ACADEMIC ASSOCIATES

STUDY GUIDE

CHEMISTRY

YEAR 12 ATAR COURSE – UNITS 3 & 4

REVISED EDITION

Michael Lucarelli & David Proctor

Periodic Table of the Elements

Alkali Metals (group 1) · *Alkali Earth Metals* (group 2) · TRANSITION ELEMENTS (groups 3–12) · *Halogens* (group 17) · *Noble Gases* (group 18)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H Hydrogen 1.008																	2 He Helium 4.003
3 Li Lithium 6.94	4 Be Beryllium 9.01											5 B Boron 10.81	6 C Carbon 12.01	7 N Nitrogen 14.01	8 O Oxygen 16.00	9 F Fluorine 19.00	10 Ne Neon 20.18
11 Na Sodium 22.99	12 Mg Magnesium 24.31											13 Al Aluminium 26.98	14 Si Silicon 28.09	15 P Phosphorus 30.97	16 S Sulfur 32.06	17 Cl Chlorine 35.45	18 Ar Argon 39.95
19 K Potassium 39.10	20 Ca Calcium 40.08	21 Sc Scandium 44.96	22 Ti Titanium 47.87	23 V Vanadium 50.94	24 Cr Chromium 52.00	25 Mn Manganese 54.94	26 Fe Iron 55.85	27 Co Cobalt 58.93	28 Ni Nickel 58.69	29 Cu Copper 63.55	30 Zn Zinc 65.38	31 Ga Gallium 69.72	32 Ge Germanium 72.63	33 As Arsenic 74.92	34 Se Selenium 78.97	35 Br Bromine 79.90	36 Kr Krypton 83.80
37 Rb Rubidium 85.47	38 Sr Strontium 87.62	39 Y Yttrium 88.91	40 Zr Zirconium 91.22	41 Nb Niobium 92.91	42 Mo Molybdenum 95.95	43 Tc Technetium (98)	44 Ru Ruthenium 101.1	45 Rh Rhodium 102.9	46 Pd Palladium 106.4	47 Ag Silver 107.9	48 Cd Cadmium 112.4	49 In Indium 114.8	50 Sn Tin 118.7	51 Sb Antimony 121.8	52 Te Tellurium 127.6	53 I Iodine 126.9	54 Xe Xenon 131.3
55 Cs Caesium 132.9	56 Ba Barium 137.3	57 La Lanthanum 138.9	72 Hf Hafnium 178.5	73 Ta Tantalum 180.9	74 W Tungsten 183.8	75 Re Rhenium 186.2	76 Os Osmium 190.2	77 Ir Iridium 192.2	78 Pt Platinum 195.1	79 Au Gold 197.0	80 Hg Mercury 200.6	81 Tl Thallium 204.4	82 Pb Lead 207.2	83 Bi Bismuth 209.0	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
87 Fr Francium (223)	88 Ra Radium 226.0	89 Ac Actinium (227)	104 Rf Rutherfordium 101.1	105 Db Dubnium (281)	106 Sg Seaborgium (271)	107 Bh Bohrium (272)	108 Hs Hassium (270)	109 Mt Meitnerium (276)	110 Ds Darmstadtium (281)	111 Rg Roentgenium (280)	112 Cn Copernicium (285)	113 Nh Nihonium (286)	114 Fl Flevorium (289)	115 Mc Moscovium (289)	116 Lv Livermorium (292)	117 Ts Tennessine (294)	118 Og Oganesson (294)

- Solid
- Liquid (at 25°)
- Gas
- Synthetically prepared

Key:

6 — *Atomic Number*
C — *Symbol*
Carbon — *Element Name*
12.01 — *Relative Atomic Mass (Atomic weight)*

R A R E   E A R T H S   (L A N T H A N I D E S)

58 Ce Cerium 140.1	59 Pr Praesodymium 140.9	60 Nd Neodymium 144.2	61 Pm Promethium (145)	62 Sm Samarium 150.4	63 Eu Europium 152.0	64 Gd Gadolinium 157.3	65 Tb Terbium 158.9	66 Dy Dysprosium 162.5	67 Ho Holmium 164.9	68 Er Erbium 167.3	69 Tm Thulium 168.9	70 Yb Ytterbium 173.1	71 Lu Lutetium 175.0
90 Th Thorium 232.0	91 Pa Protactinium 231.0	92 U Uranium 238.0	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

A C T I N I D E S

( ) = mass number of the isotope with the longest half life

Atomic weights from data published by IUPAC Commission on Atomic Weights 2018

ACADEMIC ASSOCIATES

WACE STUDY GUIDE

CHEMISTRY

YEAR 12 ATAR COURSE

Michael Lucarelli & David Proctor

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About the Author

Michael Lucarelli is a science educator, author and publisher, who has held the position of Head of Physical Sciences in Western Australian Government senior high schools. Mike founded Academic Associates and is the author of several successful educational resources.

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TO THE STUDENT

The purpose of this guide is to assist students in their preparation for tests and examinations in the new ATAR Chemistry course for Units 3 and 4. The structure of the topics will allow students to use the book throughout the year.

The guide closely adheres to the W.A. School Curriculum and Standards Authority ATAR syllabus. Essential theory is interwoven with revision exercises so that students will be able to actively review core theory and concepts.

Science Understanding

Essential core theory for each topic of Science Understanding is covered clearly and in detail. Illustrations and worked examples are used extensively to assist students in their learning. Throughout each chapter, questions and exercises are integrated with theory to help students clarify and consolidate their understanding of new concepts.

Review questions at the end of each chapter provide a wide range of problems including a more challenging 'for the experts' contextual question. All questions and review exercises have detailed answers to provide students with immediate feedback and a means of enhancing their progress.

Chemistry Calculations

Chemistry calculations are an important part of the Chemistry course and these have been treated in detail and included within each relevant section. Worked examples are included to assist students in developing their skills in this area. The review questions and solutions also provide many opportunities for further independent learning.

Trial Tests

Trial tests for each major topic provide an ideal means of self assessment. The style and structure of these tests is similar to that of the current ATAR examination. They contain a multiple choice section and a short and extended answer section. The marks allocated for each of the sections also reflect the weightings proposed by the SCSA for the examinations.

Chemistry is a most interesting and an enjoyable science to study. The practical work, in particular, holds a fascination for students. We hope that this study guide will help students to better understand the concepts they will encounter and to achieve greater success in the subject.

Michael Lucarelli and David Proctor

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UNIT 4

INTRODUCTION

SYLLABUS CHECKLIST

Please note: *The Syllabus checklist below lists only the Science as a Human Endeavour and Science Understanding sections of the Chemistry Year 12 ATAR syllabus as at the time of printing. For a more detailed and current syllabus, please check with your school or the School Curriculum and Standards Authority.*

Unit 3 – Equilibrium, acids and bases, and redox reactions

SCIENCE AS A HUMAN ENDEAVOUR

Chemical equilibrium systems

Levels of carbon dioxide in the atmosphere are rising and have a significant impact on global systems, including surface temperatures. The increasing level of carbon dioxide in the atmosphere causes more carbon dioxide to dissolve in the ocean producing carbonic acid and leading to increased ocean acidity. This is predicted to have a range of negative consequences for marine ecosystems such as coral reefs. Calcification is the process which results in the formation of calcium carbonate structures in marine organisms. Acidification shifts the equilibrium of carbonate chemistry in seawater, decreasing the rate and amount of calcification among a wide range of marine organisms. The United Nations Kyoto Protocol and the Intergovernmental Panel on Climate Change aim to secure a global commitment to reducing greenhouse gas emissions over the next few decades.

Science Understanding

- collision theory can be used to explain and predict the effects of concentration, temperature, pressure, the presence of catalysts and surface area of reactants on the rates of chemical reactions
- chemical systems include physical changes and chemical reactions and may be open (which allow matter and energy to be exchanged with the surroundings) or closed (which allow energy, but not matter, to be exchanged with the surroundings)
- observable changes in chemical reactions and physical changes can be described and explained at an atomic and molecular level
- over time, in a closed system, reversible physical and chemical changes may reach a state of dynamic equilibrium, with the relative concentrations of products and reactants defining the position of equilibrium
- the characteristics of a system in dynamic equilibrium can be described and explained in terms of reaction rates and macroscopic properties
- the reversibility of chemical reactions can be explained in terms of the activation energies of the forward and reverse reactions
- the effect of changes of temperature on chemical systems initially at equilibrium can be predicted by considering the enthalpy changes for the forward and reverse reactions; this can be represented on energy profile diagrams and explained by the changes in the rates of the forward and reverse reactions
- the effects of changes in concentration of solutions and partial pressures of gases on chemical systems initially at equilibrium can be predicted and explained by applying collision theory to the forward and reverse reactions

- the effects of changes in temperature, concentration of species in solution, partial pressures of gases, total volume and the addition of a catalyst on equilibrium systems can be predicted using Le Châtelier's Principle
- equilibrium law expressions can be written for homogeneous and heterogeneous systems; the equilibrium constant (K), at any given temperature, indicates the relationship between product and reactant concentrations at equilibrium
- the relative amounts of reactants and products (equilibrium position) can be predicted qualitatively using equilibrium constants (K_c)

SCIENCE AS A HUMAN ENDEAVOUR

Acids and bases

Models and theories are contested and refined or replaced when new evidence challenges them, or when a new model or theory has greater explanatory scope. Davy initially proposed that acids were substances that contained replaceable hydrogen (hydrogen that could be partly or totally replaced by metals) and bases were substances that reacted with acids to form salts and water. The Arrhenius model, which includes only soluble acids and bases, identified acids as substances which produce hydrogen ions in solution and bases as substances which produce hydroxide ions in solution. Subsequently, the Brønsted-Lowry model describes acid-base behaviour in terms of proton donors and proton acceptors. This approach includes a wider range of substances and can be more broadly applied.

Science Understanding

- acids are substances that can act as proton (hydrogen ion) donors and can be classified as monoprotic or polyprotic, depending on the number of protons available for donation
- the strength of acids is explained by the degree of ionisation at equilibrium in aqueous solution which can be represented by chemical equations and acidity constants (K_a)
- the relationship between acids and bases in equilibrium systems can be explained using the Brønsted-Lowry model and represented using chemical equations that illustrate the transfer of protons between conjugate acid-base pairs
- the hydrolysis of salts of weak acids and weak bases can be represented using equations; the Brønsted-Lowry model can be applied to explain the acidic, basic and neutral nature of salts derived from bases and monoprotic and polyprotic acids
- buffer solutions are conjugate in nature and resist changes in pH when small amounts of strong acid or base are added to the solution; buffering capacity can be explained qualitatively; Le Châtelier's Principle can be applied to predict how buffers respond to the addition of hydrogen ions and hydroxide ions
- • water is a weak electrolyte; the self-ionisation of water is represented by $K_w = [H^+][OH^-]$ where $K_w = 1.0 \times 10^{-14}$ at 25°C
- K_w can be used to calculate the concentration of hydrogen ions or hydroxide ions in solutions of strong acids or bases
- the pH scale is a logarithmic scale and the pH of a solution can be calculated from the concentration of hydrogen ions using the relationship $pH = -\log_{10} [H^+]$
- acid-base indicators are weak acids, or weak bases, in which the acidic form is a different colour from the basic form
- volumetric analysis methods involving acid-base reactions rely on the identification of an equivalence point by measuring the associated change in pH, using appropriate acid-base indicators or pH meters, to reveal an observable end point
- data obtained from acid-base titrations can be used to calculate the masses of substances and concentrations and volumes of solutions involved

SCIENCE AS A HUMAN ENDEAVOUR

Oxidation and reduction

Spontaneous redox reactions can be used as a source of electrical energy, including primary cells (for example, the Leclanché cell), secondary cells (for example, the lead-acid accumulator) and fuel cells (for example, the hydrogen fuel cell). Fuel cells are a potential lower-emission alternative to the internal combustion engine and are already being used to power various modes of transport. Organisations, including the International Partnership for Hydrogen and Fuel Cells in the Economy, have been created to foster global cooperation on research and development, common codes and standards, and information sharing on infrastructure development.

Science Understanding

- oxidation-reduction (redox) reactions involve the transfer of one or more electrons from one species to another
- oxidation involves the loss of electrons from a chemical species, and reduction involves the gain of electrons by a chemical species; these processes can be represented using half-equations and redox equations (acidic conditions only)
- a range of reactions involve the oxidation of one species and reduction of another species, including metal and halogen displacement reactions, and combustion in both limited and excess oxygen environments
- the species being oxidised and reduced in a redox reaction can be identified using oxidation numbers
- the relative strength of oxidising and reducing agents can be determined by comparing standard electrode potentials, and can be used to predict reaction tendency
- electrochemical cells, including galvanic and electrolytic cells, consist of oxidation and reduction half-reactions connected via an external circuit through which electrons move from the anode (oxidation reaction) to the cathode (reduction reaction)
- galvanic cells produce an electric current from a spontaneous redox reaction
- the electric potential difference of a cell under standard conditions can be calculated from standard electrode potentials; these values can be used to compare the voltages generated by cells constructed from different materials
- electrochemical cells can be described in terms of the reactions occurring at the anode and cathode, the role of the electrolyte, salt bridge (galvanic cell), ion migration, and electron flow in the external circuit
- corrosion of iron is an electrochemical process that can be prevented by a range of techniques, including by exclusion of oxygen and/or water and through cathodic protection and sacrificial anodes
- cell diagrams can be used to represent electrochemical cells
- electrolytic cells use an external electrical potential difference to provide the energy to allow a non-spontaneous redox reaction to occur
- describe the use of electrolysis in electrolytic refining, including for purification of copper, and metal electroplating, including for silver

Unit 4 – Organic chemistry and chemical synthesis

SCIENCE AS A HUMAN ENDEAVOUR

Properties and structure of organic materials

The Protein Data Bank (PDB) houses an international repository of structural data of proteins. The information is accessed and contributed to by scientists worldwide. The function of a protein is closely linked to its structure.

Science Understanding

- organic molecules have a hydrocarbon skeleton and can contain functional groups, including alkenes, alcohols, aldehydes, ketones, carboxylic acids, esters, amines and amides; functional groups are groups of atoms or bonds within molecules which are responsible for the molecule's characteristic chemical properties
- structural formulae (condensed or showing bonds) can be used to show the arrangement of atoms and bonding in organic molecules that contain the following functional groups: alkenes, alcohols, aldehydes, ketones, carboxylic acids, esters, amines and amides
- functional groups within organic compounds display characteristic chemical properties and undergo specific reactions; these reactions include addition reactions of alkenes, redox reactions of alcohols, and acid-base reactions of carboxylic acids; these reactions can be used to identify the functional group present within the organic compound
- IUPAC nomenclature is used to name organic species, including those with a parent chain of up to 8 carbon atoms with simple branching and one of the following functional groups: alkenes, alcohols, aldehydes, ketones, carboxylic acids, esters, amines and amides
- isomers are compounds with the same molecular formulae but different structures; different types of isomerism include chain and position structural isomerism and cis-trans isomerism
- all alcohols can undergo complete combustion; with oxidising agents, including acidified MnO_4^- or $Cr_2O_7^{2-}$ oxidation of primary alcohols produces aldehydes and carboxylic acids, while the oxidation of secondary alcohols produce ketones; these reactions have characteristic observations and can be represented with equations
- alcohols can react with carboxylic acids in a condensation reaction to produce esters and can be represented with equations
- organic compounds display characteristic physical properties, including boiling point and solubility in water and organic solvents; these properties can be explained in terms of intermolecular forces (dispersion forces, dipole-dipole interactions and hydrogen bonds) which are influenced by the nature of the functional groups
- empirical and molecular formulae can be determined by calculation and the structure of an organic compound established from the chemical reactions they undergo, and other analytical data
- addition reactions can be used to produce polymers, including polyethene and polytetrafluoroethene
- the structure of an addition polymer can be predicted from its monomer and the structure of an addition polymer can be used to predict the monomer from which it was derived
- condensation reactions can be used to produce polymers, including polyamides and polyesters
- the structure of a condensation polymer can be predicted and drawn from its monomer(s) and the structure of a condensation polymer can be used to predict the monomer(s) from which it was derived
- α-amino acids can be represented using a generalised structure
- the characteristic properties of α-amino acids include the formation of zwitterions and the ability to react to form amide (peptide) bonds through condensation reactions
- α-amino acids undergo condensation reactions to form polypeptides (proteins) in which the α-amino acid monomers are joined by peptide bonds
- the sequence of α-amino acids in a protein is called its primary structure
- secondary structures of proteins, (α-helix and β-pleated sheets) result from hydrogen bonding between amide and carbonyl functional groups; hydrogen bonding between amide and carbonyl functional groups within a peptide chain leads to α-helix structures while hydrogen bonding between adjacent polypeptide chains leads to β-pleated sheets
- the tertiary structure of a protein (the overall three-dimensional shape) is a result of folding due to interactions between the side chains of the α-amino acid in the polypeptide, including disulfide bridges, hydrogen bonding, dipole-dipole interactions, dispersion forces and ionic interactions

SCIENCE AS A HUMAN ENDEAVOUR

Chemical synthesis

Scientific knowledge can be used to design alternative chemical synthesis pathways, taking into account sustainability, local resources, economics and environmental impacts (green chemistry), including the production of ethanol and biodiesel.

Science Understanding

- chemical synthesis to form products with specific properties may require the construction of reaction sequences with more than one chemical reaction and involves the selection of particular reagents and reaction conditions in order to optimise the rate and yield of the product
- quantities of products in a chemical synthesis reaction can be calculated by comparing stoichiometric quantities with actual quantities and by determining the limiting reagent
- the percentage yield of a chemical synthesis reaction can be calculated by comparing theoretical versus actual product quantities
- reagents and reaction conditions are chosen to optimise yield and rate for chemical synthesis processes, including in the production of ammonia (Haber process), sulfuric acid (Contact process) and biodiesel (base-catalysed and lipase-catalysed methods)
- enzymes are protein molecules which are biological catalysts and can be used on an industrial scale to produce chemicals that would otherwise require high pressure or temperature conditions to achieve an economically viable rate, including fermentation to produce ethanol versus hydration of ethene
- chemical synthesis processes may involve the construction of reaction sequences with more than one chemical reaction, including the hydration of ethene to form ethanol and the subsequent reaction of ethanol with acetic (ethanoic) acid to produce ethyl ethanoate
- the base hydrolysis (saponification) of fats (triglycerides) produces glycerol and the salt of a long chain fatty acid (soap)
- the structure of soaps contains a non-polar hydrocarbon chain and a carboxylate group; the structure of the anionic detergents derived from dodecylbenzene contains a non-polar hydrocarbon chain and a sulfonate group
- the cleaning action of soaps and detergents can be explained in terms of their non-polar hydrocarbon chain and charged group; the properties of soaps and detergents in hard water can be explained in terms of the solubilities of their calcium salts
- industry produces a vast range of plastics, including addition polymers (for example, polyethene and polytetrafluoroethene) and condensation polymers (for example, nylon and polyethylene terephthalate [PET]) which have different properties and uses
- the varied structures of different plastics due to characteristics, including cross-linking, chain length, and intermolecular forces leads to a range of distinct properties and consequent uses (for example, the different structures, properties and related uses for polyethene, polytetrafluoroethene, nylon and polyethylene terephthalate [PET])

STUDY HINTS AND EXAM TECHNIQUES

Study Strategies

The earlier you start preparing for tests and exams, the more effective your revision will be. To get maximum benefit from your study program you need to establish a plan of attack. In brief, you need to be sure of where, how and what you will be doing to maximise your chances at test and examination time.

You will need to:

- Set up your ideal study area: Uninterrupted privacy and an organised study area are essential.
- Identify your needs: Check your areas of weakness and give them priority.
- Develop a study plan: Study timetables and setting of timelines are essential.
- Stick to the plan: A disciplined study routine will ensure your success.
- Monitor your progress: If your study plan is not working changes may be necessary.
- Your study area: The effectiveness of your study can be greatly improved by creating the right environment.

Your ideal study area should:

- be an area free from interruptions and distractions – preferably a room well away from the family room in order to minimise "visitors" or "passers through"
- be out of hearing range of the television
- have good ventilation so that you don't become drowsy
- have a good sized desk for your study needs
- be well lit so that when you sit at the desk:
  - the main light will shine from behind;
  - a second light, but not as bright, shines across the desk.
  - this second light reduces the shadows which would otherwise tire your eyes quickly.
  - have your study timetable well in view.

To be avoided in your study area: easy chair, stereo, television, phone.

Planning

Identify your needs

- list the areas that need revision for your test (or examination). Use your syllabus or school program to help you.
- prioritise areas of weakness.

Develop a timeline

- check weeks remaining to your test or Semester Examination.
- allocate time available (each week) for revision of Chemistry. Remember that you will have assignments to complete as well as study to do.
- place a sequence of areas to revise on a timeline. It is probably best to follow the sequence of your school's Chemistry program.
- allocate more time to areas in which you are weak.

Following the plan

Force yourself to stick to the plan. If time is short at any stage – prioritise in terms of what is going to be of most benefit to your long term plans.

Have a checklist (e.g. your course outline):

- tick areas you have revised, re-tick each time revised
- use the Syllabus Checklist set out in the previous pages of this book (correct at the time of printing) to tick off the course objectives as you revise them. If aiming for excellence you must know ALL areas of the course.

Study notes:

- develop a set of single page, A4, notes. One page per area revised. Try to visualise your pages of study notes – key reminder pictures or words are important tools to trigger your memory.
- you need to have set aside a section of your Chemistry file to store these revision notes. (Some students use small palm cards or record cards to store notes on small sections of the course – these are an excellent alternative.)

Using this study guide:

- read through the section appropriate to what you are revising and **highlight** all important points
- attempt **all** the questions to check your understanding
- trial tests – attempt these prior to a test or examination. To get maximum value from these tests:

  – prepare first
  – set a time
  – observe test conditions.

Monitoring your progress:
The trial tests at the back of this study guide are designed to give you immediate feedback on how your revision is proceeding and how effective it has been. If your study plan is not working, then alter it so that you can achieve your desired results.

EXAMINATION STRATEGIES

Before the examination

The evening prior to an exam should be set aside for light study and a brief review of your revision notes. If you have been provided with a copy of the examination instructions to candidates by your teacher, then it would be a good idea to go over these in detail. Avoid staying up late, as a good night's sleep will prove to be of great value to you the following day.

On the morning of the exam check that you have all that you need; examination number slip, calculator/s fitting the SCSA approved guidelines – preferably with new batteries, pens, soft pencil, eraser, and ruler. Your own watch may also be more convenient for you to use during the examination rather than the clock in the exam room.

Arrive at school with at least 20 minutes to spare. Try to relax by talking to your friends but avoid worrying about the exam, or what you may have forgotten. You will find that work you have learnt will be readily recalled during the exam.

Reading time

This ten minutes of valuable time must be used wisely. It will be natural curiosity to have a quick look at the whole paper but this will be of limited value. First, and most important, you must read the instructions and make sure you understand them. It is then best to read steadily through the questions, beginning with the short and extended answer section of the paper.

It is best to leave the multiple-choice items at this stage since you will not be able to write down an answer even though you may have read through quite a lot of detail (remember - no writing allowed during reading time). This means you will only have to *re-read* through them during the allotted 3 hours.

It is better, then to read through the questions from the beginning and to establish in your own mind the **concepts** involved and how you may tackle the question.

Working through the paper

It is best to work through the paper in the order that it is written. However this is not essential and some students prefer starting with a section they are most confident with.

Pace yourself

It is important to know how much time you have for your exam and follow the time allocations for each section. The Chemistry ATAR exam has a marks allocation for the three that is not linear. One "mark" in one of the Sections of the exam has a different weighting to one "mark" in the other two Sections of the exam. Do not allocate the same working time to a "mark" in each section. When allocating time to each section, pace yourself to spend the suggested time allocated for each section.

Section One	**Multiple Choice**	**25%**	**Suggested time – 50 minutes**
Section Two	**Short Answer**	**35%**	**Suggested time – 60 minutes**
Section Three	**Extended Answer**	**40%**	**Suggested time – 70 minutes**

Try not to spend more than the allocated time on each section of the exam.

Multiple-choice

Attempt each question as you come to it: Be sure to select an answer, even if unsure – there is no penalty for guessing. It is **wasteful** of your time to read through a question and then leave it because you are not quite sure of the answer. When you come back to it later you will only have to go through it again. If unsure, eliminate the obvious distractors and make an educated guess. Put a mark by the side of these questions so that if you do have time you can come back to reconsider them. If you do run short of time, however, you will at least have a good chance of being correct.

Read each question through carefully: Take note of any key words. Where possible, it is best to think of your answer to a question before you proceed to read through each of the alternatives given. Then look through each of the distractors to see if your answer is there. Don't immediately write this down as your answer but convince yourself that each of the other distractors is incorrect.

As you work through each distractor place a cross (x) next to those that you are sure are incorrect, a question mark (?) next to those you are not quite sure about and circle your answer when you have it. This will save time, particularly if it is a difficult question and you have to come back to it.

Changing your selections: Do this only if you are sure that your initial choice was incorrect. Usually your first choice is the best choice.

Relate to study notes: If you have difficulty with a question there are points of reference you should try to think about to work towards the best possible answer:

(i) Try to identify the syllabus concepts that the question and distractors relate to.
(ii) Try to relate the question to parts of your study notes.

A question can often become more clear when you are able to classify it according to your prior knowledge (i.e. study notes).

Short and extended answer questions

Complete all that you can—come back to others as ideas come flooding back (hopefully). When stuck on any particular question, try to associate the question with a page of your study notes—can these notes be related to the question in any way? Where appropriate chemical equations and diagrams are very useful for demonstrating your chemical literacy.

Calculations

For top marks show all your working. Be sure to state your answer to the appropriate number of significant figures and in scientific notation.

For stoichiometric calculations the balanced equation is an essential part of the solution to a question. If the equation is not given, look for clues as to what the reactants and products might be. Classify the information as to what type of reaction it might be (e.g. *acid* + *base*, *redox*, etc). It is important that you try to produce a balanced equation. It is better to have attempted to write an equation and to answer the remainder of the question than to completely disregard the question.

Before attempting a calculation note down information, produce a **simple flow diagram** if complicated information has been presented. This will help to produce a standard of working clarity that is much more logical to follow (for you and for the person marking **your** exam).

Clearly indicate the **steps or stages** to your calculation (e.g. $n(Na_2CO_3) = 2.5$). Clearly indicate which section of a multiple part question you are answering. If the question has 5 parts then your working must be broken up into 5 clearly labelled parts. **You should try to make the marker's task as easy as possible**, make your setting out clear and logical, and clearly highlight (or underline) your answer.

FORMULAE, MEASUREMENT AND QUANTITIES

Formulae

Number of moles	$n = \frac{m}{M} = \frac{mass}{molar\ mass}$
Number of moles of solute	$n = cV$
Number of moles of a gas at STP	$n = \frac{V}{22.71}$
Ideal gas law	$PV = nRT$
Parts per million	$ppm = \frac{mass\ of\ solute\ (mg)}{mass\ of\ solution\ (kg)}$
pH of a solution	$pH = -log\ [H^+]$

SI Fundamental (Base) Units

Quantity	Symbol for quantity	Unit	Symbol for unit
length	l	metre	m
mass	m	kilogram	kg
time	t	second	s
electric current	I	ampere	A
temperature	T	kelvin	K
amount of substance	n	mole	mol

Commonly used units in Chemistry

Quantity	Commonly used units and symbols		Conversions (etc)
amount of substance	mole	mol	1 mole = 6.022×10^{23} particles
concentration (solutions)	mole per litre gram per litre	mol L^{-1} g L^{-1}	mol L^{-1}
electromotive force	volt	V	
energy	joule kilojoule	J kJ	1000 J = 1 kJ
density	gram per litre	g L^{-1}	
mass	gram kilogram tonne	g kg	1 tonne = 1000 kg = 1×10^6 g
molar volume	litre per mole	L mol^{-1}	22.71 L (S.T.P. – 0.0°C, 100.0 kPa) 24.47 L (25.0°C, 101.3 kPa)
pressure	kilopascal atmosphere	kPa atm	1 atm = 101.3 kPa
temperature	kelvin degree celsius	K °C	K = °C + 273.15
time	second hour	s h	1 h = 3600 s
volume	litre millilitre cubic centimetre cubic decimetre	L mL cm^3 dm^3	1 L = 1000 mL = 1 dm^3 = 1000 cm^3

Commonly used prefixes

PREFIX	SYMBOL	FACTOR	PREFIX	SYMBOL	FACTOR
tera	T	10^{12}	milli	m	10^{-3}
giga	G	10^{9}	micro	μ	10^{-6}
mega	M	10^{6}	nano	n	10^{-9}
kilo	k	10^{3}	pico	p	10^{-12}

Some Physical Constants used in Chemistry

CONSTANT	SYMBOL	VALUE
Avogadro constant	N	6.022×10^{23} mol^{-1}
molar volume (ideal gas)	V_m	22.71 L (S.T.P.)* 24.47 L (25°C, 101.3 kPa)
universal gas constant	R	8.314 J K^{-1} mol^{-1} or 0.08206 L atm K^{-1} mol^{-1}

** S.T.P. (standard temperature and pressure) = 0.0°C, 100.0 kPa.*

Scientific notation

Scientific (or exponential) notation is used to conveniently express very large or very small numbers.Numbers are written so that there is a single non zero digit to the left of the decimal point times the appropriate power of 10.

e.g.	6275	=	6.275×10^3	
	0.06275	=	6.275×10^{-2}	
	0.00014	=	1.4×10^{-4}	
	0.000140	=	1.40×10^{-4}	
	2500	=	2.5×10^3	(if 2 sig. figures)
	2500	=	2.500×10^3	(if 4 sig. figures)

Errors and uncertainties

All measurements involve some uncertainty or error. Errors are random or systematic in nature and can be indicated using the ± notation or significant figures.

Random errors are associated with poor precision or reproducibility of a result. For example when measuring the volume of a liquid, using a graduated cylinder, we may estimate the last digit of our reading slightly differently each time. The reading could be slightly higher or slightly lower than the true value. Repeating the measurement several times and averaging the results will help minimize this type of error.

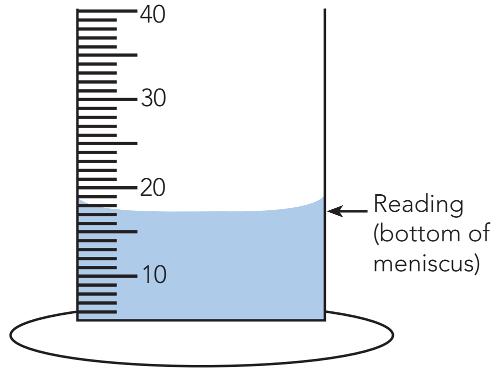
Systematic errors are associated with poor accuracy or a bias in the system of measurement. For example an incorrectly zeroed balance will always give biased readings, either always too high or always too low. Repeating the measurements several times will not minimize this type of error.

Significant figures

Significant figures are used to indicate the precision or accuracy of a particular measurement or given data. They are not to be confused with decimal points.

Recording significant figures

When a measurement is made we record all integers of which we are certain plus one other of which there is some uncertainty, e.g. a graduated cylinder is used to determine the volume of liquid as shown at right. The reading indicates a volume somewhere between 17 mL and 18 mL. Where exactly between these points is uncertain. Hence the reading (say 17.4 mL) is recorded to only three significant figures.

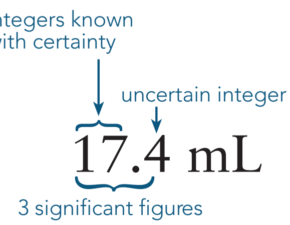


Determining significant figures

In any given data (number) a significant figure is

- any integer
- any zero that follows an integer after a decimal point

e.g. 1.46 , 0.106 , 1.10 all have 3 significant figures
2.100 × 10^3 , 1.467 , 0.02600 all have 4 significant figures
8.1 , 0.00026 , 26 all have 2 significant figures



Where a zero occurs at the end of whole number such as 250 and 5000, the correct number of significant figures is uncertain. Use of scientific notation avoids this.

e.g. 250 is written as 2.50 × 10^2 if it has 3 significant figures

250 is written as 2.5 × 10^2 if it has 2 significant figures

Using significant figures

When doing calculations, remember that your final value cannot be more precise than your least precise data. During the actual calculation leave all the digits in your calculator. However, your final result should be rounded off to have the same number of significant figures as your least significant data. In nearly all cases three significant figures are used.

Rounding off

Numbers often need to be rounded to the correct number of significant figures. To do this:

- note which are the significant digits
- look at the next digit to the right of them, and

if it is > 5 round up
if it is = 5 round up if an even number results
if it is < 5 no change

e.g. The following have all been rounded to 3 significant figures.

1.294	rounds to	1.29
0.06437	rounds to	0.0644
21.65	rounds to	21.6
21.75	rounds to	21.8
3.955	rounds to	3.96

Exact numbers

Some numbers used in chemistry calculations have an exact value and do not affect the number of significant figures in the answer. These are such numbers as:

- the coefficients in chemical equations e.g. 2HCl means 2.000 moles of HCl
- conversion ratios e.g. 1 kg = 1000.00 g

FORMULAE, COLOURS OF SELECTED SUBSTANCES, SOLUBILITY

Formulae of molecular substances

The formulae and names of some important molecular substances

Elements		Compounds			
bromine	Br_2	ammonia	NH_3	phosphoric acid	H_3PO_4
chlorine	Cl_2	carbon dioxide	CO_2	sulfur dioxide	SO_2
fluorine	F_2	carbon monoxide	CO	sulfur trioxide	SO_3
hydrogen	H_2	hydrogen chloride	HCl	sulfuric acid	H_2SO_4
iodine	I_2	hydrogen peroxide	H_2O_2	sulfurous acid	H_2SO_3
nitrogen	N_2	hypochlorous acid	$HClO$	water	H_2O
oxygen	O_2	nitric acid	HNO_3		
phosphorus	P_4	nitrogen dioxide	NO_2		
sulfur	S_8	nitrogen monoxide (nitric oxide)	NO		

Colour of species in aqueous solutions

Students should be able to use the colours of the following molecules and ions to infer and describe the products of reactions.

Cation	Colour	Cation	Colour	Anion	Colour	Halogen	Colour
$Al^{3+}_{(aq)}$	colourless	$Mg^{2+}_{(aq)}$	colourless	$Br^{-}_{(aq)}$	colourless	$Cl_{2(aq)}$	pale yellow
$NH_4^{+}{}_{(aq)}$	colourless	$Mn^{2+}_{(aq)}$	colourless*	$Cl^{-}_{(aq)}$	colourless	$Br_{2(aq)}$	orange
$Ba^{2+}_{(aq)}$	colourless	$Ni^{2+}_{(aq)}$	green	$CrO_4^{2-}{}_{(aq)}$	yellow	$I_{2(aq)}$	brown
$Ca^{2+}_{(aq)}$	colourless	$K^{+}_{(aq)}$	colourless	$Cr_2O_7^{2-}{}_{(aq)}$	orange		
$Cr^{3+}_{(aq)}$	deep green	$Ag^{+}_{(aq)}$	colourless	$I^{-}_{(aq)}$	colourless		
$Co^{2+}_{(aq)}$	pink	$Na^{+}_{(aq)}$	colourless	$MnO_4^{-}{}_{(aq)}$	deep purple		
$Cu^{2+}_{(aq)}$	blue	$Sr^{2+}_{(aq)}$	colourless	$PO_4^{3-}{}_{(aq)}$	colourless		
$Fe^{2+}_{(aq)}$	pale green	$Sn^{2+}_{(aq)}$	colourless	$S^{2-}_{(aq)}$	colourless		
$Fe^{3+}_{(aq)}$	pale brown	$Zn^{2+}_{(aq)}$	colourless				
$Pb^{2+}_{(aq)}$	colourless						

Halogen in organic solvent	
Br_2	red
I_2	purple

Halogen as free element	
$F_{2(g)}$	yellow
$Cl_{2(g)}$	greenish yellow
$Br_{2(l)}$	red
$I_{2(s)}$	purple

* very pale pink if saturated solution

Solubility rules

Students should be able to apply the following solubility rules for ionic solids in water.

Soluble in water

Soluble	Exceptions	
	Insoluble	**Slightly soluble**
Most chlorides	AgCl	$PbCl_2$
Most bromides	AgBr	$PbBr_2$
Most iodides	AgI, PbI_2	
All nitrates	No exceptions	
All ethanoates	No exceptions	
Most sulfates	$SrSO_4$, $BaSO_4$, $PbSO_4$	$CaSO_4$, Ag_2SO_4

Insoluble in water

Insoluble	Exceptions	
	Soluble	**Slightly soluble**
Most hydroxides	NaOH, KOH, $Ba(OH)_2$ (NH_4OH and AgOH do not exist)	$Ca(OH)_2$, $Sr(OH)_2$
Most carbonates	Na_2CO_3, K_2CO_3, $(NH_4)_2CO_3$	
Most phosphates	Na_3PO_4, K_3PO_4, $(NH_4)_3PO_4$	
All sulfides	Na_2S, K_2S, $(NH_4)_2S$	

Soluble = more than 0.1 mole dissolves per litre
Slightly soluble = between 0.01 and 0.1 mole dissolves per litre
Insoluble = less than 0.01 mole dissolves per litre

Colour of precipitates

The colour of the following precipitates are listed for reference only.

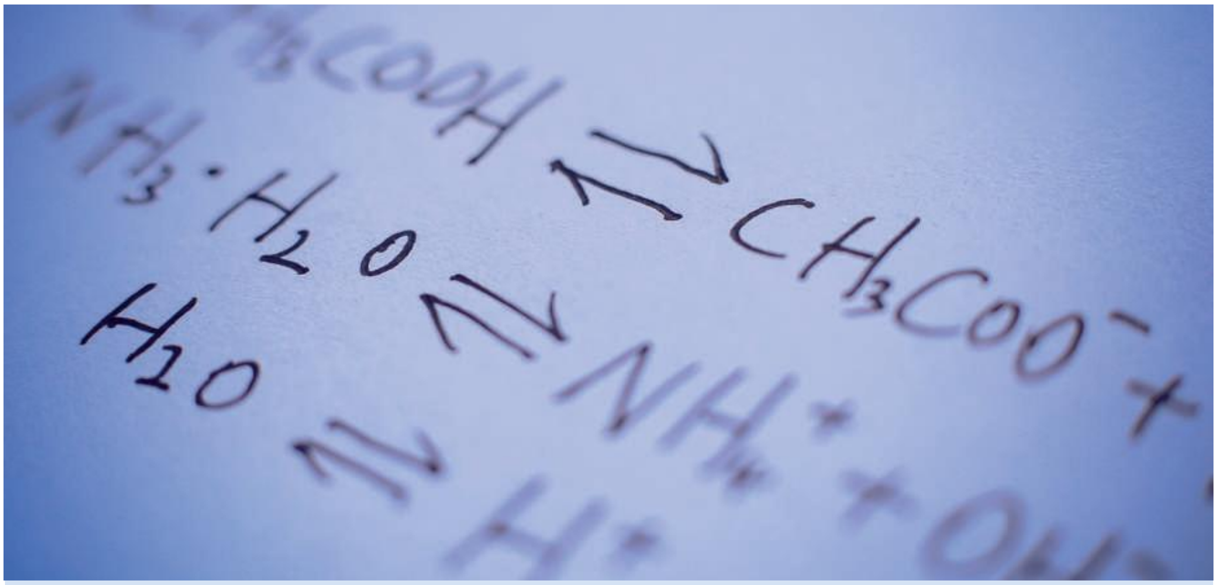
	Cl^-	SO_4^{2-}	OH^-	CO_3^{2-}		Cl^-	SO_4^{2-}	OH^-	CO_3^{2-}
Mg^{2+}	-	-	white	white	Cu^{2+}	-	-	pale blue	green
Ca^{2+}	-	white	white	white	Ag^+	white	white	(Ag_2O) brown (AgOH does not exist)	white/pale yellow
Sr^{2+}	-	white	white	white	Zn^{2+}	-	-	white	white
Ba^{2+}	-	white	-	white	Cd^{2+}	-	-	white	white
Cr^{3+}	-	-	green	- ($CrCO_3$) green	Hg_2^{2+}	white	white/ yellow	(Hg_2O) black	yellow/ brown
Mn^{2+}	-	-	pink	pink	Hg^{2+}	-	-	(HgO) red/yellow	-
Fe^{2+}	-	-	green	grey/green	Al^{3+}	-	-	white	white
Fe^{3+}	-	-	brown	brown	Sn^{2+}	-	-	white	white
Co^{2+}	-	-	red/pink	red	Pb^{2+}	white	white	white	white
Ni^{2+}	-	-	green	green		Na^+, K^+, NH^{4+} do not form precipitates.			

CHEMISTRY

UNIT 3

1

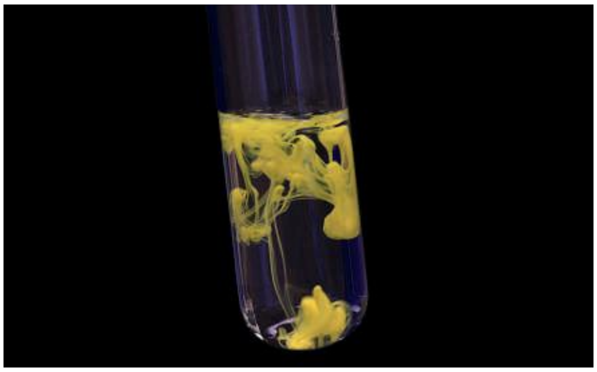
CHEMICAL EQUILIBRIUM



Topics covered in this chapter:

1.1 Reaction Rate
1.2 Collision Theory
1.3 Changing Reaction Rate
1.4 Equilibrium
1.5 Le Châtelier's Principle
1.6 Carbon Dioxide Equilibrium in Water

1.1 REACTION RATE



Some chemical reactions can be very slow, such as the rusting of an iron bolt, while others, like the formation of precipitates, are extremely fast. Chemists are particularly keen to know what makes some reactions go faster than others as this would allow them to favourably control important chemical reactions.

For example, it would be an advantage to slow down reactions such as the formation of rust and speed up reactions such as the setting of glue. Hence it is particularly important for chemists to understand the factors which influence reaction rate.

Measuring reaction rate

Several changes occur during a chemical reaction and any of them can be used to measure reaction rate. Consider the reaction illustrated at right where hydrochloric acid has been added to granulated zinc:

$$Zn_{(s)} + 2H^{+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + H_{2(g)}$$

Changes that take place during the reaction include:

- mass of zinc decreases;
- the H^+ concentration decreases;
- the Zn^{2+} concentration increases;
- the volume of $H_{2(g)}$ increases. The rate of reaction in the above situation can be determined by observing the rate of any of the changes described above. In general we can say,

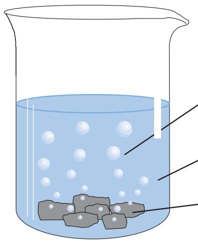


Figure 1.1 Hydrochloric acid (2.0 mol L^{-1}) added to granulated zinc. When the acid is added to the zinc there is initially a fairly rapid reaction producing hydrogen gas.

> ***The rate of reaction, at some instant, is the rate at which reactants are used up or, alternatively, the rate at which products are formed.***

Factors affecting reaction rate

The rate of a chemical reaction is affected by the:

- nature of the reactants
- concentration of the reactants
- state of subdivision of the reactants
- temperature
- presence of a catalyst.

In order to explain why these five factors affect reaction rate it is best to look at what happens at a molecular level and consider collision theory.

1.2 COLLISION THEORY

Simply writing the equation for a reaction ***does not*** explain what happens at a molecular (or particle) level. Consider the combustion of hydrogen gas. The equation for the reaction is given below as well as an illustration showing the collisions and bond breaking and bond forming that occur.

$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(g)}$$

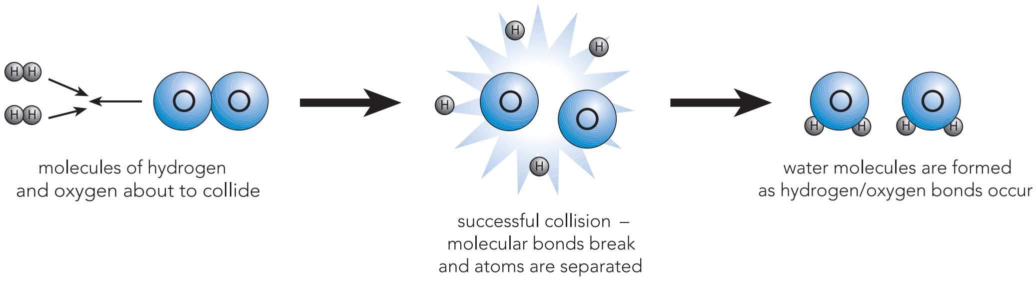


Figure 1.2 The combustion of hydrogen gas.

We can see that in order for a reaction to take place there must be successful collisions between reacting particles. The success of any collision is improved if:

- the reacting particles have an appropriate collision orientation
- the reacting particles collide with sufficient energy.

Ultimately the greater the rate of successful collisions, the faster the reaction rate.

1.3 CHANGING REACTION RATE

The nature of reactants

Chemists are able to alter the rate of a particular chemical reaction by controlling such factors as concentration and temperature. In the first instance, however, reaction rate depends on the nature of the reactants involved. In general:

- **ionic reactions** are rapid as they do not involve the breaking of bonds or electron transfer between reacting particles.

e.g. 1. $Ba^{2+}{}_{(aq)} + SO_4{}^{2-}{}_{(aq)} \longrightarrow BaSO_{4(s)}$

2. $Ag^{+}{}_{(aq)} + Cl^{-}{}_{(aq)} \longrightarrow AgCl_{(s)}$

Both reactions are almost instantaneous as no reactant bonds have to break and there is a strong electrostatic attraction between oppositely charged ions.

- **molecular reactions** are slow since they involve bond breaking and bond formation. Collisions are often unsuccessful at room temperature as there is insufficient activation energy (E_a).

e.g. 3. $C_3H_{8(g)} + 5O_{2(g)} \longrightarrow 3CO_{2(g)} + 4H_2O_{(g)}$

4. $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(g)}$

Both of these reactions are very slow (almost undetectable) at room temperature as they involve the breaking of strong covalent bonds.

Question 1.1

Which of the molecular reactions (e.g. 3 or e.g. 4) is likely to be the slowest? Why?

The concentration of reactants

Reaction rate is affected by the concentration of reactants in either the ***solution*** or ***gaseous*** phase. Collision theory tells us that for a reaction to take place the reacting particles must collide. Hence if the number of particles per unit volume is increased the number of collisions will also increase. Typically, if the pressure of two reacting gases is doubled (by doubling the number of molecules or halving the volume of each as shown below) then the reaction rate between them is increased fourfold. This occurs since the number of collisions increases by a factor of four.

