a learner who must effectively navigate and make sense of a world with many uncertainties. Chemistry is a significant part of your Diploma experience and can add to and enrich your TOK experience, particularly as you discuss the natural sciences area of knowledge. This is a reversible process: the critical thinking encouraged in TOK will deepen your understanding of what you learn in chemistry.

Does chemistry give you a 'true' picture of reality? How does the knowledge you gain in your chemistry class differ from that gained in other subjects? What are the ethical implications of developments in the subject? How have technological developments impacted our knowledge of chemistry? Chemistry has been hugely successful in giving us explanations of the material world and has also made a significant contribution to improving our quality of life. But how reliable is the knowledge that it offers?

Knowledge questions are questions about knowledge – about how it is produced, acquired, shared and used; what it is and what it is not; who has it and who does not; and who decides the answers to these questions.

Knowledge questions and the knowledge framework

Most of the questions in this book are about the chemistry of the material world and not about the nature of chemical knowledge. TOK, by contrast, focuses on **knowledge questions**. These are contestable questions about knowledge that draw on TOK concepts. The table below shows how TOK questions explore the fundamental nature of the knowledge we seek in chemistry.

Chemistry questions	Knowledge questions
What is the balanced equation for the reaction?	Can all knowledge be expressed in words or symbols?
What is the electron configuration of the sodium atom?	Are the models and theories that scientists use merely pragmatic instruments, or do they truthfully describe the natural world?
What are the acid and basic properties of the period 3 oxides?	To what extent do the classification systems we use limit the pursuit of knowledge?
Which molecule has a structure consistent with the spectral data?	How do the tools we use shape the knowledge that we produce?
Which species is acting as a Lewis acid?	How significant have notable individuals been in shaping the development of the different areas of knowledge?
Why is fluorine more reactive than chlorine?	What counts as a good explanation?

Knowledge questions draw on the 12 concepts below.

evidence	certainty	truth	interpretation	power	justification
explanation	objectivity	perspective	culture	values	responsibility

Challenge yourself

1. Identify four of the concepts above which you think are most related to chemical knowledge and explain your choices.

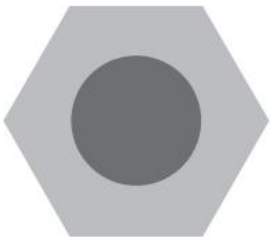
Reference to these concepts is illustrated later in the text by references in **bold**.

The different areas of knowledge can be characterized by a knowledge framework. This provides a structure for considering knowledge questions throughout the TOK course. The framework is made up of four elements: scope, perspective, methods and tools, and ethics.

The knowledge framework consists of four common elements: scope, perspectives, methods and tools, and ethics.

Knowledge and the knower

What shapes your perspective as a knower? What does Figure 1 below represent?



TOK Figure 1 A circle in a hexagon?

To many people this is simply a circle and a hexagon, but to an IB Diploma Programme chemistry student it might have more significance. It can be **interpreted** as a benzene ring or the IB Diploma Programme with six subjects as sides and a core of TOK, CAS and the Extended Essay at its centre. How you choose to interpret the figure will depend on the context in which it is presented and your prior knowledge. This illustrates the importance of perspectives, one of the elements in the TOK knowledge framework and also one of the 12 TOK concepts.

What shapes your perspective, as a knower? Why did you choose to study chemistry? How does your chemistry class differ from your other classes? How much of our knowledge depends on our interactions with other knowers? How does the knowledge that you study in class have an impact on the world outside your classes?

Chemistry is a study of the material world. How do your interactions with the material world shape your chemical knowledge? Is your motivation for studying chemistry to have a better understanding of the properties of the materials around you? What criteria can we use to distinguish between knowledge and belief? Do you know or believe that salt is made of ions? What could you do to improve your knowledge?

In a 2011 speech, Sir Harold Kroto, the 1996 Nobel Prize Laureate in Chemistry, talked about the importance of science, which, in his view, is the academic pursuit best positioned to develop the **truth** about the natural world. He also challenges us all to take **responsibility** for what we accept as knowledge.

> *'Common sense says the Sun goes around the Earth. Who agrees with me? ... It's uncommon sense that was needed to recognize that the Earth was turning on its axis... Let me just check – how many of you know the **evidence** for Galileo to say that the Earth was going around the Sun? Put your hand up. You've accepted it. Almost nobody's put their hand up. It's incredible. Look at yourself, you've accepted this. You've accepted a lot of things without evidence.'*

Do you agree with Kroto or do you think you can become too sceptical?

Chemical knowledge

The subject of chemistry has a body of highly structured and systematic knowledge. It is the work of many individuals and is in a sense anonymous – although there would have been no Hamlet without Shakespeare, atomic theory would still have been developed without Dalton. While individuals can and do contribute to this body of knowledge, their work is subject to peer review and their experimental results need to be replicated by others if they are going to be accepted by the scientific community. We all, however, have different experiences of chemistry, and this affects our knowledge of the chemical content and our procedural knowledge of how to do something such as a titration.

Challenge yourself

2. *'One aim of the physical sciences has been to give an exact picture of the material world. One achievement… has been to prove that this aim is unattainable.'*

J. Bronowski

What are the implications of this claim for the aspirations of science?

The scope of chemical knowledge

Chemistry is about understanding the nature of matter and its interactions. It helps us understand interactions between different materials and predict if and how they will react. This gives us some control of the material world and the potential to improve human life and our environment.

Chemistry has applications in the biological, material and environmental sciences. The scientific approach assumes that the material world behaves in a coherent way and is rationally comprehensible.

> *'The most incomprehensible thing about the world is that it is at all comprehensible.'*
>
> Albert Einstein

The application of chemical knowledge can have ethical, environmental, economic, cultural and social impacts.

The scope of the subject is limited by the dangerous nature of some substances to the individual and the environment.

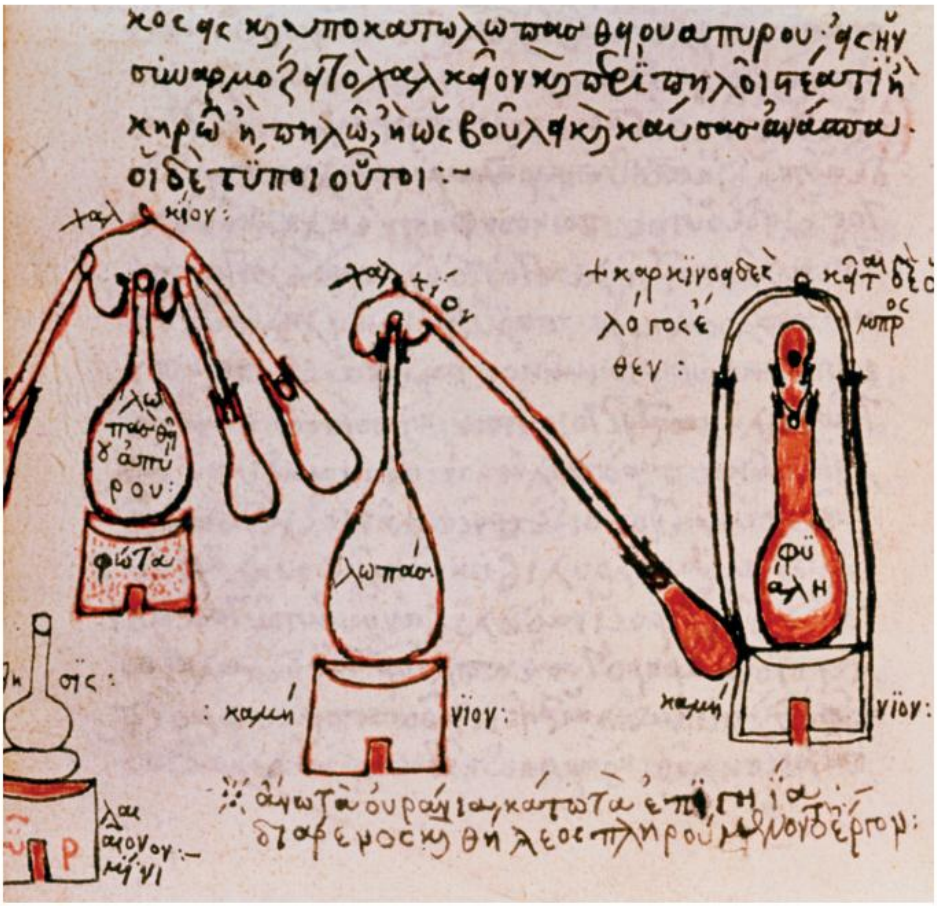
The periodic table is the map of chemistry

Maps are often used as a metaphor for knowledge in TOK and the periodic table can be thought of as the 'map' of chemistry; it suggests new avenues of research for the professional chemist and is a guide for students – it disentangles a mass of observations and reveals hidden order. Chemistry is not the study of a random collection of elements, but of the trends and patterns in their chemical and physical properties, and we should not forget that 'the map is not the territory' (Alfred Korzybski)! The periodic table is a human construct that helps us describe the elements, but it is an incomplete representation as it does not incorporate all their properties.

Perspectives in chemical knowledge

Chemistry and alchemy

It is worth reflecting that many of the experimental techniques of chemistry have their origins in the pseudoscience of alchemy, a medieval forerunner of chemistry which attempted to purify and transform matter.



A page from a treatise on alchemy written by Zosimus of Panapolitus (4th century). Some of the equipment drawn is still found in a modern chemistry laboratory.

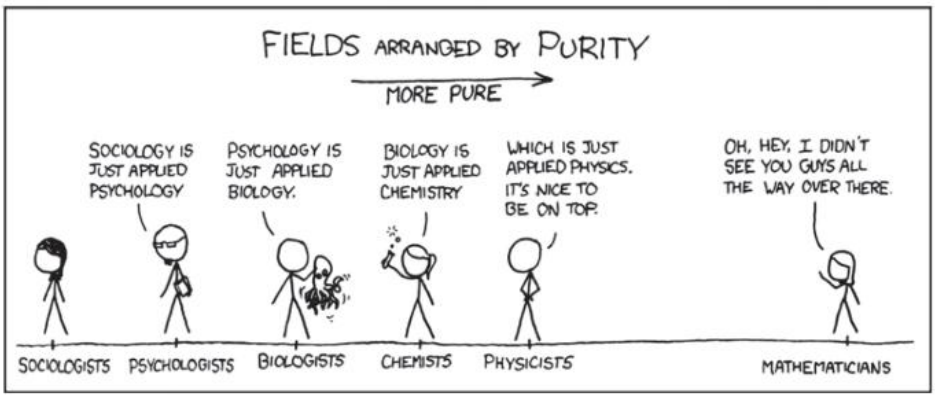
The alchemist's hunt for the Philosopher's Stone, which was believed to give eternal life and could turn base metals into gold, seems very naïve to us now. How do you think our current chemical knowledge will be viewed in 500 years?

Ernest Rutherford, the father of nuclear physics, described himself as an alchemist as he was able to change one element into another by nuclear reactions.

A web and hierarchy of disciplines

Is it possible to place the different scientific disciplines in a hierarchy, and which criteria would you use for your choice (Figure 2)? Chemical theories can help our understanding of biology: for example, hydrogen bonding explains the double helix structure of DNA. But much of chemistry relies on physics: for example, hydrogen bonding is explained in terms of electrostatic attraction.

Is this direction of **explanation** ever reversed? The view that one subject can be explained in terms of the components of another is called **reductionism**. Is physics in some way 'better' than the other sciences as it explains more? Where in this hierarchy would you place mathematics, which has been described as both the queen and the servant of the sciences? Some would argue that biology cannot be reduced to physics as it involves levels of organization that are not captured by simple concepts of physics.

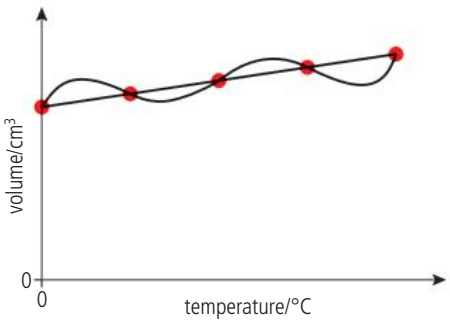


TOK Figure 2 Chemistry, the central science?

Is chemistry in some way the most complete science? Our knowledge of the periodic table and atomic structure suggests that there are limits to the number of elements in nature. Chemical knowledge is **justified** by empirical evidence which is acquired by the senses and enhanced, if necessary, by technology. Which of the natural sciences is most clearly based on direct observation?

Same data, different hypothesis: Occam's razor

It is always possible to think of a range of hypotheses that are consistent with a given set of data. For the same reason, an infinite number of patterns can be found to fit the same experimental data.



TOK Figure 3 The curve and the straight line in the graph both fit the experimental data.

You may argue that the straight line in Figure 3 is a more suitable fit to the data as it is simpler, but on what grounds do we base the assumption that simplicity is a criterion for truth? The idea that the simplest explanations are the best is inspired by the principle – named after the medieval philosopher William of Occam – known as Occam's razor that a theory should be as simple as possible while maximizing explanatory power.