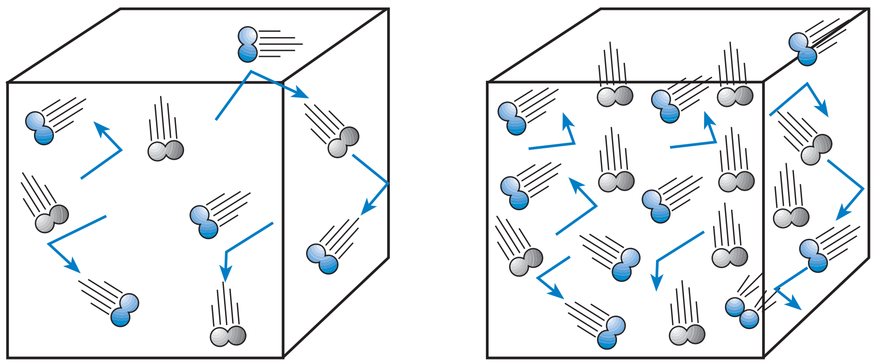


Figure 1.3 The number of collisions per second depends upon the concentration of each of the reactant particles. An increase in the rate of collisions means an increase in the rate of successful collisions and hence the rate of reaction.

The state of subdivision of reactants

A lump of sugar dissolves far more slowly in your coffee than does fine grained sugar. This observation can be readily explained in terms of collision theory. The fine grained sugar has a greater surface area than the solid lump of sugar and hence there is an increased frequency of collisions with water molecules. This results in an increased reaction rate.

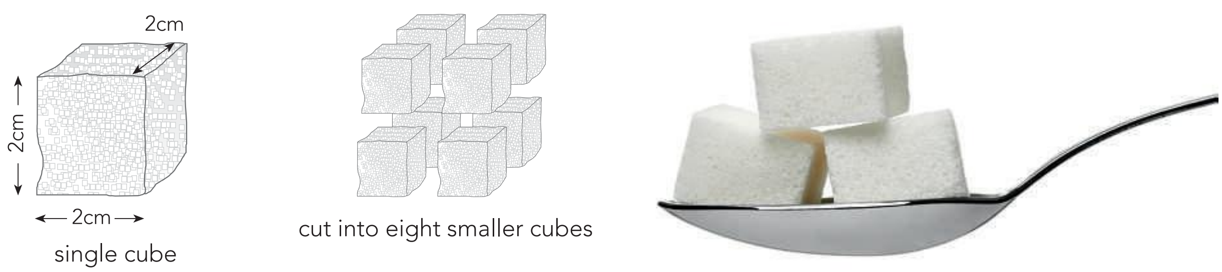


Figure 1.4 The state of subdivision increases the surface area of a reactant.

Temperature

Reaction rate is greatly affected by temperature. From the kinetic theory we know that as temperature increases so does the velocity of the reacting particles. This has a twofold effect on reaction rate.

- The number of collisions per unit time increases. This increases the number of successful collisions and hence reaction rate.

- The force, and therefore likely success, of each collision increases. More importantly, the proportion of particles with sufficient activation energy increases with temperature and hence the reaction rate increases markedly. (See kinetic energy distribution graph – Fig. 1.6).

Catalysts

The presence of some substances called catalysts helps to speed up a reaction. At the end of the reaction these substances are themselves not consumed.

The actual mechanism by which catalysts work is often complex and not always understood. However, it is evident that catalysts provide an alternate and easier reaction pathway of lower activation energy. Catalysts are involved in many important chemical reactions such as the following:

e.g.
1. Platinum in the H_2/O_2 fuel cell. $2H_{2(g)} + O_{2(g)} \xrightarrow{Pt} 2H_2O_{(g)}$
2. Iron in the Haber process. $N_{2(g)} + 3H_{2(g)} \xrightarrow{Fe} 2NH_{3(g)}$
3. Vanadium pentoxide in the Contact Process. $2SO_{2(g)} + O_{2(g)} \xrightarrow{V_2O_5} 2SO_{3(g)}$

Activation energy – effect of catalysts

Since a catalyst essentially provides an alternate, and easier pathway for a reaction, it effectively lowers the activation energy. This is true for both the forward and reverse reactions:

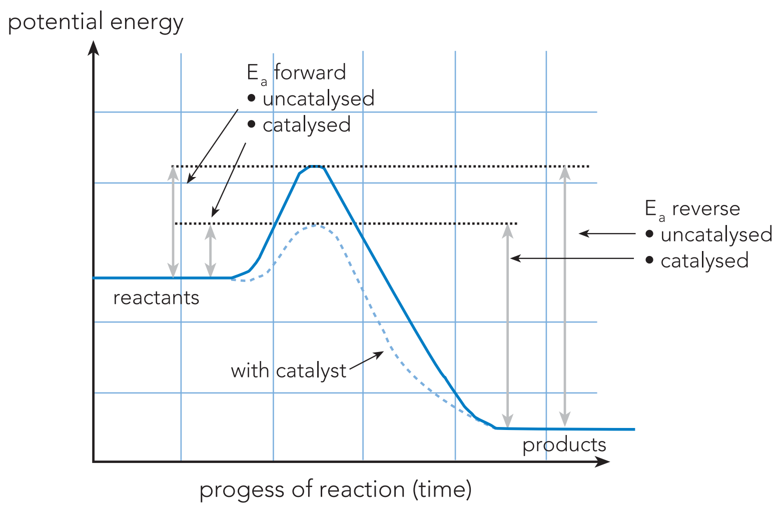


Figure 1.5 The effect of catalyst on reaction pathway. The activation energy is effectively lowered for both forward and reverse reactions by offering a new pathway.

Kinetic energy distribution and temperature

The temperature of any substance is related to the average kinetic energy of all its particles. However not all the particles (at any particular instant) are travelling at the same speed. The diagram below shows the typical distribution of molecular kinetic energies at two different temperatures. If we consider a reaction with a fairly high activation energy then very few particles have sufficient energy to undergo a reaction (shaded area). A small change in temperature however, can markedly increase the proportion of particles with energy greater than activation energy (E_a) as can be seen by a large increase in total area to the right of E_a.

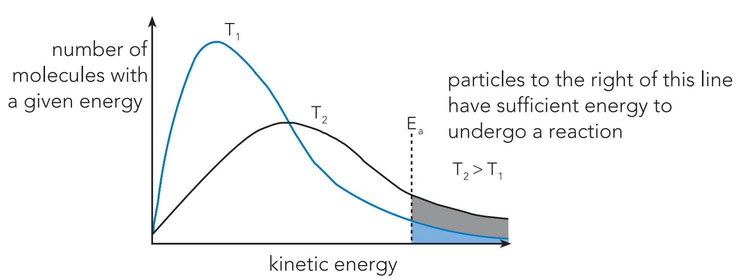


Figure 1.6 Kinetic energy distribution of particles at different temperatures.

Question 1.2

In the reaction illustrated (in Figure 1.2),

(a) how many bonds break? _______ List these. _________________________

(b) how many bonds form? _______ List these. _________________________

Question 1.3

What is meant by a successful collision between reacting particles?

____

____

Question 1.4

In the experiment illustrated in Figure 1.1, the reaction between the acid and the zinc was fastest at the beginning. Use collision theory to explain why.

____

____

____

Question 1.5

In Figure 1.4 a solid cube measuring 2 cm × 2 cm × 2 cm is cut into 8 smaller and equal cubes.

(a) Calculate the surface area of the large cube. _______________

(b) Calculate the total surface area of the eight smaller cubes. ________________

(c) Compare the surface areas. ____

Question 1.6

Catalysts are usually in the form of powders or fine wire mesh. Why is this?

____

____

____

Question 1.7

An increase in temperature of only 10°C can markedly increase reaction rate.
Use the graph in Figure 1.6 to explain the **main** reason for this.

____

____

1.4 EQUILIBRIUM

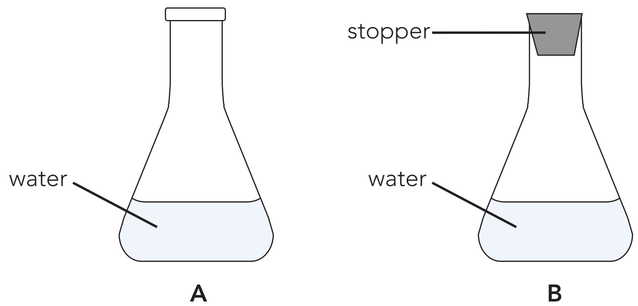
It is sometimes assumed that a chemical reaction can only go in one direction. This is not the case. Theoretically all reactions are reversible although one direction may be highly favoured.

- Where a single arrow (→) is used in an equation it indicates that the forward reaction is highly favoured.
- Where a double arrow (⇌) is used it indicates that the reaction can occur readily in either direction. The extent to which the reaction proceeds depends on the nature of the reactants and reaction conditions.

Within *a closed system* an equilibrium will always occur between reactants and products. A closed system is one which allows energy, but not matter, to be exchanged with the surroundings.

At equilibrium:
- the forward reaction rate is equal to the reverse reaction rate
- there is no change in *macroscopic properties* such as concentration, pressure or colour. (This is how we recognise that equilibrium has been reached.)

Vapour-liquid equilibrium



Consider the two flasks (A and B) shown at right. Each has the same amount of water added to them but only flask B is stoppered. They are left undisturbed on a laboratory bench for a few days. What changes would you expect to observe in each of the flasks after this time?

We would of course, find that some of the water in A would have evaporated while the water level in B would appear almost unchanged. In fact, a little of the water in B would have evaporated. That is, an equilibrium was able to be established in the closed system that exists in flask B.

The equilibrium that exists in flask B can be expressed as follows:

$$H_2O(l) \quad + \quad heat \quad \rightleftharpoons \quad H_2O(g) \qquad \text{i.e. } \Delta H = +ve \text{ (endothermic)}$$

At equilibrium:
- the rate of evaporation is equal to the rate of condensation
- the vapour pressure is constant, as is the water level.

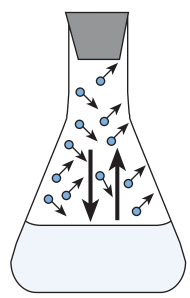


Figure 1.7 The dynamic nature of equilibrium. At equilibrium the rate at which particles leave the liquid is equal to the rate at which they return.

Assuming dry air initially, the forward reaction would predominate as there would be no water in the gaseous phase. As the vapour pressure increases the rate of condensation would also increase until it was equal to the rate of evaporation.

It is important to note that the equilibrium established is a ***dynamic*** one. On a microscopic level molecules are continually leaving and re-entering the liquid state (from the vapour).

Chemical equilibrium

Chemical reactions reach equilibrium within a closed system in a similar manner to the physical systems described above. It does not matter whether we begin just with 'reactants' or 'products' or a combination of both. The system will reach a dynamic equilibrium when the rates of forward and reverse reactions are equal.

A most important equilibrium reaction occurs in the production of ammonia using the Haber process (see also Chapter 5). This reaction is represented as follows:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H = -92 \text{ kJ mol}^{-1}$$

The progress of this reaction to equilibrium can be represented graphically as shown below. The two graphs show:

- the variation of reaction rate with time
- the variation of concentration with time.

In both cases we are considering *a closed system* which initially contained only $N_{2(g)}$ and $H_{2(g)}$.

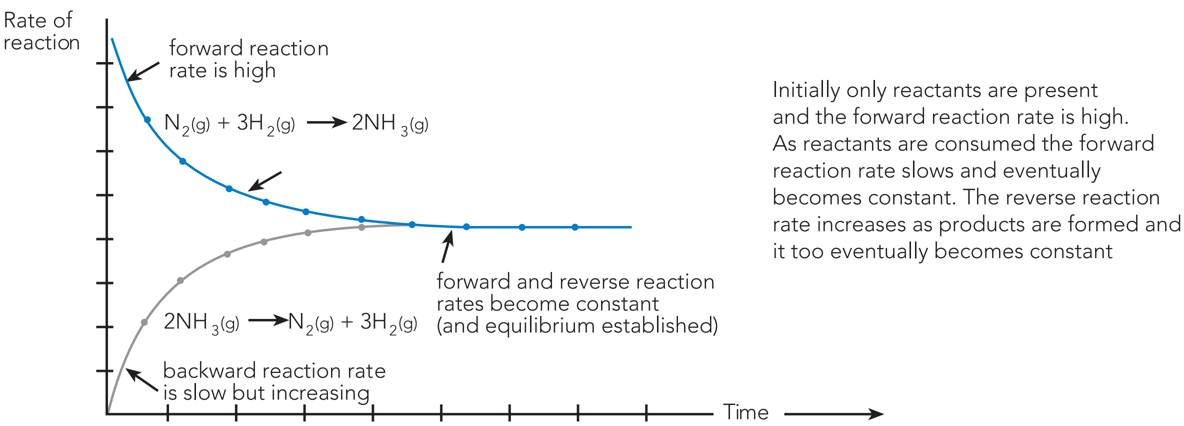


Figure 1.8 Attaining equilibrium - changes in reaction rate.

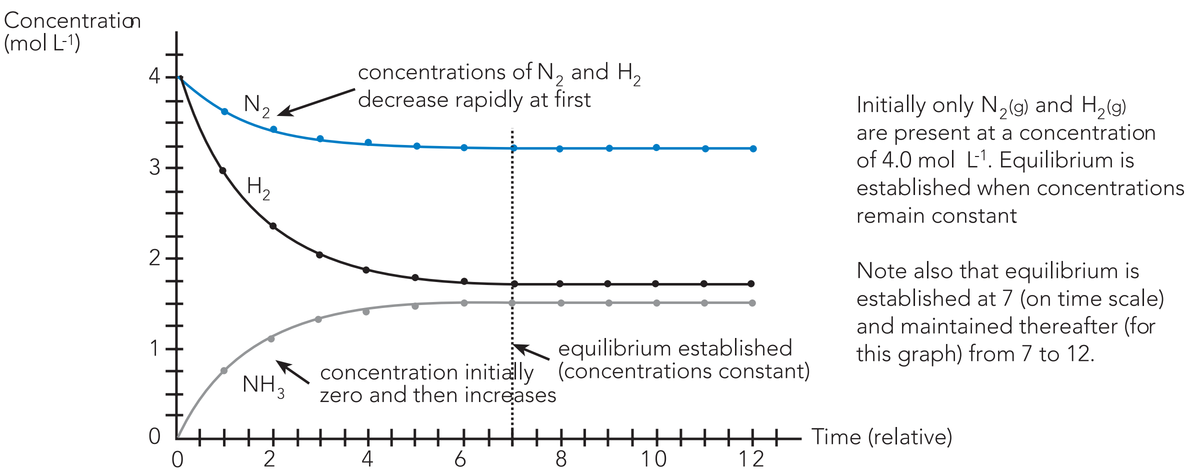


Figure 1.9 Attaining equilibrium - changes in concentration.

Question 1.8

Please refer to Figure 1.9 when answering the following.

(a) The concentration of the N_2 and H_2 decreases most rapidly at first. Why?

____

(b) The concentration of H_2 drops off much more quickly than N_2. Why?

____

Equilibrium constant (K)

For any equilibrium reaction there is an equilibrium constant (K). This constant, which is always a positive number, allows us to predict how far an equilibrium reaction will go in one direction.

- $K > 1$ — Reaction favours products (i.e. favours right hand side of $\rightleftharpoons$).
- $K >> 1$ (e.g. 10^3) — Reaction very strongly favours products. At equilibrium very little reactant remains.
- $K < 1$ — Reaction favours reactants.
- $K << 1$ (e.g. 10^{-3}) — Reaction very strongly favours reactants. At equilibrium very little product has been formed.

The equilibrium constant is derived from a mathematical relationship involving the concentration of reactants and products at equilibrium (physical states are not shown here).

If $aA + bB \rightleftharpoons cC + dD$

then $K = \dfrac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$ Note: [ ] = ***equilibrium*** concentration in mol L^{-1}

Typical examples of equilibrium constant expressions are:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad K = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$$

$$Cr_2O_7^{2-}{}_{(aq)} + 2OH^-{}_{(aq)} \rightleftharpoons 2Cr_2O_4^{2-}{}_{(aq)} + H_2O_{(l)} \qquad K = \frac{[CrO_4^{2-}]^2}{[Cr_2O_7^{2-}]\,[OH^-]^2}$$

$$Ba(OH)_{2\,(s)} \rightleftharpoons Ba^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \qquad K = [Ba^{2+}]\,[OH^-]^2$$

It is important to note that:
- Solids and liquids are NOT included in the K expression. The concentration of a solid does NOT vary, nor does the concentration of water in an aqueous solution. (Gases and aqueous solutions are OK.)
- The value of K *does not* change if you alter concentration, pressure or volume. However K varies with temperature. If temperature is increased the value of K increases for endothermic reactions (products favoured) and decreases for exothermic reactions (reactants favoured).
- The value of K refers only to the equilibrium position.

Question 1.9

Write equilibrium constant expressions for the following.

(a) $N_2O_{4\,(g)} \rightleftharpoons 2NO_{2\,(g)}$ K = ____________ $K = 0.16$ at 25°C

(b) $2HI_{(g)} \rightleftharpoons H_{2\,(g)} + I_{2\,(g)}$ K = ____________ $K = 0.018$ at 423°C

(c) $H_2O_{(l)} \rightleftharpoons H^+{}_{(aq)} + OH^-{}_{(aq)}$ K = ____________ $K = 10^{-14}$ at 25°C

(d) $AgI_{(s)} \rightleftharpoons Ag^+{}_{(aq)} + I^-{}_{(aq)}$ K = ____________ $K = 10^{-16}$ at 25°C

(e) $2SO_{2\,(g)} + O_{2\,(g)} \rightleftharpoons 2SO_{3\,(g)}$ K = ____________ $K = 20$ at 700°C

1.5 LE CHÂTELIER'S PRINCIPLE

Chemical systems that are in equilibrium can be easily affected by a change in conditions such as pressure, concentration or temperature. The French chemist, Henri Le Châtelier, summarised the effects of various changes to equilibrium systems in the Principle named after him. Le Châtelier's principle helps us predict the direction of the change. It can be stated simply as follows:

> ***If a change in conditions is made to a chemical system in equilibrium, then the system will adjust in such a way as to partially counteract the imposed change.***

For a system at equilibrium this means that

- increasing the *concentration* of a substance will favour the reaction which uses up that substance
- increasing the *pressure* of a gas will favour the reaction which decreases the pressure
- increasing the *temperature* of the system will favour the reaction which will lower the temperature.

Effect of changing concentration

Suppose that for a system at equilibrium, more of one particular substance is added. This will increase the concentration of that substance and hence the rate of the reaction that consumes it.

Consider the following system at equilibrium:

$$PCl_{3(g)} \quad + \quad Cl_{2(g)} \quad \rightleftharpoons \quad PCl_{5(g)}$$

Suppose that further $Cl_{2(g)}$ is added. Then:

- the forward reaction rate would increase while the reverse reaction rate would not initially be affected. (Since the concentration of the $PCl_{5(g)}$ has not changed.)
- as more $PCl_{5(g)}$ is produced, the reverse reaction rate also begins to increase.
- a new equilibrium would eventually be reached with identical new forward and reverse reaction rates.

The changes in concentration that occur can be illustrated graphically as shown below:

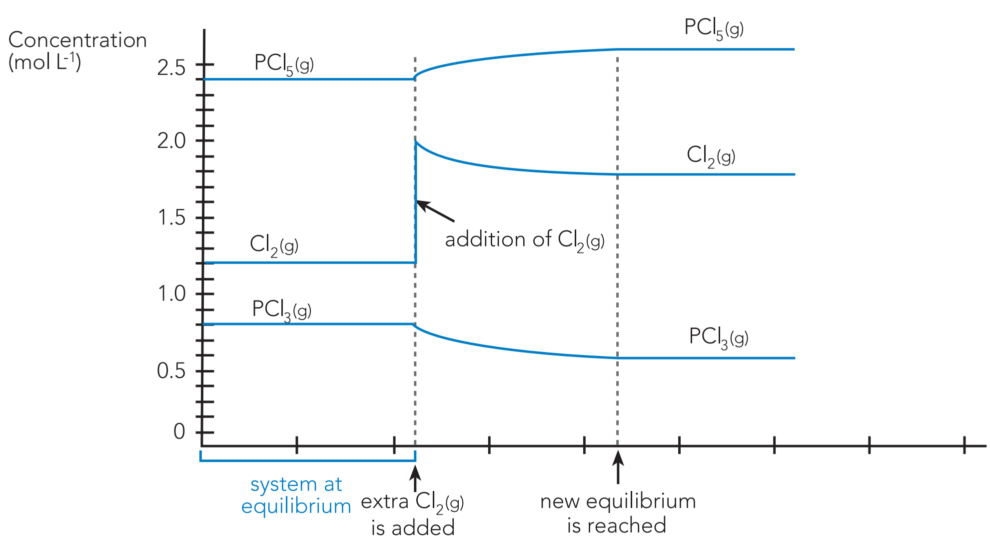


Figure 1.10 Effect of changing concentrations of a system at equilibrium.

Question 1.10

The following data refers to the equilibrium system illustrated in Figure 1.10 Complete the calculation for the equilibrium constant expression in each case and then answer the questions that follow. The numbers in the table represent concentrations in mol L^{-1}.

	$[PCl_3(g)]$	$[Cl_2(g)]$	$[PCl_5(g)]$	$\frac{[PCl_5]}{[PCl_3]\,[Cl_2]}$
Equilibrium (initial)	0.80	1.20	2.40	
Extra $Cl_{2(g)}$ added	0.80	2.00	2.40	
Equilibrium (new)	0.585	1.785	2.615	

(a) If some of the $PCl_{5(g)}$ were removed from the system at its new equilibrium how would this *initially* affect:

- forward reaction rate? ___________________________________
- reverse reaction rate? ___________________________________

(b) ***For the experts*:*** suppose that some PCl_5 is removed so that $[PCl_{5(g)}]$ is reduced from 2.62 mol L^{-1} to 2.00 mol L^{-1}. Use K to determine the approximate concentration of all species as a new equilibrium position is established. (Hint: assume a likely value for PCl_5, then use the equation of reaction to determine consequent values for PCl_3 and Cl_2. Determine value of equilibrium constant expression.)

____

____

____

____

Question 1.11

Predict the *initial* changes to reaction rate and the favoured reaction direction for the following systems, initially at equilibrium. The first case is done for you.
Note R/R = reaction rate.

System at equilibrium	Imposed change	Initial change to → R/R	← R/R	Direction favoured
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	increase $I_2(g)$	increase	nil	→
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	increase $NH_3(g)$			
$Ba(OH)_2(s) \rightleftharpoons Ba^{2+}(aq) + 2OH^-(aq)$	increase $Ba^{2+}(aq)$			
$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$	increase HCN(aq)			
$MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$	decrease $CO_2(g)$			
$MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$	decrease $MgCO_3(s)$			

* *May not be required in your course.*

Effect of changing pressure or volume of a gas

In equilibrium systems involving gases, changing the volume can alter the pressure and hence the concentration of all species. This will cause a change in both the forward and reverse reaction rates. The favoured reaction direction will depend on the number of gas particles present in the reactants and products.

Consider the following two examples where the systems are initially at equilibrium and have the pressure increased by reducing the volume of the reaction vessel.

e.g. 1. $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$

2 gas molecules → *2 gas molecules*

An increase in pressure will have no effect on the equilibrium position of this reaction. In this example above both forward and reverse reactions increase equally since the number of gas particles are the same. Hence there is no change in equilibrium position, just a change in reaction rate.

e.g. 2. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

4 gas molecules → *2 gas molecules*

An increase in pressure will favour the side with the least number of molecules. This is in accordance with Le Châtelier's Principle. When the pressure is increased (by say reducing the volume), the number of gas particles in a given volume increases. The system will oppose this change by favouring the reaction which produces the least number of particles. In the example above the favoured reaction direction would be to the right.

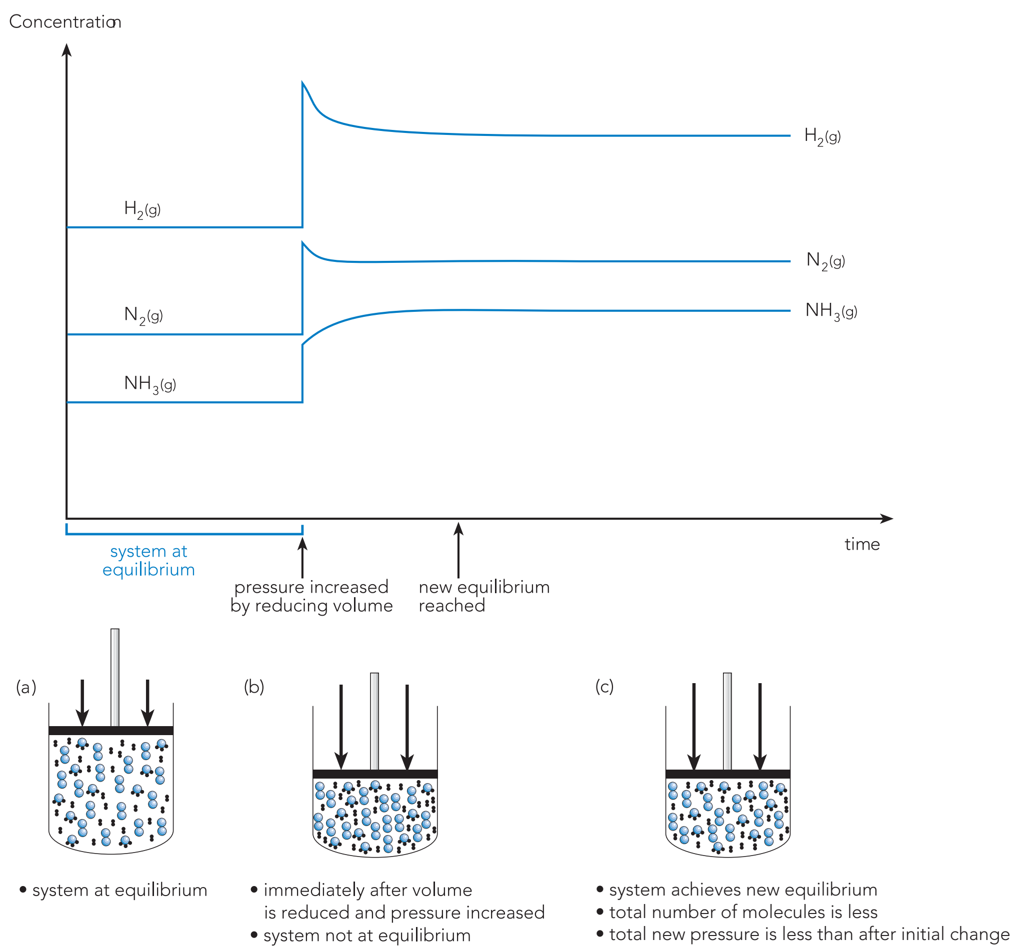


Figure 1.11 *Effect of changing pressure or volume of a gaseous system at equilibrium.*

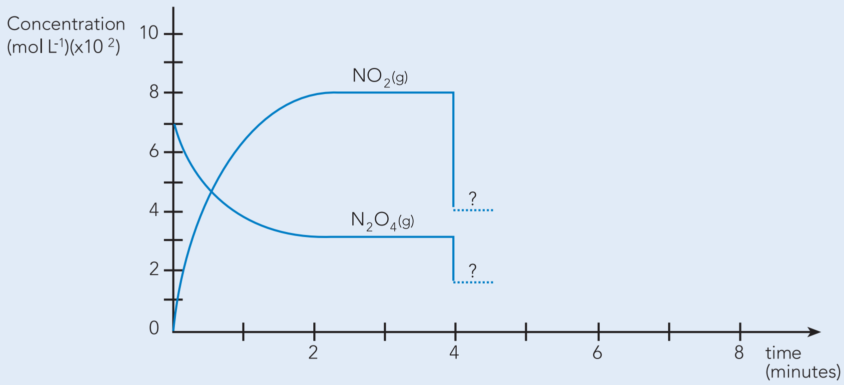
Question 1.12

Predict the favoured reaction direction in the following cases. The first case is done for you. Volume changes refer to a *gaseous* system.

System at equilibrium	Imposed volume change	Consequent pressure change	Direction favoured
$CO_{2(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$	decrease	increase	→
$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$	increase		
$N_2O_{4\,(g)} \rightleftharpoons 2NO_{2(g)}$	increase		
$2HgO_{(s)} \rightleftharpoons 2Hg_{(l)} + O_{2\,(g)}$	decrease		
$6CO_{2(g)} + 6H_2O_{(l)} \rightleftharpoons C_6H_{12}O_{6(g)} + 6O_2$	increase		
$2SO_{2(g)} + O_{2\,(g)} \rightleftharpoons 2SO_{3(g)}$	decrease		

Question 1.13

The graph below indicates the concentrations of $NO_{2(g)}$ and $N_2O_{4(g)}$ in a closed system during the first 4 minutes of an experiment.



(a) Write an equation for the reaction.

____

(b) Write an equilibrium constant expression for the reaction.

K = ______________

(c) What substance(s) were initially present in this closed system? (i.e. at t = 0).

____

(d) At what time was equilibrium reached? ______________

(e) What happened to the pressure of the gases at t = 4 minutes?
How do you think this was achieved?

____

(f) Indicate on the graph the likely changes to the concentrations of $NO_{2(g)}$ and $N_2O_{4(g)}$ as a new equilibrium is established.

Effect of changing temperature

In considering the effect of a temperature change it is best to include the heat of reaction as part of the equation. In this way heat can be considered as one of the 'reactants'.

Consider:

$$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)} \qquad \Delta H = -113 \text{ kJ mol}^{-1} \text{ (exothermic)}$$

This exothermic reaction can be rewritten as:

$$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)} + 113 \text{ kJ}$$

If heat is added to this system at equilibrium the system reaction will move in the direction that uses up heat. In this case the reverse reaction is favoured.

Note that both the forward and reverse reaction rates increase except that the reverse reaction rate increases to a greater extent initially.

Question 1.14

Predict the favoured reaction direction in the following cases. The first case is done for you.

System at equilibrium	Temperature change	Direction favoured
$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} + 92 \text{ kJ}$	decrease	$\rightarrow$
$N_2O_{4(g)} + 54 \text{ kJ} \rightleftharpoons 2NO_{2(g)}$	increase	
$CH_3OH_{(g)} + 91 \text{ kJ} \rightleftharpoons 2H_{2(g)} + CO_{(g)}$	decrease	
$S_{(s)} + O_{2(g)} \rightleftharpoons SO_{2(g)} + 297 \text{ kJ}$	increase	
$C_{(s)} + H_2O_{(l)} + 131 \text{ kJ} \rightleftharpoons CO_{(g)} + H_{2(g)}$	decrease	

Effect of using catalysts

Catalysts effectively provide a lower activation energy pathway for a reaction (see fig 1.5) and hence help increase both the forward and reverse reaction rates. Hence catalysts do not affect equilibrium position but are useful in helping reactions achieve equilibrium more quickly.

Reaction rate and equilibrium position

These two aspects of any reaction should be treated **independently** when predicting changes to a system. An increase in reaction rate, for example, does not necessarily favour products (as is often imagined).

Predicting changes to a system - complex examples

An imposed change to a system may cause changes to:

- reaction rate (forward and/or reverse)
- concentration of reactants/products

- equilibrium position (usually)
- temperature.

These situations are best dealt with in tabular form as in the following examples.

Question 1.15

The following reaction is at equilibrium:

$$2NO_{(g)} + Br_{2(g)} \rightleftharpoons 2NOBr_{(g)}$$

Determine the effect of imposing the changes indicated in the table below. The first case has been done for you. Note R/R = reaction rate, U = unchanged.

[Hint: it is best to determine the effect on the equilibrium position first.]

Imposed change	Initial change to		Final change to			New equilibrium position
	→ R/R	← R/R	[NO]	[Br_2]	[NOBr]	→, ← or U
Adding NO	inc	nil	inc	dec	inc	→
Removing some NOBr						
Decreasing volume of system						

Question 1.16

Complete the following table which relates to the reaction shown:

$$C_{(s)} + H_2O_{(l)} + 131\text{ kJ} \rightleftharpoons CO_{(g)} + H_{2(g)}$$

Imposed change	Initial change to		Final change to			New equilibrium position
	→ R/R	← R/R	[H_2O]	[CO]	[H_2]	→, ← or U
Removing some H_2						
Adding a catalyst						
Increasing temperature						
Increasing pressure						

1.6 CARBON DIOXIDE EQUILIBRIUM IN WATER

Carbon dioxide readily dissolves in water. We are all familiar with carbonated beverages which contain dissolved CO_2 and the pleasant bubbles produced when the gas escapes from the liquid.

The dissolution of carbon dioxide in water causes some of it to react with water to form carbonic acid, $H_2CO_{3(aq)}$. The carbonic acid, a weak acid, partially dissociates to form hydrogen ions ($H_3O^+{}_{(aq)}$) and bicarbonate ions ($HCO_3^-(aq)$). Further dissociation forms more hydrogen ions as well as carbonate ions($CO_3^{2-}(aq)$) . A complex chemical equilibrium exists between all these species as shown below.

$$CO_{2(g)} \rightleftharpoons CO_{2(aq)}$$

$$CO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)}$$

$$H_2CO_{3(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + HCO_3^-{}_{(aq)}$$

$$HCO_3^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + CO_3^{2-}{}_{(aq)}$$

The take up of atmospheric carbon dioxide by the water in lakes and oceans is an ongoing process that occurs fairly readily. As we can see from the equations above, this affects the acidity of the water ($H_3O^+{}_{(aq)}$ ions) but also provides the carbonate ions ($CO_3^{2-}{}_{(aq)}$) necessary for the formation of calcium carbonate structures in a variety of marine organisms.

A current concern is that the increased levels of carbon dioxide in the atmosphere cause more of it to dissolve in ocean waters. This leads to an increase in *ocean acidity* and possible negative effects on marine ecosystems. In particular the increased acidity reduces the *calcification process* necessary for many marine organisms.

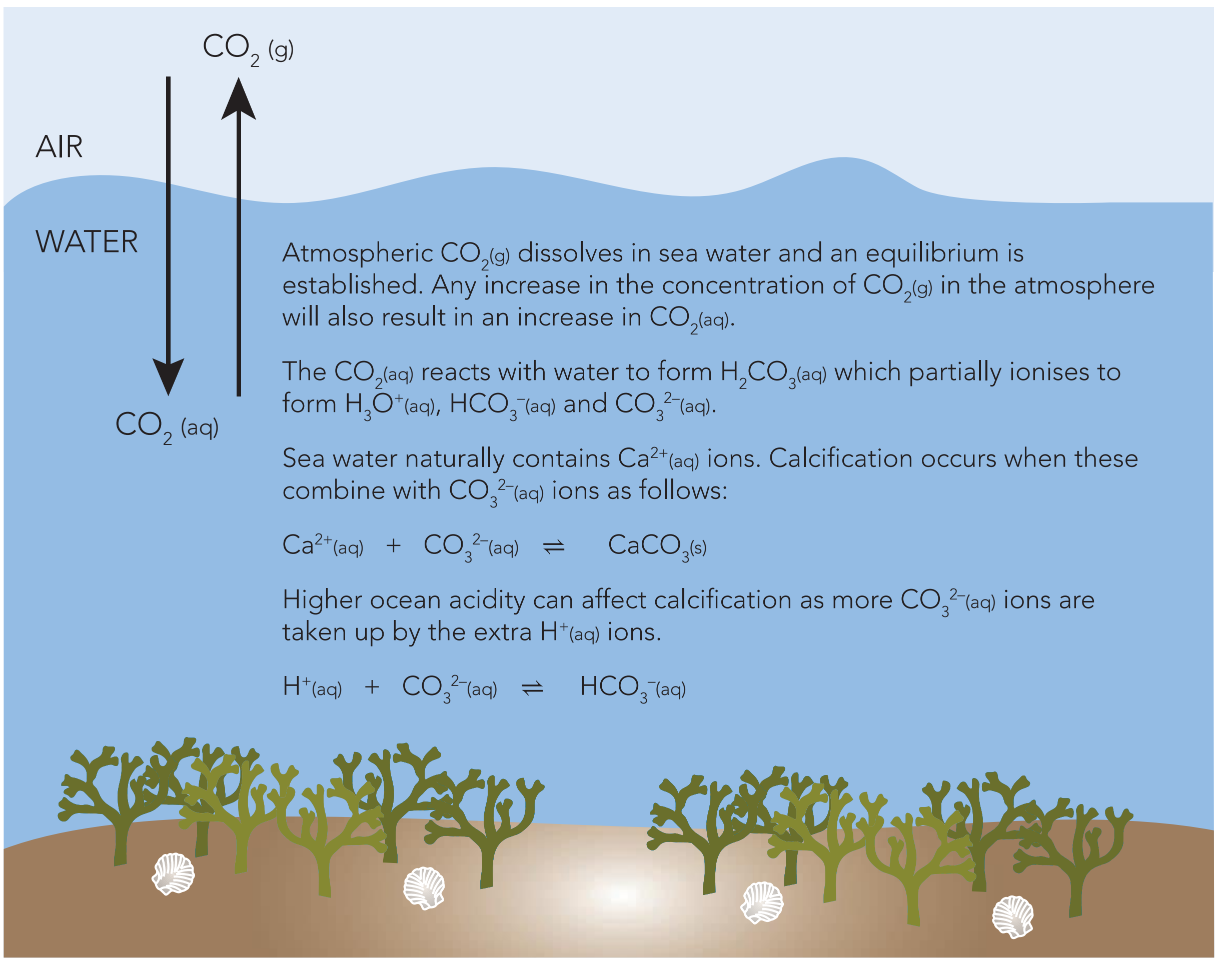


Figure 1.12 Carbon dioxide equilibrium in sea water. The dissolution of carbon dioxide in sea water is an ongoing natural process. The hydrogen ions produced affect ocean acidity while the carbonate ions make the process of calcification possible.

REVIEW QUESTIONS

Chapter 1: Chemical Equilibrium

1. Indicate whether each of the following is true or false. Alter any false statement so that they are true.
   (a) Ionic reactions are more rapid than molecular reactions.
   (b) Catalysts are not themselves consumed in a reaction.
   (c) Chemical equilibrium only exists if the reactant and product concentrations are equal.
   (d) For a chemical system in equilibrium the forward reaction rate will increase if some of the product is removed from the system.
   (e) For a chemical system in equilibrium any change made that affects the equilibrium position will cause the equilibrium to shift in the direction that will partially counteract the change.

2. (a) List 5 factors that can affect the rate of a chemical reaction.
   (b) Define the activation energy of a reaction.

3. In order to produce H_2 gas a strip of $Al_{(s)}$ was placed into 500.0 mL of a 3.50 mol L^{-1} solution of caustic soda.

$$2Al_{(s)} + 2OH^-_{(aq)} + 6H_2O_{(l)} \rightarrow 2Al(OH)_4^-{}_{(aq)} + 3H_{2(g)}$$

   State what effect **each** of the following changes will have on the rate of this reaction and use the factors listed in question 1 to state why the change occurs.

   (a) Another 100 mL of 3.50 mol L^{-1} NaOH was added as the aluminium was placed into the original caustic soda solution.
   (b) The aluminium strip was cut into smaller pieces.
   (c) The reaction vessel was placed into a trough of cold water.
   (d) 25.0 mL of 5.00 mol L^{-1} NaOH was added to the mixture.

4. During the summer months, the Health Department recommends that you do not buy sandwiches that are left on the counter for customers to see and select. The Health Department is concerned about bacteria that the food may contain.

   (a) What is the connection between the Department's concern and the summer period? You must relate your answer to the factors affecting reaction rates.
   (b) Shop owners need to have these pre-made to allow for fast service. Use your knowledge of reaction rates to suggest how the problem of rapid bacteria growth in the warm sandwiches can be overcome.

5. $I_{2(aq)} + 2S_2O_3^{2-}{}_{(aq)} \rightleftharpoons 2I^-_{(aq)} + S_4O_6^{2-}{}_{(aq)}$

   [NB: $S_2O_3^{2-}{}_{(aq)}$, $S_4O_6^{2-}{}_{(aq)}$ and $I^-_{(aq)}$ are colourless. $I_{2(aq)}$ is brown.]

   (a) What observations would you expect to make as the reaction progresses?
   (b) As the reaction progresses, what will happen to the rate of this reaction? Use a concentration versus time graph to illustrate your answer.

6. 'Catalysts are used to speed up chemical reactions. Apart from increasing the rate of a chemical reaction, catalysts also have the important feature of being reusable because they are not consumed in the reaction.'

   (a) Comment on the accuracy of this statement.
   (b) How do catalysts increase the rate of a chemical reaction?

7. A closed chemical system is one that can exchange energy with its surroundings, but not matter. What are the two characteristics of such a closed chemical system (at a constant temperature) that would indicate it is in equilibrium?

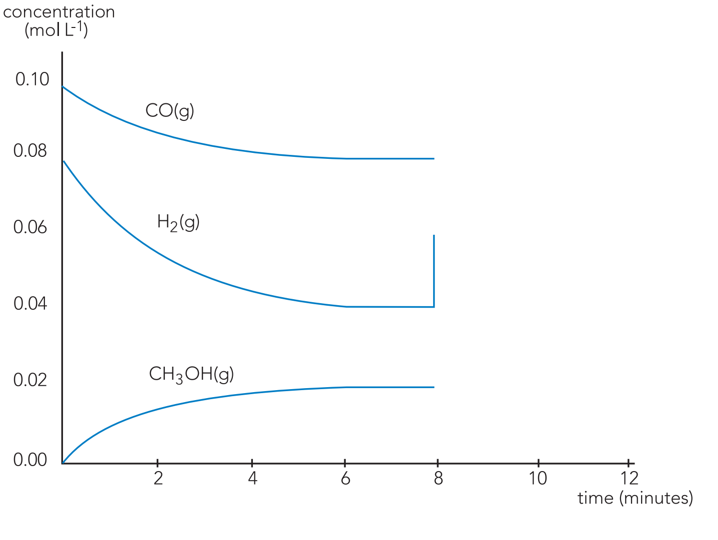
8. Consider the closed chemical system that is described by the equation below:

$$2CrO_4^{2-}{}_{(aq)} + 2H^+{}_{(aq)} \rightleftharpoons Cr_2O_7^{2-}{}_{(aq)} + H_2O_{(l)}$$

   (a) State the colours of the four chemical species listed.
   (b) What observations would indicate that the system was at equilibrium?
   (c) Write the expression for the equilibrium constant for this reaction.
   (d) Indicate the changes that may be observed if some dilute NaOH was added.

9. State Le Châtelier's principle.

10. The following graph shows the concentration of the different substances involved in an equilibrium reaction.



   (a) Write an equation for this reaction.
   (b) At what time did the system reach equilibrium?
   (c) Some hydrogen gas was added at t = 8 minutes as shown. Sketch on the graph the likely curves to t = 12 minutes.
   For Experts only: Use the expression for K to help you estimate the final concentration of $CO_{(g)}$ when a new equilibrium is reached.

11. The complex ion, iron(III) thiocyanate is blood red in colour, while at low concentrations the iron(III) and thiocyanate ions are colourless. Use Le Châtelier's Principle to predict what effects the following changes will have to the equilibrium system described by the reaction below:

$$Fe^{3+}{}_{(aq)} + SCN^-{}_{(aq)} \rightleftharpoons Fe(SCN)^{2+}{}_{(aq)}$$

[Fe $(SCN)^{2+}{}_{(aq)}$ remains soluble in basic solutions.]

State your answer as "no change", "solution becomes a deeper red" or "solution loses red colour".

(a) The concentration of Fe^{3+} ions is increased by the addition of a small amount of an iron(III) chloride solution.
(b) The volume of the system is increased with the addition of distilled water.
(c) Some 1.00 mol L^{-1} NaOH solution is added to the system.

12. Use Le Châtelier's principle to predict what effect the following changes will have on the equilibrium yield of carbon dioxide from the thermal decomposition of calcium carbonate:

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

(a) Grinding the calcium carbonate into a very fine powder before use.
(b) Increasing the pressure in the system through the addition of some helium gas.
(c) The addition of extra calcium oxide to the system.
(d) The lid of the reaction vessel was removed for a brief moment to stir the contents. During this time some of the carbon dioxide escaped.

13. The production of ethyl ethanoate from ethanol and ethanoic acid is summarised by the equation below:

$$CH_3CH_2OH_{(l)} + CH_3COOH_{(l)} \rightleftharpoons CH_3CO_2C_2H_{5(l)} + H_2O_{(l)}$$

Concentrated sulfuric acid can be used as a catalyst.

(a) How does the use of a catalyst affect the equilibrium yield of ethyl ethanoate?
(b) Why are catalysts used in industrial processes that are reversible?

14. A 2.0 L reaction vessel is set up to investigate the following equilibrium reaction at 100°C.

$$2CO_{(g)} + O_{2(g)} \rightleftharpoons 2CO_{2(g)} \quad \Delta H = +564 \text{ kJ mol}^{-1}$$

Assuming the reaction is at equilibrium indicate what will happen if the following changes to the equilibrium mixture are made. Assume in each case there has been sufficient time to reach a new equilibrium.

Change made to equilibrium mixture	Effect on total gas pressure	Effect on $[O_2(g)]$	Effect on equilibrium position	Effect on value of K
Temp reduced to 50°C				
More O_2 gas at 100°C is added				
Some Ar gas at 100°C is added				
Volume of reaction vessel is reduced to 1.5 L				
Small pellets of a catalyst are added				

15. One industrial method of producing hydrogen is to pass steam over iron:

$$3Fe_{(s)} + 4H_2O_{(g)} \rightleftharpoons Fe_3O_{4\,(s)} + 4H_{2(g)}$$

(a) Write the expression for the equilibrium constant.
(b) Suggest why this process might be conducted in an open container rather than a closed one.
(c) The steam is injected through a system of iron mesh. Suggest a reason the iron is in mesh rather than sheet form.

16. The decomposition of carbon dioxide into carbon and oxygen is an endothermic reaction. It is also reversible.

(a) Given that the ΔH for the reaction as described is +394 kJ mol^{-1}, write the balanced equation for the decomposition of CO_2. Include energy in the equation.
(b) If the volume of the reaction vessel is decreased, how will the value of the equilibrium constant be affected? (i.e. will it increase, decrease or stay the same?)
(c) If the system is heated, will the forward or reverse reaction be favoured? Use Le Châtelier's Principle to explain your answer.

17. Carbon dioxide continuously dissolves in ocean waters and equilibrium exists between the carbon dioxide in the air and that dissolved in water. When some of the carbon dioxide in the water reacts it can affect ocean acidity.

(a) Use equations to explain how ocean acidity is affected.
(b) Use Le Châtelier's Principle and relevant equations to predict any changes to ocean acidity if the concentration of carbon dioxide in the atmosphere is increased.
(c) Similarly show how the formation of calcium carbonate may be affected by the increase in atmospheric carbon dioxide.

18. The level of acidity of human blood is controlled by a carbonic acid/hydrogen carbonate equilibrium. The equation for this reaction is given below:

$$H_2CO_{3(aq)} + H_2O_{(l)} \rightleftharpoons HCO_3^-{}_{(aq)} + H_3O^+{}_{(aq)}$$

The kidneys can counteract an increase in acidity by increasing the rate of excretion of $HCO_3^-{}_{(aq)}$ into the bloodstream.

In examining this biological example of chemical equilibrium a student established this equilibrium situation in a volumetric flask. What effect would the following changes have upon the $H_3O^+{}_{(aq)}$ concentration of this experimental set up?

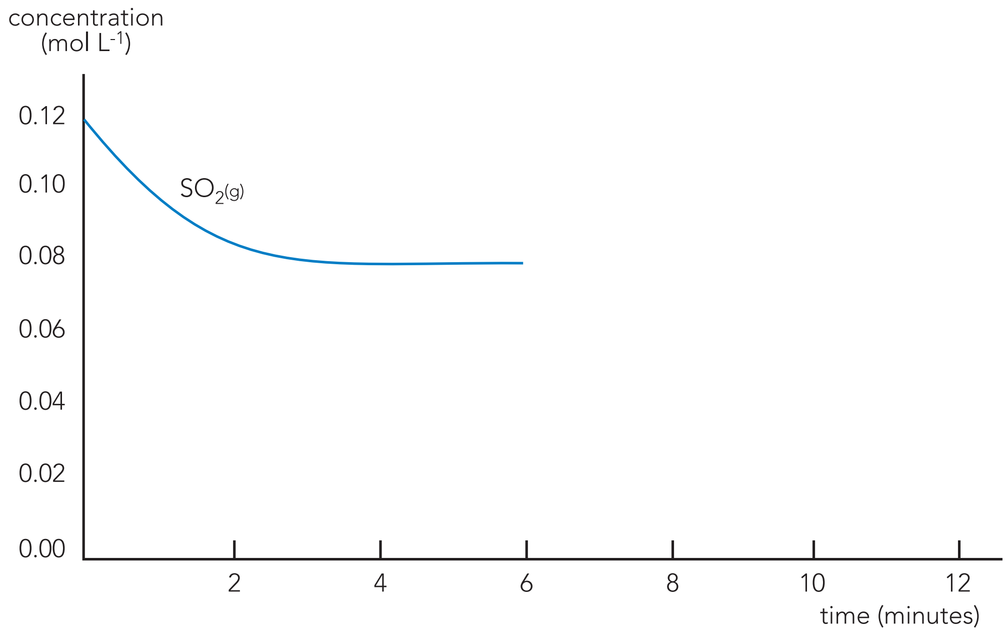
(a) The addition of $H_2CO_{3(aq)}$.
(b) The addition of an antacid powder of which the principal active ingredient is $Mg(OH)_2$.
(c) The addition of $H_2O_{(l)}$.

FOR THE EXPERTS

19. An important industrial process (see Chapter 4) involves the reaction between sulphur dioxide and oxygen to form sulphur trioxide which is itself used in the manufacture of sulphuric acid. The equation for the reaction is as follows:

$$2SO_{2(g)} \quad + \quad O_{2(g)} \quad \rightleftharpoons \quad 2SO_{3(g)}$$

In an experiment to investigate the equilibrium that exists between these gases at a particular temperature, 0.12 mol of sulphur dioxide gas and 0.08 mol of oxygen gas were placed in a 1.00 L container. As a reaction occurred, the change in concentration of sulphur dioxide was monitored for some minutes. The data was graphed as shown below.



(a) Write an expression for the equilibrium constant K for this reaction.

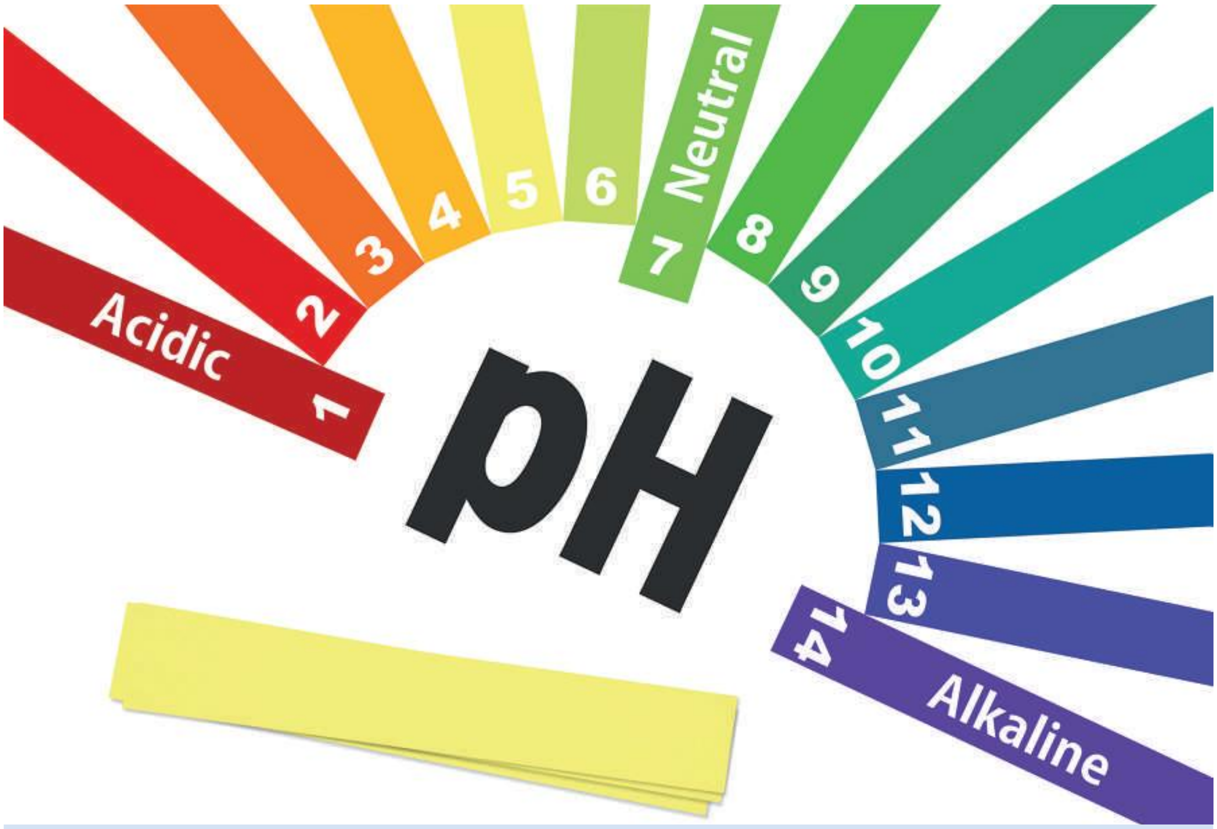
(b) Explain the significance of the horizontal part of the graph for $SO_{2(g)}$ between t = 4 to t = 6.

(c) Use the equation above to determine the concentrations of oxygen gas and sulphur trioxide gas at t = 6.

(d) On the graph sketch the variation in concentration for oxygen gas and sulphur trioxide gas from t = 0 to t = 6.

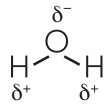
(e) All the sulphur trioxide was removed from the container at t = 6. Show graphically the approximate changes that are likely to occur to the concentrations of the gases as they reach a new equilibrium at t = 12.

2 ACIDS AND BASES



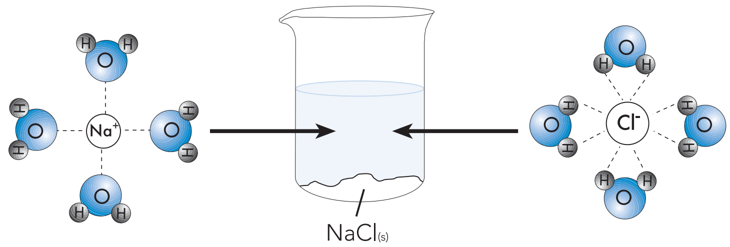
Topics covered in this chapter:

2.1 ELECTROLYTES



The size, shape and polarity of water molecules make it possible for them to pack very closely around solute particles (ions or molecules). This makes water a very good solvent.

e.g.: $NaCl_{(s)}$ in water:



- Negative region of H_2O is attracted to positive Na^+ ion.
- H_2O molecules 'pull' Na^+ ion from the Cl^- ion and disperse the Na^+ ions throughout the solution.
- Positive region of H_2O attracted to the negative Cl^- ions and the same process occurs with Cl^- ions which causes $NaCl_{(s)}$ to dissolve.

Substances that dissolve in water and form ions are called ELECTROLYTES.

STRONG ELECTROLYTES – Are good conductors of electricity in aqueous solution because water causes them to dissociate (ionic substances) or completely ionise (covalent molecular substances). Ionic substances are all strong electrolytes even if only slightly soluble since any amount dissolved completely breaks up into ions. Strong acids are also strong electrolytes as they completely ionise in solution.

$$NaCl_{(s)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$$

$$HCl_{(g)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

WEAK ELECTROLYTES – Are poor conductors of electricity in aqueous solution. Only a small percentage of molecules ionise when dissolved in water and so only a small concentration of ions is produced to conduct charge. Weak acids, and weak covalent molecular bases (such as NH_3), tend to be weak electrolytes.

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$$

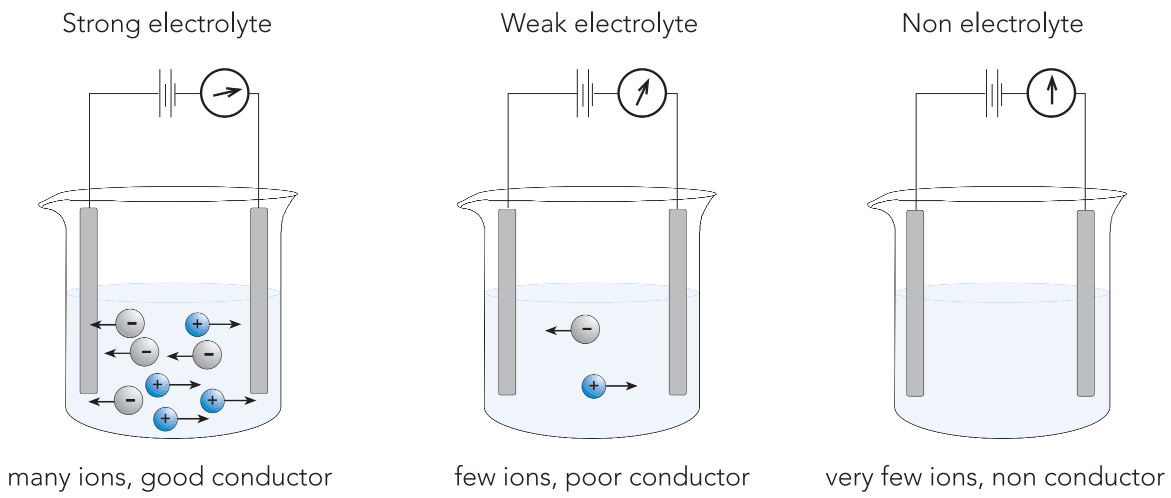
$$H_2O + NH_{3(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-_{(aq)}$$

The double arrow ($\rightleftharpoons$) is used to indicate that only a small percentage of molecules ionise.

NON ELECTROLYTES - Are non-conductors of electricity because no ions are produced when they dissolve in water.

$$C_6H_{12}O_{6(s)} \rightarrow C_6H_{12}O_{6(aq)}$$

Glucose molecules dissolve but no ions are formed.



Self-Ionisation of Water

Water, no matter how pure, is always a very weak conductor of electricity. This is due to the self ionisation of water.

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

A 1.00 litre sample of pure water at 25°C contains 1.00×10^{-7} mol of H^+ ions and 1.00×10^{-7} mol of OH^- ions.

i.e. at 25°C, $[H^+] = [OH^-] = 1.00 \times 10^{-7}$ mol L^{-1} and because $[H^+] = [OH^-]$ the water is said to be neutral.

The equilibrium constant for this self ionisation is given the symbol K_w.

$K_w = [H^+]\,[OH^-] = 1.00 \times 10^{-14}$ at 25°C

The only factor that effects K_w is the temperature. As temperature rises, so does K_w but if it is pure water, no matter what the value of K_w, $[OH^-] = [H^+]$.

ACIDIC SOLUTIONS:	$[H^+]$	$>$	$[OH^-]$
or	$[H^+]$	$>$	1.00×10^{-7} mol L^{-1} at 25°C
and	$[OH^-]$	$<$	1.00×10^{-7} mol L^{-1} at 25°C
BASIC SOLUTIONS:	$[H^+]$	$<$	$[OH^-]$
or	$[H^+]$	$<$	1.00×10^{-7} mol L^{-1} at 25°C
and	$[OH^-]$	$>$	1.00×10^{-7} mol L^{-1} at 25°C
NEUTRAL SOLUTIONS:	$[H^+]$	$=$	$[OH^-]$
or	$[H^+]$	$=$	1.00×10^{-7} mol L^{-1} at 25°C
and	$[OH^-]$	$=$	1.00×10^{-7} mol L^{-1} at 25°C

Worked Examples

2.1 Calculate the $[OH^-]$ of a 2.00×10^{-2} mol L^{-1} solution of HCl

NB: HCl is a strong acid and will completely ionise

i.e. $HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$

therefore $[H^+] = [HCl] = 2.00 \times 10^{-2}$ mol L^{-1}

$$K_w = [H^+][OH^-]$$

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.00 \times 10^{-14}}{2.00 \times 10^{-2}}$$

$$[OH^-] = 5.00 \times 10^{-13} \text{ mol L}^{-1}$$

2.2 Calculate the $[H^+]$ of a 0.350 mol L^{-1} solution of $Ba(OH)_2$.

$$Ba(OH)_{2(aq)} \rightarrow Ba^{2+}_{(aq)} + 2OH^-_{(aq)}$$

$$[OH^-] = 2 \times [Ba(OH)_2] = 0.700 \text{ mol L}^{-1}$$

$$K_w = [H^+][OH^-]$$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.00 \times 10^{-14}}{0.700}$$

$$[H^+] = 1.43 \times 10^{-14} \text{ mol L}^{-1}$$

2.3 Calculate the final pH of a solution made by mixing 25.0 mL of 0.0750 mol L^{-1} $HCl_{(aq)}$ with 32.5 mL of 0.0675 mol L^{-1} $KOH_{(aq)}$.

c.V		c.V				
HCl	+	KOH	→	KCl	+	H_2O

$n(HCl) = c.V = 0.0750 \times 0.0250 = 1.875 \times 10^{-3}$ mol
$n(KOH) = c.V = 0.0675 \times 0.0325 = 2.194 \times 10^{-3}$ mol

Enough information is known to calculate the moles ($n = c \times V$) of both HCl and KOH. This is a limiting reagent problem.

As the mole ratio from the balanced equation is 1:1, HCl is limiting reagent as n(HCl) < n(KOH).

∴ In the final solution, all HCl has been consumed and the pH is affected by n(KOH) not consumed. See next page for pH calculation.

$$n(KOH) \text{ not consumed} = 2.194 \times 10^{-3} - 1.875 \times 10^{-3} = 3.188 \times 10^{-4} \text{ mol}$$

$$c(KOH) = \frac{n}{V} = \frac{3.188 \times 10^{-4}}{(0.0250 + 0.0325)} = 5.54 \times 10^{-3} \text{ mol L}^{-1}$$

$$[H^+] = \frac{1.00 \times 10^{-14}}{5.54 \times 10^{-3}} = 1.80 \times 10^{-12} \text{ mol L}^{-1}$$

$$pH = -\log[H^+] = 11.7$$

2.2 THE pH SCALE

The pH of a solution is a measure of its acidity. It depends on the hydrogen ion concentration of the solution and is defined as follows.

$$pH = -\log_{10} [H^+]$$

pH	<	7	acidic
pH	=	7	neutral
pH	>	7	basic

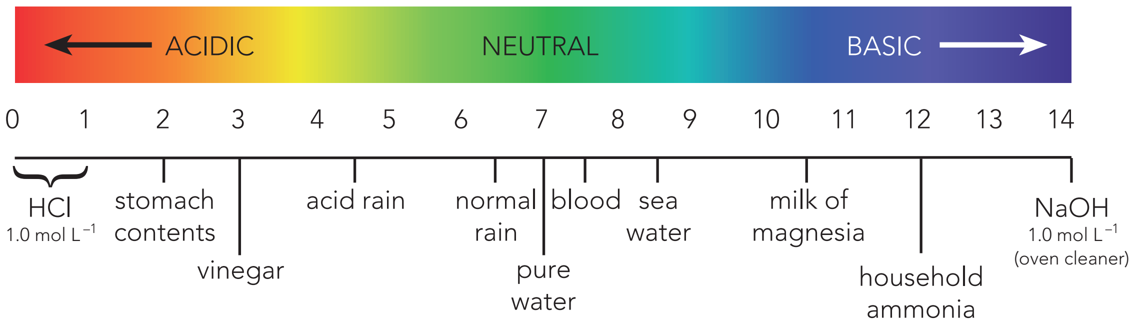


Figure 2.1 The pH acidity scale. As pH increases acidity decreases. An increase in pH by 1 means that a solution is only $\frac{1}{10}$ as acidic.

Question 2.1

Calculate the pH of 1.00 L of an antacid solution that contained 50.0 mg of $Mg(OH)_2$ as its main ingredient.

____

____

____

Question 2.2

(a) Determine the $[H^+]$ and the $[OH^-]$ of a sample of orange juice that had a pH of 3.60.

____

____

____

____

(b) Determine the $[H^+]$ and $[OH^-]$ if the orange juice was then diluted by an equal volume of water (i.e. its volume was doubled using water).

____

____

____

____

Question 2.3

At 50.0°C, pure water was found to have a Kw of 5.48×10^{-14}. Determine the pH of the water at 50.0°C.

____

____

____

Question 2.4

A sample of sulfuric acid was found to have a pH of 2.50 at 50°C. Determine the [OH-] of this sample.

____

____

____

Question 2.5

Calculate the final pH of the solution formed when 47.5 mL of 0.540 mol L^{-1} HNO_3 is mixed with 55.5 mL of 0.444 mol L^{-1} NaOH.

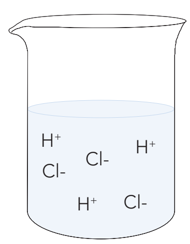
____

____

____

2.3 THEORIES ON ACIDS AND BASES

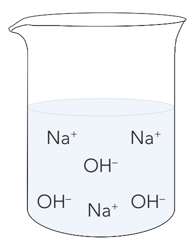
Arrhenius Theory (1880)



- acids provide hydrogen ions in aqueous solution

  $HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$

  $HNO_{3(aq)} \rightarrow H^+_{(aq)} + NO_3^-{}_{(aq)}$



- bases provide hydroxide ions in aqueous solution

  $NaOH_{(aq)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$

  $Ca(OH)_{2(aq)} \rightarrow Ca^{2+}_{(aq)} + 2OH^-_{(aq)}$

- neutralisation occurs when H^+ ion and OH^- ion combine to form $H_2O_{(l)}$

Neutralisation Reaction between $HCl_{(aq)}$ and $NaOH_{(aq)}$ is

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$$

The Arrhenius model is restricted to aqueous solutions. A more general theory with wider application was proposed in 1923 by Johannes Brønsted (Denmark) and Thomas Lowry (England).

Brønsted-Lowry Theory (1923)

- acids act as proton (H^+) donors
- bases act as proton (H^+) acceptors

e.g. 1: proton donated

$$\underset{\text{ACID}}{HCl_{(aq)}} + \underset{\text{BASE}}{NH_{3(aq)}} \rightleftharpoons NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$$

HCl is acting as an acid by donating a proton (H^+) to NH_3. NH_3, therefore, is acting as a base as it is accepting a proton.

e.g. 2: H^+ donated

$$\underset{\text{ACID}}{H_2O_{(l)}} + \underset{\text{BASE}}{NH_{3(aq)}} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

H_2O is acting as an acid (proton donor). NH_3 is acting as a base (proton acceptor)

e.g. 3: H^+ transferred

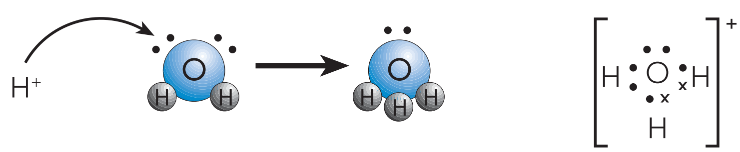
$$\underset{\text{ACID}}{H_2PO_4^-{}_{(aq)}} + \underset{\text{BASE}}{H_2O_{(l)}} \rightleftharpoons HPO_4^{2-}{}_{(aq)} + H_3O^+{}_{(aq)}$$

$H_2PO_4^-$ is acting as an acid (donating a proton). $H_2O_{(l)}$ is acting as a base (accepting a proton).

Note how H_2O can act either as an acid or a base using this theory (amphiprotic).

H+ – A closer look!

The simplest atom, hydrogen, consists of a proton surrounded by an electron. Hence the symbol **H^+** can be used to represent a **proton.** Protons are very small and readily attach themselves to the negative end of say, polar substances. In water they combine with H_2O to form the **hydronium ion, H_3O^+.**



proton | water molecule | hydronium ion (H_3O^+) | Lewis structure

Question 2.6

Complete the following equation so as to show HCO_3^- acting as (a) an acid, (b) a base.

(a) $HCO_3^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons$ ____________________

(b) $HCO_3^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons$ ____________________

Conjugate acids and bases

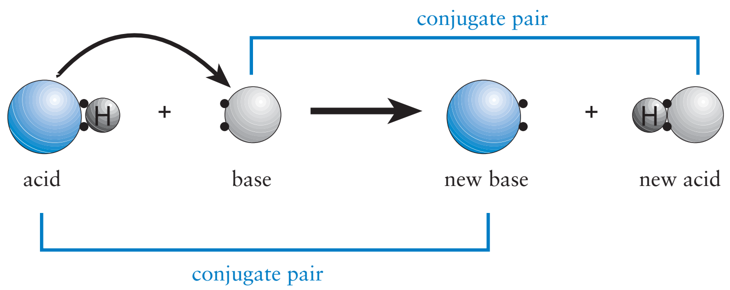
When an acid loses (donates) a proton, what is left behind is its conjugate base. Similarly when a base accepts a proton, the substance formed is its conjugate acid.

$$\underset{\text{ACID}}{CH_3COOH(aq)} + \underset{\text{BASE}}{H_2O(l)} \rightleftharpoons \underset{\text{BASE}}{CH_3COO^-(aq)} + \underset{\text{ACID}}{H_3O^+(aq)}$$

(H^+ transferred from CH_3COOH to H_2O, and from H_3O^+ to CH_3COO^-; conjugate pair: H_2O / H_3O^+; conjugate pair: CH_3COOH / CH_3COO^-)

i.e. CH_3COOH/CH_3COO^- and H_3O^+/H_2O

In general, the formation of conjugate pairs can be illustrated as follows.



Question 2.7

Complete the following tables. The first example in each case has been done for you.

(a)

acid	conjugate base
HCl	Cl^-
H_2SO_4	
HF	
H_2S	
HCO_3^-	

(b)

base	conjugate acid
CO_3^{-2}	HCO_3^-
NH_3	
$H_2PO_4^-$	
F^-	
HSO_4^-	

Question 2.8

Identify and list the conjugate acid/base pairs in each of the following.

(a) $NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$ ____________________

(b) $NH_3(aq) + PO_4^{3-}(aq) \rightleftharpoons NH_2^-(aq) + HPO_4^{2-}(aq)$ ____________________

2.4 STRENGTH OF ACIDS AND BASES

Strong acids completely ionise in water. For example, hydrogen chloride molecules in solution exist essentially as hydrogen ions, H^+ and chloride ions Cl^-.

e.g. $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$

Weak acids only partly ionise in water. For example, an ethanoic acid solution contains mostly CH_3COOH molecules.

e.g. $CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$

Notice the two arrows ($\rightleftharpoons$) are shown for the ionisation of weak acids.

Strong acids		Weak acids	
hydrochloric acid	HCl	oxalic acid	$H_2C_2O_4$
sulfuric acid	H_2SO_4	phosphoric acid	H_3PO_4
nitric acid	HNO_3	hydrofluoric acid	HF
hydrobromic acid	HBr	ethanoic acid	CH_3COOH
hydroiodic acid	HI	carbonic acid	H_2CO_3
perchloric acid	$HClO_4$	hypochlorous acid	$HClO$

Strong bases completely *dissociate* in water to produce hydroxide (OH^-) ions. Note that dissociation is simply the break up of ions that already exist within the ionic compound.

e.g. $NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$

Weak bases only partially react with water in forming hydroxide (OH^-) ions. Apart from ammonia (NH_3), most bases are anions such as CO_3^{2-} and CH_3COO^- which react with water to produce OH^- ions.

e.g. $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$

Strong bases		Weak bases	
Soluble			
sodium hydroxide	$NaOH$	ammonia	NH_3
potassium hydroxide	KOH	carbonate ion	CO_3^{2-}
Slightly soluble		ethanoate ion	CH_3COO^-
calcium hydroxide	$Ca(OH)_2$	fluoride ion	F^-
magnesium hydroxide	$Mg(OH)_2$	phosphate ion	PO_4^{3-}

Hydrolysis of Salts

Hydrolysis is the process in which an *ion* reacts with water to produce H_3O^+ ions **or** OH^- ions. Ions that produce H_3O^+ are said to be acidic while ions that produce OH^- are said to be basic.

Acidic Anions: HSO_4^- and $H_2PO_4^-$
(i.e. anion from a polyprotic acid)

Basic Anions: CH_3COO^-, HPO_4^{2-}, PO_4^{3-}, SO_4^{2-}, F^-, HCO_3^-, CO_3^{2-}, ClO^-, HS^-, CN^-
(anion from a weak acid)

Neutral Anions: Cl^-, NO_3^-, Br^-, I^-
(anions from strong acids)

Acidic Cations: NH_4^+, Al^{3+}, Fe^{3+}
(cation from a weak base or from aquated metal ions)

Basic Cations: There are no basic cations covered in the syllabus

Neutral Cations: Na^+, K^+, Ca^{2+}, Mg^{2+}, Li^+, Ba^{2+}
(Group I and II metal cations)

Worked Example

2.4 Write the equation for the hydrolysis of the following salt and classify the resulting solution as acidic or basic.

(a) Na_2SO_4:

$$SO_4^{2-}(aq) + H_2O(l) \rightleftharpoons HSO_4^-(aq) + OH^-(aq)$$

As OH^- ions are produced the solution is basic

(b) NH_4Cl:

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

As H_3O^+ ions are produced, the solution is acidic

(NB: When writing an hydrolysis equation, the neutral anion or cation is a spectator ion and omitted)

Question 2.9

Complete the following hydrolysis reactions and indicate the type of solution they form (acidic or basic).

(a) $HSO_4^-(aq) + H_2O(l) \rightleftharpoons$ ______________________

Solution becomes ______________________

(b) $CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons$ ______________________

Solution becomes ______________________

(c) $F^{-}(aq)$ + $H_2O(l)$ ⇌ ________________

Solution becomes ________________

(d) $HSO_4^{-}(aq)$ + $H_2O(l)$ ⇌ ________________

Solution becomes ________________

(e) $ClO^{-}(aq)$ + $H_2O(l)$ ⇌ ________________

Solution becomes ________________

Question 2.10

Complete the following table by predicting the nature of each salt solution as being acid, basic or neutral. The first is done for you.

Salt Solution	'Parent' base/acid	Nature
$NH_4NO_3(aq)$	weak base/strong acid	acidic
$NaCl\ (aq)$		
$Na_2CO_3\ (aq)$		
$KH_2PO_4\ (aq)$		
$MgF_2\ (aq)$		
$Ca(ClO)_2\ (aq)$		
$K_2SO_4\ (aq)$		

2.5 BUFFER SOLUTIONS

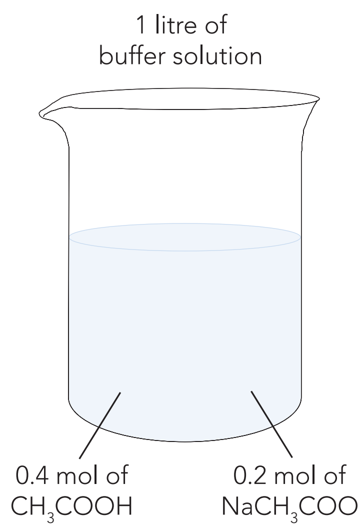
Buffer solutions are the mixture of a weak acid and its conjugate base or of a weak base and its conjugate acid. The advantage of buffer solutions is that they can maintain a relatively constant pH when quantities of acidic or basic materials are added to them. For a buffer to work, the amount of weak acid and its conjugate base must be large compared to the amount of H^+ and OH^- added or removed.

Buffer Capacity

Buffer capacity is the ability of the buffer to resist changes in pH. It refers to the amount of H^+ or OH^- that can be added without causing a 1 unit change to the pH of the buffer solution.

Buffering capacity increases as the concentration of the acid/conjugate base pair is increased. The greater the concentration of acid/conjugate base pair, the greater the amount of H^+ or OH^- that can be added without overwhelming the buffer's capacity to maintain a constant pH.

A buffer solution was made by dissolving enough CH_3COOH and $NaCH_3COO$ in water to produce a solution that contained 0.4 mol of $CH_3COOH(aq)$ and 0.2 mol of $CH_3COO^{-}(aq)$.



$$\underset{0.4\ mol}{CH_3COOH} + H_2O \rightleftharpoons \underset{0.2\ mol}{CH_3COO^-} + H_3O^+$$

The addition of only 0.01 mol of NaOH would neutralise 0.01 mol of H_3O^+. The forward reaction would be favoured to partially counteract this change. As there is 0.4 mol of CH_3COOH available for the production of H_3O^+ (as per the forward reaction), the buffer would be operating within its capacity and be able to maintain a constant pH.

However if 0.5 mol of NaOH was added to the solution, the buffer would be overwhelmed. It would not have sufficient moles of CH_3COOH to replace the H_3O^+ consumed by the NaOH. The pH of the buffer solution would change markedly.

Exercise tends to increase the acidity (reduce the pH) of blood. The presence of H_2CO_3 and its conjugate base, HCO_3^- help to maintain the bloods pH at 7.4.

Equation: $\underset{\text{ACID}}{H_2CO_{3(aq)}} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + \underset{\text{CONJUGATE BASE}}{HCO_3^-{}_{(aq)}}$

During exercise, more H_3O^+ is released into the blood from the muscles. Le Châtelier's Principle predicts that the reverse reaction would be favoured to partially counteract the increased $[H_3O^+]$ and effectively maintain a relatively constant blood pH.

Question 2.11

A second buffer solution in blood is the $H_2PO_4^-/HPO_4^{2-}$ combination.

(a) Write the equation for the reaction of the acidic ion, $H_2PO_4^-{}_{(aq)}$ with water.

____

(b) Identify the acid/base conjugate pairs in your equation.

____

(c) Use Le Châtelier's Principle to predict how this combination would respond to the addition of OH^- to the blood.

____

Question 2.12

Complete the following table by naming the conjugate base of the weak acids listed and then write the equation for the reaction of the weak acid with water.

Weak Acid	Conjugate Base	Equation
HF	F^-	$HF_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + F^-_{(aq)}$
CH_3COOH		
H_3PO_4		
NH_4^+		

Question 2.13

A 50,000 L swimming pool had a pH of 7.6.

(a) What would be the expected new pH if 100 mL of 12.0 mol L^{-1} HCl was added to the pool?

(b) After adding the 100 mL of 12.0 mol L^{-1} HCl to the pool, the owner measured the pH and found it to be 7.2. Account for the difference between the pH calculated in part (a) and the value obtained by the owner.

(c) Suggest what chemicals could be added to the pool to form a buffer solution. Write the equilibrium equation for this buffering solution and suggest two points to consider when choosing a suitable buffer for a swimming pool.

2.6 VOLUMETRIC ANALYSIS

Volumetric analysis is a quantitative method of chemical analysis. A solution of accurately known concentration is reacted with a solution of the substance of unknown concentration. By comparing the reacting volumes we can determine the concentration of the unknown.

The actual procedure of adding one solution to the other for a complete reaction is called a **titration**.

The two types of titrations are:

- Acid-base titrations
- Redox titrations.

The same principles apply to both and in particular the use of primary standards (see next page) to initially establish the concentration of solutions (standardisation). However only acid-base titrations will be covered for this course.

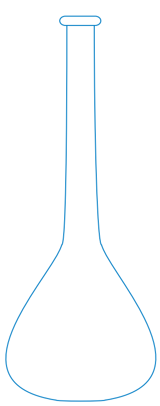
Acid-base titrations

These involve reactions between solutions of acids and bases. The point at which the reaction is complete is referred to as the equivalence point when reactants are in stoichiometric proportions. This is often not visible, as acids and bases are colourless, and so an indicator or a pH meter is required.

Since the products of an acid-base reaction may be acidic, basic or neutral, it is important to choose an indicator so that the end point matches the equivalence point. An appropriately chosen indicator will show a colour change (end point) when the reaction is complete (equivalence point). A pH meter can also be used.

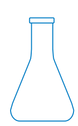
Table 2.1 Choosing a suitable indicator. Indicators are weak acids or bases whose colour changes as they change to their conjugate form. They are chosen so that this colour change occurs at equivalence point.

Indicator	pH range	Colour change acid/base	Suitable for
methyl orange	3.1 - 4.4	red → yellow	strong acid + weak base e.g. $HCl + NH_3$
methyl red	4.2 - 6.3	red → yellow	strong acid + strong base e.g. $HCl + NaOH$
phenolphthalein	8.3 - 10.0	colourless → pink	weak acid + strong base e.g. $CH_3COOH + NaOH$

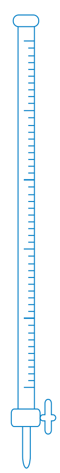


Volumetric flask
Holds accurately known volume of solution e.g. 250.0 mL, 500.0 mL. Rinse with distilled water.

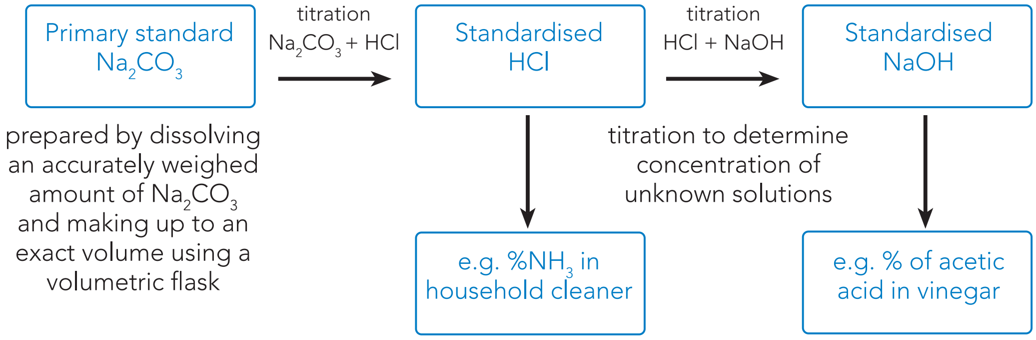
Pipette
Delivers accurately a specific volume, aliquot, of solution e.g. 20.00 mL (to ±0.02 mL). Rinse with solution.



Conical flask
Used to hold an aliquot of solution under the burette. Rinse with distilled water.



Burette
Delivers accurately a variable volume of solution (to ±0.02 mL). Rinse with solution.



Primary standards

A primary standard is required to establish the concentration of unknown solutions. Some characteristics of a good primary standard are:

- high purity and known formula
- does not react with air (e.g. not hygroscopic or deliquescent)
- reasonably high molar mass
- soluble in water.

Two commonly used primary standards are anhydrous sodium carbonate (Na_2CO_3) and hydrated oxalic acid ($H_2C_2O_4 \cdot 2H_2O$).

Standardising solutions

The procedure involved in setting up for acid-base titrations can be illustrated as follows:

Worked Example

2.5 A student prepared a primary standard of Na_2CO_3 by dissolving 1.320 g of pure anhydrous sodium carbonate and making it up to 250.0 mL in a volumetric flask.

This solution was used to standardise some HCl acid. A 20.00 mL aliquot of the Na_2CO_3 solution required on average 21.20 mL of the acid for a complete reaction. Calculate:

(a) the concentration of the Na_2CO_3 solution,
(b) the concentration of the HCl solution.

(a) $n = \frac{m}{M}$

$M(Na_2CO_3) = 22.99 \times 2 + 12.01 + 48.00 = 105.99 \text{ g mol}^{-1}$

$n = (Na_2CO_3) = \frac{1.320}{105.99}$

$= 0.012454 \text{ mol}$

$c = \frac{n}{V}$

$\therefore \ c(Na_2CO_3) = \frac{0.012454}{0.2500}$

$= 4.98 \times 10^{-2} \text{ mol L}^{-1}$

(b) $Na_2CO_{3(aq)} + 2HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + H_2O_{(l)} + CO_{2(g)}$

20.00 mL, 0.0498 mol L^{-1} (Na_2CO_3); 21.20 mL (HCl)

$n(Na_2CO_3)_{(aq)}$ used in the titration

$= cV = (4.98 \times 10^{-2})(0.0200) = 9.9616 \times 10^{-4} \text{ mol}$

$\therefore$ n(HCl) in 21.20 mL $= (2)(9.9616 \times 10^{-4})$

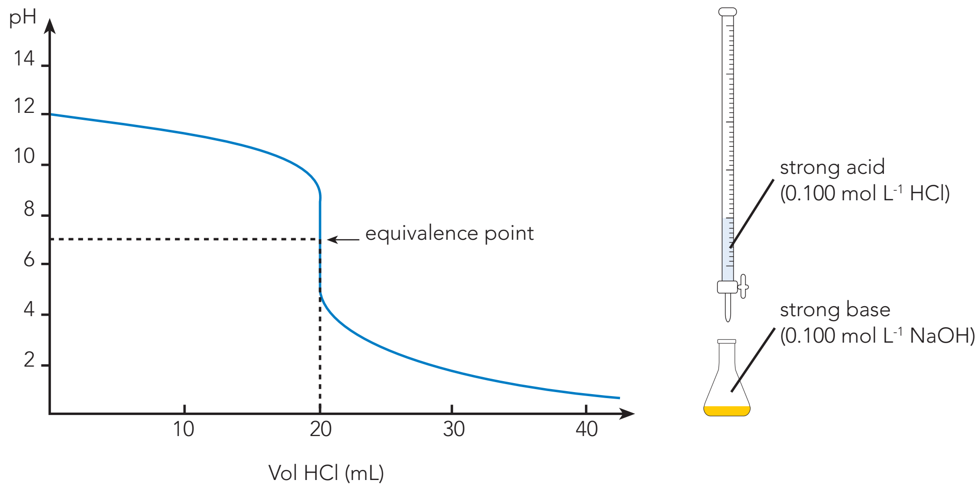
from equation $= 1.992 \times 10^{-3} \text{ mol}$

$\therefore \ c(HCl) = \frac{n}{V} = \frac{1.992 \times 10^{-3}}{0.02120}$

$= 9.40 \times 10^{-2} \text{ mol L}^{-1}$

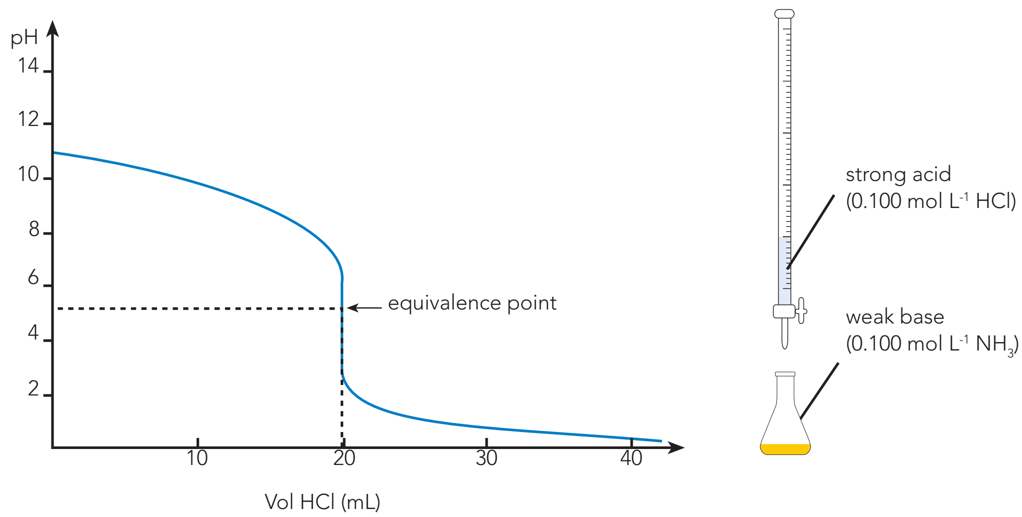
Changes in pH during acid-base titrations*

(a) Strong acid-strong base.

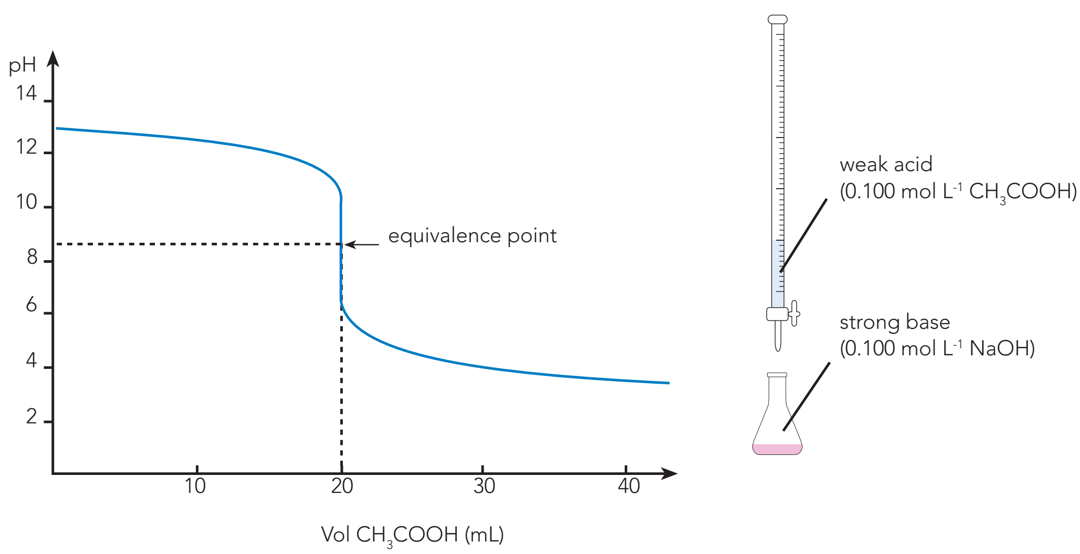


Equivalence point pH = 7.
Suitable indicator: Methyl orange or phenolphthalein. Methyl red often preferred.

(b) Strong acid-weak base.



Equivalence point pH ≈ 5.5.
Suitable indicator: methyl orange.



Equivalence point pH ≈ 9.
Suitable indicator: phenolphthalein.

** May not be required for your course.*

Question 2.14

Explain why the following substances are not suitable for use as primary standards.

(a) sodium hydroxide ______________________________

(b) hydrochloric acid ______________________________

Question 2.15

A student carrying out a titration between HCl acid and ammonia solution used phenolphthalein as an indicator.

(a) Is this an appropriate indicator? ______________________________

(b) Explain clearly why/why not.

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Complex problems – use flow diagrams

The more difficult problems are those that involve various stages or steps. It helps greatly to visualise the problem with simple sketches showing the procedure involved in the titration.

This is particularly useful when you need to work "backwards" to find percentage purity in a given sample (as in the next example).

Worked Example

2.6 A 1.252 g sample of an oven cleaner containing mostly sodium hydroxide was dissolved and made up to 250.0 mL using a volumetric flask. A 20.00 mL aliquot of this solution was titrated against 0.0950 mol L^{-1} HCl and required 23.85 mL of this acid to reach the end point. Calculate the percentage (by mass) of NaOH in the oven cleaner.

Note that 1.252 g is the mass of the oven cleaner and not the mass of NaOH. In this problem we work backwards from the titration to find out how much NaOH was actually in the sample.

$NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$

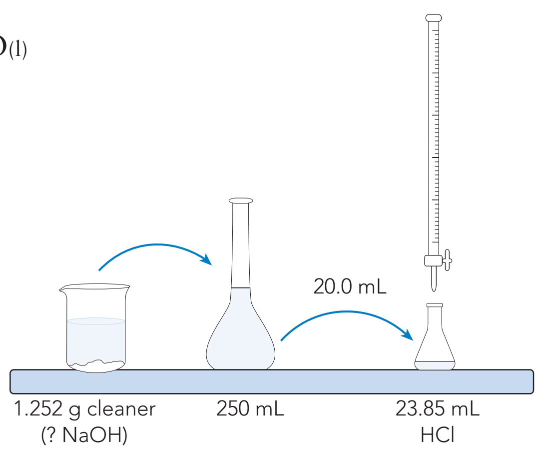
NaOH: ?; HCl: 23.85 mL, 0.0950 mol L^{-1}

n(HCl) = cV = (0.0950)(23.85 × 10^{-3})

= 2.266 × 10^{-3} mol

n(NaOH) in 20 mL aliquot

= 2.266 × 10^{-3} mol (from equation)



Now work 'backwards' to original sample.

i.e. n(NaOH) in 250 mL

$= (2.266 \times 10^{-3} \text{ mol})(\frac{250}{20})$

$= 2.832 \times 10^{-2}$ mol

$\therefore$ m(NaOH) in original sample

$m = nM = (2.832 \times 10^{-2})(40.00) = 1.133$ g

$\therefore$ % (NaOH) by mass in original sample

$= \frac{1.133}{1.252} \times 100 = 90.5\%$

Question 2.16

A 15.50 g sample of commercial vinegar was diluted and made up to 250.0 mL in a volumetric flask. A 20.00 mL aliquot (a portion of the total solution) of this diluted vinegar required 17.75 mL of a 0.05050 mol L^{-1} NaOH solution for complete neutralisation.

(a) What indicator would have been suitable for this titration?

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(b) Determine the % by mass of ethanoic acid in the commercial vinegar sample.

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(c) Determine also the concentration of ethanoic acid in commercial vinegar (in mol L^{-1} and g L^{-1}). Assume that the density of vinegar is 1.00 g mL^{-1}.

* Don't forget to draw a simple flow chart diagram to help you visualise the problem.

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Question 2.17

(a) An oxalic acid solution was prepared by dissolving 0.554 g of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) in distilled water and making it up to 500.0 mL in a volumetric flask. Determine its concentration.

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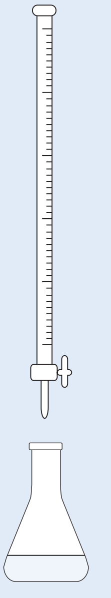
(b) This solution was placed in a burette and used to standardise a NaOH solution. A 20.00 mL aliquot of NaOH required 19.65 mL of the oxalic acid solution to reach the end point.

(i) Name an appropriate indicator for this titration. ____________________

(ii) What is the colour change at end point? __________________________

(iii) Calculate the concentration of the NaOH solution.



(c) The NaOH solution was used to determine the concentration of a diluted vinegar solution. A 20.00 mL aliquot of NaOH solution required 32.50 mL of diluted vinegar solution to complete the reaction.