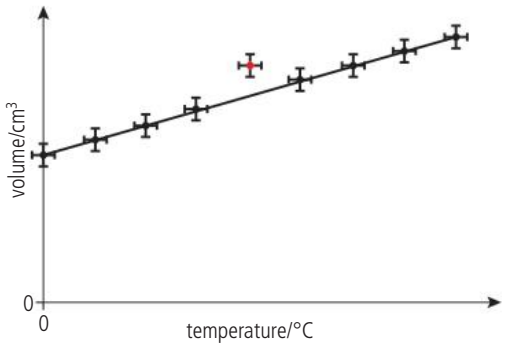
'Explanations must be as simple as possible – and no simpler.'

Albert Einstein

Do the natural sciences rely on any assumptions that are themselves unprovable by science?

Rejecting anomalous results: confirmation bias

We often dismiss results which do not fit the expected pattern as being due to experimental error. In Figure 4, is it reasonable to reject the point that is not on the line?



TOK Figure 4 When are you justified in dismissing a data point which does not fit the general pattern?

How does chemical knowledge change with time?

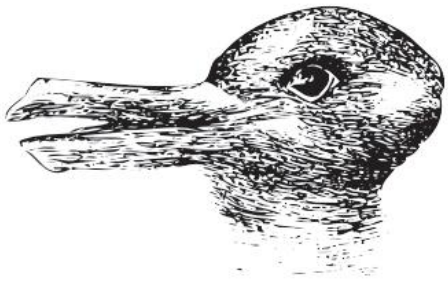
Lavoisier attached numbers to substances by measuring their masses and helped chemistry develop as a physical science. Mendeleev's periodic table systematized a mass of chemical information, and atomic theory explained the structure of the periodic table and the nature of chemical interactions. It was originally believed that a 'vital force' was needed to explain organic chemistry, but we now realize that it fits in with the rest of our chemical understanding.

Chemical knowledge has grown due to the contributions of individuals such as Boyle, Avogadro, Mendeleev, Dalton, Bohr, Lewis, Gibbs, Brønsted, Lowry and Kekulé. Their contributions have made the subject more systematic and coherent.

The above discussion suggests that there has been steady progress in chemical knowledge and our knowledge of the material world is increasing and improving in accuracy in the same way a map's description of a territory might improve with time. We will see when we discuss the ideas of Popper and the provisional nature of scientific knowledge that this view is problematic and an alternative was offered by Thomas Kuhn (1922–1996). Kuhn suggested that science does not develop by the orderly accumulation of facts and theories, but by dramatic revolutions which he called **paradigm shifts**. In this context, a paradigm can be thought of as a model or world view accepted by the scientific community. Kuhn distinguished between periods of **normal science** in which new discoveries are placed within the current paradigm and **extraordinary science** which produces results which do not fit the current paradigm. Isaac Newton, John Dalton, Charles Darwin, and Albert Einstein are all revolutionary scientists who changed the way we look at the world by proposing new paradigms.

A paradigm is a system of concepts, language, assumptions, methods, values, and interests that define research in an area of knowledge. It is related to the knowledge framework in TOK.

The idea of a paradigm shift can be illustrated by considering the picture in Figure 5.



TOK Figure 5 In one paradigm, the picture can be interpreted as a duck; in another paradigm, it can be interpreted as a rabbit. Turn the page through 90° and experience a paradigm shift.

'What were ducks in the scientists' world before the revolution, are rabbits afterwards…'

Thomas Kuhn

Atomic theory is one of the most important paradigms of chemistry. Dalton's model of the atom as indivisible spheres collapsed with the discovery of the proton, neutron and electron. And this model has developed further with advances in particle physics and the discovery of quarks.

Paradigm shifts: phlogiston theory and the discovery of oxygen

When a solid such as magnesium burns, it crumbles into ash and becomes smaller. It seems quite natural to assume that the metal is giving something off as it burns. It was originally believed that all flammable materials contain phlogiston (a word derived from the Greek for flame), which was given off and absorbed by the air as substances burn. In this theory, substances stop burning when all the phlogiston has been released or when the air is saturated with the phlogiston released. The crisis for the paradigm occurred when careful measurements showed that a mass increase occurred during combustion.



When magnesium burns, a white ash is produced. If all the ash remains in the crucible and is prevented from escaping, its mass is greater than the original magnesium. Nothing has escaped the magnesium as first thought, but oxygen has been added.

Some explained this result within the phlogiston paradigm by suggesting that phlogiston could have a negative mass, but that explanation was rejected in favour of the modern oxygen theory of combustion.

As substances burn more brightly in oxygen, the gas was originally called 'dephlogisticated air' by Joseph Priestley, one of the scientists credited with its discovery. However, the discovery of oxygen made the term 'phlogiston' meaningless.

Priority disputes

There have been some priority disputes over who discovered oxygen and arguments can be made for Scheele, Priestley and Lavoisier. Their research techniques were very different – while Priestley and Scheele heated and sniffed, Lavoisier heated, measured, and calculated. Perhaps then, it was Lavoisier who changed the biggest paradigm in the history of chemistry as he explained the mass increase during combustion as due to the combination with oxygen. Does competition between scientists help or hinder the production of knowledge?

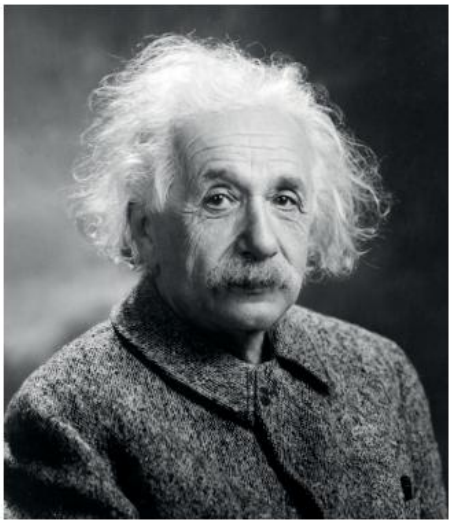
Science revolutionaries

A widely held stereotype of scientific progress is that of an idealistic young innovator challenging the ideas of the establishment. This is rationalized in Kuhn's model of science because established individual scientists are often reluctant to make such leaps. The need to be a risk-taker, one of the attributes of the IB learner profile, and thinking outside the box is emphasized by Richard Feynman:

'One of the ways of stopping science would be to only experiment in the region where you know the law.'

This emphasizes the role of creative thinking in scientific progress.





Which Einstein discovered the Theory of Relativity?

Max Planck emphasized the societal element of progress in science.

'A new scientific theory does not triumph by convincing its opponents and making them see the light, but rather because its opponents eventually die out and a new generation grows up that is familiar with it.'


Herrn Carl Wilhelm Scheele
der Königl. Schwed. Akademie der Wissenschaften Mitgliedes
Chemische Abhandlung
von
Luft und Feuer
Nebst einem Vorberichte
von
Torbern Bergmann
Professor der Chem. zu Upsal, Rittern des Königl. Schwed. Wasaord. verschied. Societ. Mitgliedes
Zweyte verbesserte Ausgabe
mit
einer eigenen Abhandlung über die Luftgattungen, wie auch mit der Herren Kirwan und Priestley Bemerkungen und Herrn Scheelens Erfahrungen über die Menge der im Dunstkreise befindlichen reinsten Luft vermehrt
und mit einem Register versehen
von
D. Johann Gottfried Leonhardi
Prof. der Arzneygelahrheit zu Leipzig, der Churfächss. ökon. Gesellschaft Mitglied.
Leipzig
bey Siegfried Lebrecht Crusius
1782.

'Air and Fire' (1782) by Scheele. Scheele discovered several new chemical elements and compounds, but was unlucky in that his contemporaries often published their findings before him. Scheele published in German.

How does the social context of scientific work affect the methods and findings of science?

Methodology and tools in chemical knowledge

Chemists follow a scientific methodology with an emphasis on experimental work. Results are explained using theories and models and evaluated by peer review. Intuition and creativity are needed to produce hypotheses' but reason must govern coherent explanations. Knowledge is shared via agreed-upon systems of language and convention including scientific terminology, chemical symbols and mathematics. Observations and measurements are made using sense perception, and emotion can provide the personal motivation for a scientist to focus on a particular area of research.

Experimental results and well-established theories count as facts and explanations which reduce chemical change and structure to simple, well-understood concepts such as mass, charge, and attractive and repulsive electrostatic forces. Models can be used to simplify a problem to simple cause and effect relationships.



▲ Zinc (Zn) and black copper(II) oxide (CuO) powders are mixed in a stoichiometric ratio. The mixture is strongly heated in a flame of a propane Bunsen burner.

What to observe?

Look at the picture (right) and make a list of observations.

Did you notice that the flame has gone orange where it heats the test tube? Many people miss this, even when they are asked to heat an empty test tube, but to the chemist' it is a significant observation. It shows that there is sodium in the glass.

'In the field of observation, chance favours only the prepared mind.'

Louis Pasteur

The scientific method

Should the natural sciences be regarded more as a method or more as a system or body of knowledge?

Richard Feynman (1918–1988), one of the great physicists of the 20th century, gave the following description of the scientific method:

'In general we look for a new law by the following process. First, we guess it. Then we compute the consequences of the guesses to see what would be implied if the law was right. If it disagrees with experiment, it is wrong. In that simple statement is the key to science… It does not make any difference how smart you are, or what is your name – if it disagrees with experiment, it is wrong… It is true that one has to check a little to check that one is wrong.'

During your IB chemistry course, you are continually challenged to think about the Nature of Science. To what extent is Feynman's view of the scientific method still a valid description today? Does a single method adequately describe scientific studies in all disciplines from astronomy to geology? Could you use your experience in the chemistry laboratory or on the collaborative sciences project to write your own definition of the scientific method?

Measurement: the observer effect

Measurement has allowed the chemist to attach numbers to the properties of materials, but the act of measurement can change the property being measured. Adding a thermometer to a hot beaker of water, for example, will cause the temperature to decrease slightly, and adding an acid–base indicator, which is itself a weak acid or base, will slightly change the pH of the solution.

Generally, such effects can be ignored, as measures are taken to minimize them. Only a few drops of indicator are used, for example, and thermometers are designed to have a low heat capacity. The **observer effect** can cause significant problems at the atomic scale, however, which led the physicist Werner Heisenberg (1901–1976) to comment:

'What we observe is not nature itself, but nature exposed to our mode of questioning.'

The observer effect is also significant in the human sciences. Can your school director observe a 'normal' chemistry class?



▲ Methyl orange is a weak acid. The addition of the indicator will change the pH of the solution it is measuring.

What is the role of inductive reasoning?

How do individual observations lead to theories and scientific laws of nature? Imagine an experiment in which you test the pH of aqueous solutions of some different oxides. The results are shown in the table.

Oxide	Acid/Alkali
$Na_2O(s)$	alkali
$MgO(s)$	alkali
$CO_2(g)$	acid
$SO_2(g)$	acid
$CaO(s)$	alkali
$N_2O_5(g)$	acid

Two possible conclusions which fit the pattern are:

- All solid oxides are alkalis. All gaseous oxides are acidic.
- All metal oxides are alkalis. All non-metal oxides are acidic.

Challenge yourself

3. Suggest another conclusion which fits the results.

We have used **induction** to draw these conclusions. Inductive logic allows us to move from specific instances to a general conclusion. Although it appeals to common sense, it is logically flawed. Both conclusions above are equally valid, based on the evidence, but both could be wrong. Just because something has happened many times in the past does not prove that it will happen in the future. This is the **problem of induction**. The philosopher Bertrand Russell illustrated the danger of generalization by considering the case of the philosophical turkey. The bird reasoned that since he had been fed by the farmer every morning, he always would be. Sadly, this turkey discovered the problem with induction on Thanksgiving Day! Are you acting in the same way as the turkey when you draw conclusions in your experimental work?

Induction means inferring general conclusions from particular examples.

How do we justify the use of induction? Consider the following form of reasoning.

- On Monday I used induction and it worked.
- On Tuesday I used induction and it worked.
- On Wednesday I used induction and it worked.
- On Thursday I used induction and it worked.
- On Friday I used induction and it worked.
- Therefore I know that induction works.

Challenge yourself

4. What does this illustrate about the problem of induction?

Falsification?

Karl Popper (1902–94) realized that scientific verification does not actually prove anything and decided that science finds theories, not by verifying statements, but by falsifying them. Popper believed that even when a scientific theory had been successfully and repeatedly tested, it was not necessarily true. Instead, it had simply not yet been proved false. Observing a million white swans does not prove that all swans are white, but the first time we see a black swan, we can firmly disprove the theory.



No matter how many times we record in our notebooks the observation of a white swan, we get no closer to proving the universal statement that all swans are white. Black swans inhabit lakes, rivers and coastal areas in Australia.

What is the role of deductive reasoning?

Deductive logic allows us to move from general statements to specific examples. The conclusion of deductive logic must be true if the general statements on which it is based are correct. Deductive reasoning is the foundation of mathematics. We can also use this reasoning to test our scientific hypotheses. Consider again the pH of the oxides tabulated earlier. The two competing hypotheses could be distinguished by considering the pH of a non-metal oxide such as phosphorus oxide, which is a solid at room temperature. If we use the two hypotheses as starting points (premises), they lead to two different conclusions using deductive reasoning.