(i) Name an appropriate indicator for this titration. ____________________

(ii) What is the colour change at end point? __________________________

(iii) Calculate the concentration of ethanoic acid (CH_3COOH) in the diluted vinegar solution.

REVIEW QUESTIONS

Chapter 2: Acids and Bases

1. Indicate whether each of the following is true or false. Alter any false statement so that they are true.
   (a) When dissolved in water all electrolytes will form ions.
   (b) Acetic acid is a strong electrolyte
   (c) Water can act both as an acid and a base.
   (d) A buffer solution can be a mixture of a weak base and a strong acid.
   (e) Pure anhydrous sodium carbonate can be used to prepare a primary standard for acid-base titrations.

2. Describe a simple experimental procedure that could be used to determine if a substance is a strong, weak or non-electrolyte. Include the comparative results for each.

3. Classify the following substances as strong, weak or non-electrolytes (when they are in solution):

   Na_2CO_3 CH_3CH_2OH HCl NH_3 $C_{12}H_{22}O_{11}$(sugar),
   $NaCl$ CH_3COOH SO_2

4. Calculate the [H$^+$] and [OH$^-$] of the following solutions:

   (a) 1.0×10^{-4} mol L^{-1} HCl (b) 1.00×10^{-4} mol L^{-1} NaOH
   (c) 3.50×10^{-6} mol L^{-1} HNO_3 (d) 4.75×10^{-2} mol L^{-1} $Ba(OH)_2$

5. Calculate the pH of the following solutions:

   (a) 1.00×10^{-3} mol L^{-1} HCl
   (b) 1.00×10^{-5} mol L^{-1} HNO_3
   (c) 4.00×10^{-2} mol L^{-1} NaOH
   (d) 3.00×10^{-4} mol L^{-1} HCl
   (e) 7.50×10^{-6} mol L^{-1} $Ca(OH)_2$

6. Copy and complete the following table by calculating the [H$^+$] and [OH$^-$] of the household materials listed (at 25°C).

Material	pH	[H$^+$]	[OH$^-$]
vinegar	3.00		
toothpaste	6.80		
oven cleaner	13.5		
window cleaner	9.75		

7. Calculate the [H$^+$], [OH$^-$] and pH of the solution that is formed when 120.0 mL of a HCl solution with a pH of 4.5 is mixed with 75.0 mL of a sodium hydroxide solution with a pH of 10.2.

8. A student was given three test tubes. One tube contained hydrochloric acid, one contained nitric acid while the third contained ethanoic acid. The three acid solutions were of equal concentration. When several drops of universal indicator were added to each test tube, the first two went red while the third turned yellow. Explain why the indicator turned a different colour in CH_3COOH.

9. (a) A sample of water was found to have a hydrogen ion concentration of 1.00×10^{-7} mol L^{-1} and was neutral. Explain how it is possible for the same sample of water to have a hydrogen ion concentration of 5.39×10^{-8} mol L^{-1} and still be considered neutral.
(b) What change would have occurred to have lowered the hydrogen ion concentration from 1.00×10^{-7} mol L^{-1} to 5.39×10^{-8} mol L^{-1}?
(c) If the water had a $[H^+]$ of 5.38×10^{-8} mol L^{-1} and was considered neutral, what would be the value of K_w.
(d) Under what conditions would K_w be greater than 1.00×10^{-14}?

10. After having their pool water tested at the local pool shop, an owner was told the pH of the water was 7.8 which was too high. To correct the problem, the owner was instructed to add 900 ml of local pool shop liquid acid to the pool. This liquid acid was 320 gL^{-1} HCl.

(a) If the pool had a volume of 45,000 L, calculate the new pH when this quantity of local pool shop liquid acid was added.

(b) The pH of the pool was reduced to 7.2 and NOT the calculated value. Suggest a reason why the pH did not reduce to the calculated value.

11. Identify the conjugate acid/base pairs in each of the following equations:

(a) $NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$
(b) $H_2PO_4^-{}_{(aq)} + HCO_3^-{}_{(aq)} \rightleftharpoons H_2CO_{3(aq)} + HPO_4^{2-}{}_{(aq)}$
(c) $H_2CO_{3(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+{}_{(aq)} + HCO_3^-{}_{(aq)}$
(d) $CH_3COO^-{}_{(aq)} + NH_4^+{}_{(aq)} \rightleftharpoons CH_3COOH_{(aq)} + NH_{3(aq)}$

12. Complete the following table about salt formation.

Reactants	Salt Formed	Nature of the salt (Acid, Base or Neutral)
$HCl + NH_3$		
$H_2SO_4 + KOH$		
$CH_3COOH + NaOH$		
	$Mg(NO_3)_2$	
	Na_3PO_4	

13. Classify the following salts as acidic, basic or neutral and write hydrolysis equations to show why the salt has been classified as acidic or basic.

(a) ammonium nitrate
(b) sodium chloride
(c) sodium sulfide
(d) potassium ethanoate

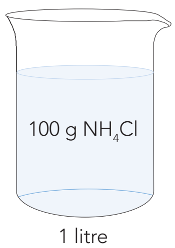
14. When the weak base, Na_2CO_3, is reacted with the strong acid, HCl, the salt produced is NaCl. Na^+ ions and Cl^- ions are both neutral but the resulting solution when Na_2CO_3 neutralises HCl is slightly acidic. Use equations to explain why.

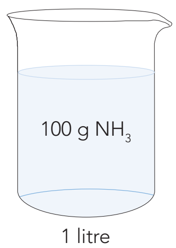
15. Give a simple test that could be used to differentiate between the following substances (give a clear statement of what observations would be expected).

    (a) 0.500 mol L^{-1} solutions of barium hydroxide and ammonia
    (b) sodium ethanoate and sodium chloride powders
    (c) 2.00 mol L^{-1} solutions of HCl and H_2SO_4

16. Rank the following 0.1 mol L^{-1} solutions in order of increasing pH:

    $NaCH_3COO$; NaCl, NaOH, NH_4Cl, HCl

17. (A) 

(B) 

    (a) What would you expect the approximate pH of the solutions in (A) and (B) to be (>7, <7, =7). Use equations to justify your answer.

    (b) When (A) and (B) are mixed together, a buffer solution is formed that has a pH of approximately 9.

    $$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

    Apart from H_2O and Cl^-, rank the chemical species in order of concentration.

    (c) When a small amount of $H^+{}_{(aq)}$ ions are added to this buffer solution, explain why they are more likely to react with $NH_{3(aq)}$ than $OH^-{}_{(aq)}$.

    (d) Use Le Châtelier's Principle to predict what the effect would be of adding the following (separately) to this buffer solution.

    (i) 2 g of HCl (ii) 2 g of NaOH

    (e) How could the buffer capacity of this mixture be exceeded?

Titrations

18. The accurate determination of the concentration of a hydrochloric acid solution, using a sodium carbonate solution of known concentration is a common analytical task carried out by high school chemistry students. Explain the meaning of the following terms used in describing titrations:

(a) primary standard	(d) equivalence point
(b) standardisation	(e) indicator
(c) end point	(f) rough titration.

19. Describe four characteristics of a **primary standard**.

20. NaOH is a chemical that can be obtained in pellet form. Explain why it is not used as a primary standard in volumetric analysis .

21. Complete the following table (for column five, assume that the acid is being added from a burette to a base in a conical flask).

Reactants (aqueous)	Salt Produced	Nature of solution at equivalence point	Suitable indicator	Expected colour change indicating end point
NaOH + HCl	NaCl	neutral	methyl orange or phenolphthalein	yellow to red pink to colourless
Na_2CO_3 + HCl				
NH_3 + HCl				
NaOH + CH_3COOH				

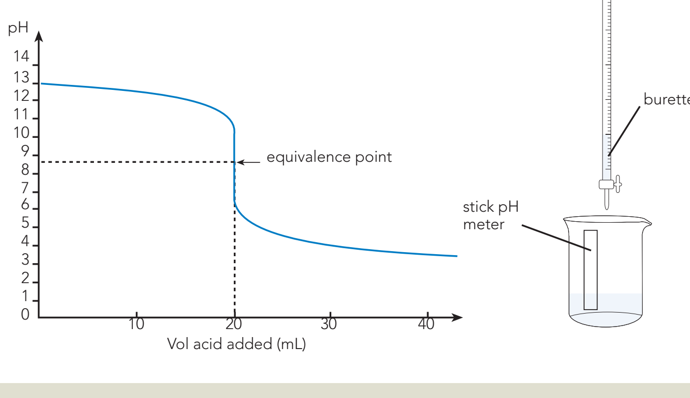
22. In determining the salt content of a sample of water a student added silver nitrate from a burette to 25.00 mL samples of the water in conical flasks. The student obtained the following results:

	Titration 1	Titration 2	Titration 3	Titration 4	Titration 5
Final Reading (mL)	21.00	41.50	26.50	46.90	23.40
Initial Reading (mL)	0.00	21.00	2.50	26.50	3.00
Volume Added (mL)	21.00	20.50	24.00	20.40	20.40

In calculating the average volume of $AgNO_3$ used in the titration, the student left the readings for titrations 1 and 3 out of the calculation. Explain why each was not included in the calculation of the average titre volume.

23. In the determination of the ammonia concentration of a window cleaning solution, a student used a previously standardised solution of hydrochloric acid. The student was unsure about what indicator to use and so chose to carry out two sets of titrations, one using methyl orange as the indicator and the other using phenolphthalein. The average volume of HCl solution used to neutralise the ammonia was 34.20 mL as indicated by the methyl orange. In general terms what would you expect the titre volume to be when phenolphthalein was used? Explain your answer.

24. Rather than use an indicator, a student used a pH meter to measure the variation of pH during a titration involving 0.0500 mol L^{-1} NaOH and 0.0200 mol L^{-1} of a certain acid. A graph of the titration results is given below. From the graph, state whether the acid was a strong acid or a weak acid. Explain your answer.



25. During a titration, a student noticed that some of the solution in the conical flask had splashed up and adhered to the inside region of the conical flask. Concerned that having some of the solution sitting above the remainder of the solution would ruin the results, the student used distilled water to wash the droplets back down into the main solution. Has this procedure altered the accuracy of the titration results?

26. In determining the ethanoic acid content of vinegar or the ammonia content of window cleaner, the household products are diluted by a factor of at least 10 before they are used in titrations. Explain the reason for the use of diluted solutions.

Calculations

27. A task carried out by high school laboratory assistants is the production of low concentration acid solutions for use in a variety of experiments. It is usual for these solutions to be produced from concentrated stock solutions. The three commonly prepared acids in school are made from 18.0 mol L^{-1} H_2SO_4, 14.0 mol L^{-1} HNO_3 or 12.0 mol L^{-1} HCl. Calculate the volume of stock acid that a lab assistant would need to obtain to make up each of the following dilute solutions:

    (a) 250 mL of 2.00 mol L^{-1} H_2SO_4
    (b) 500 mL of 0.100 mol L^{-1} HNO_3
    (c) 0.750 L of 0.500 mol L^{-1} HCl

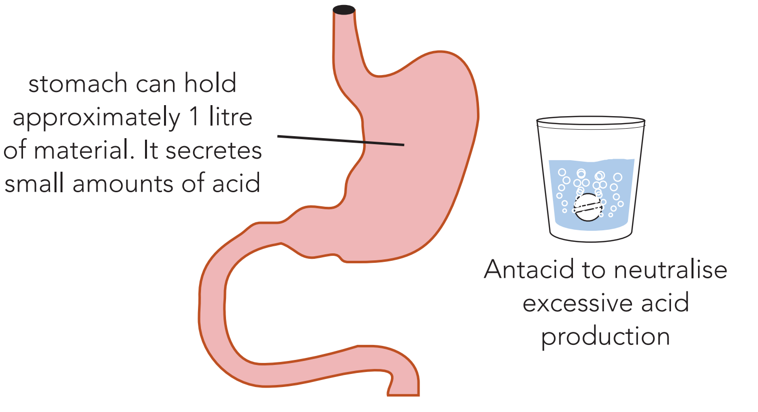
28. Upon reading the instructions for the initial setting up of a lead acid accumulator, a motorist found that they needed to obtain 2.00 L of 35.0% (by mass) H_2SO_4. This acid was stated as having a density of 1.224 g mL^{-1}. Note that density = mass/volume i.e. $D = \frac{m}{V}$

    Calculate the number of moles of H_2SO_4 that must be added to each of the six cells in the accumulator, assuming that each cell receives an equal share of the 2.00 L of solution.

29. To effectively protect against harmful bacteria and viruses, the pH of a swimming pool must be kept between 7.2 and 7.8. (The lower the pH the more effective the control but below 7.2 the conditions become uncomfortable for the swimmer.) If a swimming pool held 3.50×10^4 L of water, calculate:

    (a) the minimum acceptable hydrogen ion concentration;
    (b) the number of hydronium ions that must be present in the swimming pool when the pH is 7.8;
    (c) the number of moles of HCl that would need to be added to the swimming pool to change the pH from 7.8 to 7.2;
    (d) the volume of concentrated HCl (12 mol L^{-1}) that would need to be added to the pool to achieve this change in pH.

30. A 375 mL bottle of antacid was analysed and found to contain 30.0 g of $Mg(OH)_2$ and 30.0 g of $Al(OH)_3$. The instructions on the bottle recommend a dose of 10.0 mL of the antacid.



Calculate the quantity of stomach acid that could be neutralised by taking the recommended dosage of antacid. Stomach acid has a pH of 0.900.

31. 25.3 g of sodium hydroxide was mixed with 9.60 g of magnesium chloride and then placed into enough water to produce 8.45 L of solution. Calculate:

(a) the $[OH^-]$ ion concentration of the resulting solution;
(b) the $[H^+]$ ion concentration of the resulting solution;
(c) the pH of the resulting solution.

32. The standardisation of an approximately 0.05 mol L^{-1} HCl solution with 20.0 mL aliquots of a 0.0997 mol L^{-1} Na_2CO_3 solution produced the following table of results:

	Titration Number				
	Rough	**1**	**2**	**3**	**4**
Final Reading (mL)	45.6	43.00	46.40	44.80	49.30
Initial Reading (mL)	2.0	1.00	5.00	3.50	7.90
Titration Volume (mL)					

(a) Write a balanced equation for the reaction.

(b) Calculate the number of moles of Na_2CO_3 used in each titration.

(c) Determine the average titre volume of HCl used.

(d) Determine the concentration of the HCl solution.

33. The sodium hydroxide concentration of an oven cleaning solution was determined by the steps outlined below.

I 25.00 g of the oven cleaner was dissolved in 100 mL of distilled water.

II This solution was then added to a 250.0 mL volumetric flask and diluted by the addition of enough distilled water to correctly fill the flask.

III A 24.00 mL aliquot was removed from the volumetric flask and diluted by addition to enough water to fill another 250.0 mL volumetric flask.

IV 20.00 mL samples of this diluted solution were titrated against a standardised solution of HCl. An average of 29.80 mL of the 0.107 mol L^{-1} HCl was used.

(a) Assuming that the only basic substance in the oven cleaner was sodium hydroxide, determine the sodium hydroxide concentration of the diluted solution produced in step III.

(b) Calculate the percentage, by mass, of NaOH in the original oven cleaning solution.

34. Car battery acid contains approximately 4.500 mol L^{-1} H_2SO_4. A student carried out a series of titrations to determine the accurate concentration of H_2SO_4 in battery acid. The student followed the following steps.

STEP I Take 20.0 mL of the battery acid and dilute to 1.00 L in a volumetric flask.

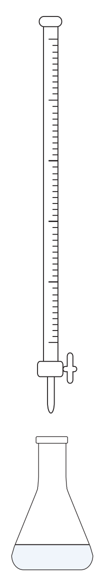
STEP II Fill a burette with the diluted battery acid.

STEP III Place 25.0 mL of standardised Na_2CO_3 (0.0939 mol L^{-1}) into a conical flask and add several drops of methyl orange.

STEP IV Conduct enough titrations to get results which are consistent to ± 0.1 mL.

Calculate the concentration of the undiluted battery acid if the average titration volume obtained in step IV was 24.7 mL.

35. When the equivalence point in a titration between a standardised 0.100 L^{-1} HCl solution and an approximately 0.10 mol L^{-1} NaOH has been reached, 24.90 mL of the acid had been added from a burette to 20.0 mL of NaOH in a conical flask. What would be the change in pH caused by the addition of another 0.100 mL drop of acid into the solution in the conical flask?



FOR THE EXPERTS

36. Washing soda is a hydrated form of sodium carbonate (i.e. $Na_2CO_3 . \times H_2O$). Also referred to as soda ash or soda crystals, washing soda is often used in laundering products as it acts as a water softener. In hard water the carbonate ions will precipitate any magnesium or calcium ions present. This prevents them from reacting with soaps or detergents giving a more effective and cleaner wash.

A sample of washing soda was analysed as follows:

A 10.96 g sample was dissolved in 500.0 mL of distilled water. A 20.0 mL aliquot of this solution was then titrated against 22.6 mL of 0.136 mol L^{-1} HCl.

(a) Write the equation for the reaction between washing soda and HCl.

(b) Determine the number of moles of HCl that were used in the titration.

(c) Determine the number of moles of sodium carbonate in 20.0 mL of the washing soda solution.

(d) Calculate the mass of sodium carbonate in the 10.96 g of washing soda.

(e) Determine the correct formula for washing soda (i.e. determine what the "x" represents in $Na_2CO_3 . \times H_2O$).

OXIDATION AND REDUCTION

3

Topics covered in this chapter:

3.1 OXIDATION AND REDUCTION

The early definition of an *oxidation* reaction was simply the combining of a substance with oxygen. For example, magnesium combines with oxygen to form MgO while carbon will burn to form CO_2.

$$2Mg_{(s)} \; + \; O_{2(g)} \; \rightarrow \; 2MgO_{(s)}$$

$$2C_{(s)} \; + \; O_{2(g)} \; \rightarrow \; 2CO_{(s)}$$

Similarly, *reduction* was considered as the opposite to oxidation and occurred when a substance lost oxygen. A typical example being the reduction of iron ore to iron metal.

$$Fe_2O_{3(s)} \; + \; 3CO_{(g)} \; \rightarrow \; 2Fe_{(l)} \; + \; 3CO_{2(g)}$$

It also became evident that oxidation and reduction reactions are interdependent and always occur together. Hence the term redox reaction (*red*uction - *ox*idation).

oxidation

$$Mg_{(s)} \; + \; H_2O_{(g)} \; \rightarrow \; MgO_{(s)} \; + \; H_{2(g)}$$

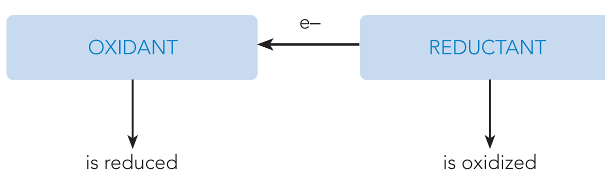
reduction

Redox reactions – a more general view

The early definitions of redox reactions are far too limiting and do not cover many similar reactions which don't involve oxygen. Redox reactions, in fact, simply involve the transfer of electrons from one species to another.

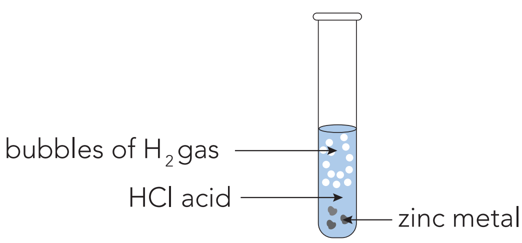
Oxidation - the loss of electrons.

Reduction - the gain of electrons.



Two quite different examples are as follows:

e.g. 1. The reaction between zinc and hydrochloric acid.



2e-   reduction

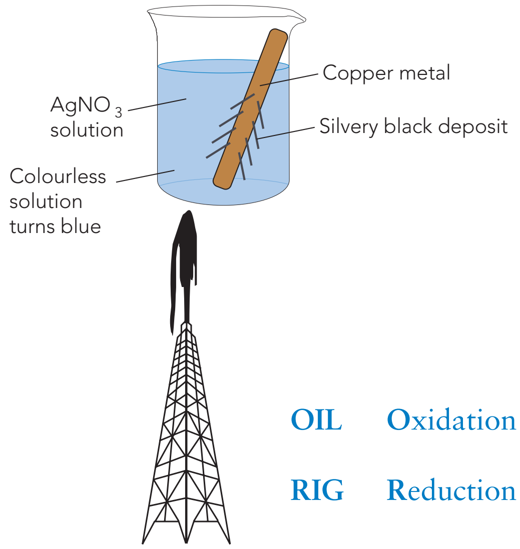
$$Zn_{(s)} \; + \; 2H^+_{(aq)} \; \rightarrow \; Zn^{2+}_{(aq)} + H_{2(g)}$$

oxidation

$Zn_{(s)} \rightarrow$ loses electrons ∴ is oxidised.

$H^+_{(aq)} \rightarrow$ gains electrons ∴ is reduced.

e.g. 2. The reaction between copper metal and silver nitrate solution.



$$2Ag^{+}(aq) + Cu(s) \rightarrow 2Ag(s) + Cu^{2+}(aq)$$

(2e⁻ transferred from Cu to Ag^{+}; oxidation: $Cu(s) \rightarrow Cu^{2+}(aq)$; reduction: $Ag^{+}(aq) \rightarrow Ag(s)$)

$Cu(s) \rightarrow$ loses electrons ∴ is oxidised.

$Ag^{+}(aq) \rightarrow$ gains electrons ∴ is reduced.

OIL Oxidation Is Loss of electrons

RIG Reduction Is Gain of electrons

Oxidising and reducing agents

Oxidation and reduction occur at the same time in a redox reaction. A redox reaction involves the transfer of electrons from the substance being oxidised to that being reduced.

Oxidising agents or *oxidants* cause a substance to be oxidised. They have a tendency to accept electrons and are themselves reduced.

e.g. O_2 Cl_2 MnO_4^{-} $Cr_2O_7^{2-}$ ClO^{-} H^{+} conc. H_2SO_4 conc. HNO_3

Reducing agents or *reductants* cause a substance to be reduced. They have a tendency to donate electrons and are themselves oxidised.

e.g. Zn C H_2 Fe^{2+} $C_2O_4^{2-}$

e.g. $$PbO(s) + CO(g) \rightarrow Pb(s) + CO_2(g)$$

(2e⁻ transferred from CO to PbO; oxidation: $CO(g) \rightarrow CO_2(g)$; reduction: $PbO(s) \rightarrow Pb(s)$)

PbO
- accepts electrons
- is reduced to Pb
- is the oxidant

CO
- donates electrons
- is oxidised to CO_2
- is the reductant

Question 3.1

The burning of magnesium metal in chlorine gas results in the formation of $MgCl_2(s)$.

(a) Write the equation for this reaction.

____

(b) Which species loses electrons? ______________

(c) Which species is oxidised? ______________

(d) Which species is the oxidant? ______________

Question 3.2

Redox reactions involve competition for electrons. Is this statement true or false? Use examples to support your reasoning.

Oxidation numbers

Oxidation numbers are a convenient way of determining if a substance has been oxidised or reduced. These numbers are arbitrarily assigned to atoms and are equal to the charge the atom would have if its bonds were purely ionic.

RULES FOR ASSIGNING OXIDATION NUMBERS	
Species	**Oxidation Number**
1. Atoms in the elemental state	0
2. Monatomic ions (Group I metals in combined state) (Group II metals in combined state)	charge on the ion +1 +2
3. Oxygen in combined state Exception 1 : peroxides e.g. Na_2O_2 , H_2O_2 Exception 2 : F_2O	–2 –1 +2
4. Hydrogen in combined state Exception : metal hydrides e.g. NaH	+1 –1
5. For polyatomic species the sum of the oxidation numbers	charge on the ion

Worked Example

3.1 Determine the oxidation number of Mn in Mn_2O_3 and MnO_4^-.

(a) Mn_2O_3 :

$$2 \times (Mn) + 3 \times (O) = 0$$
$$2 \times (Mn) + 3 \times (-2) = 0$$
$$2 \times (Mn) = +6$$
$$Mn = +3$$

(b) MnO_4^- :

$$(Mn) + 4 \times (O) = -1$$
$$(Mn) + 4 \times (-2) = -1$$
$$Mn - 8 = -1$$
$$Mn = +7$$

Question 3.3

Determine the oxidation numbers of each element in the following:

(a) $Cr_2O_7^{2-}$: Cr __________ O __________

(b) CrO_4^{2-} : Cr __________ O __________

(c) ClO_3^- : Cl __________ O __________

(d) NH_4Cl : N __________ H __________ Cl __________

(e) HSO_3^- : H __________ S __________ O __________

(f) $CaCO_3$: Ca __________ C __________ O __________

3.2 IDENTIFYING OXIDATION – REDUCTION REACTIONS

By assigning oxidation numbers to all the atoms involved in a reaction, we can determine if oxidation or reduction has occurred.

- oxidation – an increase in oxidation number
- reduction – a decrease in oxidation number

e.g.

reduction(-1)

$$Cu_{(s)} + 4H^+_{(aq)} + 2NO_3^-{}_{(aq)} \rightarrow 2NO_{2(g)} + Cu^{2+}_{(aq)} + 2H_2O_{(l)}$$

oxidation numbers → 0 +1 +5 -2 +4 -2 +2 +1 -2

oxidation(+2)

- Cu has been oxidised (O.N. 0 → +2)
- N has been reduced (O.N. 5 → 4)
- All other species have retained the same oxidation number, hence they have
- neither been reduced nor oxidised.
- This reaction is a redox reaction (both oxidation and reduction have taken place).

Question 3.4

Assign oxidation numbers to the following to determine if they are redox reactions.

(a) $Sn^{2+}_{(aq)} + Cl_{2(g)} \rightarrow 2Cl^-_{(aq)} + Sn^{4+}_{(aq)}$

(b) $H_2CO_{3(aq)} \rightarrow H_2O_{(l)} + CO_{2(g)}$

(c) $2CrO_4^{2-}{}_{(aq)} + 2H^+_{(aq)} \rightarrow Cr_2O_7^{2-} + H_2O_{(l)}$

(d) $Ca_{(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2(s)} + H_{2(g)}$

Half-equations

It is often convenient to consider a redox reaction by writing two half equations. One equation represents oxidation while the other represents reduction.

- oxidation half equation $Zn_{(s)} \rightarrow Zn^{2+}{}_{(aq)} + 2e^-$
- reduction half equation $Cu^{2+}{}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

- redox equation $Zn_{(s)} + Cu^{2+}{}_{(aq)} \rightarrow Zn^{2+}{}_{(aq)} + Cu_{(s)}$

Question 3.5

Write half-equations for:

(a) $Zn_{(s)} + 2H^+{}_{(aq)} \rightarrow Zn^{2+}{}_{(aq)} + H_{2(g)}$

oxidation ____________________________________

reduction ____________________________________

(b) $Mg_{(s)} + S_{(s)} \rightarrow MgS_{(s)}$

oxidation ____________________________________

reduction ____________________________________

Balancing Half-equations

1. Use oxidation numbers to identify the element being oxidised or reduced.
2. Write a skeleton equation (reactant → product).
3. Balance the number of atoms of the element being oxidised or reduced.
4. Balance **oxygen** atoms by adding **H_2O**.
5. Balance **hydrogen** atoms by adding **H^+**.
6. Balance **charge** by adding electrons to the side that is most positive.

Worked Example

3.2 Write a half equation for the oxidation of:
(a) $NO_3^-{}_{(aq)}$ to $NO_{(g)}$ in acidic solution.
(b) $PbO_{2(s)}$ to $Pb^{2+}{}_{(aq)}$ in acidic conditions.

(a) $NO_3^-{}_{(aq)} \rightarrow NO_{(g)}$ *skeleton equation containing element reduced (N).*

$NO_3^-{}_{(aq)} \rightarrow NO_{(g)} + 2H_2O_{(l)}$ *oxygen balanced*

$NO_3^-{}_{(aq)} + 4H^+{}_{(aq)} \rightarrow NO_{(g)} + 2H_2O_{(l)}$ *hydrogen balanced*

$NO_3^-{}_{(aq)} + 4H^+{}_{(aq)} + 3e^- \rightarrow NO_{(g)} + 2H_2O_{(l)}$ *charges balanced*

It is not necessary to actually write out each step – the previous page is an illustration of the steps involved.

(b) Similiary to (a).

$PbO_{2(s)} \rightarrow Pb^{2+}{}_{(aq)}$

$PbO_{2(s)} \rightarrow Pb^{2+}{}_{(aq)} + 2H_2O_{(l)}$

$PbO_{2(s)} + 4H^+{}_{(aq)} \rightarrow Pb^{2+}{}_{(aq)} + 2H_2O_{(l)}$

$PbO_{2(s)} + 4H^+{}_{(aq)} + 2e^- \rightarrow Pb^{2+}{}_{(aq)} + 2H_2O_{(l)}$

Question 3.6

Complete the following half-equations for acidic conditions.

(a) $MnO_4^-{}_{(aq)} \rightarrow Mn^{2+}{}_{(aq)}$

(b) $H_2C_2O_{4(aq)} \rightarrow CO_{2(g)}$

(c) $CH_3CH_2OH_{(l)} \rightarrow CH_3CHO_{(l)}$

3.3 BALANCING REDOX EQUATIONS – USING HALF-EQUATIONS

To obtain an overall reaction it is best to consider and balance each half equation first. These can then be added so that the number of electrons for each half equations is equal.

Worked Example

3.3 Balance the following redox reaction.

$$Cu_{(s)} + NO_3^-{}_{(aq)} + H^+{}_{(aq)} \rightarrow Cu^{2+}{}_{(aq)} + NO_{2(g)} + H_2O_{(l)}$$

Consider the principal reactants and write balanced half-equations.

Reduction $NO_3^-{}_{(aq)} \rightarrow NO_{2(g)}$

$NO_3^-{}_{(aq)} \rightarrow NO_{2(g)} + H_2O_{(l)}$

$NO_3^-{}_{(aq)} + 2H^+{}_{(aq)} + e^- \rightarrow NO_{2(g)} + H_2O_{(l)}$

Oxidation $Cu_{(s)} \rightarrow Cu^{2+}{}_{(aq)} + 2e^-$

Add the two half equations so that electrons cancel.

$$(NO_3^-{}_{(aq)} + 2H^+{}_{(aq)} + e^- \rightarrow NO_{2(g)} + H_2O_{(l)}) \times 2$$

$$(Cu_{(s)} \rightarrow Cu^{2+}{}_{(aq)} + 2e^-) \times 1$$

Redox equation $Cu_{(s)} + 2NO_3^-{}_{(aq)} + 4H^+{}_{(aq)} \rightarrow Cu^{2+}{}_{(aq)} + 2NO_{(g)} + 2H_2O_{(l)})$

Question 3.7

Balance the following using half-equations.

(a) $MnO_4^-(aq) + H_2S(g) + H^+(aq) \rightarrow Mn^{2+}(aq) + S(s) + H_2O(l)$

(b) $ClO^-(aq) + SO_2(g) + H_2O(l) \rightarrow Cl^-(aq) + SO_4^{2-}(aq) + H^+(aq)$

Question 3.8

Balance the following equations.

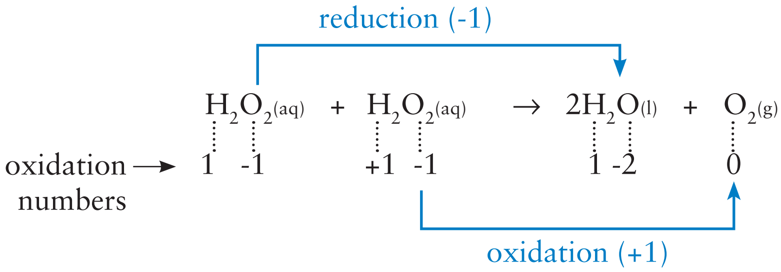
(a) $Fe^{2+}(aq) + MnO_4^-(aq) + H^+(aq) \rightarrow Fe^{3+}(aq) + Mn^{2+}(aq) + H_2O(l)$

(b) $Sn^{2+}(aq) + H^+(aq) + OCl^-(aq) \rightarrow Cl^-(aq) + Sn^{4+}(aq) + H_2O(l)$

Disproportionation reactions*

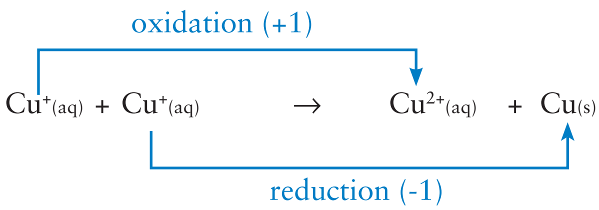
Under certain conditions some substances are able to undergo self oxidation and reduction. These types of reactions are called disproportionation reactions. Two important examples are:

(i) The decomposition of hydrogen peroxide.



or simply $2H_2O_{2(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$

(ii) The disproportionation of copper (I) ions in aqueous solution.



or simply $2Cu^{+}_{(aq)} \rightarrow Cu^{2+}_{(aq)} + Cu_{(s)}$

Question 3.9

In acidic conditions the chlorate ion (ClO_3^-) undergoes disproportionation to $Cl_{2(g)}$ and $ClO_4^-{}_{(aq)}$. Write appropriate half-equations and the overall equation.

___

___

___

___

Question 3.10

Sodium hypochlorite, NaOCl, can be prepared by bubbling chlorine gas into a solution of NaOH. Assuming the Cl^- ion is also produced, write appropriate half equations to show the disproportionation of Cl_2.

___

___

___

___

* *May not be required for your course.*

3.4 COMPETITION FOR ELECTRONS

Redox reactions involve a competition for electrons. The species being reduced has a greater ability or potential to gain electrons than the substance being oxidised. It is possible to set up experimental apparatus that can be used to compare chemical species potentials to be reduced or oxidised. By convention, the reduction of H^+ to H_2 is chosen as the standard reduction reaction to compare the potential of all other species. As it is the standard, the reduction of H^+ is said to have a potential of 0.00V

i.e. $2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$ $E° = 0.00$ V (1.0 mol L^{-1}, 25°C)

It is important to remember that reduction potentials cannot be measured separately; they must be measured with a species that is simultaneously being oxidised.

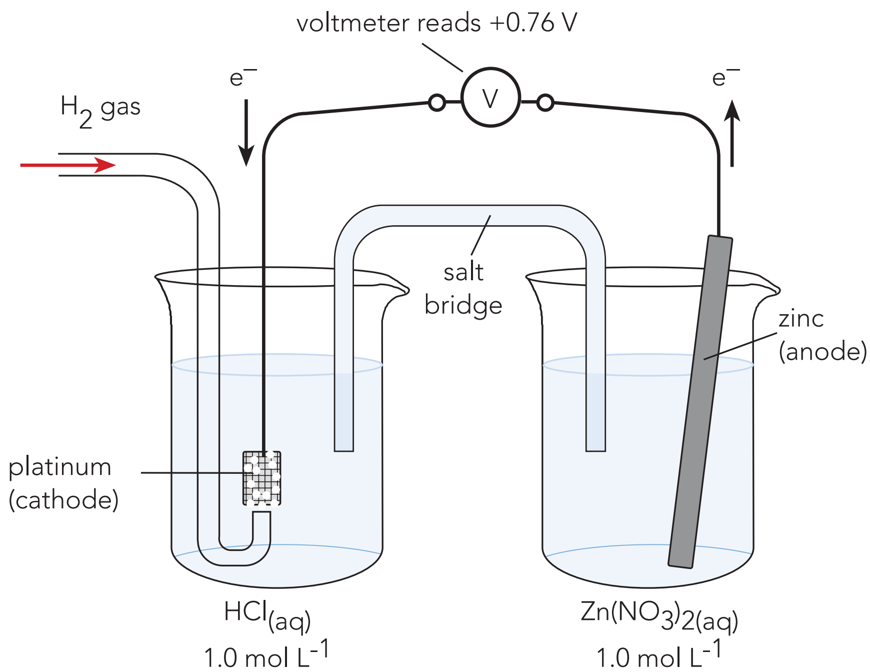


Figure 3.1 Measuring standard reduction potential of a Zn/Zn^{2+} half-cell. The H^+/H_2 half-cell is used as a reference cell. The salt bridge is a glass tube filled with electrolyte solution. This allows ion migration (transfer or charge).

Standard reduction potentials (E° values)

- are measured using the hydrogen half-cell as a reference cell
- apply to 1.0 mol L^{-1} solutions, 101.3 kPa gas pressure and 25°C temperature
- are a measure of the relative tendency of a species to be reduced
- can be used to predict:
  - electrochemical cell voltages
  - whether particular redox reactions could occur.

Some Standard Reduction Potentials

Strong oxidising agents ↑ **Weak oxidising agents**

Weak reducing agents ↓ **Strong reducing agents**

Half-reaction			E° (volts)
$F_2(g) + 2e^-$	→	$2F^-(aq)$	+2.89
$H_2O_2(aq) + 2H^+(aq) + 2e^-$	→	$2H_2O(l)$	+1.76
$PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$	→	$PbSO_4(s) + 2H_2O(l)$	+1.69
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	→	$Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$Au^{3+}(aq) + 3e^-$	→	$Au(s)$	+1.50
$Cl_2(g) + 2e^-$	→	$2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	→	$2Cr^{3+}(aq) + 7H_2O(l)$	+1.36
$O_2(g) + 4H^+(aq) + 4e^-$	→	$2H_2O(l)$	+1.23
$Br_2(l) + 2e^-$	→	$2Br_2^-(aq)$	+1.08
$NO_3^-(aq) + 4H^+(aq) + 3e^-$	→	$NO(g) + 2H_2O(l)$	+0.96
$ClO^-(aq) + H_2O(l) + 2e^-$	→	$Cl^-(aq) + 2OH^-(aq)$	+0.90
$Ag^+(aq) + e^-$	→	$Ag(s)$	+0.80
$Fe^{3+}(aq) + e^-$	→	$Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^-$	→	$H_2O_2(aq)$	+0.70
$I_2(s) + 2e^-$	→	$2I^-(aq)$	+0.54
$Cu^{2+}(aq) + 2e^-$	→	$Cu(s)$	+0.34
$2H^+(aq) + 2e^-$	→	$H_2(g)$	0 (exactly)
$Pb^{2+}(aq) + 2e^-$	→	$Pb(s)$	-0.13
$Sn^{2+}(aq) + 2e^-$	→	$Sn(s)$	-0.14
$Ni^{2+}(aq) + 2e^-$	→	$Ni(s)$	-0.24
$Fe^{2+}(aq) + 2e^-$	→	$Fe(s)$	-0.44
$Zn^{2+}(aq) + 2e^-$	→	$Zn(s)$	-0.76
$2H_2O(l) + 2e^-$	→	$H_2(g) + 2OH^-(aq)$	-0.83
$Al^{3+}(aq) + 3e^-$	→	$Al(s)$	-1.68
$Mg^{2+}(aq) + 2e^-$	→	$Mg(s)$	-2.36
$Na^+(aq) + e^-$	→	$Na(s)$	-2.71
$Ca^+(aq) + 2e^-$	→	$Ca(s)$	-2.87
$K^+(aq) + e^-$	→	$K(s)$	-2.94

difference in reduction potentials give the emf of an electrochemical cell which utilises the selected half-reactions

1.56 V

1.10 V

Predicting the direction of redox reactions

The standard reduction potentials can be used to predict the likelihood of a particular redox reaction proceeding as written.

The E° values for the two half equations are added.

- An overall + E° means that the reaction may proceed as written.
- An overall – E° means that the reaction will not occur as written.
- In general, substances listed high on the list of reduction potentials (on the left of the reaction arrow) will oxidise those listed lower (on the right of the reaction arrow).

Metals and dilute acids

e.g. 1. Could zinc react with 1.0 mol L^{-1} HCl acid?
The two possible half-equations are:

$Zn_{(s)}$	$\rightarrow$	$Zn^{2+}_{(aq)} + 2e^-$	E°	=	+0.76 V
$2H^+_{(aq)} + 2e^-$	$\rightarrow$	$H_{2(g)}$	E°	=	0.00 V
$Zn_{(s)} + 2H^+_{(aq)}$	$\rightarrow$	$Zn^{2+}_{(aq)} + H_{2(g)}$	$E°_{TOTAL}$	=	+0.76 V

The overall $E°_{TOTAL}$ is positive, hence the reaction may proceed. The $2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-$ reaction was not considered since its E° is –1.36 V and the H^+ will reduce in preference.

e.g. 2. Could copper react with 1.0 mol L^{-1} HCl acid?
As above:

$Cu_{(s)}$	$\rightarrow$	$Cu^{2+}_{(aq)} + 2e^-$	E°	=	-0.34 V
$2H^+_{(aq)} + 2e^-$	$\rightarrow$	$H_{2(g)}$	E°	=	0.00 V
$Cu_{(s)} + 2H^+_{(aq)}$	$\rightarrow$	$Cu^{2+}_{(aq)} + H_{2(g)}$	$E°_{TOTAL}$	=	-0.34 V

Reaction will not proceed since overall E° is negative.

e.g. 3. Magnesium metal is reacted with 1.0 mol L^{-1} nitric acid. Predict the reaction using E° values listed on page 59.

In this example the $Mg_{(s)}$ may be oxidised by H^+ or NO_3^-.

	$Mg_{(s)}$	$\rightarrow Mg^{2+}_{(aq)} + 2e^-$	E° =	+2.36 V
	$2H^+_{(aq)} + 2e^-$	$\rightarrow H_{2(g)}$	E° =	0.00 V
or	$NO_3^-{}_{(s)} + 4H^+_{(aq)} + 3e^-$	$\rightarrow NO_{(g)} + 2H_2O_{(l)}$	E° =	+0.96 V
	$3Mg_{(s)} + 2NO_3^-{}_{(aq)} + 8H^+_{(aq)}$	$\rightarrow 3Mg^{2+}_{(aq)} + 2NO_{(g)} + 4H_2O_{(l)}$	$E°_{TOTAL}$ =	+3.32 V

Hence $NO_{(g)}$ is produced instead of $H_{2(g)}$ since the reduction potential for $NO_{(g)}$ is higher (i.e. NO_3^-/H^+ is a stronger oxidant than H^+)

Question 3.11

Copper will not react with dilute 1.0 mol L^{-1} HCl acid but it will react with dilute 1.0 mol L^{-1} HNO_3 acid. Use E° values to determine half equations involved and overall reaction.

Metals and metal ions – Displacement reactions

Metal displacement reactions will occur if a more reactive metal is placed in a solution of a less reactive metal.

K Na Mg Al Zn Fe Pb H_2 Cu Ag Au

reactive ⟶ inert

(metal easily oxidised) (ion easily reduced)

For example, $Mg_{(s)}$ will react with $CuSO_{4(aq)}$ but $Cu_{(s)}$ will not react with $MgSO_{4(aq)}$.

e.g. 4. A strip of zinc metal is added to an aluminium nitrate solution. Predict the reaction, if any.

The two possible half-equations are:

$(Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-) \times 3 \quad E° = +0.76\ V$

$(Al^{3+}_{(aq)} + 3e^- \rightarrow Al_{(s)}) \times 2 \quad E° = -1.66\ V$

$3Zn_{(s)} + 2Al^{3+}_{(aq)} \rightarrow 3Zn^{2+}_{(aq)} + 2Al_{(s)} \quad E°_{TOTAL} = -0.90\ V$

This reaction will not proceed. The reverse reaction, of course, would be favourable. That is, aluminium metal placed in zinc nitrate solution would dissolve. A metal will displace the ions of a less active metal.

Halogens and halide ions – Displacement reactions

All the halogens are good oxidising agents with fluorine being the strongest. The trend in oxidising ability is related to their position on the periodic table.

$F_{2(g)} > Cl_{2(g)} > Br_{2(l)} > I_{2(s)}$

strong oxidant ⟶ weak oxidant

This means, for example, that $F_{2(g)}$ will displace the halide ions (e.g. Cl^-) of any of the other halogens.

e.g. 5. Predict the reaction between $Cl_{2(g)}$ and a solution of $KBr_{(aq)}$.

The two possible equations are:

$(Cl_{2(g)} + 2e^- \rightarrow 2Cl^-_{(aq)}) \quad E° = +1.36\ V$

$2Br^-_{(aq)} \rightarrow Br_{2(l)} + 2e^- \quad E° = -1.08\ V$

$Cl_{2(g)} + 2Br^-_{(aq)} \rightarrow 2Cl^-_{(aq)} + Br_{2(l)} \quad E°_{TOTAL} = +0.28\ V$

Reaction does proceed. The bromide ion will be oxidised by the $Cl_{2(g)}$.

Question 3.12

A storage plant designer needs to determine if a steel tank can be used to store copper (II) sulfate solution. Use E° values to find out if this is a good idea.

____

____

____

Limitations of the use of E° tables

The table of standard reduction potentials is useful in predicting reaction tendency and the emf of electrochemical cells.

However they do have limitations:

- The values of E° depend on concentration (1.0 mol L^{-1} solutions)

  e.g. 1.0 mol L^{-1} HNO_3 on $Cu_{(s)}$ gives $NO_{(g)}$

  conc. HNO_3 on $Cu_{(s)}$ gives $NO_{2(g)}$
- It applies only to aqueous solutions.
- The emf of a cell can depend on temperature, pressure and acidity.
- The E° values give no indication of likely reaction rate.

Question 3.13

Use standard reduction potentials to determine which of the following reactions are likely to proceed. Assume solutions are 1.0 mol L^{-1}.

(a) Iron nails are placed in zinc sulfate solution.

(b) Copper is placed in a nitric acid solution.

(c) Bromine is added to sodium chloride solution.

(d) Chlorine gas is bubbled into hydrogen sulfide solution.

(e) Potassium iodide is added to acidified potassium permanganate solution.

(f) Calcium metal is added to water.

(g) Acidified potassium permanganate solution is added to a solution of iron (II) sulfate.

Common oxidising and reducing agents

Complete the following tables showing the appropriate half equations and E° values.

Question 3.14

Common Oxidising Agents	Name	Reduction Half Equation	E°
Cl_2			
MnO_4^- (acidified)			
$Cr_2O_7^{2-}$ (acidified)			
ClO^-			
H^+			

Question 3.15

Common Reducing Agents	Name	Oxidation Half Equation	E°
Mg			
Zn			
$C_2O_4^{2-}$			
H_2			
Fe^{2+}			

3.5 ELECTROCHEMICAL CELLS

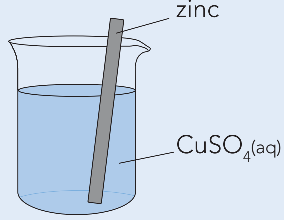
Electrochemical cells are an excellent example of a redox process put to commercial use. The two distinct types of electrochemical cells are *galvanic cells*, such as those used to power a torch or laptop, and *electrolytic cells*, which are typically used for the electrolysis of solutions.

Galvanic cells produce an electric current due to the competition for electrons between two different materials. The reaction is spontaneous. Electrolytic cells require an electrical current to produce a chemical reaction that would not otherwise occur. The process is the reverse of what occurs in a galvanic cell.

In both types of cells a transfer of electrons is involved, that is, a redox reaction. The example in the question below will help to illustrate a typical redox reaction which can be utilized in an electrochemical cell.

Question 3.16

A typical redox reaction is that which occurs when zinc metal is placed in a copper (II) sulfate solution.



(a) Give the two half-equations for this reaction.

oxidation ______________________

reduction ______________________

redox equation ______________________

(b) Describe two changes (observations) you would notice after a few minutes.

(i) ______________________

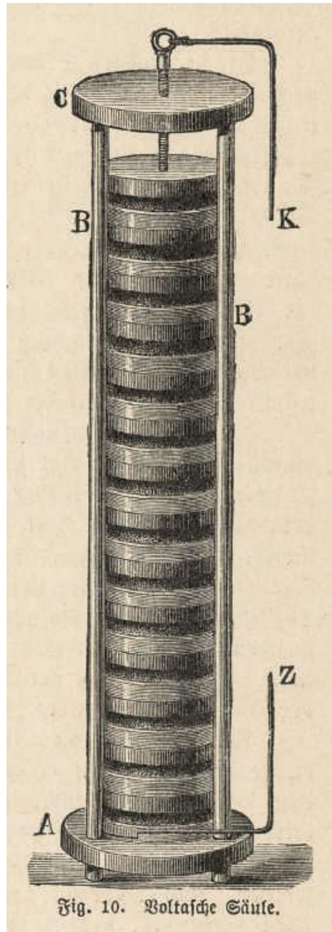
(ii) ______________________

(c) Which species has

(i) gained electrons? ______________________________

(ii) lost electrons? ______________________________

Galvanic cells



In the reaction discussed earlier (Q 3.16), the zinc metal is in direct contact with the copper (II) ions and hence electrons are transferred at the surface of the zinc metal. In this process, the chemical energy due to the redox reaction is simply given up as heat energy to the surroundings.

In a galvanic cell, such as that illustrated below, the reactants are separated and electrons are forced along an external path. The same spontaneous redox reaction takes place; however, the chemical energy from the reaction produces an external electric current.

Alessandro Volta constructed the first galvanic cell, sometimes also referred to as a voltaic cell or voltaic pile in 1799. This consisted of a series of alternating copper and zinc discs arranged as a column and separated by felt spacers soaked in salt water. (See illustration, right) Although this first galvanic cell was not so effective over long periods of time it was the first battery to provide a steady continuous flow of electricity.

Improved versions of the galvanic cell were developed during the 19th century such as that devised by John Daniell in 1836. The Daniell cell consisted of a copper can filled with copper sulphate solution in which was immersed a porous pot containing a zinc rod in a zinc sulphate solution. The porous pot prevented the solutions from mixing but allowed ions to flow between the solutions. If the zinc rod and copper can were connected by a wire then an electrical current would flow through the wire.

In the laboratory it is simpler to construct the Daniell cell using two beakers and a salt bridge as shown below. In the cell shown, zinc is oxidized and electrons flow through the external circuit to the copper. Copper ions in the Cu/Cu^{+2} cell are reduced. The salt bridge, which can simply be filter paper soaked in ammonium nitrate solution, allows ions to migrate between the two half cells and so that each cell remains electrically neutral. The choice of salt used in the salt bridge is such as to ensure no precipitation.

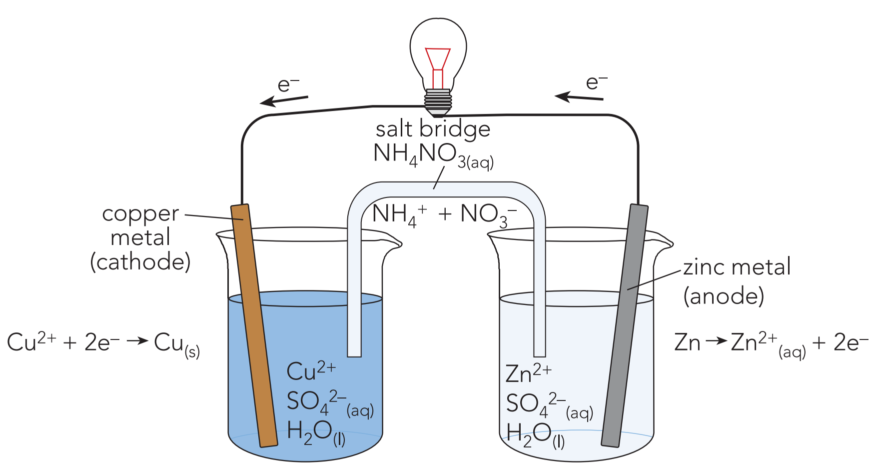


Figure 3.2 A laboratory version of the Daniell cell consisting of two half-cells, Zn/Zn^{2+} and Cu/Cu^{2+}.

Question 3.17

Refer to the Daniell cell in Figure 3.2 and answer the following.

(a) Why is a salt bridge necessary?

____

(b) Mark on the diagram the movement of ions in the salt bridge. Show:

- which ions move away from the Zn/Zn^{2+} half-cell.
- which ions move away from the Cu/Cu^{2+} half-cell.

(c) Describe the changes that would occur to:

- the zinc electrode

____

- the copper electrode

____

- the colour of the solution in the Zn/Zn^{2+} cell

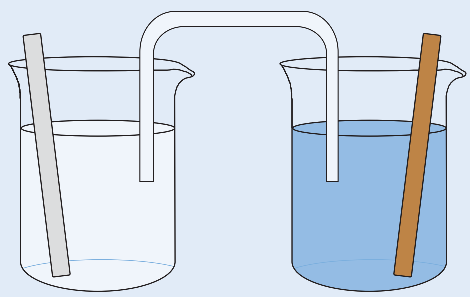
____

- the colour of the solution in the Cu/Cu^{2+} cell

____

Question 3.18

(a) Complete and fully label the diagram so as to represent a Mg/Mg^{2+}, Cu/Cu^{2+} galvanic cell. Label anode, cathode, ions, e^- movement, ion movement, etc.



(b) Anode reaction ______________________________

Cathode reaction ______________________________

Redox reaction ______________________________

(c) What is the expected emf of this cell (1.0 mol L^{-1} solution)?

(d) Eventually this cell will go flat (i.e. stop providing electrons). Detail two conditions that may cause this to happen.

(i) ______________________________

(ii) ______________________________

Determining cell voltage

The emf (voltage) produced by a cell is easily determined using standard reduction potentials (i.e. E° values). Note that these apply to 1.0 mol L^{-1} solutions, 101.3 kPa and 25°C.

e.g. for Daniell cell shown in Figure 3.2.

$Zn_{(s)}$	$\rightarrow$	$Zn^{2+}_{(aq)}$ + 2e-	E° =	+0.76 V
$Cu^{2+}_{(aq)}$ + 2e-	$\rightarrow$	$Cu_{(s)}$	E° =	+0.34 V
$Zn_{(s)}$ + $Cu^{2+}_{(aq)}$	$\rightarrow$	$Zn^{2+}_{(aq)}$ + $Cu_{(s)}$	emf =	1.10 V

Commercial cells – the dry cell*

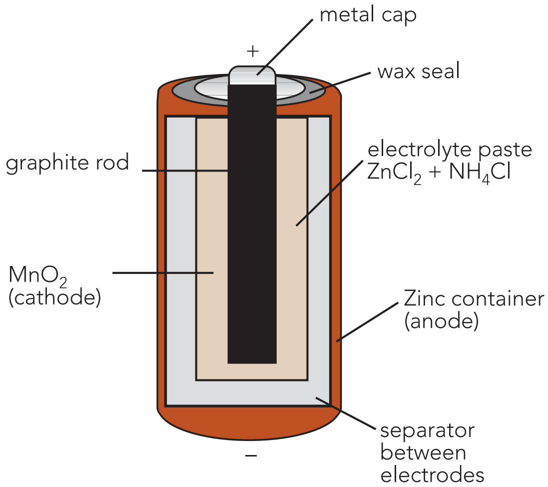


Figure 3.3 The modern dry cell. Its maximum voltage is 1.48 V.

The dry cell is fairly inexpensive and quite portable. Its compact size allows for a great many uses such as in torches, portable radios and cameras. The dry cell, or **Leclanché cell**, consists of:

- an outer case of zinc (anode)
- a carbon rod surrounded by a paste of $MnO_{2(s)}$ (cathode)
- an electrolyte paste of NH_4Cl and $ZnCl_2$.

Anode reaction $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e-$

Cathode reaction $2MnO_{2(s)} + 2H^{+}_{(g)} + 2e- \rightarrow Mn_2O_{3(s)} + H_2O_{(l)}$

Overall reaction ____________________________________
(complete this)

Question 3.19

(a) The $H^{+}_{(aq)}$ ions required in the cathode reaction of the dry cell are provided by the $NH_4^{+}{}_{(aq)}$ in the electrolyte paste. Write an equation to show how this occurs.

____

** The commercial cells discussed in this book provide important examples of redox reactions. However their detailed knowledge may not be required for your course.*

(b) Why is the Leclanché cell referred to as a primary cell?

____

(c) List the major advantages and disadvantages of this type of cell.

Advantages ____

____

Disadvantages ____

____

Question 3.20

Alkaline dry cells are also commercially available and are better performers than the acid form. An important example is the silver oxide/zinc cell commonly used in watches and calculators.

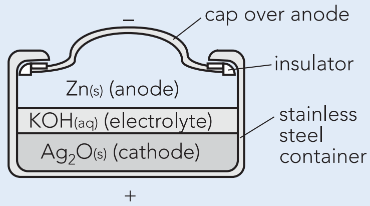


Figure 3.4 The silver oxide/zinc cell.

The zinc is oxidised to $Zn^{2+}(aq)$ while the silver oxide is reduced to silver. The silver oxide reaction is given. Complete and determine the overall equation.

anode ____

cathode $Ag_2O(s) + H_2O(l) + 2e^- \rightarrow 2Ag(s) + 2OH^-(aq)$

overall ____

The lead-acid accumulator

Lead-acid batteries are relatively inexpensive and can store large quantities of charge. Although a little bulky, their major advantage is that they can be recharged. They are widely used in motor vehicles and isolated farmhouses. Important features of the lead-acid battery are:

- electrodes
  - anode – spongy lead - large surface area
  - cathode – lead (IV) oxide packed on a metal grid
- electrolyte is concentrated sulfuric acid (4.5 mol L^{-1})
- a typical car battery consists of 6 cells placed in series (12 V total)
- it can be recharged - hence referred to as a secondary cell
- the density of the electrolyte indicates the state of charge.

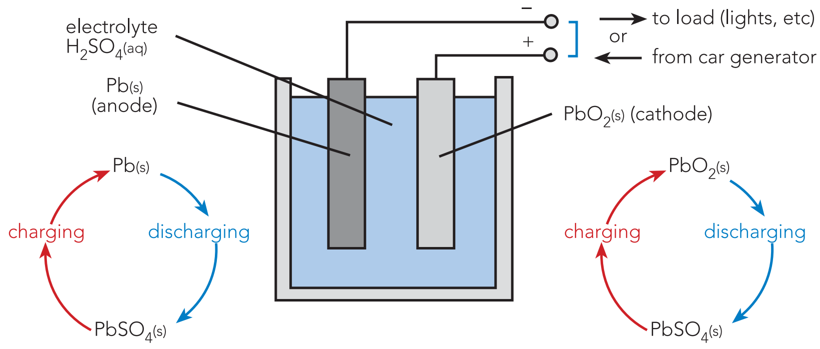


Figure 3.5 Simplified view of a lead-acid accumulator showing a single cell.

- Car batteries consist of 6 cells, each providing 2 V.
- The battery is continually being recharged by the car generator (or alternator).

The electrode reactions for *discharge* - that is for when the battery is being used - are as follows:

anode $Pb_{(s)} + SO_4^{2-}{}_{(aq)} \rightarrow PbSO_{4(s)} + 2e^-$

cathode $PbO_{2(s)} + 4H^+_{(aq)} + SO_4^{2-}{}_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)}$

Overall ______________________________
(complete this)

Question 3.21

Write the overall equation for the charging of a lead-acid accumulator.

____

Question 3.22

When an accumulator becomes flat, both electrodes become $PbSO_{4(s)}$.

(i) Explain why no emf would be possible under these conditions.

____

(ii) What other change occurs which would more easily help us to decide if the battery is flat?

____

____

The fuel cell

A fuel cell is different from both primary and secondary cells in that it does **not** store the reactants or products. Rather, a fuel cell converts the energy of a chemical reaction directly and continuously into electrical energy.

Important features of a fuel cell are:

- electrodes consist of porous platinum or graphite

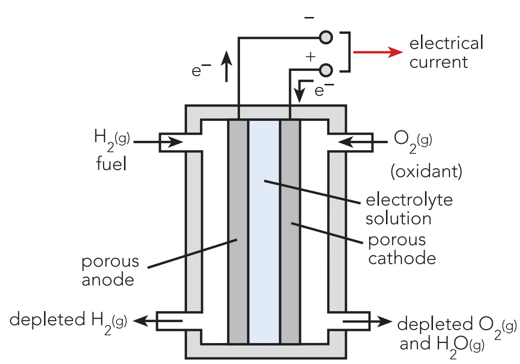


Figure 3.6 Hydrogen-oxygen fuel cell.

- electrolytes can be either basic or acidic
- reactants are usually gaseous (e.g. $H_{2(g)}$, $O_{2(g)}$)
- they supply electricity as reactants are fed into them.

The major advantages of fuel cells are their high efficiency of energy conversion and their ability to generate electricity continuously for a very long time.

Fuel cells are not widely used because of their high cost and slow rate of reaction.

If the electrolyte is acidic the electrode reactions are:

anode $H_{2(g)} \rightarrow 2H^+_{(aq)} + 2e^-$

cathode $O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)}$

overall ______________________________
(complete this)

Question 3.23

(a) Use E° values to determine the theoretical emf of the above cell (assume 1.0 mol L^{-1} solution).

____

(b) Write the half-equations for this cell in basic solution.

anode ______________________________

cathode ______________________________

(c) What is the overall reaction in both cases?

____

(d) How does this overall reaction compare with the combustion of hydrogen gas?

____

Question 3.24

A fuel cell is designed to use methane (CH_4) and oxygen in a similar manner to the H_2/O_2 fuel cell. If the electrolyte is acidic, determine the electrode reactions.

anode ______________________________

cathode ______________________________

overall ______________________________

3.6 ELECTROLYSIS

Electrolysis refers to the chemical changes that take place when an electrical current is passed through a molten substance or solution. Electrolysis occurs in an electrolytic cell and is the opposite process to that which occurs in a galvanic cell.

The reactions that occur during electrolysis are *forced reactions*, that is, they are not spontaneous reactions. By applying a suitable voltage, electrical energy is converted to chemical energy. A comparison of the processes that occur in galvanic cells and electrolytic cells is shown below.

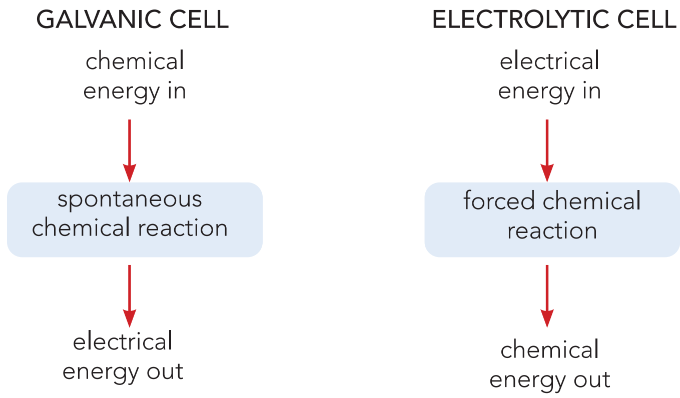


Figure 3.7 Comparing galvanic and electrolytic cells. Galvanic cells produce electrical energy due to spontaneous reactions. Electrolytic cells have an applied external voltage which causes forced reactions to occur (electrolysis). In both cases the reactions are redox reactions.

Electrolysis has many important industrial applications. Common examples are listed below. Some of these applications will be discussed in more detail later in this chapter.

ELECTROLYSIS APPLICATION	COMMON EXAMPLE
The extraction of metals	Aluminium metal from alumina (Al_2O_3)
Electrorefining	Pure copper from blister copper
Electroplating	Chrome plating, silver plating
Anodising	Corrosion resistant Al_2O_3 layer on Al metal
Chemical manufacture	Production of Na, NaOH, Cl_2, H_2
Recharging batteries	Car batteries, nickel-cadmium batteries

Electrolytic cells

Systems that bring about electrolysis reactions are called electrolytic cells. A typical example is shown below. An applied external voltage causes reactions at the two electrodes.

ANODE: Where oxidation occurs
CATHODE: Where reduction occurs
This is the same for all electrochemical cells

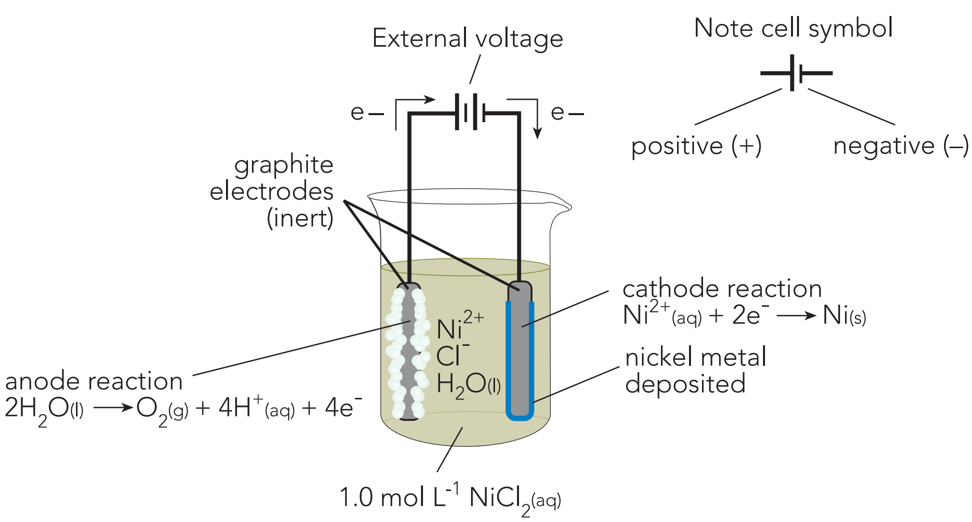


Figure 3.8 A typical electrolytic cell. An external applied voltage supplies electrons to the cathode where a reduction reaction takes place. At the anode, an oxidation reaction occurs which results in the same number of electrons being produced as those consumed at the cathode. Note that only ions flow through the solution. As they do, they complete the electrical circuit.

Predicting electrode reactions

Often, more than one reaction is possible at each electrode of an electrolytic cell. For each electrode we need to consider all substances present and whether the electrode is inert or reactive. We can to use E° values to predict reactions and voltages required. The concentration of solutions can also have a marked effect on E values and products formed. E° values apply only to 1.0 M solutions. For simplicity here we assume all 1.0 M solutions and inert electrodes. We discuss the effects of electrodes and concentration later below.

Consider the electrolytic cell shown above in Figure 3.8

Possible cathode reactions. Note that only reduction reactions can occur here:

$Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni_{(s)}$ E° = −0.24 V ✓*This reaction is favoured*
$2H_2O_{(l)} + 2e^- \rightarrow N_{2(g)} + 2OH^-_{(aq)}$ E° = −0.83 V

Possible anode reactions. Note that only oxidation reactions can occur here:

$2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-$ E° = −1.36 V
$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$ E° = −1.23 V ✓*This reaction is favoured*

Hence overall reaction:

$2Ni^{2+}_{(aq)} + 2H_2O_{(l)} \rightarrow 2Ni_{(s)} + O_{2(g)} + 4H^+_{(aq)}$ E° = −1.49 V

Note

- The least negative half reaction is always favoured.
- A minimum voltage of + 1.49 V must be applied to cause a reaction.
- Graphite electrodes can be considered inert and do not react.

Using reactive electrodes

Where reactive electrodes are used, they need to be considered in predicting reactions.
If nickel metal electrodes were used in the previous example with 1.0 mol L^{-1} $NiCl_{2(aq)}$ we would have:

Possible cathode reactions:

$Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni_{(s)}$ E° = −0.26 V ✓*This reaction is favoured*
$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$ E° = −0.83 V

Possible anode reactions:

$Ni_{(s)} \rightarrow Ni^{2+}_{(aq)} + 2e^-$ E° = +0.26 V ✓*This reaction is favoured*
$2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-$ E° = −1.36 V
$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$ E° = −1.23 V

Hence overall reaction:

$Ni_{(s)}$ → $Ni_{(s)}$
(at the anode) (at the cathode)

We can see that by using nickel electrodes one of the preferred reactions is different from the previous example. At the anode nickel metal reacts rather than water. Effectively, nickel metal is oxidized at the anode and the resulting ions are reduced back to the metal at the cathode. This type of reaction is very important in electroplating and the electrorefining of metals like copper.

Question 3.25

(a) If the nickel electrodes in the previous example were replaced with copper electrodes, the overall reaction would be different. Consider the possible electrode reactions to determine the overall result.

Possible cathode reactions:

____

____

Possible anode reactions:

____

____

Overall reaction:

____

____

(b) The reactions within this electrolytic cell may change after some time. Explain why.

____

____

____

____

Aqueous solutions – concentration effect

The concentration of an aqueous solution can affect the preferred reactions that occur in an electrolytic cell. E° values apply only to 1.0 M solutions. At other concentrations the E values change and other competing reactions may be more favoured.

In all aqueous solutions water is always a possible reactant; at either electrode. In fact if a low concentration solution of say NaCl or H_2SO_4 is used, then *electrolysis of water* will occur. The products would be oxygen gas at the anode and hydrogen gas at the cathode.

Let us consider the electrolysis of a NaCl solution at different concentrations. Assume inert electrodes. The possible electrode reactions and E° values (1.0 M solutions) are listed. For neutral solutions the (non standard) E value for the water reactions is also given.

Possible cathode reactions:

$Na^{+}_{(aq)} + e^{-} \rightarrow Na_{(s)}$ E° = -2.71 V

$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$ E° = –0.83 V *(E = –0.41 V at pH = 7)*

Possible anode reactions:

$2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-$ E° = -1.36 V

$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$ E° = -1.23 V (*E = -0.82 V at pH = 7*)

Aqueous NaCl (1.0 M solution). At the cathode, water is reduced rather than the sodium ions as indicated by the E° values. Hydrogen gas is the only product at both high and low concentrations of solution. At the anode we can see that for 1.0 M solutions the E° values for the possible reactions are very similar. Oxygen gas is produced in preference to chlorine gas although some chlorine gas may also be produced. At very low concentration only oxygen gas is produced.

Aqueous NaCl (concentrated solution). At high concentrations only chlorine gas is produced at the anode. Hydrogen gas is still produced at the cathode. The electrolysis of a concentrated aqueous solution of sodium chloride is an important industrial process.

The *Nelson cell* is used to electrolyse a concentrated brine solution to produce hydrogen, chlorine and sodium hydroxide, all important industrial chemicals. The hydrogen and chlorine are produced as discussed above and the sodium hydroxide is the result of the hydroxide ions produced at the cathode combining with the sodium ions in solution. Essentially the $NaCl_{(aq)}$ solution becomes a $NaOH_{(aq)}$ solution.

Question 3.26

Consider the electrolysis of sodium chloride solutions at different concentrations as discussed above. Assuming inert electrodes give the electrode reactions and list the products formed for the following concentrations.

(a) Aqueous NaCl (1.0 mol L^{-1})

Anode reaction ______________________________

Cathode reaction ______________________________

Products are ______________________________

(b) Aqueous NaCl (concentrated solution)

Anode reaction ______________________________

Cathode reaction ______________________________

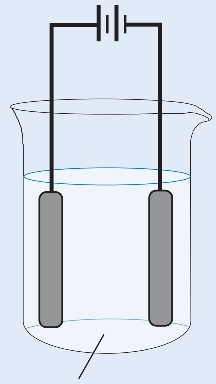
Products are ______________________________

Question 3.27

A 1.0 mol L^{-1} solution of $HCl_{(aq)}$ is to be electrolysed using inert electrodes as shown.

(a) Fully label the diagram showing:

- species in the beaker
- electron flow
- anode and cathode



(b) Determine possible reactions at each electrode and give the overall reaction. Include E° values.

anode ______________________________

____

cathode ______________________________

____

overall ______________________________

____

Electrolysis of molten salts

As we have seen above, the electrolysis of aqueous solutions often involves the reaction of water itself. Solid ionic salts do not conduct electricity. However if they are heated sufficiently they become molten and can be electrolysed. In this situation the ions of the ionic salt will react at the electrodes. For example, if sodium chloride is heated to above 800ºC it melts and can be electrolysed as shown below.

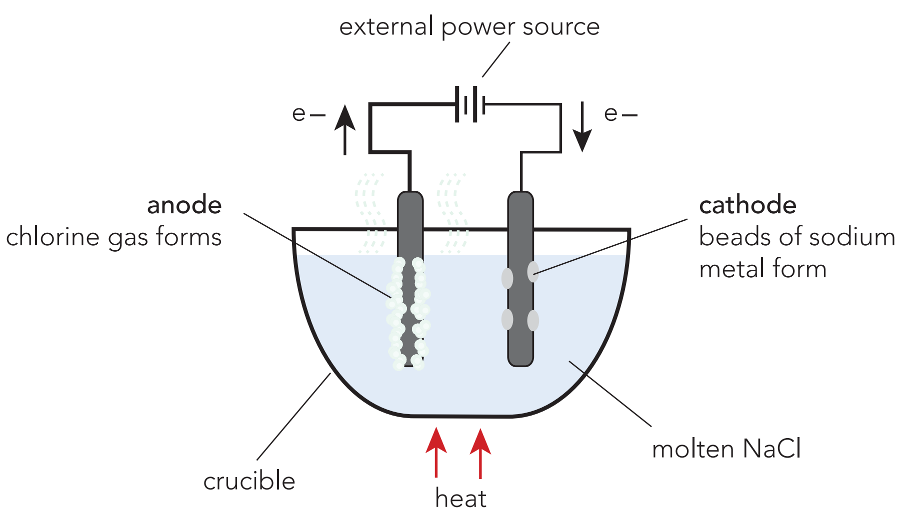


Figure 3.9 Electrolysis of molten sodium chloride. Only sodium and chloride ions are available to react at the inert electrodes. Sodium liquid is produced at the cathode and chlorine gas at the anode.

Question 3.28

Consider the electrolysis of molten sodium chloride as discussed above. Assuming inert electrodes, give the electrode reactions for the following examples.

(a) Molten NaCl

Anode reaction ______________________________

Cathode reaction ______________________________

Products are ______________________________

(b) Molten PbI_2

Anode reaction ______________________________

Cathode reaction ______________________________

Products are ______________________________

Electroplating

Metals may be electroplated by adding a very thin layer of another metal by the process of electrolysis. This important industrial process is used in order to improve the appearance of more base metals such as iron and also improve their resistance to corrosion.

Silver plating, for example, can enhance the looks of items such as bracelets, necklaces, cutlery and ornamental objects. A very thin layer of silver is coated on the object by attaching them to the cathode of an electrolytic cell as shown. The finished product will have the look of silver but cost much less than if the item was solid silver.

Gold similarly can be used for electroplating items of jewellery. It is also used in the electronics industry in a similar way to produce tarnish resistant contacts and switching gear. Other important examples of electroplating are tin plating, zinc plating and chrome plated steel.

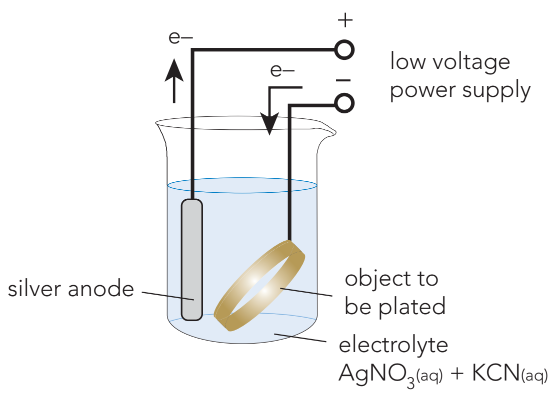


Figure 3.10 Electroplating with silver. The metal object to be plated is always attached to the cathode. The anode is made of the metal used for the coating. It does not need to be pure.

Question 3.29

For the electroplating of silver as shown above, give the relevant reactions.

anode ______________________________

cathode ______________________________

overall ______________________________

Question 3.30

To get a really smooth finish when electroplating with silver, the silver ion concentration in solution must be very low. This is why KCN is added to the electrolyte solution. An equilibrium is established as follows:

$$Ag^{+}_{(aq)} + 2CN^{-}_{(aq)} \rightleftharpoons Ag(CN)_2^{-}{}_{(aq)}$$

Explain how this equilibrium reaction helps.

____

____

Electrolytic refining of copper

Copper is produced from its ores by a series of processes. The final smelt contains about 98.5% of copper. However the purity required for electrical wiring, one of the main uses of copper, is very high (≈ 99.9%). To achieve this high purity, crude copper or 'blister' copper is refined as shown below.

This electrolytic process is very similar to electroplating. The copper and other reactive metals within the anode are oxidised and become part of the electrolyte solution. The high cost of electrorefining is partly offset by the recovery of valuable impurities such as silver and gold. The use of a very low voltage, approximately 0.3 V, ensures that only copper is deposited at the cathode and that the less active silver and gold are not oxidised at the cathode but are left behind as part of the anode mud.

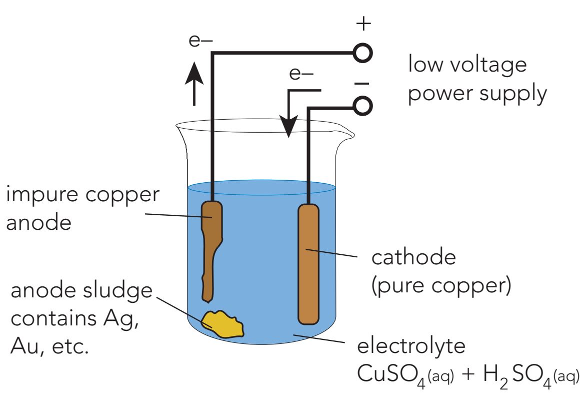


Figure 3.11 Electrolytic refining of copper. Industrially, copper anodes consist of large copper slabs produced from crude copper (≈ 98.5%) or recycled high grade copper scrap. Impurities mostly include gold, silver, lead and nickel. These impurities are recovered from the anode mud or from solution.

Question 3.31

(a) For the electrorefining of copper as shown above, give the relevant reactions.

anode ____

cathode ____

overall ____

(b) The gold and silver impurities not oxidised at the anode simply fall to the bottom and become part of the anode *sludge* or *slime*.

(i) Explain why this is the case. Refer to E° values in your answer.

____

____

(ii) Of what use might the anode mud be?

____

____

(c) Oxidised metal impurities such as Ni^{2+} and Pb^{2+} are not deposited at the cathode.

(i) Explain why this is the case. Refer to E° values in each case.

____

____

(ii) Suggest how the nickel and copper ions may be removed or recovered.

____

3.7 CORROSION OF METALS

Corrosion is an electrochemical process that occurs when metals are oxidised by substances in their environment.

Anode (metal oxidises): Metal $\rightarrow$ (Metal ions) $^{x+}$ + x e-

Cathode: Four common, but not exhaustive, reduction processes are given below:

(i)	$2H^+ + 2e^- \rightarrow H_2$	metal exposed to moist, acidic conditions
(ii)	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	metal exposed to moisture and oxygen (very common)
(iii)	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	metal exposed to moisture but a low concentration of oxygen, e.g. shovel blade in the soil
(iv)	$(\text{Metal ions})^{x+} + x\, e^- \rightarrow \text{Metal}$	metal in contact with another metal with a greater reduction potential

Preventing corrosion is often about limiting the contact of the metal with these four processes.

Question 3.32

List the following metals in order of increasing tendency to be oxidised.

Fe, Zn, Au, Mg, Na, Ag, Al, Pb, Cu

____

When some metals oxidise, they form a tough, protective oxide coating that greatly limits the ability of the oxidising agent to come in contact with the metal. Aluminium is a common example. Even though Al will oxidise rapidly, the oxide coating protects the underlying Al from further corrosion. Iron, however forms a oxide coating that is easily penetrated by O_2 and H_2O and subsequently the oxide layer does not protect the Fe from further corrosion.

Rust – A Special Example of Corrosion

The most common and important example of corrosion is the oxidation of iron. This is caused by the action of oxygen and water vapour in the air.

The formation of rust involves a series of reactions.

- *The initial oxidation of the iron.*

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^- \quad \text{(anodic reaction)}$$
$$O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)} \quad \text{(cathodic reaction)}$$

- *The further oxidation of the $Fe(OH)_{2(s)}$ formed.*

$$\underset{\text{pale green}}{4Fe(OH)_{2(s)}} + 2H_2O_{(l)} + O_{2(g)} \rightarrow \underset{\text{red brown}}{4Fe(OH)_{3(s)}}$$

- *The partial dehydration of the $Fe(OH)_{3(s)}$ to rust. One possible reaction is shown.*

$$2Fe(OH)_3 \rightarrow Fe_2O_3.H_2O_{(s)} + 2H_2O_{(l)}$$

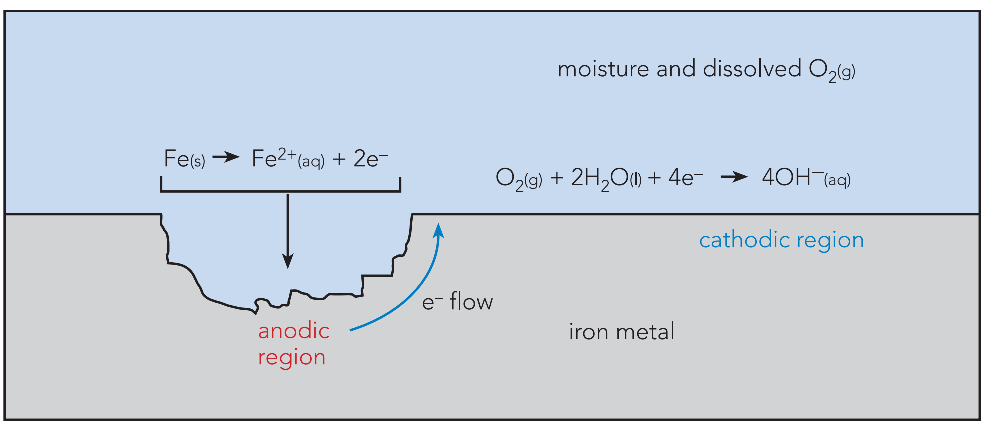


Figure 3.12 Corrosion of iron by the action of oxygen and water.

This is an electrochemical process. Areas of stress in the iron become anodic while areas of high oxygen concentration become cathodic. Electrons flow through the metal from the anode to the cathode. The moisture acts as the electrolyte.

Corrosion prevention

Prevention of corrosion is of tremendous economic importance (future millionaires – here is an area where you can make money). To prevent corrosion we must inhibit the reactions discussed on the previous page. This can be done by:

- excluding air and/or water from the metal surface by
  - protecting the iron surface with paint, grease, plastic
  - plating the iron surface with metals such as chromium or metallic tin
- using a sacrificial anode (more reactive metal) by
  - galvanising iron with zinc – zinc corrodes in preference
  - attaching magnesium and aluminium to ships
- using cathodic protection so that jetties and pipelines are rendered negative by a low voltage dc current. The anodes may be made of scrap iron (e.g. old engine blocks) or titanium coated inert electrodes.

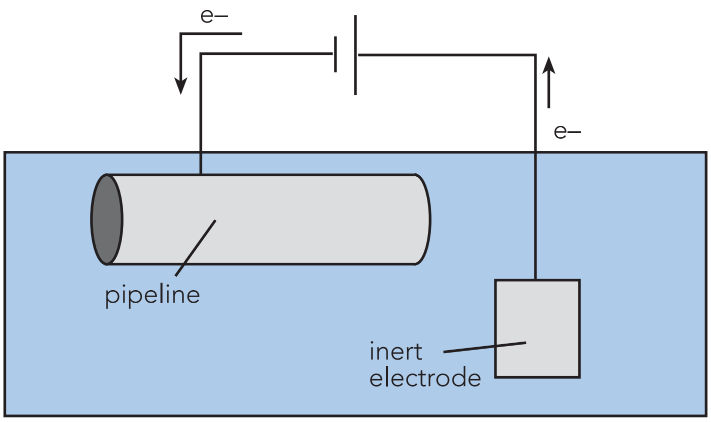


Figure 3.13 Cathodic protection. The pipeline is made negative to prevent its oxidation. Instead, H_2O is reduced at the pipeline, and oxidised at the inert electrode.

REVIEW QUESTIONS

Chapter 3: Oxidation and Reduction

Redox

1. Indicate whether each of the following is true or false. Alter any false statement so that they are true.
   (a) Oxidising agents are electron acceptors.
   (b) When a species is oxidised, there is an increase in its oxidation number.
   (c) Standard reduction potentials (E0 values) are measured using a platinum half-cell as a reference cell.
   (d) The salt bridge in a simple Daniell electrochemical cell allows electrons to migrate through it so that each half-cell remains electrically neutral.
   (e) A metal used as a sacrificial anode is more reactive than the metal it protects from corrosion.

2. Determine the oxidation number of the element in bold print in each of the following:

   (a) $\mathbf{Cu}(NH_3)_4^{2+}$ (b) $K_2\mathbf{Cr}_2O_7$

   (c) $Mg\mathbf{H}_2$ (d) $\mathbf{Mn}_2O_3$

   (e) $\mathbf{H}_2O_2$ (f) $H_2C_2O_4.2H_2O$

   (g) $(NH_4)_2SO_4.\mathbf{Fe}SO_4.6H_2O$

3. Use oxidation numbers to identify the element that has been oxidised (if any has) in each of the following:
   (a) $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

   (b) $2Na(s) + H_2S(g) \rightarrow Na_2S(s) + H_2(g)$

   (c) $MnO_2(s) + 4H^+(aq) + 2Cl^-(aq) \rightarrow Mn^{2+}(aq) + Cl_2(g) + 2H_2O(l)$

   (d) $AgBr(s) + 2S_2O_3^{2-}(aq) \rightarrow [Ag(S_2O_3)_2]^{3-}(aq) + Br^-(aq)$

   (e) $5H_2C_2O_4(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$

4. Use oxidation numbers to identify the element that has been reduced (if any has) in each of the following:
   (a) $4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s)$

   (b) $Cu(s) + 4H^+(aq) + 2NO_3^-(aq) \rightarrow Cu^{2+}(aq) + 2H_2O(l) + 2NO_2(aq)$

   (c) $4Au(s) + 8CN^-(aq) + 2H_2O(l) + O_2(g) \rightarrow 4Au(CN)_2^-(aq) + 4OH^-(aq)$

   (d) $Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$

5. Complete the following table by classifying the substances listed as **oxidising agents** or as **reducing agents**.

   Oxalic acid, zinc, oxygen gas, hydrogen gas, chlorine gas, carbon, potassium permanganate (acidified), iron (II) ions, concentrated sulfuric acid, potassium dichromate (acidified), hydronium ion, and concentrated nitric acid.

Oxidising Agents (oxidants)	Reducing Agents (reductants)

6. Complete the following table showing the observations you would expect to make when the following substances are mixed.

Equation	Colour of Reactants	Colour of Products
$Br_{2(aq)}$ + $I^{-}_{(aq)}$ →		
$Br^{-}_{(aq)}$ + $Cl_{2(aq)}$ →		
$I^{-}_{(aq)}$ + $Cl_{2(aq)}$ →		
$Ag^{+}_{(aq)}$ + $Cu_{(s)}$ →		
$Mg_{(s)}$ + $Cu^{2+}_{(aq)}$ →		

7. Use oxidation numbers and half equations to balance each of the following equations (assuming acidic conditions).

(a) $S_2O_3^{2-}{}_{(s)} + I_{2(s)} \rightarrow S_4O_6^{2-}{}_{(aq)} + I^{-}_{(aq)}$

(b) $Br^{-}_{(aq)} + SO_4^{2-}{}_{(aq)} \rightarrow SO_{2(g)} + Br_{2(l)}$

(c) $Ag_2S_{(s)} + H^{+}_{(aq)} + NO_3^{-}{}_{(aq)} \rightarrow Ag^{+}_{(aq)} + NO_{(g)} + S_{(s)} + H_2O_{(l)}$

(d) $CrO_4^{2-}{}_{(aq)} + H^{+}_{(aq)} + Cl^{-}_{(aq)} \rightarrow Cr^{3+}_{(aq)} + Cl_{2(g)} + H_2O_{(l)}$

(e) $MnCl_{2(s)} + OH^{-}_{(aq)} + Br_{2(aq)} \rightarrow MnO_{2(s)} + Cl^{-}_{(aq)} + Br^{-}_{(aq)} + H_2O_{(l)}$

8. Use oxidation numbers and half equations to write balanced nett equations for each of the following reactions. You will also need to use your knowledge of solubility rules, etc, to produce the correct **ionic** equations.

(a) Silver metal being dissolved in concentrated nitric acid to produce silver nitrate, nitrogen dioxide and water.
(b) Sulfur powder is thoroughly mixed with a solution of acidified sodium dichromate to produce sodium sulfate and the insoluble chromium (III) oxide.
(c) Hydrogen sulfide gas is bubbled through dilute nitric acid producing sulfur, nitrogen monoxide and water.
(d) Chlorine water is made dissolving bleaching powder, $CaCl_2.Ca(ClO)_2$ in water and then adding some dilute hydrochloric acid. When bleaching powder dissolves in water it forms $Ca(ClO)_2$ solution.
(e) An iron (II) sulfate solution is mixed with an acidified potassium permanganate solution.
(f) A potassium iodide solution is mixed with an acidified solution of potassium dichromate.
(g) A solution of acidified potassium permanganate is mixed with a solution of hydrogen peroxide.

9. Disproportionation is said to occur when an element is simultaneously oxidized and reduced. Show how this can occur with hydrogen peroxide by using appropriate half equations.

10. Sodium hypochlorite and calcium hypochlorite are two sources of the OCl^- ion which is a commonly used oxidising agent. Give two uses of the hypochlorite ion.

Reaction Tendency

11. Rewrite the following list of elements so that they are in increasing order of strength as reducing agents.

Silver, chlorine, hydrogen, lead, gold and calcium.

12. MnO_2 can be reduced according to the following equation:

$$MnO_{2(s)} + 4H^+_{(aq)} + 2e^- \rightarrow Mn^{2+}_{(aq)} + 2H_2O_{(l)}$$

Which halide ions could be oxidised by manganese (IV) oxide?

13. Rewrite the following list in order of increasing strength as oxidising agents.

H_2O_2 , Cr^{3+} , Br_2 , $Cr_2O_7^{2-}$, MnO_4^- , K^+ , Au^{3+}.

14. (a) Name two substances that will oxidise Sn^{2+} to Sn^{4+}.

(b) Name two substances that will reduce Fe^{3+} to Fe^{2+}.

(c) Name a substance that will oxidise solid gold.

(d) Name a substance that will oxidise silver but that will not oxidise platinum.

15. What might happen if aluminium rivets are used to fasten zinc coated gutters to a roof?

16. The standard reduction potential for the half cell containing 1.00 mol L^{-1} Al^{3+} ions and Al solid at 25°C and 101.3 kPa pressure is –1.68 V.

(a) Use the Al^{3+}/Al half cell (and others if necessary) to explain what is meant by the term **standard reduction potential.**

(b) Is it possible to have this half cell operating in isolation from any other chemical species that may react?

(c) Name two chemical species that could be used to cause Al^{3+} to be reduced to Al solid.

17. Use a table of standard reduction potentials to determine if a reaction is possible between the following chemical species. If a reaction is possible, use half equations to write a balanced net equation.

(a) A strip of Cu is added to a 1 mol L^{-1} HCl solution.

(b) Solutions of copper (I) nitrate and iodine water are mixed.

(c) An acidified potassium permanganate solution is added to a sample of hydrogen peroxide.

(d) A strip of copper metal is placed in a solution of concentrated nitric acid. Use E° values listed on page 59.

(e) A piece of sodium metal was placed into a beaker containing a 1 mol L^{-1} solution of calcium nitrate.

(f) An acidified 1 mol L^{-1} $KMnO_4$ solution is mixed with a 1 mol L^{-1} solution of HCl.

(g) An acidified 1 mol L^{-1} $K_2Cr_2O_7$ solution was mixed with a 1 mol L^{-1} solution of HCl.

(h) A piece of iron was submersed in a recently boiled beaker of pure water.

18. A table of standard reduction potentials would predict that aluminium metal will oxidise when placed into a beaker of water.

i.e. $Al_{(s)} \rightarrow Al^{3+}{}_{(aq)} + 3e^-$ E° = +1.68 V

$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-{}_{(aq)}$ E° = –0.83 V

Explain why aluminium window frames do not oxidise on exposure to water.

Galvanic cells

19. In any galvanic cell:

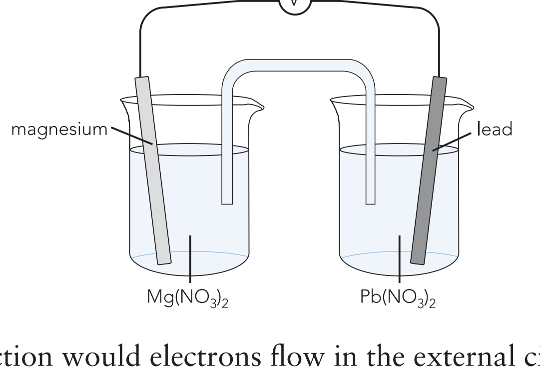
(a) What process occurs at the anode?

(b) What process occurs at the cathode?

(c) What charge is assigned to the anode?

(d) What charge is assigned to the cathode?

20. Consider the following simple galvanic cell:



(a) What direction would electrons flow in the external circuit?

(b) What would be the charge carriers in the external circuit?

(c) What would be the charge carriers in the solutions?

(d) What would be a suitable solution to use in the salt bridge?

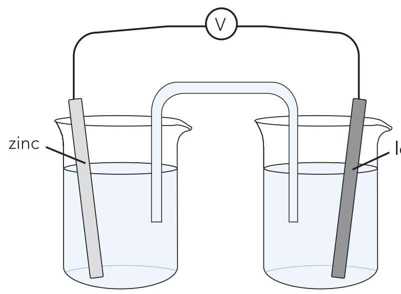
(e) Write the equation to show the oxidation process.

(f) Write the equation to show the reduction process.

(g) If the cell was set up according to standard conditions, what would be the reading on the voltmeter?

(h) Why is a salt bridge necessary in cells that have this style of construction?

21. A galvanic cell was constructed using the following set up:



The solution in both beakers was dilute hydrochloric acid and potassium nitrate was used in the salt bridge.

(a) Would the cell still work if the zinc strip was removed from its beaker and placed into the same beaker as the lead strip (but not touching the lead)?

(b) Would a reaction occur if lead and zinc strips were allowed to touch? How would the reading on the voltmeter be affected?

22. For each of the following combinations, write the equation for the process occurring at the anode and the cathode and predict the cell emf (assume standard conditions).