- All solid oxides are alkalis.
- Phosphorus oxide is solid.

Therefore: phosphorus oxide is an alkali.

OR

- All non-metal oxides are acidic.
- Phosphorus oxide is a non-metal oxide.

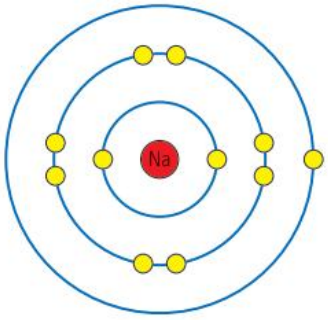
Therefore: phosphorus oxide is an acid.

When the pH of phosphorus oxide solution is tested and shown to be an acid, we can be certain that the first hypothesis is false, but we cannot be sure that the second is definitely true. If it survives repeated tests, it may, however, become accepted as scientific truth, but does not mean that it is certain. No matter how many tests a hypothesis survives, we will never prove that it is true in the same way as a mathematical proof is true. All scientific knowledge is **provisional**.

There are still problems, however, with this view of science. When your results do not match up with the expected values in a chemistry investigation, do you abandon the accepted theories, or do you explain the differences as being due to experimental error, faulty instruments, or contaminated chemicals?

Are the models and theories that scientists use merely pragmatic instruments or do they actually describe the natural world?

We started the chapter with the metaphor of a map for knowledge. Models play a similar role to maps. Scientists use models to clarify certain features and relationships. They can become more and more sophisticated, but they can never become the real thing. Models are just a representation of reality. For example, in pre-IBDP courses, the sodium atom can be represented by the diagram in Figure 6 with a nucleus at the centre of the atom and electrons orbiting the nucleus like planets orbiting the Sun. This model helps us understand the reactivity of the element. Sodium reacts by losing its outer electron to adopt the electron arrangement of neon with only complete energy levels.

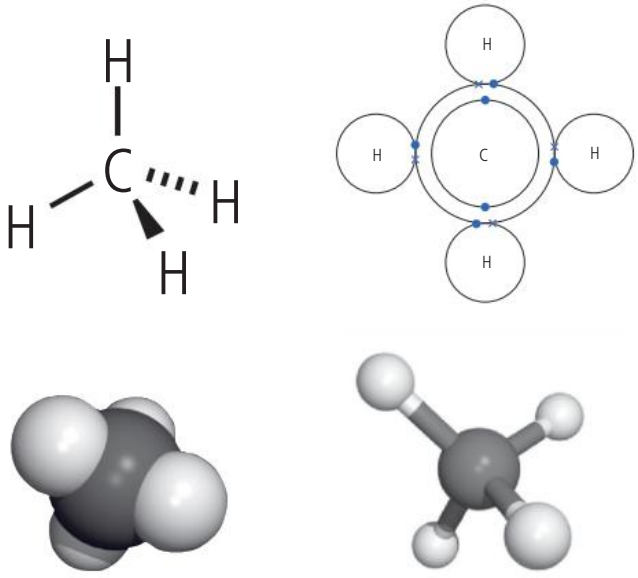


TOK Figure 6 A model you may have used to explain the chemistry of sodium.

The model is not complete, however, as it fails to explain the electron arrangement of atoms after calcium in the periodic table. To explain the chemistry of all the elements, we need a more sophisticated model, that of electrons occupying orbitals. Can an inaccurate model give us knowledge?

Models are not the territory

The methane molecule can be represented in a number of ways (Figure 7).

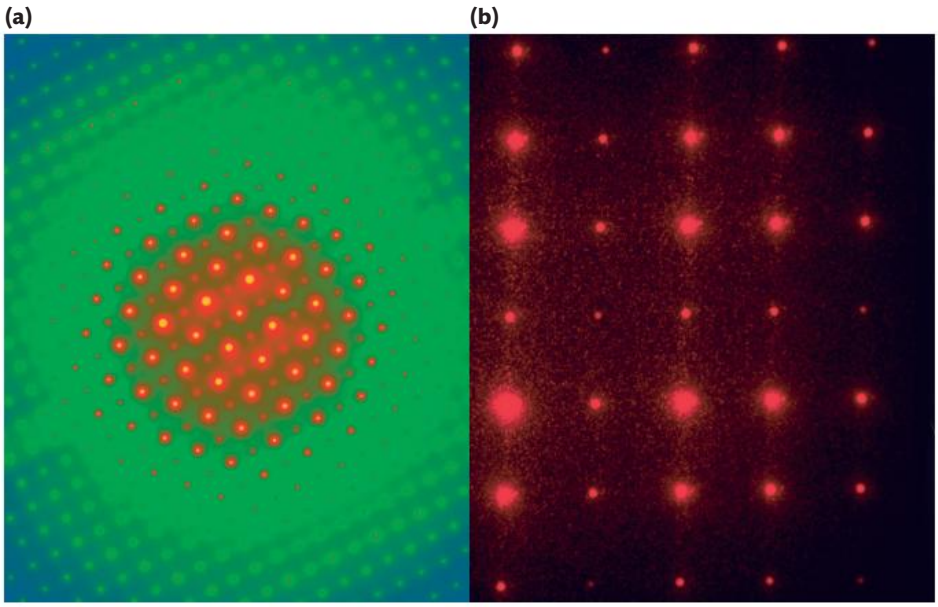


TOK Figure 7 Different models of the methane molecule.

Since a model is a simplified representation of the world, it tends to focus on features that are directly relevant. This highlights the need to consider the relationship between the model and the context in which it has been applied.

What is the role of imagination?

The evidence for the wave nature of electrons comes from the diffraction pattern observed when a beam of electrons is passed through a metal structure, which is similar to that observed when light is passed through a diffraction grating (see below).



(a) The electron diffraction pattern of molybdenum trioxide (MoO_3). **(b)** Diffraction grating pattern formed by laser light (red).

We now recognize that the 'true' nature of the electron, or indeed of anything, cannot be completely described by a single model. Both the wave and particle models are needed. This should not surprise us as models are often based on our everyday experience which does not apply to the small scale of the atom. To understand nature at this level, scientists must go beyond their experience and use their imagination. Scientists need imagination to form a mental representation of something when it is beyond sense experience. Imagination is also associated with creativity, problem-solving and originality, all key skills of scientists.

The wave–particle duality of the electron illustrates a general knowledge issue. Two sources of knowledge can often give conflicting results and it is for us to see if the conflict is real or a limitation of human knowledge.

E.J. Corey, who was awarded the Nobel Prize for his work on retrosynthetic analysis, also stressed the role of imagination in synthetic chemistry. The retrosynthetic approach starts with the target molecule and works backwards by focusing on the functional group to identify possible precursors leading to a possible starting material.

'The synthetic chemist is more than a logician and strategist; he is an explorer strongly influenced to speculate, to imagine and even to create.'

J.J. Thomson won the 1906 Nobel Prize in Physics for measuring the mass of an electron, that is, for showing it to be a 'particle'. His son G.P. Thomson won the 1937 Nobel Prize in Physics for showing the electron to be a 'wave'. This is not necessarily a contradiction. It is a question of particles sometimes behaving as waves. Our everyday classification of phenomena into 'wave' and 'particle' breaks down at the subatomic scale. This limitation of our experience should not, however, shackle our understanding of the subatomic world.

Our imagination can help us to solve problems and develop original ideas. We may use imagination to make connections between separate ideas, to build models or to create theories. But to what extent should we trust our imagination, given that it is derived in the mind rather than through sense perception? Can imagination reveal truths that reality hides? What other examples of discoveries in chemistry illustrate the importance of imagination?

Science and pseudoscience: homeopathy

If you have ever dropped a Mentos candy into a bottle of a carbonated drink you would have noticed that it fizzes with an eruption of foam. Can you explain this? If someone suggested that it was because of an 'evil demon' hidden in the drink responding angrily to being assaulted by a solid lump, you would probably reject it as a non-scientific explanation. But what makes this non-scientific? A scientific theory must be testable. It is difficult to imagine an experiment which could be designed to prove the 'evil demon' theory *false*. A theory that can be used to explain everything explains nothing.

There are a number of activities that are claimed by those who practise them to be scientific, such as astrology, homeopathy, and crystology (crystal therapy). The label 'science' is used to add authority to the claims, but how do we distinguish a genuine science from a fake or **pseudoscience**? It is the methods used in the natural sciences that are the key distinguishing factor – what is it about these methods which makes the knowledge they generate reliable?

Homeopathy is an alternative therapy that aims to treat diseases by giving extremely dilute doses of compounds that cause the same symptoms as the disease. The more dilute the dosage, the more powerful the remedy. Some doses are so dilute that it is likely they do not contain a single molecule of the active substance. Practitioners attribute this to the 'memory' of the water in which they have been diluted. Conventional science has subjected these claims to intense scrutiny, but firm evidence of anything other than the placebo effect has not yet been found.



Homeopath preparing herbal remedies.

Ethics

Progress in science and technology can profoundly affect our lives. Often these effects are positive – medicines have made our lives safer, and the development of new materials has made our lives more comfortable – but technological developments can also bring suffering and injustice. Industry and technology have had a negative impact on the environment. How do we decide what is the right and wrong use of science? These are ethical questions. There is often disagreement about what is 'right', and ideas of what is considered to be acceptable often change over time. Ethical issues raise difficult questions about risk versus benefits. In many cases, the science is so new that judging long-term benefits and risks is difficult. Developments in chemistry can create new ethical issues. There are also more direct concerns about how scientists should conduct their work. Scientists generally work in communities, not in isolation, and are expected to report their results honestly and openly in an atmosphere of trust. How would you respond if a student you were working with wanted to 'make up' their experimental results? What are your responsibilities in such a situation? The IB's mission statement and academic honesty policy is clear about the active role students have on their own learning. Your work should be authentic and genuine.

Science is, however, a human endeavour and scientists, like the rest of humanity, can be motivated by envy, vanity and ambition.

Is science, or should it be, **value**-free? Some would argue that it is the aim of science to describe the world as it is and not as it should be.

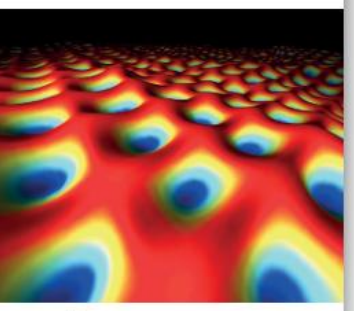


Dioxin pollution can be produced by the incomplete combustion of plastics. Dioxin toxicity research has involved tests on rats. Are such tests ethically justified?

Some people do, however, fear the consequence of scientists 'interfering with nature'. Who decides what is and what is not a legitimate area of scientific research? The scientific community or society at large?

What are the responsibilities of the scientific community in controlling the quality of knowledge? It was originally believed, for example, that the medicine thalidomide was so safe that it was prescribed to pregnant women to control morning sickness, but this led to tragic consequences as the drug can cause many malformations in the fetus. Who is responsible when things go wrong?

Individual chemists have to take some responsibility. They must use their knowledge responsibly and consider the full implications of their work. There are ethical considerations that limit the scope of inquiry.



This picture is obtained by firing a beam of polarized ^{3}He atoms towards a metal surface. The metal can be seen as a lattice of positive metal ions (blue) in a sea of electrons (red).

Chemistry and the optional themes

The TOK optional themes are focused on issues beyond the school experience that have a huge impact on the world today and a particularly key role in shaping your perspectives and identity. Some possible links can be made between the optional themes and what you study in chemistry. We outline some examples here.

Knowledge and technology

Chemistry deals with what is acquired by the senses, and enhanced, if necessary, by technology. We are now able to see things which are beyond the direct limits of our senses. Look at the photograph (right). Is this what a metal surface really looks like?

Does technology merely extend the range of the human senses, or does it give a new way of seeing the world?

Technology has also had a big impact on experimental work. You will have used data loggers to collect and analyze experimental data and spreadsheets to analyze and present results. You may have also made measurements with new instruments that would not have been possible a few years ago. You will have used the internet to collaborate with other students, possibly from different schools in different parts of the world. How are the questions you explore limited by the technology that is available to you?

How have these technologies shaped your knowledge? Will the chemical knowledge of future IB Diploma Programme students progress as technologies continue to develop?

Robots are already used to perform some experimental procedures. Can a machine have procedural knowledge in the same way as an experienced laboratory chemist? Could these practical skills be one day redundant and not worth learning?



Robotic arm pouring a chemical into a flask.

Part of the final assessment of your chemical knowledge includes a multiple-choice paper where you are asked to choose the best answer from a selection of four answers. This is marked by a computer which has the answers stored as data. The computer does not know the answer in the same way that you hopefully will! In this assessment, your knowledge is demonstrated by your response to a list of questions. With developments in Artificial Intelligence, it may not be too long before computers can be programmed to perform equally well in the different assessment tasks. Would this make the knowledge of the computer in some way equivalent to yours? In what sense, if any, can a machine be said to 'know' something?