(a) $\{Zn/Zn^{2+}\}$ and $\{Cu/Cu^{2+}\}$

(b) $\{Ag/Ag^{+}\}$ and $\{Fe/Fe^{2+}\}$

(c) $\{I_2/I^{-}\}$ and $\{Al/Al^{3+}\}$

(d) $\{Br_2/Br^{-}\}$ and $\{F_2/F^{-}\}$

(e) $\{MnO_4^{-}/H^{+}/Mn^{2+}/H_2O\}$ and $\{H_2O_2/O_2/H^{+}\}$

Electrolysis

23. Complete the following table which compares and contrasts galvanic and electrolytic cells.

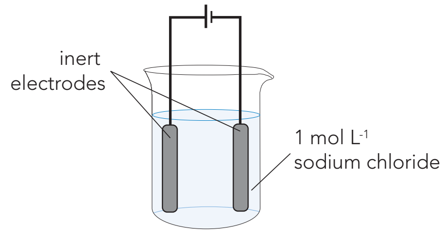
Galvanic Cells	Electrolytic Cells
	Forced chemical reaction
Oxidation occurs at the:	
	Polarity of anode is:
Electrical energy is created by a chemical change.	

24. Write the oxidation and reduction half equations for the reactions that occur when an electrical current is passed through the following molten salts. Inert electrodes have been used. Give the minimum voltage required to produce the reaction in each case.

(a) sodium chloride (b) zinc bromide

(c) lead (II) iodide (d) potassium fluoride

25. Consider the following electrolytic cell:



(a) Identify all chemical species in this cell.

(b) List those that can be oxidised.

(c) Use the table of standard reduction potentials to identify the species that is most likely to be oxidised.

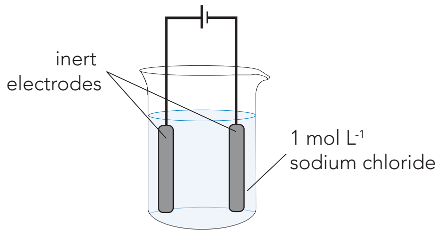
(d) Repeat parts (b) and (c) to identify what species is most likely to be reduced.

(e) Write the half equations and nett equation for the reaction that occurs.

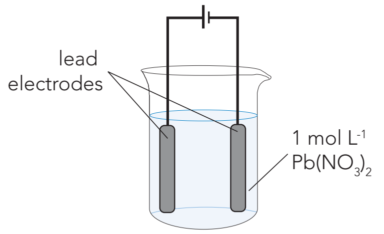
(f) What minimum voltage does the battery need to supply to make the reaction occur?

26. In which of the following cells is water oxidised or reduced?

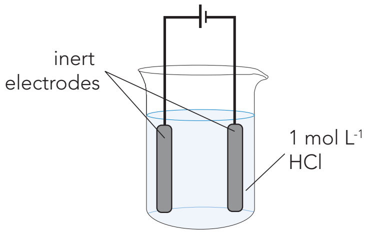
(a)



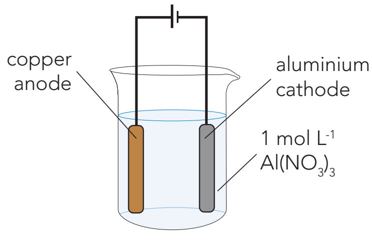
(b)



(c)



(d)



27. Write the oxidation half equation, reduction half equation, nett equation and voltage required for each of the reactions that occur in question 25, parts (a) to (d).

28. With the aid of a labelled diagram and appropriate equations, explain how a steel bracelet could be given a coating of silver. Clearly indicate in your diagram what the cathode; anode and electrolyte are composed of.

29. Two commonly used classroom reagents are 1 mol L^{-1} H_2SO_4 and 1 mol L^{-1} NaOH. Write the nett equations for the electrolysis of each of these reagents (individually) if inert electrodes are used.

Corrosion

30. The corrosion of iron to form rust is a complicated process and it is often best to break it down into several simpler stages. Complete the following by filling in the blank spaces in the explanation or in the paragraph.

- Iron corrodes (oxidises) at the anode: $Fe_{(s)} \rightarrow Fe^{2+} + 2e^-$
- For the iron to be oxidised, some other chemical must be ________________.
- If oxygen and water are present at the ________________ then hydroxide ions will form:

  $O_{2(g)} + 2H_2O_{(l)} +$ __________________ $\rightarrow 4OH^-_{(aq)}$
- The Fe^{2+} and OH^- ions form the insoluble ________________ hydroxide.
- The presence of dissolved oxygen in the water will cause the further oxidation of the iron to form a compound called 'rust'.
- Two possible formulae for rust are ________________ and ________________.

31. Using the information from question 28, explain why the addition of an organic base such as ethylene glycol helps to inhibit the corrosion of car engines.

32. Tin is often used to coat iron cans which are subsequently called tin cans.

(a) Why is tin used as a coating for iron?

(b) Use half equations and E° values to explain why this coating will only work while it is coherent and no iron is exposed.

(c) Use half equations and E° values to explain why a zinc coating is much more effective in preventing the corrosion of iron.

33. Hot water storage tanks sometimes have a metal rod (magnesium or zinc) inserted into them to act as a sacrificial anode. Explain how this anode would help prevent a steel tank from corroding.

34. To reduce the likelihood of car doors corroding it is often recommended to apply a coating of light oil to the internal parts of the door and to clean the drain holes regularly. Explain how these two procedures help prevent corrosion.

35. Long pipelines are expensive to construct and so minimising maintenance problems after construction is an economic necessity. One such method is to connect the pipeline to a DC electricity supply. The pipeline is made the cathode while pieces of metal at various distances along the pipeline are connected as the anode.

(a) Explain why this procedure would help to reduce the overall cost of pipe maintenance.

(b) What is likely to happen to the metal that is connected as the anode?

36. In the extraction of iron from iron ore in a blast furnace, carbon monoxide is the main reducing agent. The blast furnace is filled with iron ore (e.g. Fe_2O_3), coke (carbon) and limestone ($CaCO_3$, SiO_2) and heated to temperatures of nearly 2000°C.

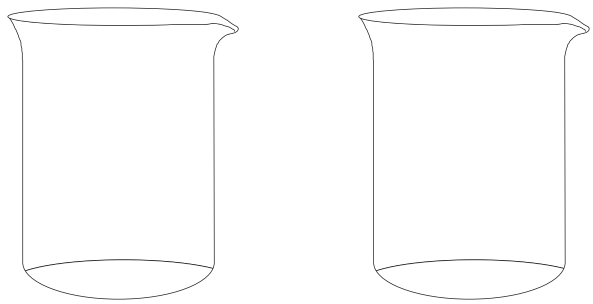
(a) How is the carbon monoxide produced in the blast furnace? Give relevant equations.

(b) Write the equation for the reduction of Fe_2O_3 to Fe by CO.

FOR THE EXPERTS

37. A student sets out to build a galvanic cell using the following components:
    - Freshly cleaned strips of Al and Sn.
    - Solutions (1.0 m) of aluminium nitrate, tin (II) nitrate and potassium nitrate.
    - Glassware to construct the cell.
    - Electrical leads and a voltmeter.

    (a) Draw a labelled diagram to show how these materials could be used to make a galvanic cell. Your diagram must include the materials to be used as the salt bridge, the anode and the cathode.



    (b) Write equations for the processes occurring at the anode and the cathode.

    (c) Predict the emf of the cell (if at standard conditions).

    (d) Using chemical symbols and arrows, show the direction of movement of the chemical species in this galvanic cell.

    (e) After some time it was noticed that the emf of the cell was lower. Suggest possible reasons for this.

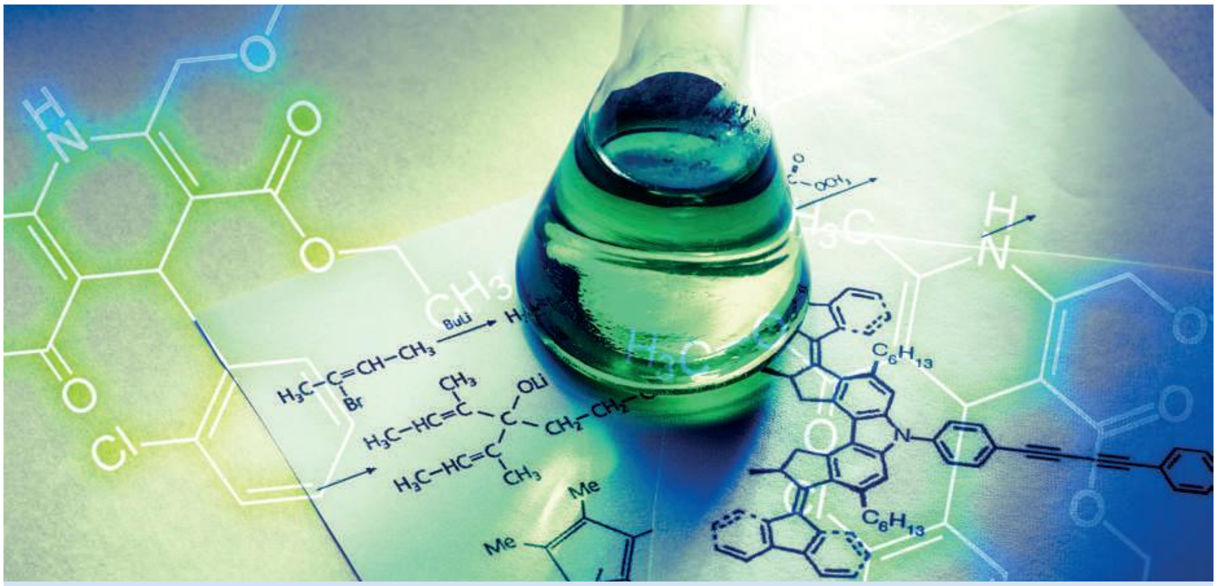
    (f) Which of the electrodes is likely to have increased in mass? Explain.

CHEMISTRY

UNIT 4

ORGANIC CHEMISTRY

4



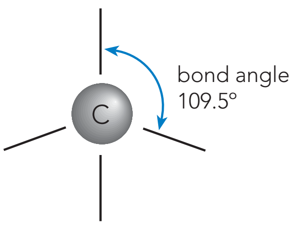
Topics covered in this chapter:

4.1 INTRODUCTION TO BONDING AND TERMINOLOGY

Carbon has the electron structure **2 4** (**$1s^2$ $2s^2 2p^2$**). To obtain the same electron configuration as the nearest noble gas, neon; carbon can form four covalent bonds. Carbon has the unique ability to form *very stable (strong) covalent bonds* with itself and other elements such as hydrogen, oxygen, nitrogen and the halogens. The stability of the bonds allows carbon to form a virtually unlimited number of straight chain, branched chain and ring molecules.

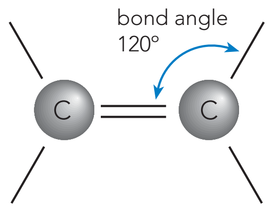
The bonding options for carbon atoms are:

1. four single covalent bonds with a tetrahedral structure as the basic shape.



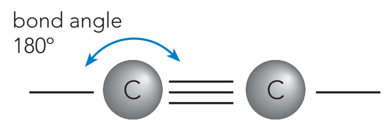
An **alkane** is a carbon chain that contains only single bonds between carbon atoms. Alkanes have the general formula C_nH_{2n+2}

2. one double bond and two single bonds with a triangular planar structure as the basic shape.



An **alkene** is a carbon chain that contains at least one double bond between carbon atoms. Alkenes have the general formula C_nH_{2n} (also cycloalkanes)

3. one triple bond and one single bond with a linear structure as the basic shape.

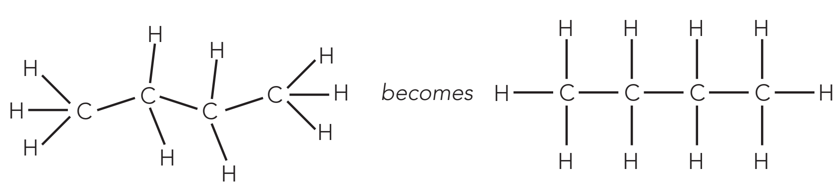


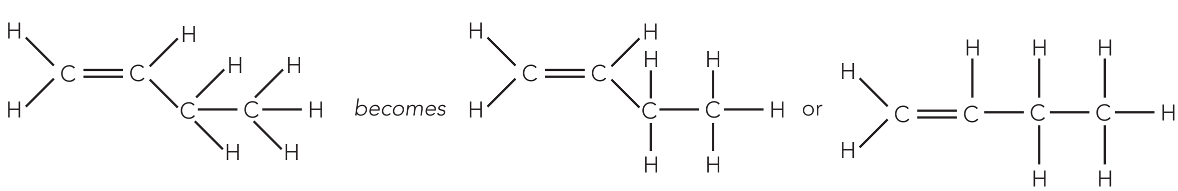
An **alkyne** is a carbon chain that contains at least one triple bond between carbon atoms. Alkynes have the general formula C_nH_{2n-2} (also cycloalkenes)

- Carbon often forms single bonds with *other carbon atoms, hydrogen, oxygen, nitrogen and the halogens.*
- Carbon often forms double bonds with *other carbon atoms and oxygen.*
- Carbon often forms triple bonds with *other carbon atoms and nitrogen.*

Drawing Organic Molecules

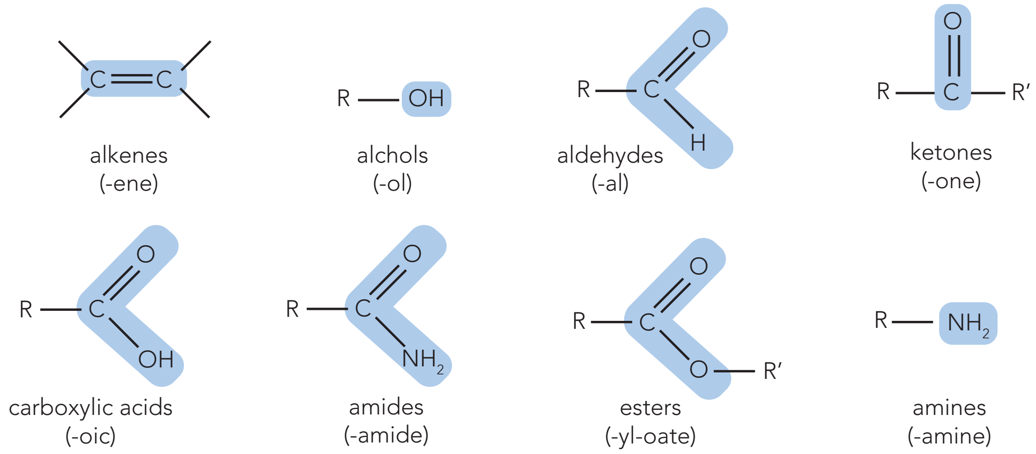
Most organic molecules are based on a tetrahedral shape in which the bonding electron pairs assume a maximum angle of separation in 3-dimensional space. In tetrahedral molecules the bond angles are 109.5°. Representing 3-dimensional figures on 2-dimensional paper is sometimes confusing, the general procedure followed in drawing the 3-D tetrahedral shape on 2-D paper is to draw the bond angles as 90°. Two examples are given below:





Functional Groups

These are the chemically reactive part of an organic molecule. Some important functional groups are:



Alkyl Groups

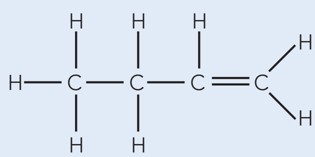
These are saturated carbon chains (what does saturated mean?) which, together with functional groups, compose organic molecules.

Alkyl groups are hydrocarbon chains that are missing one hydrogen. The place where the hydrogen atom is missing is where the alkyl group is attached to the main carbon chain. Alkyl groups have the general formula C_nH_{2n+1} and are often indicated by the symbols R, R_1, R_2, etc.

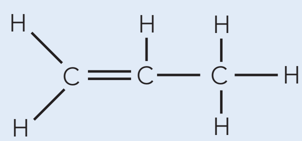
Question 4.1

Examine the following diagrams (structural formulae) and identify the functional **group** present.

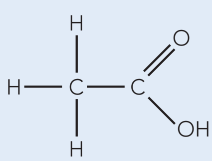
(a)



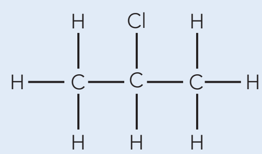
(b)



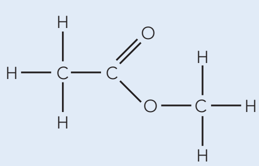
(c)



(d)



(e)



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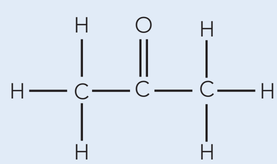
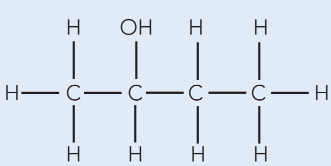


(g)



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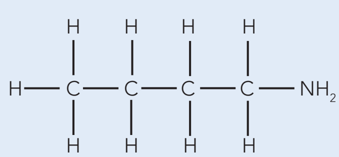


IUPAC rules for naming organic molecules

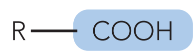
These rules are open to some degree of interpretation and so there will always be some disparity between names given by different chemists.

A small selection of the IUPAC Rules are:

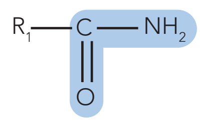
1. Identify the functional groups in the molecule and determine which group has the highest priority in naming (order of priorities given below).
2. Select the longest continuous carbon chain containing the highest priority functional group.
3. Number the chain from the end which gives the main functional group the lowest number.
4. Number all functional groups using the order from #3.
5. Use the appropriate prefix or suffix to name each functional group.
6. Use one word to name the compound. The name for each group is preceded by a numeral indicating its attachment position in the parent chain. Alphabetical order is used when more than one group is involved.
7. Numerals are separated from words by a hyphen and from other numerals by a comma.
8. The priorities for selecting functional groups (R– is a carbon chain of zero or more carbon atoms in length):

decreasing priority

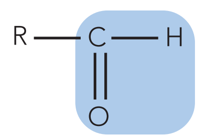
(i) carboxylic acids



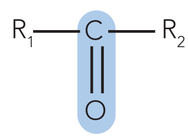
(ii) amides



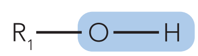
(iii) aldehydes



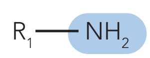
(iv) ketones



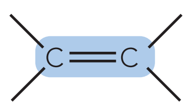
(v) alcohols



(vi) amines



(vii) alkenes



(viii) alkyl groups, C_6H_5 - , halides, etc

Question 4.2

Complete the following table to show the prefixes that are used for indicating the number of carbon atoms in a chain.

Number of carbon in chain	alkane	alkene (with 1 double bond only)	alkyl group
1	methane	***	methyl
2	ethane	ethene	ethyl
3	propane		
4	butane		
5	pentane		
6	hexane		
7	heptane		
8	octane		

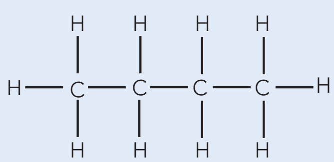
When naming molecules that have more than one of a functional group attached the following prefixes are used:

2	3	4	5	6	7	8	9	10
di	***tri***	***tetra***	***penta***	***hexa***	***hepta***	***octa***	***nona***	***deca***

Question 4.3

Use IUPAC Rules to name the following organic compounds.

(a)



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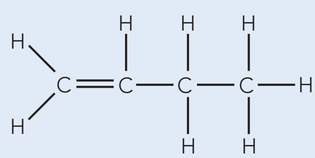
(b)



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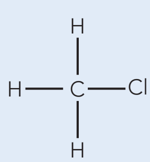
(c)



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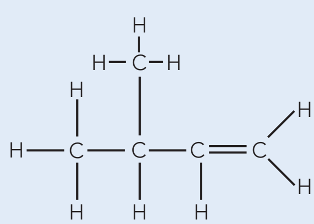
(d)



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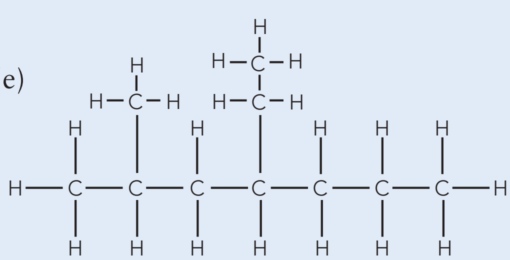
(e)



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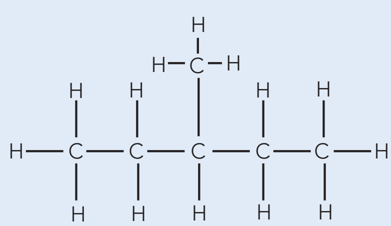
(f)



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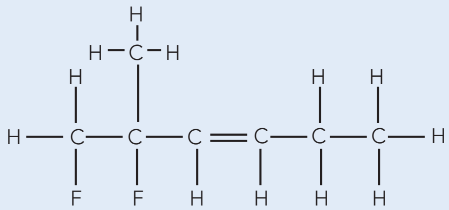
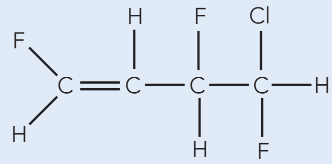
(g)



(h)



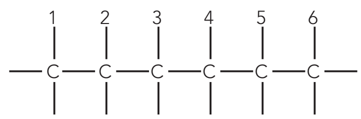
Structural Formula

A structural formula diagram gives a 2-dimensional representation of the organic molecule. It provides important information about where each different atom is attached to a carbon chain. A molecular formula provides the correct number of atoms of each element in a compound, a structural formula provides that **plus** the bonding position of each atom of each element.

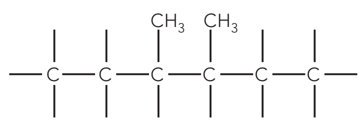
Worked Example 4.1

Draw the structural formula for 3,4-dimethylhexane.

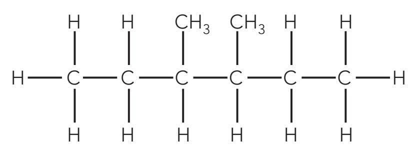
(i) Identify the longest chain by reading the end of the name - hexane.



(ii) Identify what is attached to the longest chain and where it is attached - two methyls at carbons numbered 3 & 4.



(iii) Complete the diagram by drawing the remaining hydrogens.



Question 4.4

Draw the structural formulae of the following compounds.

(a) 3,4-diethyloctane

(b) 1,3,4-triiodohexane

(c) 1,1-dichloropent-2-ene

(d) 3,6-diethylnon-4-ene

Question 4.5

Identify what is **incorrect** about the name of each of the following.

(a) but-3-ene ______________________

(b) 2-ethylprop-1-ene ______________________

(c) pent-4-ene ______________________

(d) 3,4-dimethylpent-4-ene ______________________

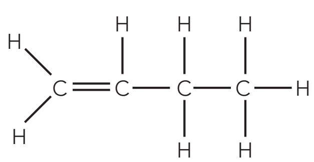
4.2 ISOMERISM

Structural isomers

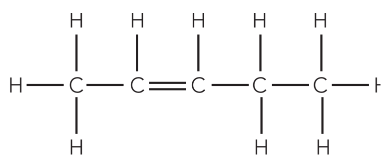
Structural isomers are molecules that have the same molecular formula but have different properties. They have different chemical and physical properties because they have different arrangements of the atoms in the molecule, i.e. they have different structures.

Some examples of structural isomers:

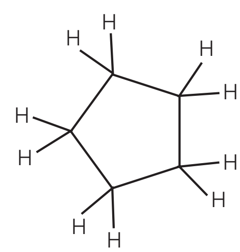
Molecular formula: C_5H_{10}



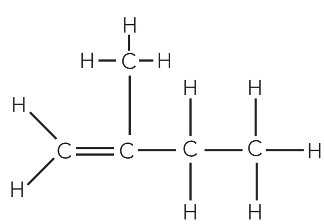
isomer 1: pent-1-ene



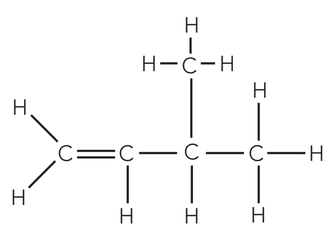
isomer 2: pent-2-ene



isomer 3: cyclopentane



isomer 4: 2-methylbut-1-ene



isomer 5: 3-methylbut-1-ene

Question 4.6

Draw the structural formula for each of the following molecules. They all have the molecular formula C_5H_{10}, so identify which are structural isomers of those drawn above. For those that are not isomers – identify why not.

(a) 2-methylbut-2-ene

(b) 3-methylbut-2-ene

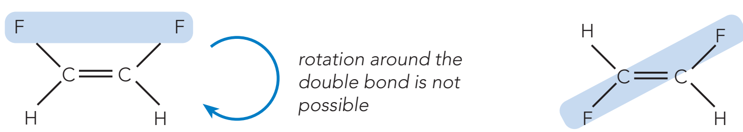
(c) methylcyclobutane

(d) pent-3-ene

Cis and trans isomers

Cis and trans isomers occur only in alkenes. The existence of the double bond stops rotation and so molecules with the same structural formula can have different geometries and hence different properties.

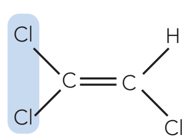
e.g. 1,2-difluoroethene has two isomers:



cis-1,2-difluoroethene *trans*-1,2-difluoroethene

The cis prefix refers to the different structures being on the same side of the axis splitting the double bond while the trans prefix refers to the different structures being across the axis splitting the double bond.

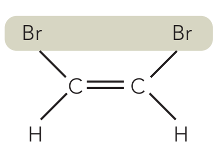
Not all alkene compounds exhibit cis/trans isomerism, e.g.



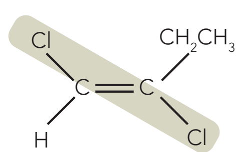
Worked Example 4.2

Name the following cis/trans isomers.

(a)



(b)



Step 1: Name the compound as per normal.

Step 2: Identify both examples, identify the species that are on the same side (*cis*) or opposite sides (*trans*) of the double bond.

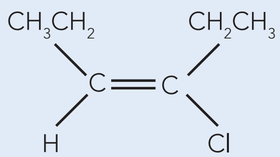
Step 3: Place the appropriate suffix (*cis* or *trans*) in front of the name.

(a) *cis*-1,2-dibromoethene (b) *trans*-1,2-dichlorobut-1-ene

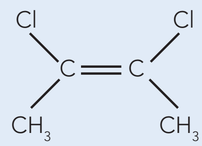
Question 4.7

Name the following compounds using the prefixes "cis" and "trans".

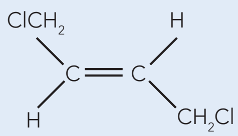
(a)



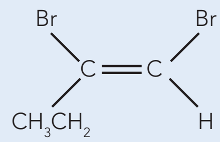
(b)



(c)



(d)



Question 4.8

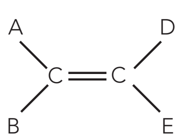
Draw the *cis* and *trans* isomers for each of the following (if the isomers exist).

(a) hept-1-ene (b) 1,2-dichloroethene (c) 1-chloropent-1-ene

SUMMARY – ISOMERS

Structural isomers have the same molecular formula but have:

- different carbon configurations,
- the same functional group in different positions on the chain,
- the same carbon chain with different functional groups.



Cis/trans isomers must be alkenes and have the general form:

where A ≠ B and D ≠ E and C is a carbon atom.

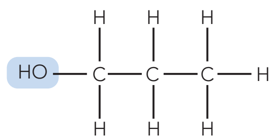
4.3 FUNCTIONAL GROUPS

Alcohols

General formula: -C-OH, or R-OH.

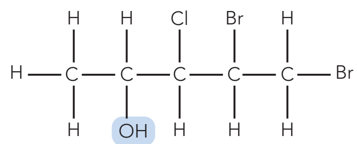
Naming: the compound's name will end in -ol.

e.g. 1:



is propan-1-ol

e.g. 2:

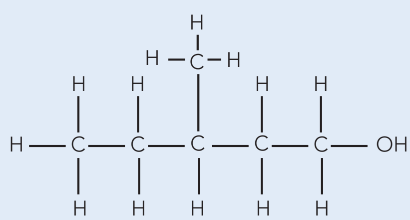


is 4,5-dibromo-3-chloropentan-2-ol

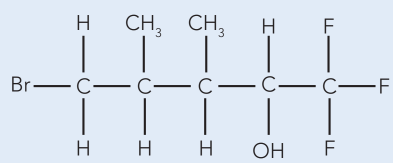
Question 4.9

Name the following compounds.

(a)



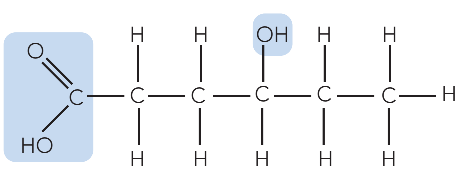
(b)



______________________ ______________________

Note: Using **-ol** as a suffix will not occur when a functional group of higher priority is attached to the carbon chain. In this case the presence of the -OH functional group is indicated using the prefix **-hydroxy-**.

e.g.



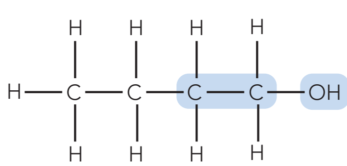
is 4-hydroxyhexanoic acid

Primary, Secondary and Tertiary Alcohols

Alcohols can also be identified according to how many carbon atoms are bonded to the carbon atom attached to the hydroxy group.

Primary alcohol: – OH is attached to a carbon which is attached to **one** other carbon atom.

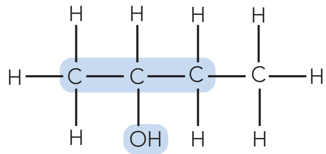
e.g.



butan-1-ol

Secondary alcohol: – OH is attached to a carbon which is attached to **two** other carbon atoms.

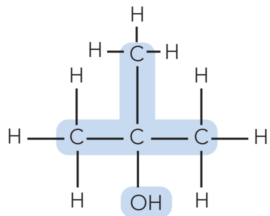
e.g.



butan-2-ol

Tertiary alcohol: – OH is attached to a carbon which is attached to **three** other carbon atoms.

e.g.



methylpropan-2-ol

Reactions of alcohols

1. oxidation of primary alcohol → aldehyde → carboxylic acid

e.g. Write the half equations and full equation for the oxidation of propan-1-ol by acidified potassium permanganate to form propanal.

Oxidation: $CH_3CH_2CH_2OH \rightarrow CH_3CH_2C(=O)H + 2H^+ + 2e^-$ (× 5)

Reduction: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ (× 2)

Nett: $5CH_3CH_2CH_2OH + 2MnO_4^- + 6H^+ \rightarrow 5CH_3CH_2C(=O)H + 2Mn^{2+} + 8H_2O$

NB: propanal could be oxidised further to form propanoic acid.

$CH_3CH_2C(=O)H + H_2O \rightarrow CH_3CH_2C(=O)OH + 2H^+ + 2e^-$

2. oxidation of a secondary alcohol → ketone

e.g. Write the half equations and nett equation for the oxidation of propan-2-ol by acidified potassium dichromate.

Oxidation: $CH_3CH(OH)CH_3 \rightarrow CH_3C(=O)CH_3 + 2H^+ + 2e^-$ (× 3)

Reduction: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

Nett: $3CH_3CH(OH)CH_3 + Cr_2O_7^{2-} + 8H^+ \rightarrow 3CH_3C(=O)CH_3 + 2Cr^{3+} + 7H_2O$

3. NB: tertiary alcohols are not oxidised by acidified $KMnO_4$, etc

4. alcohol + carboxylic acid $\xrightarrow{H^+}$ ester + water

See section on esters for more detail.

Properties of alcohols

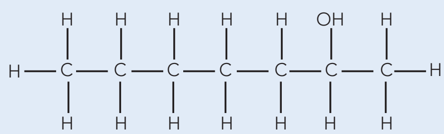
Due to the presence of the -OH group, alcohols exhibit hydrogen bonding. This means that alcohols will tend to have higher melting points and boiling points than other hydrocarbons of similar molar mass. The hydrogen bonding leads to alcohols having a relatively high solubility in water – although the solubility decreases as the length of the hydrocarbon chain increases.

Because of the openness of the hydrocarbon chain primary alcohols tend to have higher boiling points than secondary alcohols which tend to have higher boiling points than tertiary alcohols (this only applies to alcohols of similar molar mass).

Question 4.10

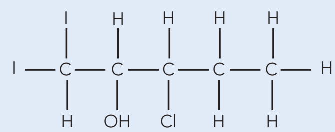
Name the following organic compounds.

(a)



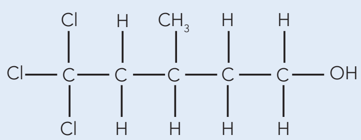
____

(b)



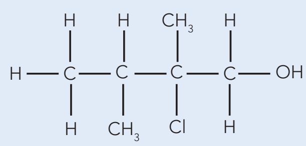
____

(c)



____

(d)



____

Question 4.11

Draw the structural formula for each of the following.

(a) 2-iodopropan-2-ol

(b) 4,5-difluoro-6-methyloctan-2-ol

Question 4.12

(a) Use half equations to write the balanced equation for acidified $K_2Cr_2O_7$ oxidising butan-1-ol to form butanal.

Oxidation: ______________________

Reduction: ______________________

(b) Use half equations to write the balanced equation for the reaction between acidified $KMnO_4$ and pentan-3-ol.

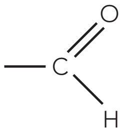
Oxidation: ______________________

Reduction: ______________________

(c) Write the equation for the complete oxidation of butan-1-ol by oxygen gas.

____

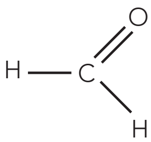
Aldehydes

General formula:  or – CHO

Naming: aldehydes are named using the suffix **-al** in place of the "e" on the end of the hydrocarbon's name.

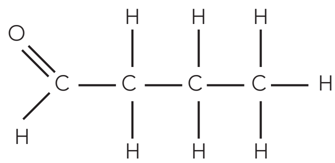
Aldehydes (and ketones) contain the –C=O functional group which is named the carbonyl group. The presence of this carbonyl group causes aldehydes to exhibit dipole-dipole interactions. This gives aldehydes higher melting points, boiling points and solubilities in water than other hydrocarbons of similar size. (These properties are not as pronounced or magnified as in alcohols which exhibit hydrogen bonding.)

e.g. 1



methanal (formaldehyde)

e.g. 2



butanal

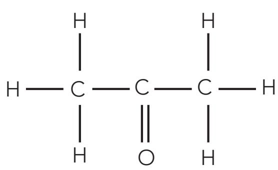
As previously discussed, aldehydes are formed by the oxidation of primary alcohols. Aldehydes can be oxidised to form carboxylic acids.

Ketones

General formula: $-\overset{\overset{\displaystyle O}{\|}}{C}-$ or $R_1\text{–}\overset{\overset{\displaystyle O}{\|}}{C}\text{–}R_2$

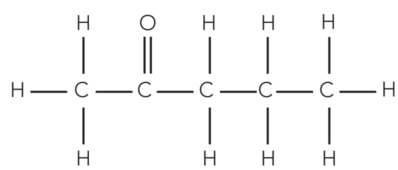
Naming: ketones are named using the suffix **-one** in place of the "e" on the end of the hydrocarbon's name.

e.g. 1



propanone (acetone)

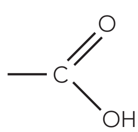
e.g. 2



pentan-2-one

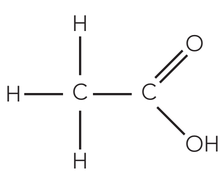
The properties of ketones are very similar to those of aldehydes. However, unlike aldehydes, ketones are not oxidised to form carboxylic acids. Ketones are formed by the oxidation of secondary alcohols.

Carboxylic acids

General formula: –COOH or  or RCOOH

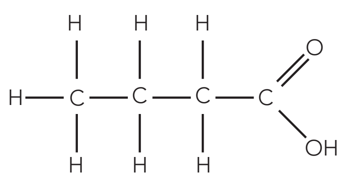
Naming: carboxylic acids are named using the suffix **-oic acid** in place of the "e" on the end of the hydrocarbon's name.

e.g. 1



ethanoic acid

e.g. 2



butanoic acid

NB: aldehydes and carboxylic acids must be at the end of the carbon chain and so are assumed to be number 'one' in a name.

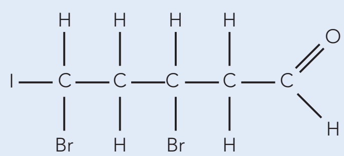
Because of the presence of the –C=O and –OH groups carboxylic acids have high solubilities in water, melting points and boiling points when compared to other organic compounds of similar molar mass. As with alcohols, aldehydes and ketones; the solubility of carboxylic acids decreases as the length of the carbon chain increases.

Carboxylic acids are weak acids as they do not completely ionise when dissolved in water. Carboxylic acids are formed by the oxidation of primary alcohols and aldehydes.

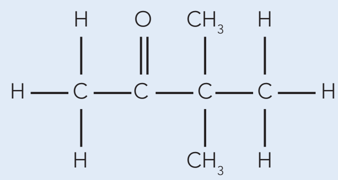
Question 4.13

Name the following compounds.

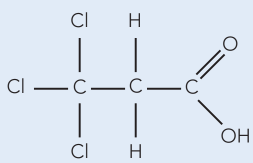
(a)



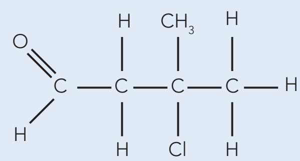
(b)



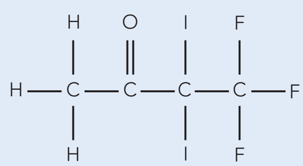
(c)



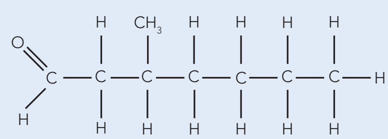
(d)



(e)



(f)



Question 4.14

Draw the structural formula for each of the following.

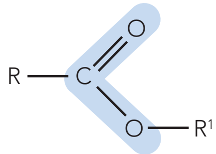
(a) 3,4-dichloropentanal

(b) 3-methyloctan-4-one

(c) hexanoic acid

(d) 3,3,3-triiodopropanal

Esters

General formula: 

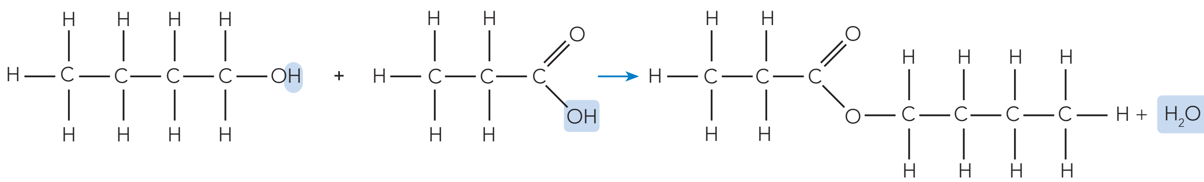
Naming: esters are made by reacting a carboxylic acid with an alcohol. Their name is derived from the two reacting components.

e.g. 1 ethan**ol** + methan**oic acid** $\xrightarrow{H^+\text{(catalyst)}}$ **ethyl** methan**oate** + water
where the **yl** comes from the alcohol reactant and the **oate** comes from the acid reactant.

Esterification is the name for the chemical reaction in which esters are made.

e.g. 2 Write the equation for the reaction between butan-1-ol and propanoic acid.

butan-1-**ol** + propan**oic acid** $\xrightarrow{H^+}$ butyl propan**oate** + water



Question 4.15

Name the ester formed in each of the following, and draw its structural formula.

(a) methanol + propanoic acid $\xrightarrow{H^+}$

(b) hexanoic acid + propan-1-ol $\xrightarrow{H^+}$

(c) heptan-1-ol + ethanoic acid $\xrightarrow{H^+}$

Question 4.16

What organic reactants could be used to produce the following esters?

(a) ethyl propanoate ______________________

(b) octyl butanoate ______________________

(c) propyl methanoate ______________________

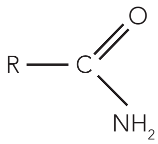
Properties of esters: Esters have similar boiling points to aldehydes and ketones with the same number of C atoms because of dipole-dipole force of attraction and dispersion forces. Small esters are soluble in water but the solubility decreases as the length of the carbon chain increases. Many esters have their own distinctive fruity smell.


methyl butanoate


ethyl butanoate

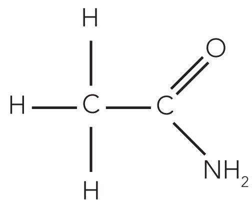

pentyl ethanoate

Amides

General Formula: 

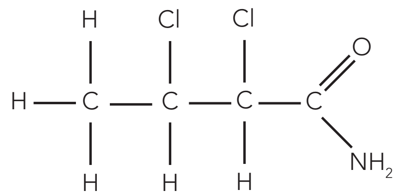
Naming: amides are named using the suffix **-amide** in the place of the "e" on the end of the hydrocarbon's name.

e.g. 1:



ethanamide

e.g. 2:



2,3-dichlorobutanamide

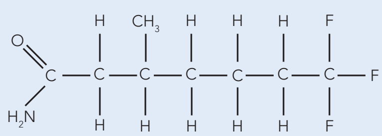
Amides can be produced by reacting ammonia with a carboxylic acid. The product is then heated to remove the water.

$$RCOOH + NH_3 \xrightarrow{\text{Heat}} RC=ONH_2 + H_2O$$

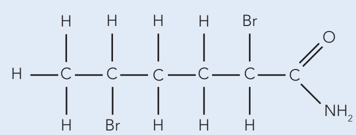
The presence of the NH_2 and C=O groups mean that amides form strong hydrogen bonds and consequently have high melting points for their size and are soluble in water. As is usual with organic molecules the solubility decreases as the size of the molecule increases. Although the presence of the $-NH_2$ would suggest otherwise, amides tend to form neutral solutions.

Question 4.17

Name the following compounds.

(a) 

____

(b) 

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Question 4.18

Draw the structural formula of the following

(a) 4,5,6-triiodoheptanamide

(b) 3-chloro-4-methylpentanamide

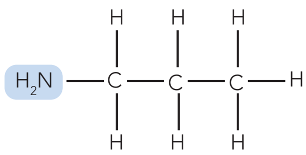
4.4 AMINES AND α-AMINO ACIDS

Amines

General formula: $-NH_2$ or $R-NH_2$.

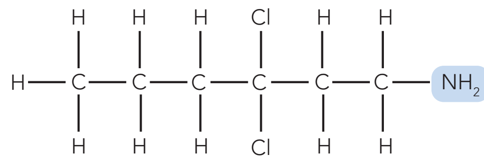
Naming: the compound's name will end in –amine.

e.g. 1



propan-1-amine

e.g. 2



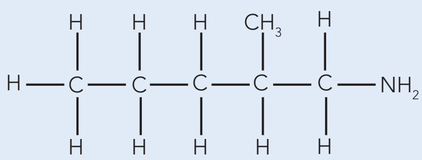
3, 3-dichlorohexan-1-amine

Note: **–amine** as a suffix is not used when a functional group of higher priority is attached to the carbon chain. In this case the presence of the **$-NH_2$** functional group is indicated using the prefix **–amino-**

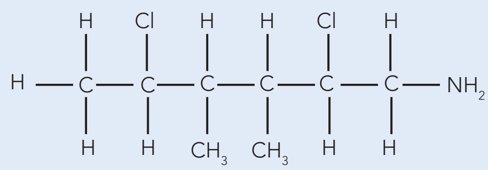
Question 4.19

Name the following compounds:

(a)



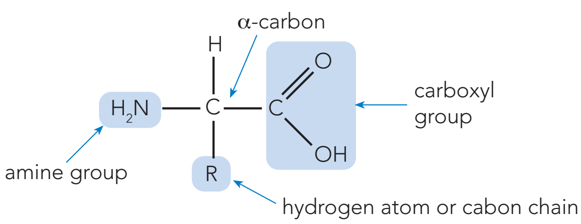
(b)



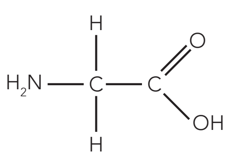
α-Amino Acids

All α-amino acids have a structure that is centred around an **alpha** carbon. The alpha carbon is always bonded to four distinct groups:

(i) A carboxyl group (–COOH)
(ii) An amine ($-NH_2$)
(iii) A carbon chain often represented by "–R". (Glycine is the only alpha amino acid that does not have this carbon chain, it has a hydrogen atom)
(iv) A hydrogen atom (in glycine's case, a second hydrogen atom)

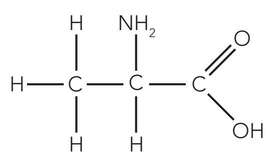


e.g. 1



glycine (2-amino ethanoic acid)

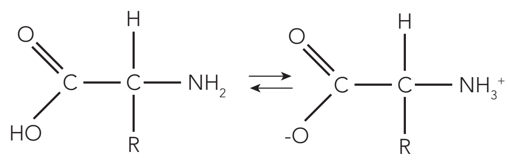
e.g. 2



alanine (2-amino propanoic acid)

α-amino acids having boiling points above 200°C which is higher than other amines or carboxylic acids of similar molar mass. This is because in solid form or in neutral solution, the amine group removes a proton from the carboxyl group which results in the α-amino acid having both a positive ion ($–NH_3^+$) and negative ion ($–COO^–$). In this form, the α-amino acid is a neutral ion as it possesses both a positive and a negative charge and is an example of a **zwitterion**. α-amino acids are generally soluble in water and insoluble in non-polar solvents. To a large extent this is due to the α-amino acids forming zwitterions in the solid and aqueous phase. The comparative solubilities of the α-amino acids depends upon the size of the –R side chain and what functional groups are contained in the side chain.

e.g.



Generally, the properties of α-amino acids are determined by the properties of the carbon side chain (–R) that is attached to the α carbon. The polarity of the side chain is very influential on the properties of the α-amino acid as it influences interactions with other molecules. As α-amino acids are the building blocks of proteins, the properties of the side chain greatly influence the properties and structure of the protein.

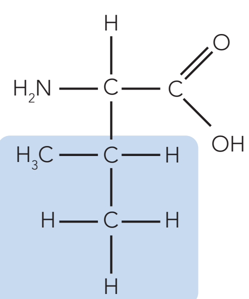
It is often useful to group the α-amino acids according to the polarity of the side chain.

1. **Non-polar, –R chain is an alkyl or phenyl group** (in the case of glycine, a H atom only).

   Interactions with other molecules due to dispersion forces.