Knowledge and language

The language of alchemy was cryptic and secretive because the knowledge it communicated was thought to be too powerful to share with the general public. The names of many chemicals were derived from their natural origin and were not related to their composition. The language of modern chemistry, by contrast, is precise, and is an effective tool for thought. When asked to draw the different isomers of C_7H_{16} it is very easy to draw the same structure twice by mistake. The IUPAC nomenclature, however, allows you to distinguish between the different isomers. They have different structures if they have different names.

The nine isomers of C_7H_{16}. The names help you to distinguish the different structures.

heptane	2-methylhexane	3-methylhexane
2,2-dimethylpentane	2,3-dimethylpentane	2,4-dimethylpentane
3,3-dimethylpentane	3-ethylpentane	2,2,3-trimethylbutane

The use of oxidation states has also allowed us to develop a systematic nomenclature for naming inorganic substances. The IUPAC aims to provide scientists with a common language as it saves time and resources. How does language allow humans to pool resources and share knowledge?

Today if a scientist is going to coin a new term, or publish a new discovery, it is most probably in English. Back in the late 19th century, however, the dominant language in chemistry was German and learning the language was often required to study chemistry at university. The change from German to English was influenced by the politics of the times. What role does language play in allowing knowledge to be shared with future generations?

Chemistry, of course, also has its own universal language. Balanced equations allow us to use mathematics to solve chemical problems. The ability to attach numbers to substances allows the chemist to use mathematics as a precise tool to investigate the material world. Language should be a tool and not an obstacle to knowledge.

Knowledge and politics

Chemistry has applications in many important areas of our lives such as food, energy security, environment, defence and health, and so can have an impact on politics. Developments in scientific knowledge can often trigger political controversies.

Cans of genetically modified tomato puree. Different countries have adopted very different approaches to the marketing of GM foods. In the European Union (EU), strict rules apply to the labelling of GM foods, while in the USA and Canada there is no mandatory labelling of GM content. It has been said that the EU is adopting the 'precautionary principle' in this regard, and this raises several concerns for international trade.



Knowledge and religion

There have been many historical conflicts between science and religion but are they necessarily irreconcilable? The chemist Peter Atkins argues that there is no evidence and no reason to have religious belief. He argues that science and religion are incompatible, and science can answer the questions that religion has traditionally answered.

To others, however, science and religion are complementary areas of knowledge which are concerned with different spheres of experience, asking different questions, and justified in different ways. According to Einstein: science is concerned with *what is* whereas religion with *what should be*.

> *'Science without religion is lame, religion without science is blind.'*
>
> Albert Einstein

To what extent do scientific developments have the power to influence thinking about religion?

Knowledge and indigenous societies

Many modern medicines have primitive origins based on folklore. In 400 BCE Hippocrates recommended a solution derived from a willow leaf as a treatment for the pain of childbirth, and the bark of the willow tree was later used as a treatment for fever. As chemical techniques advanced, the active chemical salicylic acid was extracted; its structure was modified, and the analgesic aspirin synthesized.

The traditional knowledge of many indigenous societies is rooted in their long-standing and close relationships with the natural world. It is more dependent on the direct use of the senses than modern science. The French anthropologist Claude Lévi-Strauss, in his essay on The Science of the Concrete, contrasts indigenous knowledge with chemistry by giving an example of how similar discoveries can be made but in different ways. The fragrances of lavender, wintergreen and bananas have a common feature identified by indigenous societies and so they group them together. Analytical chemistry related this feature to them all being esters. Similarly, wild cherries, cinnamon, vanilla and sherry, which are grouped together by indigenous societies by their fragrances, are all identified as aldehydes by the analytical chemist.

In this case the indigenous knowledge of the plants is related to a sense of smell and a basic process of categorization which, according to Lévi-Strauss, is more 'concrete' in nature than chemistry. This suggests that indigenous knowledge is very highly empirical and pragmatic in nature.

Chemistry and TOK assessment

TOK in Chemistry assessment

In your chemistry exams the questions use different command terms which indicate the depth of treatment required. 'Describe' and 'outline' questions require less depth of knowledge than 'explain' and 'predict' questions.

Is there a categorical distinction between a description and an explanation?

Chemistry in TOK assessment

The TOK exhibition

The TOK exhibition explores how TOK manifests itself in the world around you. You are required to create an exhibition of three objects that connect to **one** of the 35 'IA prompts' in the TOK guide. You are encouraged to choose objects of personal interest that you have come across in your school studies and/or your lives beyond the classroom.

An extremely wide variety of objects are suitable for use in a TOK exhibition. For example, the pictures of experimental equipment, molecular models or the periodic table discussed in this chapter, as well as many of the illustrations in the text or the textbook itself, are all objects of interest. It is, however, strongly recommended that you base your exhibition on one of the TOK themes, either the core theme or one of the optional themes and not areas of knowledge such as the natural sciences.

The TOK essay

In your TOK essay, you are expected to make connections between the knowledge question and your own experiences as a learner. It is helpful to support your argument with examples drawn from your IB diploma courses as well as from other sources. This includes your chemistry class.

Some examples of prescribed essay titles for you to consider.

- Do good explanations have to be true? (May 2019)
- To produce knowledge just observe and then write down what you observe. Discuss the effectiveness of this strategy in two areas of knowledge. (Nov 2019)
- Is there a trade-off between scepticism and successful production of knowledge? (Nov 2019)
- 'There is a sharp line between describing something and offering an explanation of it.' To what extent do you agree with this claim? (May 2020)
- 'Present knowledge is wholly dependent on past knowledge.' Discuss this claim with reference to two areas of knowledge. (May 2020)
- 'Reliable knowledge can lack certainty.' Explore this claim with reference to two areas of knowledge. (Nov 2020)
- 'If all knowledge is provisional, when can we have confidence in what we claim to know?' Answer with reference to two areas of knowledge. (Nov 2021)
- 'We are rarely completely certain, but we are frequently certain enough.' Discuss this statement with reference to two areas of knowledge. (Nov 2021)

Internal Assessment

Purpose

During your two-year IB Diploma Programme, you are expected to carry out a **scientific investigation.** This must be written up as a full report and is an integral part of your final assessment for the course.

Your investigation will be based on a topic of your own interest, and have a focused research question, which is rationalized through appropriate scientific context. Your topic may be selected individually or through collaboration within a group of no more than three students (yourself included). Your approach and methodology can rely on the collection and analysis of primary data through experimental work, or the analysis of secondary data from a database or from the use of an open-ended simulation. Your investigation may also use a mix of approaches and data sources.

In all cases, the investigation will be assessed according to the same **four** assessment criteria which are summarized below.

Note the following general points:

- The scientific investigation may be completed individually or collaboratively. Details on group work are presented later in this chapter.
- The scientific investigation contributes 20% towards your final chemistry grade.
- Your written report will be marked internally by your teacher who will allocate a predicted grade.
- A sample of the reports from your class will be submitted to the IB for moderation and standardization to ensure fairness in applying the standards across all candidates. The mark awarded upon moderation may be different from the mark predicted by your teacher.
- The scientific investigation should take approximately 10 hours to complete including any preparatory work, lab work and write up.
- The report has an upper word-limit of 3000 words. The following words are not included in the word count:
  - charts and diagrams
  - data tables
  - equations, formulae and calculations
  - citations/references
  - bibliography
  - headers
- The topic selected for the scientific investigation can be based on the course content, or it can be on extension material beyond the specifications of the chemistry subject guide.
- It is recommended that you are proactive and initiate a discussion with your teacher early on regarding your scientific investigation ideas, and always seek to obtain advice and information from teachers and peers.

Academic honesty

There is a strong expectation from IB candidates to show the highest level of academic integrity and academic honesty. Under no circumstances is plagiarism and/or collusion in your scientific investigation or any other piece of work submitted to the IB for assessment acceptable. It is encouraged that an appropriate web-based plagiarism detection engine is used prior to submitting work.

Appropriate referencing to sourced information used in the scientific investigation report is *required*. You can follow any of the accepted referencing styles.

Remember that, as stated in the IB chemistry subject guide, *omitted or improper referencing will be considered as academic malpractice* and flagged for investigation as a potential breach of regulations.

The assessment criteria

The scientific investigation will be marked using a best-fit approach to match the level of work with the descriptors given at each mark band. Each criterion is marked separately and contributes to the final mark of 24 (later scaled to 20% of overall grade) as shown below:

Criterion	Maximum number of marks available	Weighting (%)
Research design	6	25
Data analysis	6	25
Conclusion	6	25
Evaluation	6	25
Total	**24**	**100**

The descriptors of each criterion are presented below. Guidance *in addition to* what is already presented in the chemistry subject guide is given. You are strongly recommended to focus on the highest mark-band level descriptors each time – there is no point in aiming for less!

Research design

Marks	Level descriptor
0	The report does not reach the standard described by the descriptors below.
1–2	• The research question is stated without context. • Methodological considerations associated with collecting data relevant to the research question are stated. • The description of the methodology for collecting or selecting data lacks the detail to allow for the investigation to be reproduced.
3–4	• The research question is outlined within a broad context. • Methodological considerations associated with collecting relevant and sufficient data to answer the research question are described. • The description of the methodology for collecting or selecting data allows for the investigation to be reproduced with few ambiguities or omissions.
5–6	• The research question is described within a specific and appropriate context. • Methodological considerations associated with collecting relevant and sufficient data to answer the research question are explained. • The description of the methodology for collecting or selecting data allows for the investigation to be reproduced.

Checklist

A downloadable copy of this checklist is available in the eBook.



- ✓ My research question investigates the relationship between two correlated variables.
- ✓ I have provided a justification for the relationship between the dependent and independent variables hypothesized using appropriate scientific context.
- ✓ I have provided additional background which is focused and deepens the understanding of the investigated research question.
- ✓ I have clearly stated and defined the variables (dependent/independent/controlled) involved in my investigation.
- ✓ My choice of investigation methodology is justified. I have explained why the methodology chosen is appropriate to answer the research question within specific parameters.
- ✓ I have highlighted and explained any decisions taken in the design of a new *(or* the modification of an existing) methodology.
- ✓ I have explained and justified key steps of the methodology and I have ensured that my report is clear on why specific conditions are used in the methodology and what the importance of these conditions are.
- ✓ I have assessed and reported any associated Health and Safety considerations including Ethical and Environmental risks, which may not be immediately obvious.
- ✓ My methodology is clearly stated. Another student may potentially repeat the work by following the methodology that I have described.
- ✓ I have reviewed the methodology and any unnecessary steps or repetition of steps have been removed.
- ✓ My methodology allows for the collection of enough data.

- ✓ My presented methodology is an honest representation of the work undertaken in the lab, stating the procedure I used and not the one that I should have used in retrospect.
- ✓ My methodology is internally consistent with the work presented in the report.

Data analysis

Marks	Level descriptor
0	The report does not reach the standard described by the descriptors below.
1–2	• The recording and processing of the data is communicated but is neither clear nor precise. • The recording and processing of data shows limited evidence of the consideration of uncertainty. • Some processing of data relevant to addressing the research question is carried out but with major omissions, inaccuracies or inconsistencies.
3–4	• The communication of the recording and processing of the data is either clear or precise. • The recording and processing of data shows evidence of a consideration of uncertainties but with some significant omissions or inaccuracies. • The processing of data relevant to addressing the research question is carried out but with some significant omissions, inaccuracies or inconsistencies.
5–6	• The communication of the recording and processing of the data is both clear and precise. • The recording and processing of data shows evidence of an appropriate consideration of uncertainties. • The processing of data relevant to addressing the research question is carried out appropriately and accurately.

Checklist



A downloadable copy of this checklist is available in the eBook.

- ✓ My qualitative and quantitative data are presented appropriately.
- ✓ The origin of the presented data is clear.
- ✓ Tables, graphs, figures and schemes are clearly labelled, and in-text citations are used when appropriate to help the reviewer follow my work and thinking process.
- ✓ My data are presented in a consistent manner following SI conventions.
- ✓ My data-analysis protocol is clearly shown. I have provided an example of my calculations.
- ✓ I have taken into consideration the uncertainties in my measurements and the error propagation in the various mathematical operations used.
- ✓ My data analysis protocol is relevant, and the produced results are appropriate to address the research question.
- ✓ I have presented/visualized my results with appropriate graphs that enhance the reader's understanding of my work and are relevant in addressing my research question.

Conclusion

Marks	Level descriptor
0	The report does not reach the standard described by the descriptors below.
1–2	• A conclusion is stated that is relevant to the research question but is not supported by the analysis presented. • The conclusion makes superficial comparison to the accepted scientific context.
3–4	• A conclusion is described that is relevant to the research question but is not fully consistent with the analysis presented. • A conclusion is described and makes some relevant comparison to the accepted scientific context.
5–6	• A conclusion is justified that is relevant to the research question and fully consistent with the analysis presented. • A conclusion is justified through relevant comparison to the accepted scientific context.

Checklist

A downloadable copy of this checklist is available in the eBook.



- ✓ My conclusion directly addresses the research question and is justified by the data and the data-analysis I have presented in the report.
- ✓ I have correctly interpreted my processed data, considering the associated uncertainties and their impact on the conclusion.
- ✓ I have compared my conclusion to the established scientific context, such as journal articles, science textbooks, encyclopedia articles or other peer-reviewed sources. I have considered the extent of my agreement or disagreement with the established scientific understanding and I have explored the reasons that may have contributed to my conclusion.

This point is critical as it will enable you to appropriately evaluate your work!

Evaluation

Marks	Level descriptor
0	• The report does not reach the standard described by the descriptors below.
1–2	• The report states generic methodological weaknesses or limitations. • Realistic improvements to the investigation are stated.
3–4	• The report describes specific methodological weaknesses or limitations. • Realistic improvements to the investigation, that are relevant to the identified weaknesses or limitations, are described.
5–6	• The report explains the relative impact of specific methodological weaknesses or limitations. • Realistic improvements to the investigation, that are relevant to the identified weaknesses or limitations, are explained.

Checklist

A downloadable copy of this checklist is available in the eBook.



- ✓ I have considered the **weaknesses** related to the control of variables, the choice of equipment, the choice of methodology and any choices regarding

the data-analysis processes used. I have considered how these choices affected my conclusion. I have considered whether I would have made different choices given the opportunity.

✓ I have considered the **limitations** of my investigation. I took into consideration any assumptions made in the data-analysis, the range of the collected data, and the boundaries of the system investigated. I have considered the extent to which the obtained results are applicable.

✓ Considering the above, I have proposed *realistic* changes that could lead to more accurate results and/or extend the range and/or scope of the investigation.

Group work

The table below distinguishes between individual and collaborative work with regards to the scientific investigation.

Individual work	**Student works individually**	Students formulate and investigate their individual research question. Students develop their own methodology to answer their research question. A student cannot present the same raw dataset as another student.
Collaborative work	**Small group (no more than 3 students in a group)**	Students collaborate in selecting a topic of investigation. Each student formulates and investigates their individual research question by choosing: **A** A different independent variable than the other members of the group -or- **B** The same independent variable but with a dependent variable different than the one considered by the rest of the group -or- **C** A different part of the dataset to that used by the other members of the group from within a larger data set that the group has collected together. **Each student submits their own individual report**, clearly indicating that the investigation was developed through collaboration in a group. A student cannot present the same raw dataset as another student within the group.
	Class collaboration	A school or a class may participate or undertake a large-scale activity collecting data to generate a database. A student may participate in adding data to the database by using standardized protocols that they did not develop themselves. The student may then use the database to generate data for a scientific investigation that is treated as a scientific investigation that utilized secondary data from an external source. A student cannot present the same raw dataset as another student.

If you decide to work in a group, you still have to develop your own research question within the group-selected topic (see table above). While working in a group you may collaborate in developing a methodology or a standardized protocol that will allow for the collection of different sets of raw data that can address the needs of each group member's research question.

You may help, and receive help from, other group members in collecting the data and running the experiment(s), but in the end, you need to produce and submit your own individual report according to the criteria discussed on the previous page.

Types of investigations

Below you are presented with some examples of types of investigations and some important factors you need to consider when planning your scientific investigation.

Hands-on practical laboratory work

Hands-on laboratory work is the most traditional type of investigation. When planning for hands-on laboratory work, you need to ensure that your school:

- has the chemical materials needed
- has the required equipment available and in good shape
- and that the physical space and time needed will be available to you.

Time management is essential as practical work can be delayed by unexpected experimental procedure failures, for example, broken equipment, shipping delays in materials or other procedural challenges.

Fieldwork

Fieldwork has similar constraints as hands-on laboratory work with the additional requirement of collecting data in the field prior to analyzing/processing it in a lab. You need to ensure that you have collected more than enough data in the field before returning to the lab, as multiple visits to perform fieldwork may be unfeasible and, in some cases, reduce the validity of your work, as environmental conditions will vary in each visit.

Use of spreadsheet for analysis and modelling

The use of spreadsheets for analysis and modelling is becoming more and more popular and allows for faster processing of extended datasets. You need to collect your own primary data and then process them with the use of a spreadsheet or application.

Therefore, one of the challenges is that you need to be, or become, familiar with using a spreadsheet program such as Microsoft Excel® and its required syntax. Furthermore, when analyzing large datasets, you must be very careful in considering your personal bias in selecting the range and type of data to analyze.

Extraction and analysis of data from a database

The use of databases is very similar to the use of spreadsheets for analysis; the difference is that instead of generating your own primary data to use in the spreadsheet, you make use of secondary data found in publicly available databases. There are numerous databases available online that you can refer to, and examples are provided later in this chapter.

Use of a simulation

Simulations have also increased in popularity. As such, any open-ended simulation can be used to produce primary data that can be then analyzed as part of your

scientific investigation. The challenge here is to find a good open-ended simulation that will enable you to design your own experiment rather than follow a set of instructions that will lead to a pre-defined result.

Developing a research question

All journeys start with a first step. In your scientific investigation journey, your first step is developing your own research question. This can be challenging at the beginning and your ideas may be rejected by your teacher, either because they are not open-ended enough, they have been overdone in the past or, simply, your school does not have the equipment or resources necessary for the work you are proposing.

Remember that your work does not need to be groundbreaking or world-changing, even though it could be. You also need to consider that you only have 10 hours to research, experiment and write up your report for your scientific investigation, so be realistic in your goal setting.

In general, your scientific investigation should be looking to investigate the relationship between two correlated variables within a system. Your research question can be simply stated as:

How does the change of an <independent variable> in <specific system> affect a <dependent variable>?

Hulley *et al.* (2007) have suggested a set of criteria (FINER) that should be considered when developing your research question. These are presented below, adapted to the requirements of the scientific investigation in IB chemistry.

Feasible	You can address the question within the allowed time. The required equipment and materials are available. You have, or you will be able to develop, the required technical skills to be successful in researching your question.
Interesting	Your research question is open-ended, and it is not a simple yes or no question. The research question is of personal interest and will keep you, as well as your peers and eventually the moderators, intrigued and interested.
Novel	Your research question confirms, refutes, or extends previous findings.
Ethical	You have considered significant ethical, environmental and health concerns related to the research question posed.
Relevant	Your research question is relevant to chemistry.

Depending on the type of your investigation, your research question may be developed in slightly different ways.

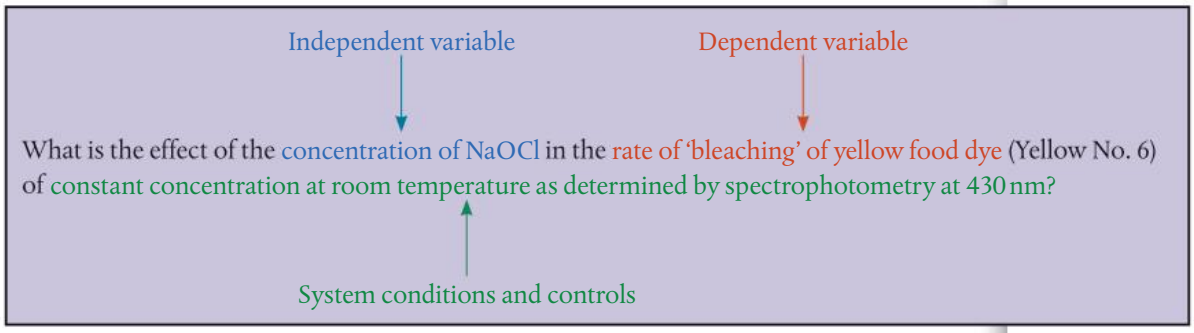
Manipulation of an independent variable

Consider the following:

You have a well-defined chemical system where a causal relationship between two variables is obvious.

You develop a protocol that can test and establish the mathematical relationship between the dependent and independent variables.

Example research question:



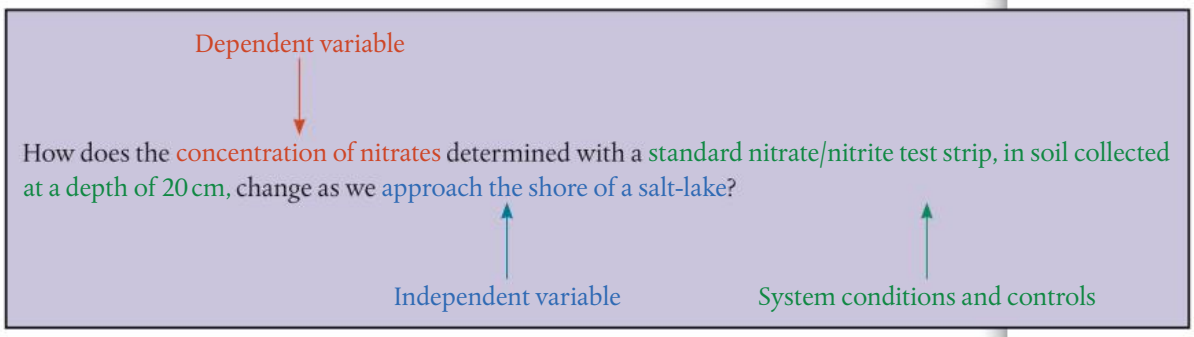
When reviewing the above example research question, the dependent and independent variables are immediately obvious. The system investigated, as well as the specific conditions that focus the scope of the investigation, are also stated.

Selecting variables through fieldwork

Consider the following:

You want to investigate how a dependent variable is affected by manipulating an independent variable on samples collected in the field under specific conditions.

Example research question:



In the example above, the variable is the concentration of nitrates in a solid sample that is collected at specific distances from the shore of a salt lake. The system of investigation and the range of the scope of the investigation are also clearly stated.

Selecting data from databases

Analyzing topics from databases such as (but not limited to) those from EPA, European Environment Agency, United Nations Environment Programme, Database of Environmental Education, NETROnline, World Health Organization, EMA, CDC, ECDC, NASA, PubMed, NIST, ChemExpert etc., can allow for various research questions to be developed.

See a comprehensive list of databases by following the links on the right.

As you are using secondary data and you are not generating your own through experimentation, these scientific investigations are expected to have a large dataset and rely heavily on the mathematical analysis of said dataset.

The use of spreadsheets and/or models in the analysis of these data sets is highly encouraged.

Using data generated by simulations

The use of simulations to generate data is approached in a similar fashion to databases. Predictive software such as MOPAC, WebMO, GAMESS, SAPT, Spartan Student, Molden or Tinker (among others) as well as PhET simulations can be adapted to generate data for this use.

Example research question:

> What are the trends observed in the dissociation enthalpy of the O–H bond of straight-chain alcohols with no side-chain substituents in respect to their increasing mass, as reported by the National Standard Reference Data Series, National Bureau of Standards, no. 31, Washington, 1970?

In the example above, the variable is the dissociation enthalpy of the O–H bond in a well-focused area of investigation, that of straight-chain alcohols with no side-chain substituents. Notice how the scope and the range of the investigation are very clearly stated. The question is also very clear that it is a data-based investigation, as the database of reference is stated at the end.

When utilizing databases, the sheer amount of available data can obscure the focus and the scope of your investigation and easily take you on a tangent from what you are investigating. It is, therefore, extremely important to limit the range of your investigation and set a very clear boundary on the extent of your investigation. By doing so, you will allow yourself to run a robust analysis of the dataset that can lead to a valid conclusion relevant to your research question.

If you expand the boundary of your investigation too much, then you may fall prey to several *unknown unknowns* – or variables whose influence on your hypothesis you are unaware of – that can and will affect the validity of your conclusion.



Data paralysis: in the words of Winston Churchill: 'too much analysis can lead to paralysis'. It is of high importance to narrow the scope and range of your scientific investigation, no matter the kind of investigation you have decided to pursue. It can be very tempting to do more experiments, collect additional data or explore further avenues of investigation; but there is simply not enough time to do so well. It will eventually become difficult to separate meaningful data from irrelevant data that 'muddy' your analysis, prohibiting you from reaching a meaningful conclusion to your question. Focus on the question at hand instead, and any ideas or observations that you may have had during the investigation that could have been worthy of their own investigation can be included at the end of your work under 'Further Investigation'. It may also help your teacher in designing new experiments or providing ideas to new students the year after.

Bibliography

Hulley, S., Cummings, S., Browner, W., Grady, D. and Newman, T. (2007). *Designing clinical research, 3rd ed.* Philadelphia (PA): Lippincott Williams and Wilkins.

Skills in the study of chemistry

Central to learning chemistry is the application of techniques and gaining experimentation skills. This course is designed to provide a number of activities to enrich your understanding of chemical concepts through experimentation and inquiry. These skills are integrated into the learning throughout the course, as illustrated in the tables that follow.

Tools

Tool 1: Experimental techniques

Chemistry is an experimental science. Through the ages, chemistry emerged from the domain of craftspeople and artisans such as smelters, metallurgists, painters, potters and bakers who were the initial lore-masters of chemistry. Understandings in the fundamentals of chemistry were developed from their experimental knowledge and observations. Technological advancement has allowed the development of increasingly sophisticated instrumentation that enables scientists to collect ever more accurate data and make highly detailed observations to further refine our chemistry models and understandings.