   Glycine, alanine, valine, leucine, isoleucine, phenylalanine, tryptophan, methionine and proline.

   e.g. **valine:**

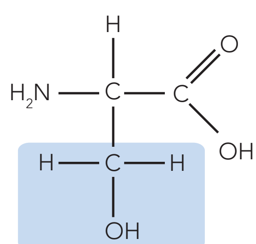


2. **Polar but neutral, –R chain has an amide, hydroxy or thiol (–RSH) group**

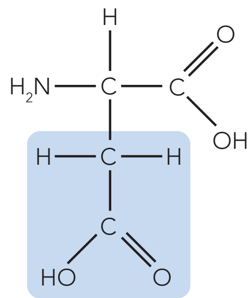
   Side chain can be involved in hydrogen bonding. Cysteine can form disulfide bonds.

   Serine, threonine, cysteine, tyrosine, asparagine and glutamine. (NB cysteine and tyrosine can form negative ions but these ions are not favoured at the average pH of human cells.)

   e.g. **serine:**



3. **Acidic and polar as the –R chain contains carboxyl group**
At the average pH of human cells, the –COOH exists as the negative $–COO^-$ ion
Aspartic acid and glutamic acid.
e.g. **aspartic acid**



4. **Basic and polar as the –R chain contains an amine group**
At the average pH of human cells, the $–NH_2$ will as the positive $–NH_3^+$ ion (or $=NH_2^+$ ion).
Histidine, lysine and arginine.
e.g. **lysine:**

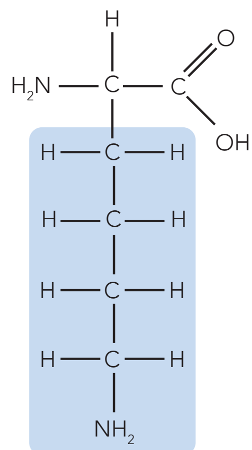
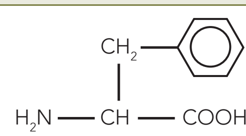
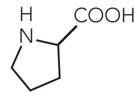
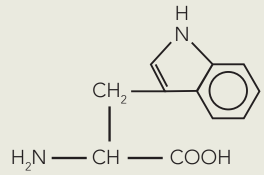
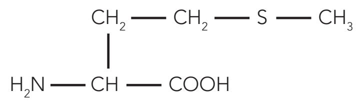
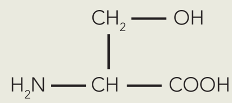
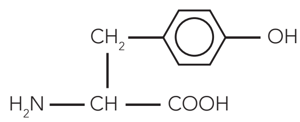
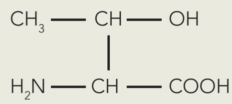
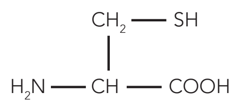
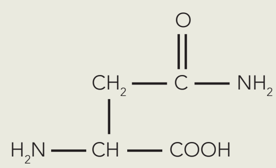
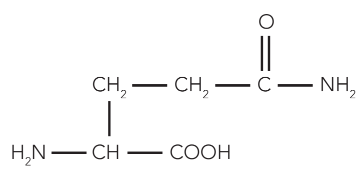
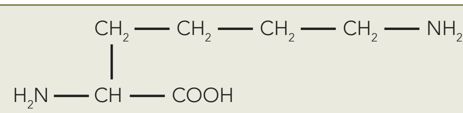
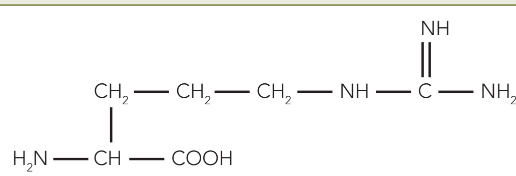
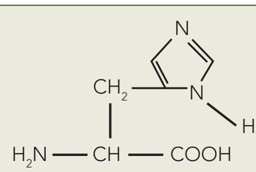
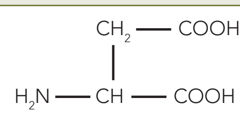
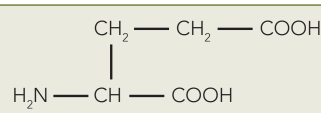


Table 4.1

α-amino acid (polarity of side chain)	Abbreviation	Structure
Glycine (no side chain)	Gly	$H_2N — CH_2 — COOH$
Alanine (non-polar)	Ala	CH_3 | $H_2N — CH — COOH$
Phenylalanine (non-polar)	Phe	
Valine (non-polar)	Val	$CH_3 — CH — CH_3$ | $H_2N — CH — COOH$
Leucine (non-polar)	Leu	$CH_3 — CH — CH_3$ | CH_2 | $H_2N — CH — COOH$
Isoleucine (non-polar)	Ile	$CH_3 — CH — CH_2 — CH_3$ | $H_2N — CH — COOH$

α-amino acid (polarity of side chain)	Abbreviation	Structure
Proline (non-polar)	Pro	
Tryptophan (non-polar)	Trp	
Methionine (non-polar)	Met	
Serine (polar)	Ser	
Tyrosine (polar)	Tyr	
Threonine (polar)	Thr	
Cysteine (polar)	Cys	
Asparagine (polar)	Asn	
Glutamine (polar)	Gln	
Lysine (Basic and +vely charged)	Lys	
Arginine (Basic and +vely charged)	Arg	
Histidine (Basic and +vely charged)	His	
Aspartic Acid (Acidic and -vely charged)	Asp	
Glutamic Acid (Acidic and -vely charged)	Glu	

Question 4.20

Alanine is an α-amino acid. Comment on its polarity and acidity.

Question 4.21

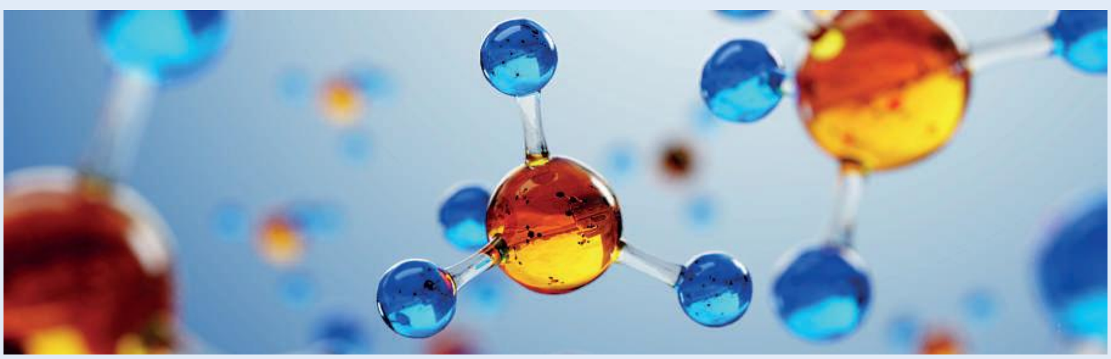
(a) Write the equation for alanine dissolving in water.

(b) Draw the structural formula for alanine when it is in a 0.1 mol L^{-1} NaOH solution.

(c) Draw the structural formula for alanine when it is in a 0.1 mol L^{-1} HCl solution.

Question 4.22

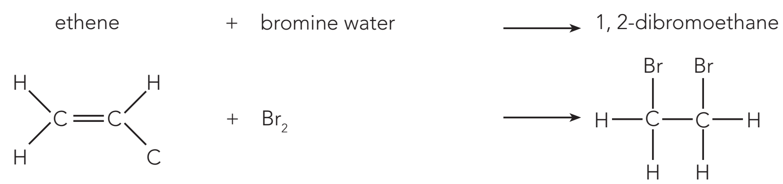
Using the Table 4.1, would you expect alanine or isoleucine to have the more hydrophobic side chain. Justify your answer.



4.5 REACTIONS OF HYDROCARBONS

Addition reactions

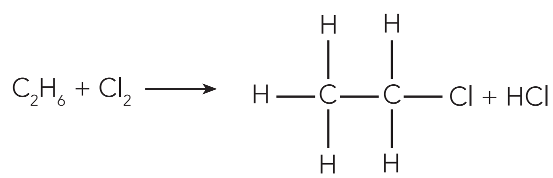
Addition reactions occur when **alkenes** and **alkynes** have their double or triple bond broken and elements such as halogens added into the carbon chain.



Substitution reactions

Substitution reactions occur when alkanes and aromatic compounds react such that a hydrogen atom is removed and another element such as a halogen is substituted into its position on the hydrocarbon chain.

e.g.



Alkanes and aromatic compounds are relatively inert compounds. Substitution reactions need to occur at moderately high temperatures (250°C) or with UV light added and are slower than addition reactions (typically).

Combustion

All hydrocarbon compounds can be burnt in oxygen. If complete combustion occurs then the only products are carbon dioxide and water vapour. The production of energy by burning organic fuels (fossil fuels) is the major form of energy production on Earth.

Question 4.23

Write the equation for the following reactions. Show the structural formula of all organic compounds.

(a) ethene + Cl_2 ________________________________

(b) hexane + Br_2 ________________________________

(c) but-1-ene + HBr ________________________________

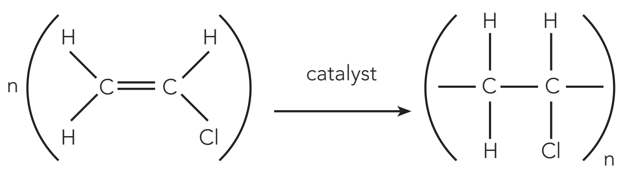
(d) C_7H_{16} + O_2 ________________________________

4.6 POLYMERISATION

A **monomer** is a small molecule that can be joined many times to form a polymer. **Polymerisation** is the chemical process by which many monomers are linked to each other to form large chain molecules called polymers.

Two types of polymerisation are:

i) **Addition Polymerisation:** the monomer is an alkene and the polymer is formed by the breaking of the double bond in the simple alkene and then linking the pieces together.



vinyl choride (chloroethene) polyvinyl choride

ii) **Condensation Polymerisation:** one monomer is a di-carboxylic acid and the other is either a di-alcohol or a di-amine. If the non-acidic monomer is a di-alcohol the polymer formed will be a polyester but if it is a di-amine then the polymer is a polyamide. In either case the other product will be water and hence the name condensation polymer.

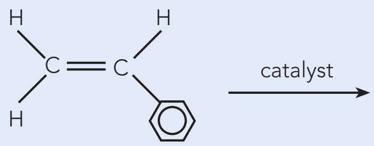
n(HOOC–R–COOH)	+	n(HO–R´–OH)
–dioic acid	+	–diol
→ (–OC–R–COOR´O–)n	+	$2H_2O$
polyester	+	water
n(HOOC–R–COOH)	+	n(H₂N – R´– NH₂)
–dioic acid	+	–diamine
→ (–OC–R–CONHR´NH–)n	+	$2H_2O$
polyamide	+	water

Wool, silk, nylon and Kevlar™ are examples of polyamides while terylene and polyethylene terephthalate (PET) are examples of polyesters.

Question 4.24

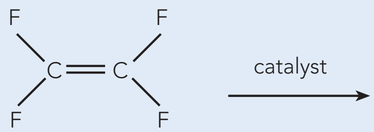
Show what polymers can be formed from the following monomers.

(a)



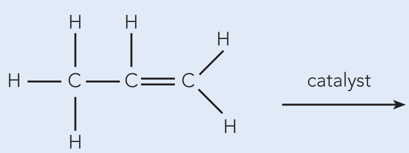
monomer = styrene polymer = ____________________

(b)



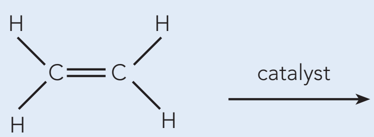
monomer = tetrafluoroethene polymer = teflon

(c)



monomer = propene polymer = ____________________

(d)



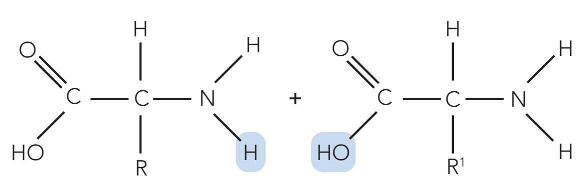
monomer = ethene polymer = ____________________

Polypeptides and Proteins

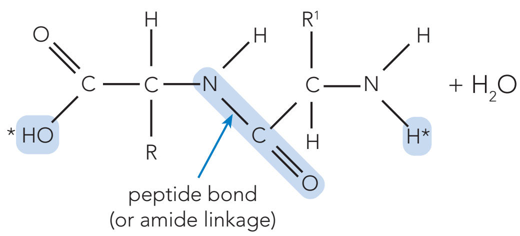
α-amino acids are characterised by the amine group and the carboxyl group attached to the end carbon. Having these two functional groups at the end of the chain leads to α-amino acids being the monomers in the formation of a condensation polymer called a polypeptide. Proteins form when polypeptides join together to create an even larger molecule.

The mechanism by which α-amino acids polymerise is:

1. A hydrogen atom is removed from the amine group from one a-amino acid molecule and an OH group is removed from the carboxyl end of another a-amino acid molecule.



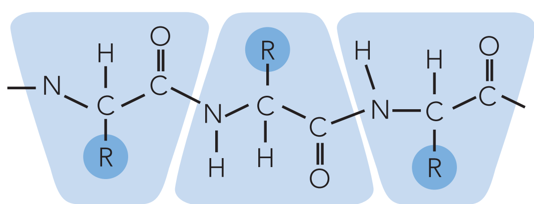
2. The two molecules then join at the sites where the H and OH are missing in what is called a peptide bond.



3. This also occurs at the other ends of the α-amino acid molecules as indicated by the asterisk in (2). When many α-amino molecules join together, the polymer is called a polypeptide.

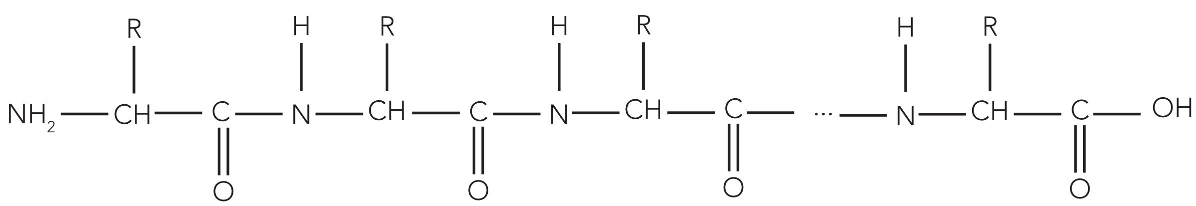
4. One polypeptide molecule can join or bond to another polypeptide molecule because of interactions (dispersion forces, dipole-dipole interactions or hydrogen bonds) between the side chain section labelled R and R_1 in the diagrams of points (1) and (2).

5. The amide linkage, or peptide bond, is the key structure to identify when describing proteins. It is usual to start at the amine (-NH-) end and go to the carbonyl end (-C=O). The diagram below shows the repetition of a small number of amino acid monomers in a protein.



The sequence of the repeating amino acid monomers gives the protein its **primary** structure. The **primary** structure of a protein relates to structure governed by the covalently bonded atoms in the protein but not including any disulfide bridges.

The diagram below shows a common representation for the primary structure of a protein.



A protein may contain between 50 and 2000 repetitions of the amino acid monomers. The "R" side chain represents the remaining carbon chain region (not the NHCHC=O section) of any of the 20 amino acids that make up proteins. It is common practice to use a 3-letter or a 1-letter abbreviation for the amino acid rather than "R" when drawing proteins. The polarity of the side chain tends to affect the interaction of that region of the molecule with water. Generally the non-polar side chain regions of the protein tend to be at the core of the protein whereas the polar or charged regions tend to be at the surface.

Question 4.25

How many monomer units are drawn in the protein structure above?

Structure of Proteins

Proteins are very large molecules and as such there are numerous influences on their properties and structure. The structure of proteins is often broken down to the following categories according to what sections of the protein are interacting:

PRIMARY STRUCTURE: describes the sequence of α-amino acids in the protein polymer chain. The atoms are held to each other in the polymer by covalent bonds. The primary structure is often illustrated using the 3 letter abbreviations for the α-amino acids present.

…–Ala–Asn–Ser–Asp–Cys–Asn–Glu–Arg–Val–Phe–Met–Thr–Gln–His–Gly–…

SECONDARY STRUCTURE: this describes the effect that hydrogen bonding between the amide and carbonyl groups in the protein polymer chain have on the structure of the protein. These strong secondary forces of attraction will pull sections of the protein chain together as coiled helix structure (α-helix) or cause folds or sheets (β-pleated sheets) between sections of the protein.

TERTIARY STRUCTURE: this describes the effect that bonding between the –R side chains has on the shape of the protein. The bonding between the side chains in the protein molecule may be hydrogen bonding, dipole-dipole interactions, dispersion forces or ionic interactions. As the cysteine -R side chain ends with a HS group, two cysteine functional groups in a protein can form covalent disulfide bridges (–S–S– covalent bonds) between the –HS groups.

Question 4.26

(a) Could the following monomer be part of the primary structure of a protein? Explain your answer.

$HOOCCH_2CHNH_2CH_2CH_2CH_2CH_3$

(b) A section of a protein had the following sequence of α-amino acids, –Ala–Val–Leu–Phe–. These α-amino acids are all considered to be non-polar and their interactions with similar sections of the same protein chain tend to be by dispersion forces. They tend to avoid water and arrange themselves towards the centre of the protein structure. Which level of structure of the protein is this describing?

4.7 ORGANIC SOLVENTS

The solubility of one substance in another is difficult to predict and is dependent on factors such as the nature of intermolecular forces within the solvent (and solute), intermolecular forces between solvent and solute molecules, quantities of solvent and solute, temperature, etc.

A **general** guide to the solvent qualities of organic substances is:

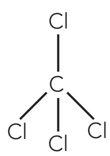
Polar solutes dissolve in *polar* solvents,
non-polar solutes dissolve in *non-polar* solutes,
BUT
non-polar solutes do not dissolve in *polar solvents,*
polar solutes do not dissolve in *non-polar solvents*.

For organic compounds the following table may be useful:

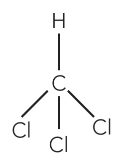
Polar Solvents	Non-polar Solvents
alcohols (–OH)	alkanes
amines (–NH_2)	alkenes
aldehydes (–CHO)	alkynes
ketones (–C=O)	esters
carboxylic acids (–COOH)	

- As the length of the hydrocarbon chain increases, the molecules listed as polar solvents tend to become less polar and more non-polar in nature.
- The polar nature of alkyl halides is not predictable and needs to be determined through examining the shape and dipole moment or overall polarity of the molecules involved. Alkyl halides that are polar tend not to have as strong a polar nature as water and are often only slightly soluble in water.

e.g.



CCl_4 contains polar covalent bonds because of its shape is non-polar.



$CHCl_3$ is polar but is only slightly soluble.

Petrol, kerosene, carbon tetrachloride, mineral turpentine and some esters are common non-polar solvents.

Ethanol, acetone (propanone) and methylated spirits are common polar solvents.

Question 4.27

Explain how a small amount of motor oil could be removed from a concrete driveway.

Question 4.28

Methylated spirits is useful for cleaning windows. Explain what sort of materials methylated spirits would have trouble removing and explain why it doesn't leave streaks on the window.

____

____

____

____

Question 4.29

Complete the following table.

Functional group	General formula	Name ends in:	Solubility in water	Produced by: (give an example of a typical reaction)
–Cl –I –Br (haloalkane)				substitution addition
>C=C< (alkene)				NA
$-NH_2$ (primary amine)				NA
–OH (alcohols)				hydration of an
–CHO (aldehydes)				oxidation of a
–C(=O)– (ketones)				oxidation of a
–COOH (carboxylic acids)				oxidation of a or of an
–C(=O)–O– (esters)				alcohol with

Question 4.30

Complete the following table.

Reactants	Organic Products	Observations
Primary alcohol + $KMnO_4$ (acidified)		
Secondary alcohol + $K_2Cr_2O_7$ (acidified)		
Tertiary alcohol + $KMnO_4$ (acidified)		
Alkane + Cl_2 (with UV light)		
Alkyne + Cl_2		

Question 4.31

Complete the following organic reactions.

Combustion

[Hydrocarbons / Alcohols / Aldehydes, ketones / Esters / Carboxylic acids] + O_2 → ______________ + ______________

Substitution and Addition

Alkane + Halogen → ______________ + ______________

Alkene + Halogen → ______________

Oxidation of Alcohols

Primary Alcohol + $KMnO_4$ *acidified* or $K_2Cr_2O_7$ *acidified* (Oxidising agent) → ____________ → ____________

Secondary Alcohols + $KMnO_4$ *acidified* or $K_2Cr_2O_7$ *acidified* (Oxidising agent) → ____________

Tertiary Alcohols + $KMnO_4$ *acidified* or $K_2Cr_2O_7$ *acidified* (Oxidising agent) → ____________

Reactions of Esters

In acidic conditions: Ester + Water → ________________ + ________________

*Ester + Hydroxide → –R + ________________

* Soap making is an example of alkaline hydrolysis of an ester. See section on soaps in Chapter 5.

e.g.
CH_2OOCR
|
$CHOOCR$ + 3NaOH → ________________ + ________________
|
CH_2OOCR

4.8 EMPIRICAL FORMULA CALCULATIONS

Students need to be able to determine by calculation, the empirical and molecular formulae and the structural formula of a compound from the analysis of combustion or other data. When analysing data, the determination of a(n):

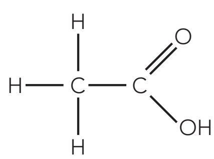
Empirical Formula: provides the simplest whole number ratio of moles of each element present

Molecular Formula: shows the actual whole number ratio of moles of each element present

Structural Formula: indicates how the atoms of each element are bonded to each other

e.g. Ethanoic Acid:

- empirical formula CH_2O
- molecular formula $C_2H_4O_2$
- structural formula is:



but this is often simplified to CH_3COOH.

Table 4.2 Compounds and their formulae.

Compound	Semi-structural formula	Molecular formula	Empirical formula
water	–	H_2O	H_2O
methane	–	CH_4	CH_4
ethane	CH_3CH_3	C_2H_6	CH_3
ethanoic acid	CH_3COOH	$C_2H_4O_2$	CH_2O
methyl methanoate	$HCOOCH_3$	$C_2H_4O_2$	CH_2O
* glucose			
* ethyne			
* benzene			

*(complete these)

Solving empirical formula problems is fairly straight forward. Just remember that we are trying to find the simplest mole ratio of the elements in the compound.

Empirical formula problems may either be:

- simple i.e. the masses of the elements in the compound (or %) are given.
- complex (one sample) – a single sample is burnt or reacted.
- complex (multi-sample) – two or more different sized samples are reacted.

Worked Example 4.3

Empirical Formula - 'simple type'.

A 12.00 g sample of a substance contains 6.54 g of carbon, 1.10 g of hydrogen while the remainder is oxygen.
(a) Find its empirical formula.
(b) If its molecular mass is 88.1, find its molecular formula.

		C	H	O
12.00 g sample	Mass	6.54 g	1.10 g	4.36 g
n =	Moles	6.54 / 12.01 = 0.5445	1.10 / 1.008 = 1.091	4.36 / 16.00 = 0.2725
to get this divide by smallest value (e.g. 0.2725)	Mole ratio	1.998	4.004	1.000
NB – do not round until the end	Simple ratio	2	4	1

(a) Hence empirical formula = C_2H_4O

(b) EF mass = 2 (12.01) + 4 (1.008) + 16.00
= 44.05

MF mass (given) = 88.1
∴ MF = 2 (EF) = $C_4H_8O_2$

Question 4.32

A compound was found to contain 40.0% carbon, 6.67% hydrogen and 53.3% oxygen. Its relative molecular mass is 60.0. Find its empirical formula and molecular formula.

	C	H	O
Mass			
Moles			
Mole ratio			
Simple ratio			

Hint: For % problems assume that you have a 100 g sample

Hence empirical formula	=	______________________
Also EF mass	=	______________________
MF mass	=	______________________
Hence molecular formula	=	______________________

Worked Example 4.4

Empirical Formula - 'complex type'.

An organic compound was known to contain only carbon, hydrogen and oxygen. A 6.36 g sample was burnt and the products formed collected (3.01 g of water and 7.36 g of carbon dioxide).

(a) Determine the empirical formula.

(b) Find the molecular formula if the molecular mass is 228 g.

$$C?H?O? \quad + \quad O_2 \quad \rightarrow \quad \underset{7.36\text{ g}}{CO_2} \quad + \quad \underset{3.01\text{ g}}{H_2O}$$

Step 1 Find the masses of C, H, O in the original sample.

$\frac{m}{M}$

mass of C $= \frac{12.01}{44.01} \times 7.36 = 2.008$ g

mass of H $= \frac{(2)(1.008)}{18.016} \times 3.01 = 0.337$ g

$\therefore$ mass of O $= 6.36 - 2.008 - 0.337 = 4.015$ g

We now have a 'simple' Empirical Formula problem. Complete this example:

	C	H	O
Mass			
Moles			
Mole ratio			
Simple ratio			

Hence empirical formula	=	______________________
Also EF mass	=	______________________
MF mass	=	______________________
Hence molecular formula	=	______________________

Worked Example 4.5

Empirical Formula - 'complex type' - two samples, same mass.

A 0.6578 sample of a compound which was known to contain only C, H, O and S was completely burnt in excess oxygen. This produced 0.7413 g of carbon dioxide and 0.4551 g of water. The sulfur present was oxidised to the sulfate and precipitated as barium sulfate - 1.966 g being recovered.

(a) **Determine the empirical formula.**

Sample 1	C?H?O?S?	+	O_2	→	CO_2	+	H_2O	+	?
	0.6578 g				0.7413 g		0.4551 g		
Sample 2	C?H?O?S?	+	SO_4^{2-}	→	$BaSO_4$				
	0.6578 g				1.966 g				

Note: the sulfur in the $BaSO_4$ all came from the original 0.6578 sample.

(b) **A sample of the compound was vapourised and found to have a density of 3.49 g L^{-1} at S.T.P. Determine the molecular formula.**

(a) Step 1
Find the masses of C, H, O and S in the sample. Because the samples are the same size we can assume that the amount of sulfur in the sample 1 is the same as sample 2.

* *complete all calculations.*

* Sample 1 mass of C $= \frac{12.01}{44.01} \times 0.7413 =$

mass of H = ____________ × ____________ =

* Sample 2 mass of S = 32.07 × ____________ =

∴ mass of O = 0.6578 – (   ) – (   ) – (   ) = g

We now have a 'simple' Empirical Formula problem. Complete this example:

	C	H	S	O
Mass				
Moles				
Mole ratio				
Simple ratio				

Hence E.F. = ____

(b) Determine molecular formula by first finding molecular mass.

mass of 1 L	=	3.49 g
∴ mass of 22.41 L	=	?
∴ molecular mass	=	(3.49) (22.41) = ________________
Now EF mass	=	________________ , MF mass = ________________
∴ MF	=	____

Worked Example 4.6

Empirical Formula - 'complex type' - two samples of different mass.

A compound containing carbon, hydrogen, nitrogen and oxygen was analysed as follows. First a 1.476 g sample was burnt and 2.320 g of CO_2 and 0.3168 g of H_2O were formed. A second sample (1.167 g) was treated to convert all the nitrogen into ammonia. The ammonia was titrated and found to be 0.01389 mol.

(a) Calculate the empirical formula of the compound.

(b) A third sample of the compound (2.520 g) was vapourised and occupied 336 mL at STP. Use this information to determine its molecular formula.

(c) Sketch a possible structure for this organic compound.

Note: this problem involves two different sized samples for finding the empirical formula - so it is best to tackle it by finding the % of each element within each sample - then we will have a 'simple' problem.

Sample 1	C?H?N?O?	+	O_2	→	CO_2	+	H_2O	+	?
	1.476 g				2.320 g		0.3168 g		

Step 1 Find the % by mass of C, H in sample 1.

$$\text{mass of C} = \frac{12.01}{44.01} \times 2.320 = 0.6331 \text{ g}$$

$$\therefore \text{ \% C in sample 1} = \frac{0.6331}{1.476} \times 100 = 42.89\%$$

$$\text{mass of H} = \frac{(2)(1.008)}{18.016} \times 0.368 = 0.337 \text{ g}$$

$$\therefore \text{ \% H in sample 1}$$

Sample 2	C?H?N?O?	+	?	→	NH_3	+ ?
	1.167 g				0.01389 g	

Step 2 Find the % by mass of N in sample 2.

n (NH_3)	=	0.01389 mol		
∴ n (N)	=	0.01389 mol		
∴ m (N)	=	(0.01389) (14.01)	=	0.1946 g

$$\therefore \text{ \% N in sample 2} = \frac{0.1946}{1.167} \times 100 = 16.68\%$$

Step 3 Determine the % by mass of O by subtraction from 100%.

∴ % O = 100.0 – 42.89 – 2.402 – 16.68
= 38.03%

We now have a 'simple' EF problem. * *assume a 100 g sample – complete all calculations*

	C	H	N	O
Mass				
Moles				
Mole ratio				
Simple ratio				

(a) Hence E.F. = ______________________________

(b) To find the molecular formula we need to find the molecular mass.

2.520 g occupy 336 mL at STP
? g occupy 22.41 L at STP?

∴ molecular mass $= (2.520)(\frac{22410}{336}) = 168$ g

Now EF mass = ______________________________

MF mass = 168 g

∴ MF = ______________________________

(c) Sketch a possible structure for this organic compound.

REVIEW QUESTIONS

Chapter 4: Organic Chemistry

1. Indicate whether each of the following is true or false. Alter any false statements so that they are true.

   (a) The IUPAC name for $CH_3COCH_2CCl_3$ is 1,1,1-trichlorobutanone.

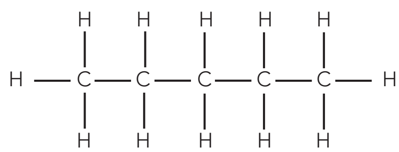
   (b) $C_5H_8F_2$ has multiple isomers including cyclic compounds and geometric isomers.

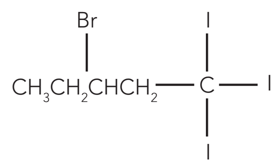
   (c) Alcohols, ketones and aldehydes can be oxidised by acidified potassium permanganate solutions to form carboxylic acids.

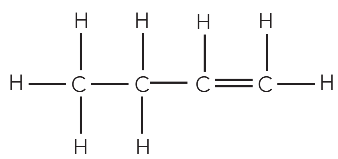
   (d) On chemical analysis a hydrocarbon was found to contain 81.71% carbon. Further analysis found the molar mass to be 44.094 g mol^{-1}. This compound's empirical formula is the same as its molecular formula.

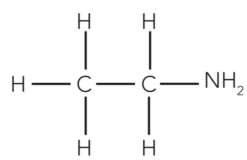
   (e) The α-amino acids, cysteine and methionine are the only two α-amino acids that contain sulfur. They can affect the secondary structure of proteins through the formation of disulfide bridges.

2. Use the IUPAC rules to name the following compounds.

   (a)


   (b)


   (c)


   (d)


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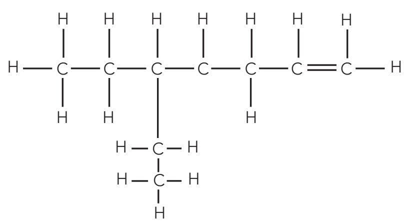

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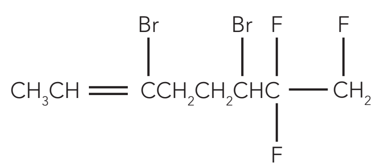

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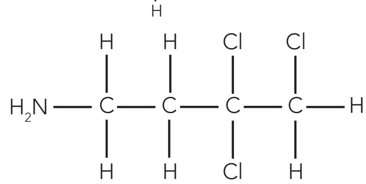

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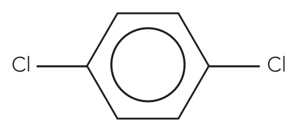
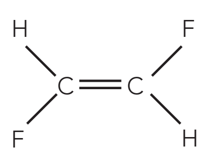


   (i)


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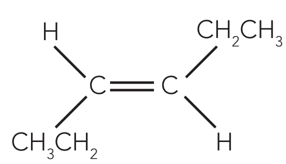
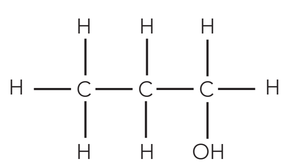
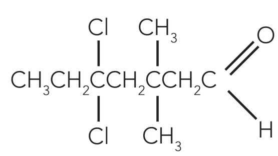
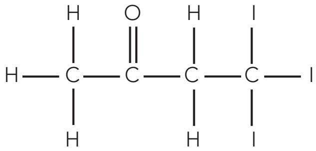
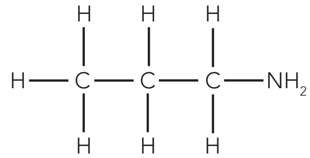
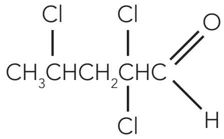


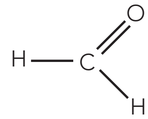
   (k)


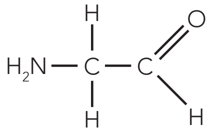
   (l)


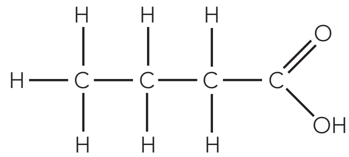
(m) 

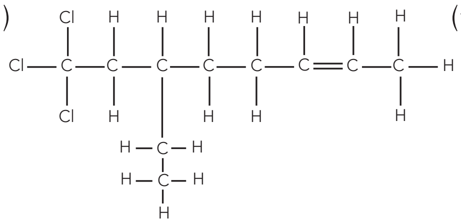
(n) 

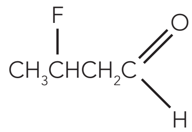
(o) 

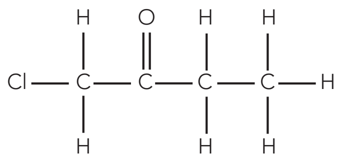
(p) 

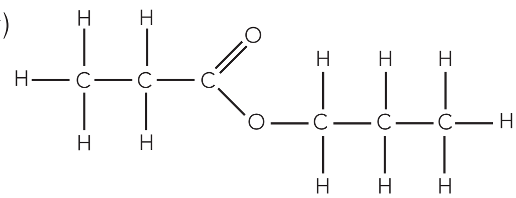
(q) 

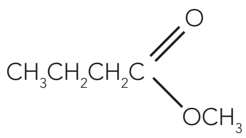
(r) 

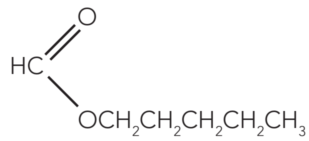
(s) 

(t) 

(u) 

(v) 

(w) 

(x) 

3. Draw the structural formula of each of the following compounds.

(a) hexane

(b) 1,1,1-trichloroethane

(c) 2-methylbut-1-ene

(d) 4,4-diethylheptane

(e) heptan-1-amine

(f) 2-bromo-2-methylpropane

(g) 2-ethyl-3-methylpent-1-ene

(h) 2-chloro-3,3-diethyl-2,5-dimethylhexane

(i) *cis*-hept-3-ene

(j) *trans*-1,2-dibromobut-1-ene

(k) 4,4-dichloro-3-methylhexan-2-ol

(l) *trans*-1-chloropropene

(m) 4,5,5,5-tetrafluoropentan-2-one

(n) 3,4-diiodopentan-1-ol

(o) propanoic acid

(p) 3-hydroxybutanal

(q) *cis*-pent-2-ene

(r) 2,2,2-trichloroethanoic acid (s) 1,2,3-tribromohexane

(t) 2,2-dichloropentan-1-amine (u) 5-ethyl-5-methyloctan-4-one

(v) *trans*-1-chloropropene

4. Give a test and an observation that would permit the identification of each of the compounds in the pairs listed below.

   (a) butanal and butanone (b) butanal and hexane

   (c) ethanol and propanone (d) butan-1-ol and 2-methylpropan-2-ol

   (e) methanol and pentan-1-ol

5. For each of the following redox reactions, write:

   (i) the oxidation and the reduction half equations

   (ii) the nett equation

   (iii) an expected observation.

   (a) Acidified potassium dichromate is mixed with ethanol to form ethanal.

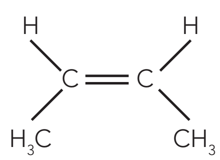
   (b) Acidified potassium permanganate is reacted with methanol to form methanoic acid.

   (c) Acidified potassium permanganate is mixed with butan-2-ol.

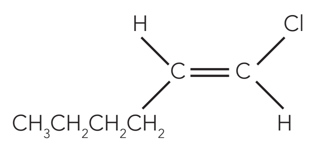
   (d) Acidified potassium permanganate is reacted with pentanal.

6. Name the following:

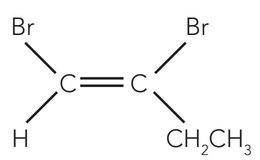
   (a)



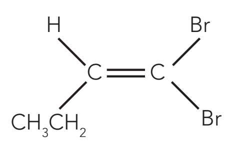
   (b)



   (c)



   (d)



7. Write the balanced equation for the following reactions. Write the structural formula of any organic compound. (Assume correct reaction conditions are produced, e.g. catalyst present, UV light added, etc.)

   (a) propene + Br_2 (b) hex-1-ene + Cl_2

   (c) methane + O_2 (d) butane + Cl_2

   (e) hex-2-ene + HCl (f) octane + O_2

8. Name the type of substance whose properties are described below.

(a) Fruity smelling compound that has a low solubility in water.

(b) High melting point compared to other organic compounds of similar molar mass; ionise to some extent when dissolved in water.

(c) Very soluble in water, reacts with acidified $KMnO_4$ and with carboxylic acids.

(d) Not soluble in water; decolourises bromine water; can be used to form polymers.

9. Name the esters produced in the reactions below.

(a) methanol + methanoic acid

(b) butan-1-ol + ethanoic acid

(c) heptanoic acid + hexan-1-ol

(d) pentanoic acid + ethanol

10. Write the balanced equations for the production of the following esters.

(a) butyl heptanoate

(b) methyl pentanoate

(c) ethyl methanoate

(d) ethyl ethanoate

11. Esters can undergo hydrolysis. In acidic conditions a carboxylic acid and an alcohol are formed while in basic conditions an alcohol and a salt of a carboxylic acid will form.

(a) Complete the following equations for the hydrolysis of an ester.

(i) $CH_3CH_2COOCH_3 + H_2O \rightarrow$ (in acidic conditions)

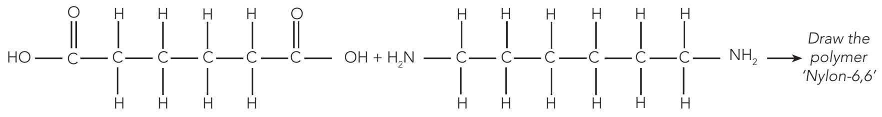
(ii) $CH_3CH_2COOCH_3 + OH^- \rightarrow$ (in basic conditions)

(b) What common household substance is produced by the hydrolysis of a complex ester in basic conditions? (See section 5.1.)

12. Dicarboxylic acids contain two carboxylic acids on the one hydrocarbon chain. Some dicarboxylic acids can be reacted with dialkanamines or dialkanols to produce polymers.

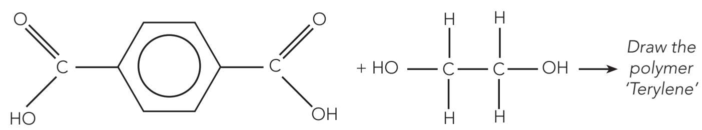
For each example below, draw a unit of the polymer that will form. The other product in each of the examples below is water.

(a)



hexanedoic acid hexan-1,6-diamine

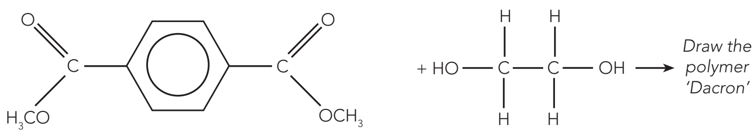
(b)



terephthalic acid ethan-1,2-diol

A third polymer can be made from the ester derivative of a dicarboxylic acid; e.g.

(c)

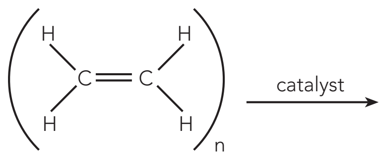


dimethyl terephthalate ethan-1,2-diol

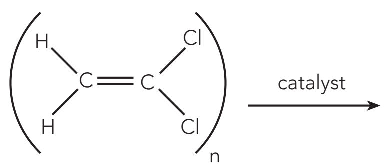
(d) Parts (a) and (b) show the formation of condensation polymers. Apart from the polymer, what is the other product formed?

13. Complete the following equations to show the formation of an addition polymer from an ethene based monomer.

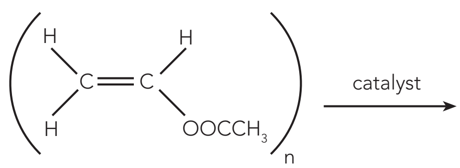
(a)



(b)



(c)



14. (a) What does the "α" refer to in α-amino acids?

(b) Using leucine as an example, explain what a zwitterion is.

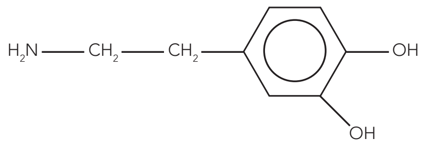
(c) Draw the structural formula for valine when it is an acidic solution.

(d) Draw the structural formula for methionine when it is alkaline solution.

(e) Using serine as the example, write an equation to show the formation of a single peptide bond. If this was repeated to form a polymer, what type of polymerisation reaction would this be classified as?

15. Dopamine is a neurotransmitter produced primarily by the brain from an α-amino acid. Parkinson's Disease is said to be the result of a large reduction in the production of dopamine by the brain.

Dopamine has the chemical structure



In the production of dopamine, the α-amino acid has a hydroxy group added while losing the carboxyl (COOH) group. Using the structure above identify the α-amino acid that is converted by the brain into dopamine.

16. (a) A section of a protein was found to be α-helix in shape. Identify the interactions that cause the α-helix shape and say what sections of the protein would lead to these interactions?

(b) Explain the difference between the secondary and the tertiary structure of a protein.

17. An organic compound was found to be a liquid at room temperature and composed of carbon, hydrogen and oxygen only. Complete combustion of a 9.994 g sample of the compound produced 14.65 g of carbon dioxide and 5.997 g of water.

A set of chemical tests on a different sample of the compound found that 2.22 g of the compound required 37.5 mL of 0.986 mol L^{-1} NaOH for neutralisation.

(a) Determine the empirical formula of the compound.

(b) Assuming the compound is monoprotic determine its molecular formula.

(c) Suggest a likely structural formula for the compound.

18. Qualitative analysis of an organic compound showed that it contained carbon, hydrogen and oxygen only.

When 0.392 g of this sample was burnt in excess oxygen it produced 0.320 g of water and 547 mL of carbon dioxide at 100.0°C and 101.3 kPa pressure.

When another 0.392 of the sample was heated to 250.0°C, the vaporised sample was found to create a pressure of 194 kPa in a 1.00×10^2 mL container.

(a) Determine the empirical formula of the compound.

(b) Determine the molecular formula of the compound.

(c) When this compound was reacted with methanol it was found to produce a liquid that smelt like apples.

(i) Draw the structural formula of the compound.

(ii) Name the product formed when it reacts with methanol.

19. A 5.945 g sample of a substance was found to be composed of 25.45% copper, 12.84% sulfur, 57.67% oxygen and 4.04% hydrogen.

(a) Determine its empirical formula.Further analysis of another 5.945 g of the sample found that when converted from its normal hydrated form to the anhydrous form a weight loss of 2.145 g occurred.

(b) Determine the molecular of the compound showing the water of crystallisation.

20. An organic compound containing oxygen, carbon and hydrogen was labelled X and was subject to the following set of experiments:

I. Substance X was found to be oxidised by potassium permanganate to produce substance Y.

II. Substance X reacted with substance Y to produce a sweet smelling substance labelled substance Z.

III. Substance X and substance Y reacted with sodium.

IV. Substance X was found to be a straight chain compound containing less than 5 carbon atoms.

V. Substance Z underwent hydrolysis in acidic conditions to produce substances X and Y.

VI. 11.62 grams of substance Z was burnt in oxygen and produced 26.41 g of carbon dioxide and 10.81 g of water.

(a) Determine the empirical formula of substance Z.

(b) Draw a possible structural formula of substance Z.

21. When 3.990 g of an organic compound, containing only C, H and N, was burnt in excess oxygen, 8.927 g of carbon dioxide, 5.478 g of water vapour and 3.111 g of nitrogen dioxide were produced.

(a) Determine the empirical formula of the compound.

When a further 3.990 g sample of the compound was vapourised and collected at 210.0°C and 101.3 kPa pressure, it was found to occupy a volume of 2.680 L.

(b) Calculate the molecular formula of the compound.

(c) Given that the only functional group was in a “primary” location draw the structural formula of the compound and give its IUPAC name.

FOR THE EXPERTS

Modern Lifestyles

22. Monosodium glutamate (MSG) is a sodium salt of the ∝-amino acid glutamate, or glutamic acid. MSG is a popular flavour enhancer because it gives food a savoury taste as against the four standard tastes of bitter, salty, sour and sweet.

One method of producing MSG is the hydrolysis of vegetable proteins such as wheat gluten or sugar beet molasses. In this process, the protein is mixed with water and acid before being heated. The glutamate produced is reacted with caustic soda (NaOH) to produce monosodium glutamate.

(a) The α-amino acid glutamate has the formula $C_5H_9NO_4$. Draw its structural formula.

(b) Comment on the acidity and polarity of glutamate.

(c) Write the equation for the production of MSG from glutamate.

(d) Predict the solubility of MSG in water, give a reason for your answer.

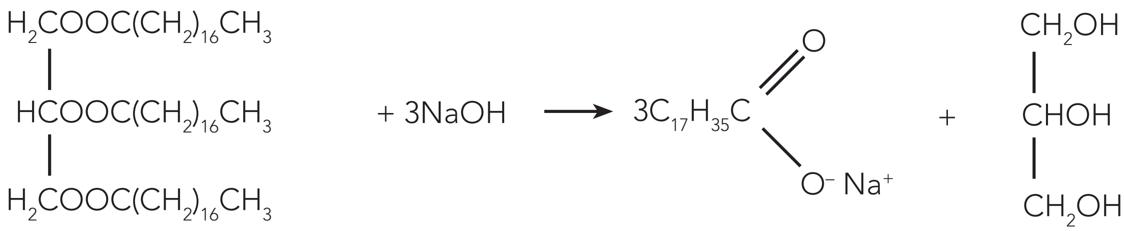
5 CHEMICAL SYNTHESIS

Topics covered in this chapter:

5.1 SOAPS AND DETERGENTS

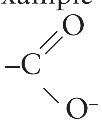
Saponification is the alkaline hydrolysis (NaOH or KOH) of a plant oil or an animal fat (i.e. a long chain ester).

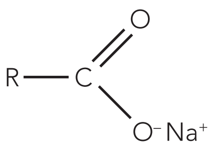
e.g.