Skill	Description	Section references
Addressing safety of self, others and the environment In the duration of the course, you will be involved in many hands-on and other experimental activities. When in the lab, you must always be aware of the potential risks and hazards associated with the work at hand and always comply with related safety regulations. These risks may be **chemical** due to the nature of the materials used, or **environmental** due to the potential harm that the direct disposal of the materials used, as well as the products formed, can have on the environment and on health. Besides these obvious risks and hazards, an investigation may have ethical implications which may not be as obvious but still need to be taken into consideration.	***Recognize and address relevant safety, ethical or environmental issues in an investigation.***	S1.1.1 S1.4.4 S1.4.5 S2.1.3 S1.5.4 S2.2.9 S2.2.10 S2.3.1 S3.1.10 HL R1.1.2 R1.1.4 R2.1.3 R2.2.1 R2.2.3 R2.2.10 HL R3.1.4 R3.1.6 R3.1.7 R3.1.8 R3.1.13 HL R3.1.14 R3.2.2 R3.2.3 R3.2.16 HL

SKILLS

You should consider the environmental effects of your work in the laboratory and learn safe protocols for the storage, use and disposal of chemicals. Micro-scale chemistry and Green Chemistry can be considered here.

SKILLS

The best sources of information for carrying out risk assessments for the use of chemicals are material safety data sheets (MSDS), which should be available whenever you are handling chemicals. The Laboratory Safety Institute (LSI) has developed useful guidelines on laboratory practice.

Choosing apparatus for carrying out reactions and for accurate measurement involves considerations of safety, efficiency, precision and availability.

SKILLS

Measuring variables Measurement is an important part of chemistry. In the laboratory, you will use different measuring equipment and there will be times when you will need to select the instrument that is most appropriate for your task from a range of possibilities. The conclusions reached from a scientific investigation are only as good as the data collected and the quality of the analysis that follows. For these reasons it is imperative to understand how to accurately measure variables to ensure high-quality data collection and analysis.	***Understand how to accurately measure with an appropriate level of precision:***	
	• mass	S1.4.4 S1.4.5 R1.1.4 R2.1.3 R2.2.1 R2.2.3
	• volume	S1.4.5 S1.5.4 R2.1.3 R2.2.1 R2.2.3
	• time	R2.2.1 R2.2.3 R2.2.10 HL
	• temperature	S1.5.4 R1.1.2 R1.1.4 R2.2.1 R2.2.3
	• length	S2.2.2
	• pH of solution	R2.2.1 R2.2.3 R3.1.4 R3.1.6 R3.1.8 R3.1.13 HL R3.1.14 HL
	• electric current	S2.1.3 S2.2.9 S2.3.1 R2.2.1 R3.1.6
	• electric potential difference	R2.2.3 R3.2.3
Related activities	• Reading an SDS • Common laboratory equipment • Treatment of waste • Measuring mass and volume • Use of a pH meter and universal indicator to measure pH	

Applying techniques There are some techniques that are considered fundamental for any chemistry student. Extended practice and familiarization with these techniques are essential for students in chemistry designing their scientific investigation.	***Show awareness of the purpose and practice of:***	
	• preparing a standard solution	S1.4.5 S2.2.9 R2.2.1
	• carrying out dilutions	S1.4.5
	• drying to constant mass	S1.4.4
	• distillation and reflux	S1.1.1 R3.1.7 S2.2.9
	• paper or thin layer chromatography	S1.1.1 S2.2.10
	• separation of mixtures	S1.1.1 R3.1.7
	• calorimetry	R1.1.2 R1.1.4 R2.2.1
	• acid–base and redox titration	R2.2.1 R2.2.3 R3.1.4 R3.1.6 R3.1.8 R3.2.2 R3.2.3
	• electrochemical cells	R3.2.3 R3.2.16 HL
	• colorimetry or spectrophotometry	S3.1.10 HL R2.2.3
	• physical and digital molecular modelling	S1.5.4 S2.1.3 S2.2.9
	• recrystallization	S.1.1.1
	• melting point determination	S1.1.1 S2.2.9



It is not expected that you will have individual access to all of the equipment specified. During the course you should gain experience of carrying out these processes in small groups, or of using simulations, or observations of demonstrations as needed.

Related activities	• filtering and separating heterogeneous mixtures • preparing solutions • preparing a calibration curve for spectrophotometric determinations • thin-layer chromatography (TLC) in a sample of paracetamol • setting up a reflux and distillation apparatus • preparation of AgI(s) precipitate from aqueous solutions • sublimation of iron and iodine • the heat curve of water • preparation and standardization of aqueous solutions • racing compounds on TLC

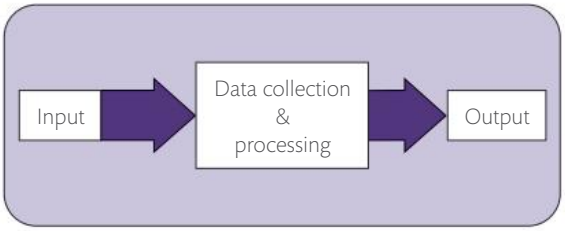
Tool 2: Technology

Chemistry does not only happen on the bench by heating and mixing solutions. A lot of modern chemistry, especially research related to the evaluation of theoretical models, identification of trends in large data sets and/or predictions from large data sets, takes place behind a computer screen. Computational chemistry is a well-established field that finds applications in both theoretical and applied chemistry.

In general, when we want to generate data from models and simulations, the logical path employed is that shown in Figure 1.

Skill	Description	Section references
Applying digital technology to collect data Early analysts relied on their senses and their skills in collecting data but continuous improvement in instrumentation and technology has not only allowed us to explore the world beyond the constraints of our senses but also to collect large datasets in short time with relative ease. Modelling and manipulating data Molecular modelling and prediction of properties	Use sensors.	S1.5.3 R1.1.2 R3.1.4 R3.1.8
	Identify and extract data from databases.	S1.5.3 S2.1.3 S3.1.4
	Generate data from models and simulations.	S1.5.3 S3.1.4 S3.2.3

Applying technology to process data Digital technology can be used not only to generate but also to process data. Whether data are generated/collected digitally or in traditional investigations, they can be analyzed with the help of computers through spreadsheets or more specialized analysis/ modelling software.	Use spreadsheets to manipulate data.	S1.5.3
	Represent data in a graphical form.	S1.5.3 S3.1.4 R3.1.4
	Use computer modelling.	S1.5.3



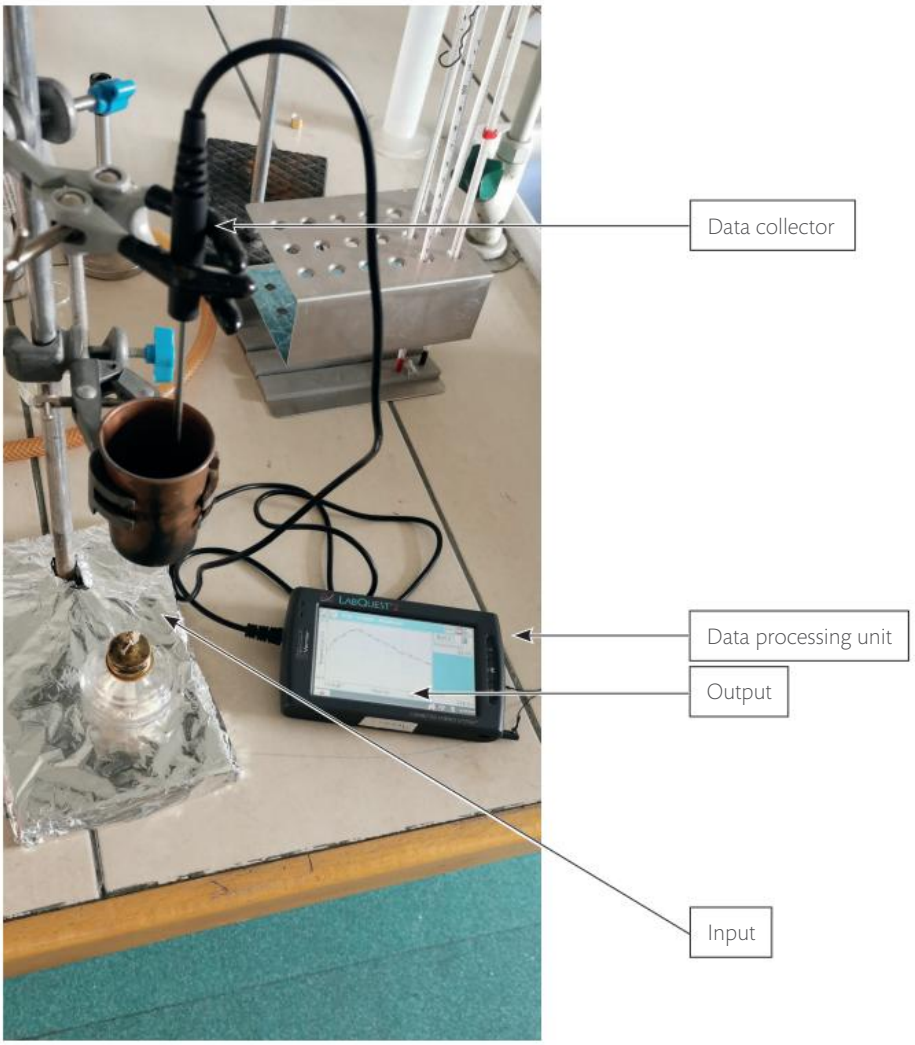


Figure 1 Experimental set-up for calorimetry using a temperature probe for data collection.

Tool 3: Mathematics

It has been stated that a chemist is *someone who can solve a problem you did not know you have.* Chemistry problems are usually of low mathematical complexity in the sense that you do not need advanced mathematics or calculus to solve them, but can rely on simple mathematical operations as itemized below.

The challenging part in chemistry problem solving is, more often than not, understanding what the question is asking and having a good grasp of the underlying concepts at play. Problem-solving strategies will be presented in each topic to help you master this skill.

Skill	Description	Section references
Applying general mathematics Data is the lifeblood of scientists. It may be qualitative, obtained from observations, or quantitative, collected from measurements. Quantitative data are generally more reliable as they can be analyzed mathematically but nonetheless will still suffer from unavoidable uncertainties. This analysis helps identify significant relationships and eliminate outliers. Scientists look for relationships between the key factors in their investigations. The errors and uncertainties in the data must be considered when assessing the reliability of the data. Errors and uncertainties in chemistry	Use basic arithmetic and algebraic calculations to solve problems.	S1.1.1 S1.4.4 S1.4.5 S1.5.3 R1.1.4 R2.2.1 R2.2.3 R2.2.10 HL R3.1.4 R3.1.8
	Carry out calculations involving decimals, fractions, percentages, ratios, reciprocals, exponents.	S1.4.4
	Carry out calculations involving logarithmic functions.	R3.1.4
	HL Carry out calculations involving exponential functions.	S1.3.6 R3.1.4
	Determine rates of change from tabulated data.	R2.2.1
	Calculate mean and range.	Errors and uncertainties
	Use and interpret scientific notation (e.g. 3.5×10^6).	S1.3.6 R3.1.4
	Use approximation and estimation.	S1.4.4
	Appreciate when some effects can be ignored and why this is useful.	TOK – What are the implications of our experimental choices?
	Compare and quote values to the nearest order of magnitude.	Errors and uncertainties
	Understand direct and inverse proportionality, as well as positive and negative correlations between variables.	S1.5.3
	Calculate and interpret percentage change and percentage difference.	Errors and uncertainties
	Calculate and interpret percentage error and percentage uncertainty.	Errors and uncertainties
	Distinguish between continuous and discrete variables.	R2.2.1

<table>
<tr>
<td>Using units, symbols and numerical values
The measurement of a physical property is always expressed as:
physical property = numerical value × unit
Units are treated in the same way that any algebraic symbol is used in calculations.
SI stands for Système International d'Unités, an internationally agreed system of units established by the International Bureau of Weights and Measures and endorsed by IUPAC.
The system, which is metric in nature, has 7 base units from which all other units are derived.
<table><tr><td>metre</td><td>m</td><td>length</td></tr><tr><td>kilogram</td><td>kg</td><td>mass</td></tr><tr><td>second</td><td>s</td><td>time</td></tr><tr><td>ampere</td><td>A</td><td>electric current</td></tr><tr><td>kelvin</td><td>K</td><td>temperature</td></tr><tr><td>mole</td><td>mol</td><td>amount of substance</td></tr><tr><td>candela</td><td>cd</td><td>luminous intensity</td></tr></table>This book contains some updates to the definitions of units agreed by IUPAC, now based on established and timeless universal constants.</td>
<td>Apply and use SI prefixes and units.
Identify and use symbols stated in the guide and the data booklet.
Express quantities and uncertainties to an appropriate number of significant figures or decimal places.</td>
<td>S1.5.3
R1.1.4
Errors and uncertainties
S1.3.6</td>
</tr>
<tr>
<td>Processing uncertainties
An uncertainty range applies to any experimental value. Some pieces of apparatus state the degree of uncertainty; in other cases, you will have to make a judgement. Appropriate consideration of the impact of measurement uncertainty on the analysis is a requirement in any experimental process.
The experimental error in a result is the difference between the recorded value and the generally accepted or literature value. Errors can be categorized as random or systematic.</td>
<td>Understand the significance of uncertainties in raw and processed data.
Record uncertainties in measurements as a range (±) to an appropriate precision.
Propagate uncertainties in processed data, in calculations involving addition, subtraction, multiplication, division and (HL only) exponents.
Express measurement and processed uncertainties – absolute, fractional (relative), percentage – to an appropriate number of significant figures or level of precision.
Apply the coefficient of determination (R^2) to evaluate the fit of a trend line or curve.</td>
<td>Errors and uncertainties</td>
</tr>
</table>

Graphical representations of data are widely used in areas such as finance and climate modelling, and can be the basis of predicted trends.

Graphing Data collected from investigations are often presented in graphical form. This provides a pictorial representation of how one quantity is related to another. A graph is also a useful tool to assess errors as it identifies data points which do not fit the general trend and so gives another measure of the reliability of the data.	Sketch graphs, with labelled but unscaled axes, to qualitatively describe trends.	R2.2.1 R2.2.10
	Construct tables, charts and graphs for raw and processed data including bar charts, histograms, scatter graphs and line and curve graphs.	R2.2.3 R2.2.10 HL
	Plot linear and non-linear graphs showing the relationship between two variables with appropriate scales and axes.	S1.4.5 R2.2.1 R2.2.3 R2.2.10 HL
	Draw lines or curves of best fit.	R2.2.3 R2.2.10 HL
	Interpret features of graphs including gradient, changes in gradient, intercepts, maxima and minima, and areas.	S1.4.5 R2.2.1 R2.2.3 R2.2.10 HL R3.1.8
	Draw and interpret uncertainty bars.	Errors and uncertainties
	Extrapolate and interpolate graphs.	S1.4.5 R2.2.1 R2.2.3 R2.2.10 HL R3.1.8
Related activities	Coffee-cup calorimeter Comparing the enthalpy of isopropanol and ethanol Finding the enthalpy change of hydration Comparing the enthalpy of pentane and hexane. Synthesis and purification of Aspirin HL Investigating rates of reaction HL Determination of the concentration of ethanoic acid in vinegar Determination of the level of rust in a rusted nail Redox titrations	

Inquiry process

The components of the Inquiry cycle and their links in the book are presented below, and they are individually discussed in more detail in the Internal Assessment chapter of this book.

Inquiry 1: Exploring and designing

Skill	Description	Section references
Exploring	Demonstrate independent thinking, initiative and insight.	R1.1.4 R2.1.3
	Consult a variety of sources.	
	Select sufficient and relevant sources of information.	
	Formulate research questions and hypotheses.	
	State and explain predictions using scientific understanding.	
Designing	Demonstrate creativity in the designing, implementation and presentation of the investigation.	
	Develop investigations that involve hands-on laboratory experiments, databases, simulations, modelling.	
	Identify and justify the choice of dependent, independent and control variables.	
	Justify the range, interval and quantity of measurements.	
	Design and explain a valid methodology.	
	Pilot methodologies.	
Controlling variables	***Appreciate when and how to:***	
	calibrate measuring apparatus including sensors	
	maintain constant environmental conditions of reaction systems	
	insulate against heat loss/gain	

SKILLS

Laboratory work usually involves 'hands-on' experimental work, which leads to the collection of primary data. These are data obtained directly, such as by measuring changes in a variable during an experiment or by collecting information through surveys or observations. Secondary data refer to data obtained from another source, such as via reference material or third-party results. The source of secondary data must always be cited in a report. Analysis of secondary data can also form an important part of experimental work.

Inquiry 2: Collecting and processing data

Skill	Description	Section references
Collecting data	Identify and record relevant qualitative observations.	S1.3.2 S1.4.5 S1.5.4 S2.1.3 S2.2.9 S2.3.1 S3.1.4 S3.1.10 HL R1.1.2 R1.1.4 R1.3.2 R2.1.3 R2.2.1 R2.2.10 R3.1.6 R3.1.14 HL R3.2.2 R3.2.3
	Collect and record sufficient relevant quantitative data.	
	Identify and address issues that arise during data collection.	
Processing data	Carry out sufficient, relevant and accurate data processing.	
Interpreting results	Interpret qualitative and quantitative data.	
	Interpret diagrams, graphs, and charts.	
	Identify, describe, and explain patterns, trends and relationships.	
	Identify and justify the removal or inclusion of outliers in data (no mathematical treatment required).	
	Assess accuracy, precision, reliability and validity.	

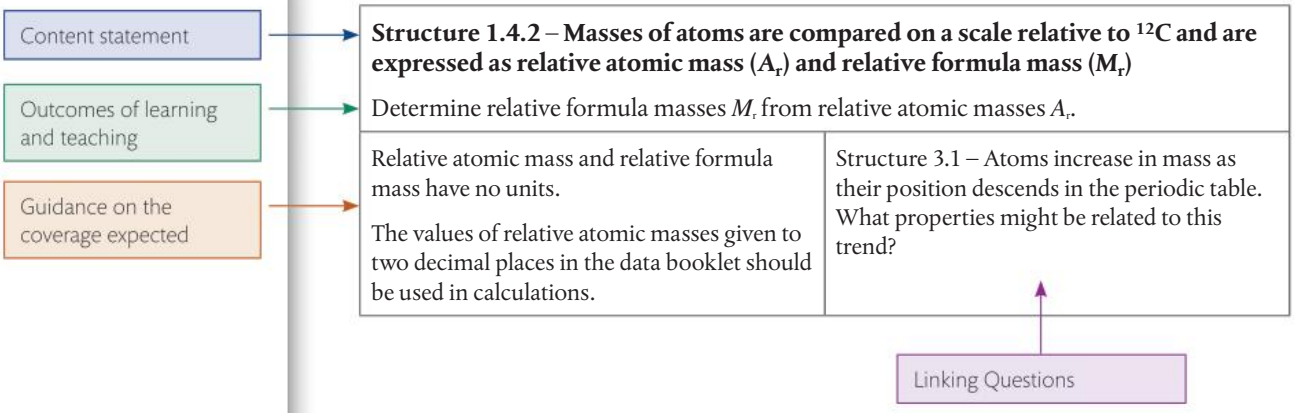
Inquiry 3: Concluding and evaluating

Skill	Description	Section references
Concluding	Interpret processed data and analysis to draw and justify conclusions.	R1.1.4 R2.1.3 R2.2.3
	Compare the outcome of an investigation to the accepted scientific context.	
	Relate the outcome of an investigation to the stated research question or hypothesis.	
	Discuss the impact of uncertainties on the conclusions.	
Evaluating	Evaluate hypotheses.	
	Identify and discuss sources and impacts of random and systematic errors.	
	Evaluate the implications of methodological weaknesses, limitations, and assumptions on conclusion.	
	Explain realistic and relevant improvements to an investigation.	

Strategies for success in IB chemistry

During the course

Take responsibility for your own learning. As you finish your study of a topic, it is a really good time to check back through the numbered Understandings for each chapter and make sure that you are comfortable with all the expectations.
Each Understanding is shown as a three-part box, for example:



Spend extra time on parts where you are less confident of your knowledge and understanding. Use additional sources of information such as online simulations, videos, other books and journals to help spark your curiosity and grasp the wider contexts of the topic. The more you do, the more you will enjoy the course and the more successful you will be.

As you learn more about each topic, you should be able to answer the Guiding Question at the start of each chapter with increasing depth. For example from Structure 1.1:

Guiding Question

How can we model the particulate nature of matter?

Use the Guiding Question revisited at the end of each chapter as a checklist summary of what has been covered and a prompt for more work if anything is not clear. For example, from Structure 1.2:

Guiding Question revisited

How do the nuclei of atoms differ?

The Linking Questions help you to find interconnections between different parts of the course, linking the concepts in different topics. Brief answers to these questions are given in the text, and you can also try to make up your own questions to explore the connections between different parts of the course.

Structure 2.4 – Why are some substances solid while others are fluid under standard conditions?

Note that laboratory work and other skills are an integral part of the course to support your learning of the topics. These skills are assessed in both the Internal Assessment and parts of the External Assessment.

Make sure that you have completed all the exercises at the end of each Understanding and checked your answers in the eBook. The practice questions at the end of each chapter are mostly questions from previous years' IB exam papers, so they are a very good way of testing yourself at the end of each topic. The answers and guidance used by examiners in marking the papers are also given in the eBook.

SKILLS

The halogen–halide reactions can be investigated in the lab. Full details of how to carry out this experiment with a worksheet are available in the eBook.

Exercise

Q1. What increases **in equal steps of one** from left to right in the periodic table for the elements sodium to argon?

A the relative atomic mass

B the number of occupied electron energy levels

C the number of neutrons in the most common isotope

D the number of electrons in the atom

Practice questions

1. Which is a conjugate Brønsted–Lowry acid–base pair?

$$CH_3COOH(aq) + H_2O(l) \rightarrow CH_3COO^-(aq) + H_3O^+(aq)$$

A CH_3COO^- / H_3O^+ **B** H_2O / CH_3COO^-

C H_2O / H_3O^+ **D** CH_3COOH / H_2O

Preparing for the examination

Organize your time for review well ahead of the exam date on a topic-by-topic basis. While you are studying make sure that you test yourself as you go – being able to recognize the content on the page is very different from being able to produce it yourself on blank paper. Effective revision generally involves using lots of scrap paper for testing your knowledge and understanding. Practise writing balanced equations, and drawing diagrams, structural formulas and so on.

Remember that you need to cover the work from the entire course. So try to make your studying cumulative; this means building up a connected picture of knowledge and understanding by recognizing how the topics are interrelated and reinforce the same concepts. It can feel a bit like doing a jigsaw, where the more you have done, the easier it gets to add in the new pieces.

There is no choice of questions in the exam so make sure that you do not miss anything out. When you have finished your review of a particular topic, it is a good idea to test yourself with IB questions and time yourself according to how much time you are given for each type of question.

In the examination

The External Assessment accounts for 80% of the final grade awarded for Higher Level Chemistry. The assessment consists of two exam papers, which are scheduled separately, and total 4.5 hours.

	Duration / hours	Total marks	Description of examination	% of total mark
Paper 1 Paper 1A Paper 1B	2	75	Paper 1 is presented as two separate booklets, 1A and 1B, which are both to be completed within the allocated time, with no break between. • 40 multiple-choice questions • data-based questions • questions on experimental work	**36**
Paper 2	2.5	90	• short-answer and extended-response questions	**44**

In both Paper 1 and Paper 2:

- calculators may be used
- a clean copy of the IB data booklet will be provided
- all questions are compulsory
- questions may test a general understanding and application of the nature of science (NOS)
- you are given 5 minutes reading time at the start of the exam when you can look at the questions but are not allowed to start writing.

Guidance for the exam papers

At the start of the exam, use the 5 minutes reading time to turn through all the pages of the exam booklets, to make sure you are aware of the full extent of the paper.

In Paper 1 you are responsible for the division of time between 1A and 1B. As the two sections are worth similar numbers of marks, you should aim to spend approximately 1 hour on each part.

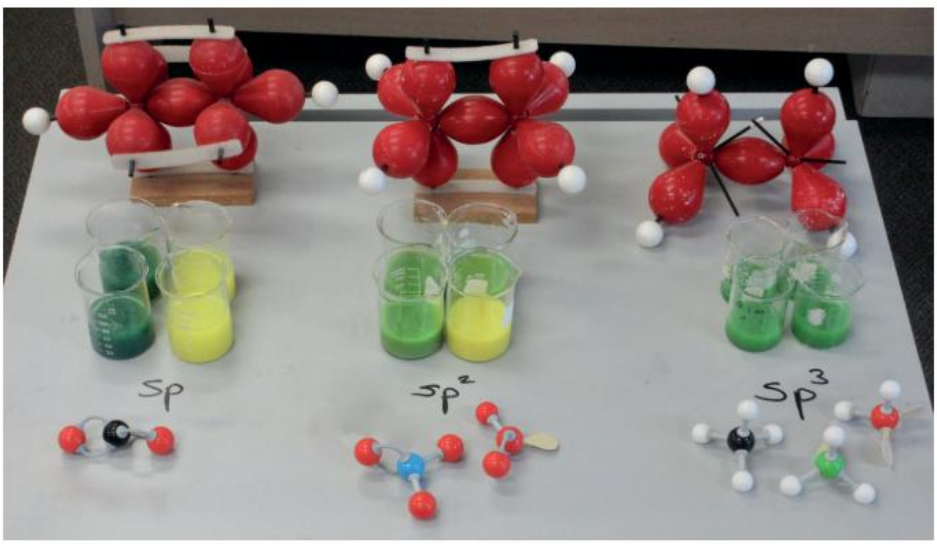
Multiple choice questions (Paper 1A)

- There is no penalty for wrong answers in multiple-choice questions, so make sure that you do not leave any blanks.
- Read *all* the given answers A–D for each question. It is likely that more than one answer is close to being correct but you must choose the best answer available.

Written response questions (Paper 1B and Paper 2)

- Note the number of marks given in parentheses for each part of a question and use this to guide you in the detail required. In general, one mark represents one specific fact or answer.

- Take note of the command terms used in the questions as these also give an important clue about exactly what is required. It is a good idea to underline the command terms on the question paper to help you focus your answer.
- Sometimes questions include several different instructions, and it can be easy to miss a part of the question; avoid this by crossing off the parts of the question on the paper as you go so you can see what you might have missed.
- Remember these questions are testing your knowledge and understanding of *chemistry,* so be sure to give as much relevant detail as you can, with equations and specific examples where possible. You can only be given credit for what you write down so do not assume anything – show off!
- In calculations, it is essential that you show all your workings very clearly. Also pay attention to significant figures and include units always. When a question has several parts which all follow on from each other, you will not be penalized more than once for the same mistake. So, for example, if you make a mistake in part (a) of a question, but then use that wrong answer correctly in part (b), you will still get full marks for part (b) – *provided your method is clear*. So never give up!
- Be careful with your writing of formulas and structures. Notation in chemistry is very picky, and you need to be precise with upper vs lower case letters, the exact positions of bonds between atoms etc. For example, Co means something completely different from CO; a hydroxyl group is —OH, not OH—.



▲ Understanding of concepts in chemistry, such as hybridization, is often helped by the use of models and visual analogies. Can you identify the molecules and explain the bond angles of the models in the foreground?

Advice on the Extended Essay

The Extended Essay is a compulsory part of the IB Diploma Programme. It is an independent 40-hour research project in an IBDP subject of your choice. The final essay, of up to 4000 words of formally presented, structured writing, is the longest assignment of the two-year programme. Although this may sound daunting, it is a great opportunity to investigate a topic of particular interest and produce knowledge that is new to you. It shares with the theory of knowledge (TOK) course a focus on interpreting and evaluating evidence and constructing reasoned arguments. The marks awarded for the Extended Essay and TOK are combined to give a maximum of three bonus points.

An Extended Essay in chemistry must have a clear chemical emphasis and deal with chemical reactions, chemical bonding or chemical analysis. Sometimes you need to be careful that it is not more closely related to another subject. For example, a chemistry Extended Essay in an area such as biochemistry will be assessed on its chemical and not its biological content. It should include chemical principles and theory.

Some advice

Why do an Extended Essay in chemistry?

If chemistry is your favourite subject and you want to study it at university, an Extended Essay in chemistry can support your university application as it shows that you have a genuine interest in the subject. Most chemistry essays are from Higher Level students, but this is not a requirement, and many Standard Level students have submitted excellent essays. This is something you can discuss with your supervisor.

Possible approaches

There are a number of possible approaches to an Extended Essay in chemistry.

Experimental	Design and implementation of an experimental procedure and the collection and analysis of the data.
Data-based	Location and extraction of raw or processed secondary data which are analyzed and evaluated.
Theoretical or computer simulation	Development of a quantitative or semi-quantitative model. Perhaps best done in combination with another approach.
Literature or survey	The essay must have a firm chemical basis. Essays written at the level of a newspaper or news magazine article are unlikely to achieve a high mark.
Combination	Some combination of the approaches listed above.

Although it is not a requirement, the best chemistry Extended Essays tend to be those based on experiments performed in a school laboratory. It is easier to have personal

input if you are able to plan and modify your experimental procedures and use familiar equipment. If the investigation is undertaken in an external laboratory, you must show clearly that you understand the methods and materials, and describe your role in collecting the data.



The best chemistry Extended Essays are often based on experiments carried out in a school laboratory.

The chemistry Extended Essay and the Internal Assessment

An Extended Essay (EE) is different from the Internal Assessment (IA) and is not a lab report. The IA is more likely to be directly related to syllabus content, whereas the EE could explore aspects of chemistry not covered in the syllabus. An EE must construct a theoretical framework for the underlying chemistry of the chosen topic, whereas the IA task focuses on the application of the scientific method to a problem of interest and will only include some background information. The EE explicitly assesses your ability to analyze and evaluate scientific arguments. The assessment criteria for the two tasks are distinct. The IA is discussed in the Internal Assessment chapter.

Before you start

Read a copy of the subject-specific details of an Extended Essay in chemistry, including the assessment criteria. Read some previous essays and try to identify their strengths and weaknesses. Draw up a list of possible research questions including the techniques you would use to address them. Many of the best essays involve investigations of relatively simple phenomena using apparatus and materials found in most school laboratories.

You may find it useful to consider some of the following techniques when planning your research; it is often appropriate to use a combination of two or more of these approaches:

- titration: acid–base or redox
- chromatography: paper, partition, thin-layer, column
- electrophoresis
- spectrophotometry
- measuring mass or volume changes
- calorimetry
- qualitative and quantitative analysis
- separation and purification techniques in organic chemistry
- use of data-logging probes for some of the above.

The research question

Spend time working out your research question. This is the key to a successful Extended Essay as the overall quality of an essay often depends on the quality of the research question. You should choose a topic that interests you as you will be spending 40 hours on it! Do not choose anything that is too complicated or difficult. Your question must be sharply focused and capable of being addressed in 40 hours and 4000 words. For example, *The ratio of oxygen and chlorine produced at the anode during the electrolysis of different concentrated solutions of aqueous sodium chloride solution* is better than *The electrolysis of salt*. It is likely that your research question will be modified during the process as you complete your research. The crucial thing is that your essay is a true analysis of the research question. You need to directly address the research question in your conclusion.

The research process

- Safety is a priority. Do not do anything in the laboratory without first checking with your supervisor.
- If your approach is experimental make sure that you can produce results that you can analyze and evaluate in detail.
- Use a range of resources to find out what others have done in the area. Textbooks should never be the only source of information. Do not spend all your time online! Use your school and other local libraries if possible. Peer-reviewed articles in scientific journals are the most reliable sources.
- Keep written records of everything that you do and make a note of all references, including the date when internet sites were accessed so that you can build up your footnotes and bibliography as you go along.
- Record all experimental data, including the dates when the experiments were performed and any uncertainties in your measurements. In your preliminary investigations, write down any problems and challenges you encounter and record any modifications. Use your imagination to design new equipment if necessary.

Writing the essay

- Make sure that you address your research question and the Extended Essay assessment criteria.
- Include explanations of any theory not covered in the IB subject guide, including the chemistry of any specialized techniques you have used.
- Use the appropriate chemical language and make sure that all chemical equations are balanced.
- Include sufficient details of any experimental procedures to allow others to repeat the work.
- Check any calculations and make sure that all experimental data are presented correctly including units and significant figures.
- Discuss the limitations of the experimental method and any systematic errors.
- Consider any questions that are unresolved at the end of your research and suggest new questions and areas for possible further investigation.
- Let your enthusiasm and interest in the topic show and emphasize clearly your own personal input.
- Ensure that your word count is close to 4000. You will often find you can cut quite a number of words as you polish your essay at the end.

After completing the essay

Check and proofread the final version carefully.

Use the assessment criteria to grade your essay. Are you satisfied with the grade you award yourself?

Assessment

An excellent Extended Essay

The grade descriptor for an excellent Extended Essay is as follows:

Demonstrates effective research skills resulting in a well-focused and appropriate research question that can be explored within the scope of the chosen topic; effective engagement with relevant research areas, methods and sources; excellent knowledge and understanding of the topic in the wider context of the relevant discipline; the effective application of source material and correct use of subject-specific terminology and/or concepts further supporting this; consistent and relevant conclusions that are proficiently analyzed; sustained reasoned argumentation supported effectively by evidence; critically evaluated research; excellent presentation of the essay, whereby coherence and consistency further support the reading of the essay; and present and correctly applied structural and layout elements. Engagement with the process is conceptual and personal, key decision making during the research process is documented, and personal reflections are evidenced, including those that are forward-thinking.

The assessment criteria

All Extended Essays are assessed according to five criteria, A–E. Each criterion is made up of a series of strands that act as the core focus for that criterion. The tables in the following section give a checklist to help you achieve the highest level for each criterion. The notes in italics refer specifically to essays in chemistry.

A. Focus and method

Strand	Checklist
Topic	Is the topic communicated accurately and effectively? Is the research topic clearly identified and explained? Is the purpose and focus of the research clear and appropriate? *The topic for study may be generated from the chemistry course or may relate to a subject area beyond the syllabus content.*
Research question	Is the research question focused and clearly stated in the introduction? Does the research question address an issue appropriately connected to the discussion in the essay?
Methodology	Have an appropriate range of relevant source(s) and/or method(s) been selected? Is there evidence of an effective and informed selection of sources and/or methods? *You must research the existing literature on the topic and choose an appropriate methodology to pursue the investigation. If practical work is undertaken, the rationale for choosing the procedure should be clearly explained.*

Do	Don't
✓ Cite the source of the method used. ✓ Discuss possible alternative methods (experimental or otherwise) and justify your choice. ✓ Discuss any modifications you have made to a standard procedure. ✓ Avoid repetition.	✗ State multiple research questions. ✗ Make statements that are not justified including unsupported generalizations. ✗ Include superficial, irrelevant or unresearched background information.

B. Knowledge and understanding

Strand	Checklist
Context	Are the source materials clearly relevant and appropriate to the research question? Is the knowledge of the topic clearly demonstrated and coherent? Are the sources used effectively with understanding? *Literature cited should generally come from acknowledged scientific sources.*
Communication	Are subject-specific terminology and concepts used accurately and consistently? Does the essay demonstrate effective knowledge and understanding? *Chemical nomenclature and terminology should be used consistently and effectively. This includes relevant chemical and structural formulas, balanced equations with state symbols, reaction mechanisms, significant figures and SI units.*

Do	Don't
✓ Maintain a consistent linguistic style throughout the essay. ✓ Select a range of sources. ✓ Explain the chemistry behind the techniques used. ✓ Process data correctly and show sample calculations.	✗ Give unnecessary explanations for basic chemistry.

C. Critical thinking

Strand	Checklist
Research	Is the research appropriate to the research question? Is the research consistently relevant? Does the research support the argument?
Analysis	Is the research analyzed effectively and clearly focused on the research question? Are conclusions to individual points of analysis effectively supported by the evidence? *Analysis often includes mathematical transformations, tables of processed data and graphs. Do not use statistical analysis unless it adds to the chemistry aspect of the question. The analysis should support and clarify the argument leading to the conclusion.*
Discussion and evaluation	Is an effective and focused reasoned argument developed from the research? Is the conclusion reflective of the evidence presented? Is the reasoned argument well-structured and coherent? Is the research critically evaluated? *Unresolved issues should be identified, and suggestions made as to how these could be explored further. Any weaknesses in experimental design or systematic errors should be identified. The quality, balance and quantity of sources should be evaluated. The validity and reliability of any data, including measurement uncertainties, should be evaluated and discussed.*

Do	Don't
✓ Consider different approaches or counterarguments. ✓ Question the reliability of any sources used. ✓ Include any experimental uncertainties. ✓ Discuss any assumptions made in your arguments. ✓ Address the research question in the conclusion.	✗ Write a descriptive or narrative account. ✗ Introduce new material into the conclusion that has not been referred to earlier. ✗ Suggest superficial or unrealistic areas for further investigation.

D. Presentation

Strand	Checklist
Structure	Is the structure of the essay appropriate in terms of the expected conventions for chemistry, the topic, and the argument? *Large tables of raw data are best included in an appendix, where they should be carefully labelled. Tables of processed data should be designed to clearly display the information in the most appropriate form. Graphs or charts drawn from the analyzed data should be selected to highlight only the most pertinent aspects related to the argument. Too many graphs, charts and tables will distract from the overall quality of the communication.*
Layout	Do the structure and layout support the reading, understanding and evaluation of the essay? *If an experimental method is long and complex, you may include a summary of the methods in the body of the essay but be careful to ensure that the summary contains all elements that contribute to the quality of the investigation.*

Do	Don't
✓ Acknowledge any unoriginal material. ✓ Label diagrams clearly. ✓ Use the appendix to show materials, unsuccessful trials, risk assessment, preparation of solutions, etc.	✗ Use superficial diagrams or images.

E. Engagement

Strand	Checklist
Research focus	Are your reflections on decision-making and planning evaluative? Do your reflections communicate a high degree of engagement? Do your reflections demonstrate initiative and/or creativity?
Planning and process	Do you discuss the challenges you experienced in the research process and include any actions taken or new ideas generated? *Reflections include the relative success of approach and strategies chosen, and the approaches to learning skills you developed during the process.*

Do	Don't
✓ Discuss the challenges you faced and details of how you overcame them. ✓ Include questions that emerged as a result of the research. ✓ Discuss how your understandings developed or changed during the process.	✗ Give a simple descriptive account of what you have done.

Bibliography and references

It is required that you acknowledge all sources of information and ideas in an approved academic manner. Your supervisor or school librarian will be able to give you advice on which format to follow.

World studies Extended Essays

As you think about topics for an Extended Essay in chemistry, it may be that you find an area of current global interest which overlaps with another subject. In this case, it may be appropriate to submit the essay as world studies, which is a separate IB Extended Essay subject. An essay in world studies must have the following characteristics:

- it must focus on an issue of contemporary global significance
- it must involve an in-depth interdisciplinary study, making reference to at least two IB subjects.

The most successful topics reveal connections between specific or local places, people, phenomena or experiences and the larger global framework in which they take place.



Remember to use a range of resources including the internet and any libraries available.

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