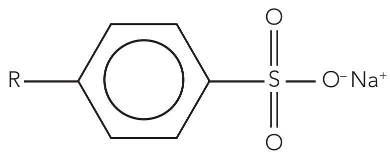
triglyceride (fat) + sodium hydroxide → sodium stearate (soap) + propan-1,2,3-triol (glycerol)

The soap chain is a long chain organic salt in which the hydrocarbon chain portion ($C_{17}H_{35}$ in the example above) is hydrophobic ('water hating' - non-polar) and the carboxylate end

() is hydrophilic ('water loving' - polar).



Simplified soap structure



Simplified detergent structure

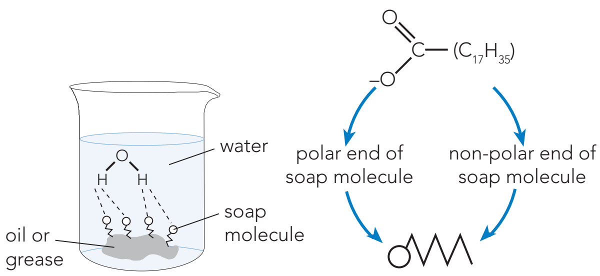
Soaps are not as effective in water that contains calcium ions or magnesium ions, ie hard water. When used in hard water the insoluble salts $Mg(C_{17}H_{35}COO)_2$ and $Ca(C_{17}H_{35}COO)_2$ are formed and the solubility of the soap to form $C_{17}H_{35}COO^-$ ions is greatly reduced which consequently, reduces the cleaning ability of the soap. Detergents are often used in preference to soaps because they do not form insoluble calcium or magnesium salts.

Cleansing Action of Soaps: (based on sodium stearate as the soap)

The cleansing action of a soap is dependent on the soap molecule dissociating into Na^+ and $C_{17}H_{35}COO^-$ ions. The negative end of the $C_{17}H_{35}COO^-$ ion is hydrophilic and allows the soap to dissolve in water. The long hydrocarbon portion of the $C_{17}H_{35}COO^-$ ion is hydrophobic and is responsible for breaking up the non-polar materials such as oil and grease.

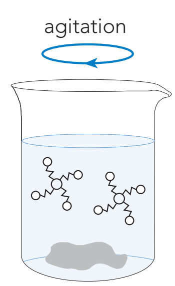
Step 1:

Non-polar region of the soap molecule is attracted to the non-polar oil or grease. The polar end of the soap molecule is attracted to the water molecules. This attraction tries to pull pieces of the oil or grease away from the main chunk.



Step 2:

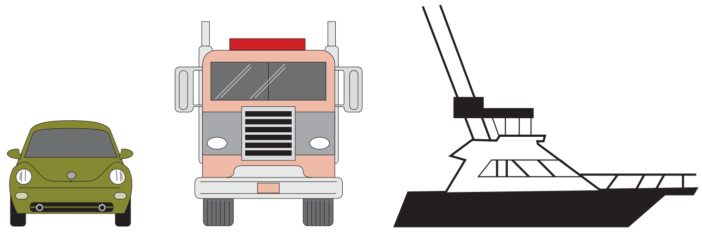
Agitation will help the soap molecules to break the oil and grease down into smaller pieces. Micelles are formed when soap ions completely surround the tiny oil droplets. The negative COO- region of the soap aligns outwards towards the surrounding water molecules. The non-polar hydrocarbon region of the soap is attracted to the oil droplets. The formation of these micelles causes the oil to be broken down into very small pieces which are then dispersed throughout the water. Agitation and hot water will increase the rate at which the oil is dispersed throughout the water.



The cleaning action of detergents is very similar to that of the soap.

5.2 SYNTHESIS OF BIOFUELS

In 2009 Australia consumed approximately 5.5×10^{10} litres of petroleum products, by 2019 this had increased to 7.6×10^{10} litres. Nearly all of this fuel was fossil fuels and consequently it is expected that in future years worldwide competition for this non-renewable resource will lead to a decrease in its availability and a potential rapid increase in its cost. There is also growing pressure worldwide to reduce greenhouse gas emissions by using alternative fuels. At present two alternative fuels are ethanol and biodiesel with hydrogen gas and ammonia being touted as near future alternatives.



Ethanol as a fuel

The first mass-produced car, the 1908 Model T Ford, was a hybrid vehicle. It was designed to run on ethanol, petrol or a mixture of these two fuels. The use of ethanol in conjunction with petrol was common up until the 1940's. From 1940's to 1970's the ready availability and low cost of petrol saw the use of alcohol as a fuel greatly reduced. Since the petrol price hikes that begun in 1970's, alcohol has again started to be used as a supplement to petrol.

The addition of ethanol to petrol can decrease the CO emissions from cars and increase the octane rating of the petrol. As ethanol can be produced from renewable sources, its addition to petrol reduces the consumption of the non-renewable petrol. The amount of ethanol in the fuel is represented by an "E" value, E10 containing 10% ethanol E85 containing up to 85% ethanol. In Western Australia in 2021, the Fuel Watch website (www.fuelwatch.wa.gov.au) no longer lists any service stations selling E10 in WA (19 listed in 2015) and 11 selling E85. New South Wales has legislation that requires 6% of all petrol sold to be ethanol and in Queensland legislation requires 4%.

In the USA at the time of the Model T Ford, ethanol was mainly produced from corn through a fermentation/distillation process. Most of the world's ethanol is still produced by **fermentation** but it can also be produced by the **hydrolysis of ethene**, which is produced by the cracking of petroleum.

Production by Fermentation

Fermentation: in this process, yeast converts simple sugars or monosaccharaides from plants to alcohol and carbon dioxide. Corn, sugar cane and sorghum are common sources of the simple sugars.

Step 1: Grains such as corn and sorghum contain starch which is a polymer made up of repeating units of the monosaccharaides, glucose or fructose. The grain is dried and crushed to release the starch.

Step 2: Water and the **enzymes**, amylase and amyloglucosidase are added to the starch. The **enzymes** are biological catalysts, that is they increase the rate at which the starch polymer is broken down to the glucose monomer by providing an alternate reaction pathway with lower activation energy. Typically, an enzyme is a protein in which the catalytic action is controlled by the sequencing of the amino acids on the protein.

Step 3: Yeast converts the glucose to alcohol with the aid of a group of enzymes.

$$C_6H_{12}O_6 + \text{enzymes} \rightarrow 2\ C_2H_5OH + CO_2$$

Step 4: The alcohol produce by fermentation is an aqueous solution with a maximum concentration of 15%. This is increased to 95% via **distillation**.

Step 5: The final step is to pass the distilled alcohol through a molecular sieve. The alcohol is passed through beds of zeolite. The zeolite sieve separates the smaller water molecule from the larger ethanol molecule and allows for the collection of relatively pure ethanol. This ethanol can then be added to petrol.

Production by Hydrolysis of Ethene

Hydrolysis of Ethene: pure ethanol can be produced by the hydrolysis of ethene, i.e. gaseous ethene reacts with steam. This is a reversible, exothermic reaction with a change in enthalpy of -45 kJ mol^{-1}. The reaction vessel is usually at pressures of 65 atm, a temperature of 300°C and contains H_3PO_4 catalyst that is supported on a SiO_2 mesh.

Question 5.1

Write the equation for the production of ethanol by the hydrolysis of ethene.

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Question 5.2

Use Le Châtelier's principle to predict the temperature and pressure conditions that would favour a high yield of ethanol.

Temperature

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Pressure

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Question 5.3

Explain how the concentration of the reactants will affect the yield of the ethanol.

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It would be a cheap and simple task to increase the concentration of the steam, however the increased yield would be offset by a decrease in the concentration of the catalyst. The decrease in concentration of the catalyst would cause the reaction rate to be uneconomically slow. The worst case would that the excess steam would wash the H_3PO_4 off its SiO_2 support.

Question 5.4

The temperature used is 300 °C which is not particularly low. Why would the chemical engineer design a plant for this temperature rather than the much cheaper low temperature of 25°C?

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The production yield of ethanol would be favoured by an even higher pressure than 65 atm, however this pressure is chosen as balance between yield of ethanol and the cost of building and maintaining a vessel to withstand the higher pressures. The use of higher pressures would also create a chemical problem in that they would favour the polymerisation of ethene to polyethene.

Question 5.5

Draw 3 repeating units of the polymer polyethene.

Apart from its uses as a fuel and in beverages, ethanol is also used in the production of ethyl ethanoate.

Uses of ethyl ethanoate:
- Solvent to decaffeinate tea and coffee
- Alternate to acetone as a nail polish remover
- Artificial flavour in confectionary
- Solvent for perfumes
- Solvent to clean circuit boards
- Hardener in paints

Question 5.6

Write the equation for the production of ethyl ethanoate.

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Biodiesel

Rudolf Diesel demonstrated the prototype of the first diesel engine at the Paris World Expo in 1900. This engine ran on the biofuel peanut oil.

Diesel fuel accounts for about 38% of transport fuel used in Australia and it is almost entirely a fossil fuel. Consideration into the use of biofuels as a replacement fuel or as additive to diesel has been made over a number of years. The European Union has established a target that 10% of fuels used for transport would be biofuels by the year 2020. At present the major biofuel used in the European Union is biodiesel that is produced by the transesterification of bio-oils. The common raw materials to produce biodiesel are conventional vegetable oils, rapeseed (including canola), sunflower, soybean, coconut and palm.

The oils or fats used to produce biodiesel are usually triglycerides with 15 to 23 carbons in each of the molecule's straight chains. Transesterification is the process in which an ester reacts with an alcohol so that the alky section of the alcohol replaces the alkyl section on the ester that is attached to the O. The alkyl section that is removed from the ester becomes the replacement for the alky section on the alcohol.

The general equation below shows the glyceride section of the triglyceride being replaced by CH_3O from methanol and the products formed are three methyl R-oate esters and glycerol (propan-1,2,3-triol). The methyl R-oate esters are isolated and used as the biodiesel. (Remember, methyl R-oate is not the correct name for the ester as R simply represents a carbon chain of unspecified length.)

Question 5.7

Comment on the validity of the statement: Sodium hydroxide is added to the reaction mixture as a catalyst to increase the equilibrium yield of the biodiesel (methyl R-oate).

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To favour the production of the biodiesel (methyl R-oate) the concentration of the methanol is kept high. Water is removed from the system as its presence can lead to the triglyceride reacting with the sodium hydroxide catalyst to form a salt of the triglyceride, i.e. soap. The formation of the soap reduces the yield of biodiesel.

This method of production of biodiesel is often referred to as **base-catalysed** esterification. Lipase is an enzyme found in most living things, in humans it catalyses the breakdown or digestion of fats and oils. Research and trials are ongoing into the use of **lipase-catalysed** esterification as more cost effective method of producing biodiesel than base catalysed esterification. The enzyme will allow the industrial processes to be carried out at temperatures and pressures closer to normal, thereby reducing the amount of energy and expensive equipment needed. The use of the lipase enzyme has the environmental advantage of removing the need to use a caustic (basic) catalyst such as NaOH.

5.3 INDUSTRIAL PROCESSES – ECONOMIC FACTORS

In many industrial processes, reaction rates and equilibrium yield are important considerations.

However, while it is desirable to achieve a high equilibrium yield, it is also important to consider:

- rate of attainment of equilibrium. Exothermic reactions, for instance, give a much higher yield at low temperatures. However at low temperatures reaction rate is low.
- cost of providing high temperatures and/or pressures where these give high equilibrium yields.
- safety aspects – particularly with high temperatures and pressures.
- environmental impact – are there alternatives that provide similar results with lower costs to the environment.

Often a compromise is made in providing desirable reaction conditions, so that maximum amount of product can be produced safely and at lowest cost.

World wide, sulfuric acid and ammonia are synthesised in larger quantities than any other industrial chemical compounds. The economic output of a country's industry can be predicted by its production of H_2SO_4 and NH_3. Consequently it is important that you understand the methods by which these chemicals are produced, the economical factors affecting the production and the common uses of each.

Ammonia

Uses:

1. Nitric acid production
2. Fertilizers
   a) Ammonium nitrate
   b) Ammonium sulfate
   c) Ammonium hydrogen phosphate
   d) Urea
3. Explosives
   a) Ammonium nitrate
   b) Nitroglycerine
   c) Trinitrotoluene (TNT)
4. Cyanide (HCN, NaCN)
   a) Production of polymers such as polyamides (nylon) and acrylics
   b) Gold refining
5. Refining of nickel and zinc
6. Industrial refrigerant
7. Rocket propellant (hydrazine, N_2H_4)
8. Household window and floor cleaner

Production:
Ammonia, NH_3, is produced in several steps from air (N_2 and O_2), methane (CH_4) and water.

Step 1: Steam is reacted with methane to produce hydrogen gas

$$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3\,H_{2(g)}$$

700°C and a Ni catalyst

Step 2: Air is added to the mixture to convert more CH_4 to H_2, this is also the source of nitrogen gas for step 4.

$$2\ CH_4(g) + O_2(g) \rightleftharpoons 2\ CO(g) + 4\ H_2(g)$$

700°C and Ni catalyst

Step 3: Mixture passed over an iron oxide catalyst to create more H_2. Carbon dioxide is removed at this stage by the addition of an organic base into which the carbon dioxide dissolves.

$$CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g)$$

Step 4: Haber Process, hydrogen reacted with nitrogen to form ammonia.

$$N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g) \qquad \Delta H = -92\ kJ\ mol^{-1}$$

Maximising Yield and Minimising Cost

Temperature: Low temperature favours the formation of ammonia but the reaction rate would be very slow.

Compromise: ≈ 500°C gives an acceptable rate and yield

Pressure: High pressure gives the best yield and reaction rate but increases the costs of building and running the plant.

Compromise: ≈ 350 atmospheres

Catalyst: An iron/iron oxide catalyst is used to increase the rate of reaction. The catalyst does not increase the yield of ammonia but it enables equilibrium to be reached faster.

Sulfuric Acid

Uses

Sulfuric acid is the most widely used chemical in the world. The largest use of sulfuric acid is in the production of fertilizers such as superphosphate, ammonium phosphate and ammonium sulfate. Sulfuric acid is used in the production of other acids, dyes, detergents and explosives, it is used in the refining of petrol and as the electrolyte in car batteries.

Production

The raw materials in the production of sulfuric acid are sulfur and oxygen. Although sulfur is found in its pure or elemental state, worldwide nearly all sulfur used for the production of sulfuric acid is extracted from crude oil or natural gas. In Western Australia, sulfur dioxide is obtained from the smelting of non-ferrous ores such as nickel sulfide.

Step 1: Sulfur is burnt in air to produce sulfur dioxide

$$S(s) + O_2(g) \rightleftharpoons SO_2(g) \qquad \Delta H = -297\ kJ\ mol^{-1}$$

Step 2: Sulfur dioxide formed reacts with oxygen to form sulfur trioxide

$$2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g) \qquad \Delta H = -198\ kJ\ mol^{-1}$$

V_2O_5 catalyst

Even though Le Châtelier's Principal would suggest that a higher pressure would favour the formation of SO_3, the reaction is carried out at the relatively low pressure of 1 or 2 atmospheres. This is because the reaction yield at the low pressures is still very high and the improvement in yield created by high pressures is not economically justifiable.

Step 3: Sulfur trioxide is dissolved in sulfuric acid to form oleum.

$$SO_{3(g)} + H_2SO_{4(l)} \rightarrow H_2S_2O_{7(l)}$$

The sulfur trioxide could be dissolved in water to form sulfuric acid, however this a very exothermic reaction and the heat generated causes the sulfuric acid to form a vapour or mist which is very difficult to work with.

Step 4: Oleum reacts with water to form sulfuric acid

$$H_2S_2O_{7(l)} + H_2O_{(l)} \rightarrow 2\ H_2SO_{4(l)}$$

Question 5.8

The production of SO_3 is carried out at a 400°C to 450°C and a pressure of between 1 and 2 atmospheres.

Does a temperature of 450°C favour a high yield of SO_3? Explain your answer.

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Explain why the equilibrium yield of SO_3 is favoured by a high pressure.

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Explain why the the production of SO_3 is carried out at the moderately high temperature of 450°C.

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5.4 CHEMICAL SYNTHESIS AND STOICHIOMETRY

Limiting Reagents

In most stoichiometric problems, we are usually given the amount of only one of the reactants. It is then assumed, or stated, that the other reactant is in excess. If we are given the amounts of two (or more) reactants, then we need to determine which is the limiting reagent and which reactant is in excess.

The limiting reagent is the reagent that is consumed first. It is the reactant that runs out and when this occurs, the reaction stops.

Consider the reaction between methane (CH_4) and oxygen:

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$$

We can see from the balanced equation that 1 mole of CH_4 will react with 2 mole of oxygen. Suppose we are given that there are 4 mol of CH_4 and 6 mole of oxygen available for the reaction. Which will run out first?

Since, from the balanced equation we can say:

1 mole of CH_4 reacts with 2 mole of oxygen
∴ 4 mole of CH_4 would react with 8 mole of oxygen

As there are only 6 mole of oxygen available, it will run out first. Oxygen is the limiting reagent and methane is in excess.

(1) Recognising limiting reagent question
If you are given sufficient information to calculate the number of moles of two reactants, then you will need to determine which is the limiting reagent.

(2) Identifying the limiting reagent
You are given amounts of two reactants, say A and B, and need to determine which is the limiting reagent. As you would do for any stoichiometric calculation you will firstly need to:

- Write a balanced equation
- Calculate the moles available of both A and B from information given.

You can now determine which is the limiting reagent either by;

Method 1 Visual check of moles available and comparison
Choose reactant A for comparison. From the balanced equation, determine how many moles of reactant B would be needed to consume all the moles of reactant A available.
- If there are sufficient mol or more of reactant B then reactant A is the limiting reagent
- If there are insufficient mol of reactant B then reactant B is the limiting reagent

OR

Method 2 Comparison of stoichiometric and actual mole ratios
An alternate method is to compare the stoichiometric ratio (from the balanced equation) with the actual mole ratio. See worked example.

(3) Calculating products and excess reagents

Only the limiting reagent can be used to calculate products and amounts of other reactants consumed. See worked example.

Worked Example 5.1

Hydrochloric acid containing 10.0 g of HCl was reacted with 10.0 g of calcium carbonate to produce carbon dioxide gas. Determine: (a) the limiting reagent; (b) the mass of $CO_{2(g)}$ produced; (c) the mass of unused reactant.

(a) STEP 1 $CaCO_{3(s)} + 2HCl_{(aq)} \rightarrow CaCl_{2(aq)} + H_2O_{(l)} + CO_{2(g)}$

10.0 g (CaCO₃) *10.0 g* (HCl)

STEP 2 $n(CaCO_3)_{(s)} = \frac{m}{M} = \frac{10.0}{100.1} = 0.0999 \text{ mol}$

$n(HCl) = \frac{m}{M} = \frac{10.0}{36.58} = 0.2743$ mol

Extra step: Determine limiting reagent

- *Method 1* *Visual check of moles available and comparison*

  There are 0.0999 mol of $CaCO_3$. This would require (2)(0.0999)mol of HCl to react with. Since there are 0.2743 mol of HCl available there is more than sufficient. Hence HCl is in excess and $CaCO_3$ is the limiting reagent.

- *Method 2* *Compare stoichiometric and actual mole ratios*

  stoichiometric ratio $\frac{n(HCl)}{n(CaCO_3)} = \frac{2}{1} = 2$ (from equation)

  actual mole ratio $\frac{n(HCl)}{n(CaCO_3)} = \frac{0.2743}{0.0999} = 2.75$

  actual ratio > than stoichiometric ratio, hence HCl in excess, $CaCO_3$ is limiting reagent.

(b) Steps 3/4

To find mass of $CO_{2(g)}$ produced consider only the limiting reagent $CaCO_{3(s)}$.

hence $n(CO_2) = n(CaCO_3)$ (from equation)

$= 0.0999$ mol

$\therefore\ m(CO_2) = nM = (0.0999)(44.01) = 4.40$ g

(c) Extra Step To find mass of unused reactant you must first find how much of the excess reagent was used.

$n(HCl)$ used $= 2 \times n(CaCO_3) = (2)(0.0999) = 0.1998$ mol

$\therefore\ m(HCl)$ used $= (0.1998)(36.458) = 7.284$ g

$\therefore\ m(HCl)$ remaining $= 10.0\text{ g} - 7.285\text{ g} = 2.72$ g

Worked Example 5.2

A 1.250 g sample of NaCl is dissolved in 75.0 mL of water. To this solution 25.0 mL of 0.615 mol L^{-1} $AgNO_3$ solution is added. Find:

(a) mass of silver chloride produced;

(b) concentration of any remaining ions.

(a) Step 1 $NaCl_{(aq)} + AgNO_{3(aq)} \rightarrow AgCl_{(s)} + NaNO_{3(aq)}$

1.25 g	*25.0 mL*
75.0 mL	*0.615 mol L^{-1}*

Step 2 $n(AgNO_3) = cV = (0.615)(0.0250) = 0.0154$ mol

$n(NaCl) = \frac{m}{M} = \frac{1.250}{58.44} = 0.0214 \text{ mol}$

∴ The limiting reagent is $AgNO_3$.

STEPS 3/4 ∴ $n(AgCl)$ produced = $n(AgNO_3)$ used

= 0.0154 mol

∴ $m(AgCl) = nM = (0.0154)(143.35)$

= 2.21 g

(b) To find concentration of all ions remaining.

(i) Ag^+ ions are all consumed

$c(Ag^+) = 0 \text{ mol L}^{-1}$

(ii) NO_3^- ions are still in solution (Why?)

$c(NO_3^-) = \frac{n}{V} = \frac{0.0154}{0.100}$ ← *total solution volume*

= 0.154 mol L^{-1}

(iii) Na^+ ions are all in solution

$c(Na^+) = \frac{0.0214}{0.100} = 0.214 \text{ mol L}^{-1}$

(iv) Cl^- ions - some have combined with the Ag^+ ions to form $AgCl_{(s)}$.

Excess Cl^- ions= 0.0214 – 0.0154 = 0.0060 mol

∴ $c(Cl^-)$ ions $= \frac{n}{V} = \frac{0.0060}{0.100}$

= 0.060 mol L^{-1}

Question 5.9

A 3.200 g sample of NaOH is added to a solution containing 1.125 g of H_2SO_4. Determine:

(a) the limiting reagent;

(b) the mass of sodium sulfate formed in solution;

(c) the mass of unused reactant remaining in solution.

Step 1 ____________________

Steps 2/3/4 ____________________

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Question 5.10

When 20.0 mL of 0.450 mol L^{-1} NaOH solution is mixed with 30.0 mL of 0.540 mol L^{-1} magnesium chloride solutions, a precipitate of magnesium hydroxide is produced. Calculate:

(a) mass of the precipitate;

(b) concentration of any remaining ions.

Step 1 ____

Steps 2/3/4 ____

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Percentage Purity Problems

In these type of problems we tend to work "backwards" to find the actual mass of the substance we wish to know.

Worked Example 5.3

In an experiment to find the purity of a 5.642 g sample of anhydrous sodium carbonate, it was reacted with excess hydrochloric acid. A volume of 1.170 L of CO_2 gas was collected at STP. Find the % purity of the Na_2CO_3 sample.

STEP 1 $$Na_2CO_{3(s)} + 2HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + H_2O_{(l)} + CO_{2(g)}$$

? g

STEP 2 $$n(CO_2) = \frac{V}{22.71} = \frac{1.170}{22.71} = 0.0515 \text{ mol}$$

STEP 3 $$n(Na_2CO_3) = n(CO_2) \text{ (from equation)}$$
$$= 0.0515 \text{ mol}$$

STEP 4 $$m(Na_2CO_3) = nM = (0.0515)(105.99)$$
$$= 5.461 \text{ g}$$

Extra step: Find % purity

$$\% \ Na_2CO_3 \text{ in sample} = \frac{5.461}{5.642} \times 100 = 96.8\%$$

Question 5.11

A 154.5 g ore sample containing copper (I) sulfide was roasted in air and 12.25 g of copper were recovered. The equation for the reaction is as follows.

$$Cu_2S_{(s)} + O_{2(g)} \rightarrow 2Cu_{(s)} + SO_{2(g)}$$

Determine the % of copper (I) sulfide in the ore sample.

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Multi-reaction Problems

Some problems involve a series of reactions such as the manufacture of sulfuric acid. It is usually best to get an **overall equation** before proceeding. Alternatively, it is possible to follow the mole ratios through each reaction.

Worked Example 5.4

Sulfuric acid can be manufactured from iron pyrites (FeS_2) by the sequence of reactions shown. Calculate the mass of sulfuric acid which could be obtained from 100.0 kg of pure iron pyrites if the overall process is 85% efficient.

(i) $4FeS_{2(s)} + 11O_{2(g)} \rightarrow 2Fe_2O_{3(s)} + 8SO_{2(g)}$

(ii) $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{2(g)}$

(iii) $SO_{3(g)} + H_2O_{(l)} \rightarrow H_2SO_{4(l)}$

***Method 1:** Get an overall equation. Multiply each line so that common substances on opposite sides of the equation cancel.*

e.g.			
	(i)	leave	$4FeS_{2(s)} + 11O_{2(g)} \rightarrow 2Fe_2O_{3(s)} + \cancel{8SO_{2(g)}}$
	(ii)	× by 4	$\cancel{8SO_{2(g)}} + 4O_{2(g)} \rightarrow \cancel{8SO_{3(g)}}$
	(iii)	× by 8	$\cancel{8SO_{3(g)}} + 8H_2O_{(l)} \rightarrow 8H_2SO_{4(l)}$

STEP 1 (overall equation) $4FeS_{2(g)} + 15O_{2(g)} + 8H_2O_{(l)} \rightleftharpoons 2Fe_2O_{3(s)} + 8H_2SO_4$

100 kg *? g*

STEPS 2,3,4 $n(FeS_2) = \dfrac{n}{M} = \dfrac{100.0 \times 1000}{119.98}$ ← *don't forget to convert to grams*

$= 833.5$ mol

$\therefore n(H_2SO_4) = \dfrac{8}{4} \times n(FeS_2)$ (from equation)

$\therefore m(H_2SO_4) = nM = (1667)(98.08) = 163.5$ kg

Process only 85% efficient

$\therefore m(H_2SO_4) = \dfrac{85}{100} \times 163.5 \text{ kg} = 139.0$ kg

Method 2 *Carry molar relationships through from one equation to the other.*

Hence as before $4FeS_2 \rightarrow 8SO_2 \rightarrow 8SO_3 + 8H_2SO_4$

$n(FeS_2) = 833.5$ mol

$\therefore n(H_2SO_4) = \frac{8}{4} \times 833.5$ mol $= 1667$ mol

$\therefore m(H_2SO_4) =$ ______________________ (please complete)

$\therefore m(H_2SO_4) =$ ______________________

Which method do you like?

Note however: Method 2 is difficult to use if the required element splits into different products during the reactions.

Question 5.12

Sodium carbonate can be produced by the Solvay process which involves the following reactions:

$NH_3 + H_2O + CO_2 \rightarrow NH_4HCO_3$

$NH_4HCO_3 + NaCl \rightarrow NH_4Cl + NaHCO_3$

$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$

$Na_2CO_3 + 10H_2O \rightarrow Na_2CO_3 . 10H_2O$

Calculate the mass of ammonia and sodium chloride required to produce 1000 kg of sodium carbonate-10-water. Assume the process is 90% efficient.

Step 1 ____

Steps 2/3/4 ____

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REVIEW QUESTIONS

Chapter 5: Chemical Synthesis

1. (a) Write the balanced equation for the production of a soap.

   (b) Explain why a soap, which has a large carbon chain, is able to dissolve in water.

   (c) Explain why it is important for a soap to have a long carbon chain section.

2. Soaps have difficulty cleaning materials when they are used in hard water. (Hard water being water in which soap will not lather.)

   (a) What are the substances commonly contained in hard water that prevent lathering?

   (b) Why do these materials stop the soap from lathering?

   (c) Why are detergents more commonly used as a cleaning aid?

   (d) Draw the structural formula for a typical detergent molecule.

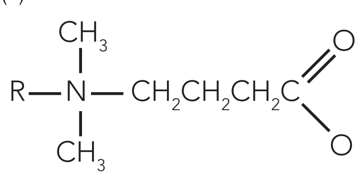
3. Some skin care products do not use traditional soaps and detergents to clean the skin, instead they use a surfactant that forms a zwitterion as it is much less likely to irritate the skin.

   (a) In general, what is a zwitterion?

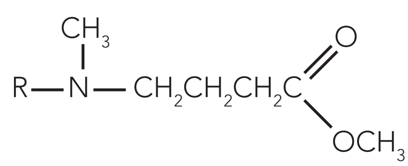
   (b) Explain the purpose of a surfactant.

   (c) The two diagrams below show a molecule and its zwitterion (but charges missing). Draw the zwitterion with positive and negative regions correctly labelled.

(i)



(ii)



   (d) Explain the role in cleaning oils from skin of the section of the zwitterion labelled R.

4. The acid catalysed hydrolysis of propene is very similar to the hydrolysis of ethene. It is a reversible, exothermic reaction, however it has two possible organic products rather than one.

   (a) Name the two possible organic products for this reaction.
   (b) Write the balanced equation for the production of one of these products.
   (c) What pressure conditions, high or low, would favour a high yield of the product? Explain your answer.

(d) The formation of the organic product is an exothermic process, explain why the reaction is carried out at moderately high rather than low temperatures.

5. Use the production of alcohol, by fermentation and hydrolysis, as an example to explain the advantages that enzymes offer over traditional catalysts in the industrial synthesis of materials.

6. Write the sequence of equations to summarize how ethyl ethanoate can be produced from the ethene and water.

7. Over three quarters of the worlds production of ethanoic acid is by the oxidation of methanol by carbon monoxide.

$$CH_3OH + CO \rightarrow CH_3COOH$$

This process is carried out at 150°C to 200°C, 30 - 60 atm pressure and with a catalysts such as rhodium metal iodide complex and iridium metals iodide complex.

Explain reasons why ethanoic acid would be synthesised under these conditions rather than 20°C to 30°C and 1 atm.

8. Calculate the mass of ethanoic acid that could be produced if 9.44×10^6 g of methanol is reacted with 6.38×10^6 g of carbon monoxide.

9. A major use of ethanoic acid is in the production of the monomer vinyl acetate (ethenyl ethanoate).

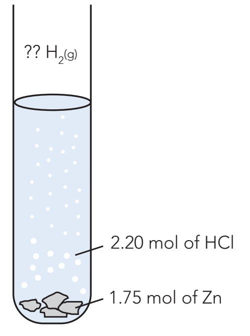
$$CH_3COOH + C_2H_2 + O_2 \rightarrow 2\ CH_3COOCHCH_2 + 2\ H_2O$$

The vinyl acetate monomer is used in an addition reaction to produce polyvinyl acetate (PVA) which is commonly used in making wood glues and school glues.

Draw a section of the polymer PVA showing at least 3 monomer units.

10. (a) Biodiesel is produced by the base catalysed transesterification of a triglyceride. Write the equation for the production of biodiesel from palmitic acid, the major triglyceride in palm oil. The hydrocarbon chain sections of palmitic acid are 16 carbons in length.
(b) Trials are being carried out with the commercial production of biodiesel from triglycerides such as palm oil using lipase as the catalyst rather than a base. What advantages might an enzyme catalysed process offer?
(c) Give 2 advantages of using a biodiesel over a conventional petro-based diesel.

11. A student prepared some hydrogen gas by reacting 120 mL of 1.50 mol L^{-1} hydrochloric acid with 7.34 g of zinc.



The hydrogen gas was collected at 18°C and 105 kPa.
(a) Write an equation for the reaction.
(b) Which is the limiting reagent?
(c) What volume of hydrogen gas was collected at the conditions given?
(d) Determine the mass of any unused reactant.

12. If sodium carbonate powder is added to a solution of nitric acid, an effervescent reaction occurs producing carbon dioxide gas.
    (a) Write an equation for the reaction.
    (b) If 15.5 g of sodium carbonate is added to 100 mL of 0.242 mol L^{-1} nitric acid, determine:
        (i) the volume of CO_2 gas produced at STP.
        (ii) the concentration of any ions remaining in solution.
        (Assume that the sodium carbonate powder did not significantly change the volume of solution.)

13. A mixture of the gases propane and oxygen was placed in a sealed container with (a movable piston) and then sparked. The reaction which occurred is:

    $C_3H_8(g) \; + \; 5O_2(g) \; \rightarrow \; 3CO_2(g) \; + \; 4H_2O(g)$

    The original mixture contained 200 mL of propane and 500 mL of oxygen. Determine the volume of all gases present after the reaction. (All volumes measured at the same temperature and pressure.)

14. A mixture is made up by adding 50.0 mL of 1.15 mol L^{-1} sodium iodide solution to 100 mL of 0.50 mol L^{-1} potassium iodide solution. To this mixture 20.0 g of lead (II) nitrate crystals was added. A bright yellow precipitate formed.
    (a) Write an equation for the precipitation reaction that occurred.
    (b) Determine the mass of precipitate that formed.
    (c) Assuming the volume of the final mixture is not affected by the crystals added or precipitate formed, determine the concentration of all remaining ions in solution.

15. The production of sulfuric acid in the Contact Process is represented by the following series of equations:

    $S(s) \; + \; O_2(g) \; \rightarrow \; SO_2(g)$

    $2\,SO_2(g) \; + \; O_2(g) \; \rightarrow \; 2\,SO_3(g)$

    $SO_3(g) \; + \; H_2SO_4(l) \; \rightarrow H_2S_2O_7(l)$

    $H_2S_2O_7(l) + H_2O(l) \; \rightarrow \; 2\,H_2SO_4(l)$

    Calculate the mass of acid produced if 3.25 tonnes of sulfur are converted to sulfur dioxide and the acid produced in this process 98.5% H_2SO_4.

16. Phosphoric acid can be produced burning liquified phosphorous at a temperature of approximately 2000ºC. The gaseous phosporous pentoxide is then passed through a hydration tower where it is converted to the acid.

    $P_4(l) \; + \; 5\,O_2(g) \; \rightarrow \; 2\,P_2O_5(g)$
    $P_2O_5(g) \; + \; H_2O(l) \; \rightarrow \; 2\,H_3PO_4(aq)$

    Calculate the mass of phosporous required to produce 1.50 tonne of final acid solution that is 85.0% H_3PO_4.

17. Palm oil is is a mixture of triglycerides where the average number of carbons on the ester carbon chain is 17 (i.e. the R group is on average 17 carbon long). Calculate the mass of biodiesel (ester) that could be produced from each kilogram of the palm oil triglyceride if the base catalysed esterification process is 85% efficient.

18. In 2015 it is predicted that Australia will export 1.40 billion tonnes of iron ore. The reduction of the iron ore to steel by carbon can be summarised as follows:

$2\ C + O_2 \rightarrow 2\ CO$
$Fe_2O_3 + 3\ CO \rightarrow 2\ Fe + 3\ CO_2$

The equations show the steel produced as pure iron however it is actually a mixture of the carbon and iron. By varying the amount of carbon in the steel, manufactures can vary properties of the steel produced.
Calculate the mass of plain carbon steel that would be produced if 33.3 % of the iron ore exported by Australia in 2015 was converted to plain carbon steel which contains 1.00% carbon.

Determine the mass of carbon dioxide produced when all of the exported iron ore is converted to steel.

19. Sphalerite is commercially, the most important ore of zinc. In sphalerite the zinc occurs as a sulfide ore. Zinc is obtained by converting the sulfide to an oxide which is then reduced by carbon.

$2\ ZnS + 3\ O_2 \rightarrow 2\ ZnO + 2\ SO_2$
$ZnO + C \rightarrow Zn + CO$

Calculate the mass of zinc that could be produced from a 235 kg sample that contained 65.0% zinc sulfide.

20. Pure aluminium is obtained from its ore, bauxite in a three-stage process:

Stage 1: The aluminium oxide is removed from the other impurities in the ore by dissolving it in a NaOH solution.

$$Al_2O_{3(s)} + 2\ OH^-_{(aq)} + 3\ H_2O_{(l)} \rightarrow 2\ Al(OH)_4^-{}_{(aq)}$$

Stage 2: The resulting solution is seeded with $Al_2O_3.3H_2O$. The precipitated alumina is then roasted to form Al_2O_3

$$2\ Al(OH)_4^-{}_{(aq)} \rightarrow Al_2O_3.3H_2O_{(s)} + 2\ OH^-_{(aq)}$$

$$Al_2O_3.3H_2O_{(s)} \rightarrow Al_2O_{3(s)} + 3\ H_2O_{(g)}$$

Stage 3: Electrolysis is used to reduce Al_2O_3 to pure Al

$$2\ Al_2O_3 + 3\ C \rightarrow 4\ Al + 3\ CO_2$$

If the bauxite ore is 60.0% aluminium oxide, calculate the mass of the ore required to produce 3.50 tonnes of pure aluminium.

FOR THE EXPERTS

Industrial Chemistry

21. Nitric acid can be produced by the Ostwald Process. This is a multistage process that begins with the oxidation of ammonia (produced via the Haber Process)

STEP 1: $4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O$

STEP 2: $2\ NO + O_2 \rightarrow 2\ NO_2$

STEP 3: $4\ NO_2 + 2\ NO + 2\ H_2O \rightarrow 4\ HNO_3$

The nitric acid produced at this stage is concentrated but not pure. Purification often involves the distillation of the concentrated HNO_3 from P_2O_5.

(a) Calculate the theoretical mass of pure HNO_3 that could be produced via steps $1 \rightarrow 3$ from 1.50 tonnes of ammonia gas.

An industrial chemist wanted to test the purity of the nitric acid after step 3, 20.0 g of the acid (concentrated but not pure) was removed from the reaction vessel and placed in a 500 mL volumetric flask. The volumetric flask was then filled to the mark with distilled water.

A 25.0 mL aliquot of this solution was removed from the volumetric flask and reacted with excess zinc in alkaline solution to reduce the nitric acid to ammonia.

$$4Zn_{(s)} + NO_3^-{}_{(aq)} + 7OH^-{}_{(aq)} + 6H_2O_{(l)} \rightarrow 4[Zn(OH)_4]^{2-}{}_{(aq)} + NH_{3(g)}$$

The solution was heated to drive off all of the $NH_{3(g)}$. This NH_3 gas was collected and re-dissolved in distilled water. The resulting ammonia solution required 39.6 mL of 0.2725 mol L^{-1} HCl for neutralisation.

$$NH_{3(aq)} + H^+{}_{(aq)} \rightarrow NH^+{}_{(aq)}$$

(b) Determine the percentage of mass of HNO_3 in the original 20.0 g of concentrated acid removed from the reaction vessel.

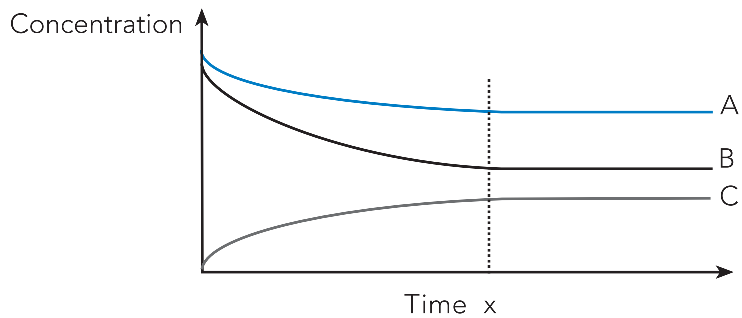
(c) Determine the concentration (mol L^{-1}) of the concentrated acid if it has a density of 1.41 g mL^{-1}.

TRIAL TEST 1:
CHEMICAL EQUILIBRIUM

Time allowed:	**70 minutes**	**Section 1 –** Multiple Choice	20 marks
Total marks:	**80**	**Section 2 –** Short & Extended Answer	60 marks

SECTION 1 – MULTIPLE CHOICE (20 MARKS)

1. The graph below shows the change in concentration for gases present over a period of time for the reaction that occurs when sulfur dioxide is burnt in oxygen in a closed system.



REACTION: $2SO_2 + O_2 \rightarrow 2SO_3$, $\Delta H = -99$ kJ mol^{-1}.

Which of the following is correct?

(a) Line A represents the change in concentration for SO_3.
(b) Line B represents the change in concentration for SO_3.
(c) Time x represents the time when the concentration of SO_2 and SO_3 become equal.
(d) Time x represents the time when the forward reaction and the reverse reaction rates become equal.

2. For the reaction given in question 1,

(a) $K = \dfrac{[SO_2]^2.[O_2]}{[SO_3]}$
(b) The equilibrium yield of sulfur trioxide can be increased by raising the temperature of the system.
(c) The equilibrium yield of sulfur trioxide can be increased by raising the pressure in the reaction vessel.
(d) The rate of attainment of equilibrium can be increased by increasing the volume of the reaction vessel.

3. Which of the following reactions is endothermic?

(a) $CO_{2(s)} \rightarrow CO_{2(g)}$
(b) $Mg^{2+} + 2e^- \rightarrow Mg$
(c) $H + H \rightarrow H_2$
(d) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

4. When a catalyst is added to an exothermic reaction,

(a) a new reaction pathway of lower activation energy is created.
(b) the energy released, per mole of reactant, is increased.
(c) the reaction mechanism alters to reduce the energy of the products.
(d) more energy is absorbed from the surroundings and the reaction rate is increased.

5. Silver ions react with chloride ions and ammonia according to the following equations:

$$Ag^{+}{(aq)} + Cl^{-}{(aq)} \rightleftharpoons AgCl{(s)}$$
$$Ag^{+}{(aq)} + 2NH_{3}{(aq)} \rightleftharpoons Ag(NH_{3})_{2}^{+}{(aq)}$$

If ammonia solution was added to a saturated solution of silver chloride,

(a) there will be no change to the solubility of the AgCl as ammonia is less reactive than chlorine.
(b) the NH_3 will increase the solubility of the AgCl by removing Ag^+ ions from the solution.
(c) as AgCl is not part of the process forming the complex ion, it solubility will not be affected.
(d) the AgCl will become more soluble because the NH_3 is more polar than water.

6. The thermite process is summarised by the equation below:

$$2Al{(s)} + Fe_{2}O_{3}{(s)} \rightarrow 2Fe{(l)} + Al_{2}O_{3}{(s)} + \text{energy}$$

Which of the following statements is correct?

(a) Adding HCl will increase the reaction rate by increasing the state of sub-division of the Al.
(b) Grinding both reactants into a fine powder will increase the amount of Fe produced.
(c) Removing the Fe as it is produced will increase the reaction rate.
(d) Grinding the solids to powder will increase the rate at which the Al is consumed.

7. If the following reaction is carried out at a higher temperature the yield of HI(g) will be greater. Which of the following best explains the reason for this.

$$H_{2}{(g)} + I_{2}{(g)} \rightleftharpoons 2HI{(g)} \qquad \Delta H = +52 \text{ kJ mol}^{-1}.$$

(a) Increasing the temperature causes the forward reaction to increase.
(b) Increasing the temperature causes a nett forward reaction because the reaction is endothermic.
(c) Increasing the temperature causes the activation energy to be lowered and hence it is easier for products to form.
(d) Increasing the temperature causes a greater number of collisions between reacting particles and hence more product is formed.

8. When developing black and white film in photography, sodium thiosulfate ($Na_2S_2O_3$) can be used to wash out any unexposed silver bromide salt.

$$AgBr{(s)} + 2S_{2}O_{3}^{2-}{(aq)} \rightarrow Ag(S_{2}O_{3})_{2}^{3-}{(aq)} + Br^{-}{(aq)}$$

The rate at which the thiosulfate ion ($S_2O_3^{2-}$) dissolves the silver bromide could be increased by:

(a) adding more silver bromide to the solution.
(b) removing bromide ions from the solution.
(c) increasing the temperature of the solution.
(d) increasing the pressure on the system.

9. A solution of potassium dichromate actually contains a mixture of chromate ions and dichromate ions in equilibrium (equation given below). The position of equilibrium being determined by the conditions present.

$$Cr_2O_7^{2-}(aq) + H_2O(l) \rightleftharpoons 2CrO_4^{2-}(aq) + 2H^+(aq)$$

orange solution *yellow solution*

Which of the following imposed changes would favour the formation of dichromate ions?

(a) The addition of more water to the system.
(b) The addition of a chemically selective catalyst.
(c) The addition of concentrated sodium hydroxide to the system.
(d) The addition of concentrated hydrochloric acid to the solution.

10. A sealed tube of the brown gas nitrogen dioxide actually contains a mixture of nitrogen dioxide and dinitrogen tetroxide. The equation for the equilibrium that exists between these two gases is:

$$2NO_2(g) \rightleftharpoons N_2O_4(g) + 57\text{ kJ}$$

Any change to this equilibrium system that favours the formation of $NO_2(g)$ causes the system to become a darker brown colour, while any change that favours the formation of $N_2O_4(g)$ causes the system to become a lighter brown colour.

Given the above information, which of the statements below is correct?

(a) Placing the tube in hot water would cause the gas mixture to become a lighter brown colour.
(b) Increasing the pressure would cause the system to become a lighter brown colour.
(c) Injecting a suitable catalyst would cause the system to become a lighter brown colour.
(d) Injecting more N_2O_4 into the cylinder would cause the system to become a lighter brown colour.

SECTION 2 – SHORT AND EXTENDED ANSWER (60 MARKS)

Answer each question in the space provided.

11. An important chemical reaction is the combustion of petrol in the cylinder of a motor of a vehicle.

$$2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g) + \text{Energy}$$

Use the collision theory to explain three ways by which the rate of this reaction could be increased.

(a) ____

(b) ____

(c) ____

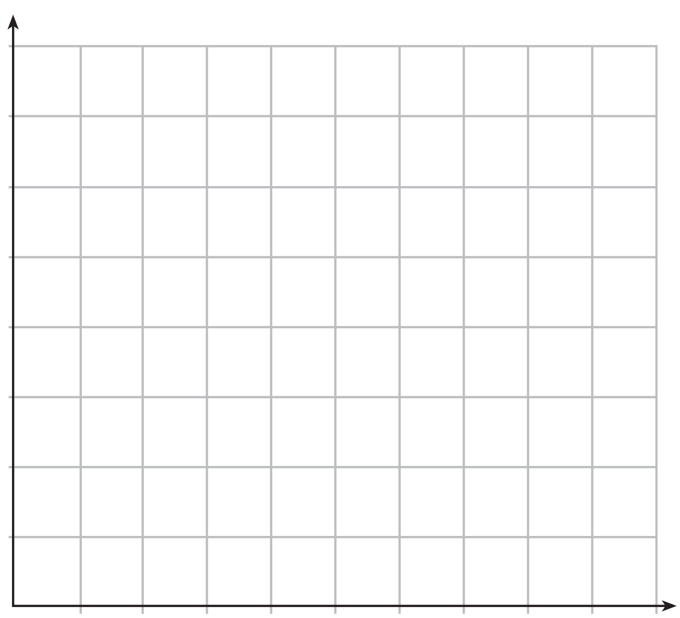
[6 marks]

12. Use the axes below to draw the energy profile diagram for the combustion of methane.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \quad ; \quad \Delta H = -890 \text{ kJ mol}^{-1}$$
$$E_a = 320 \text{ kJ mol}^{-1}$$

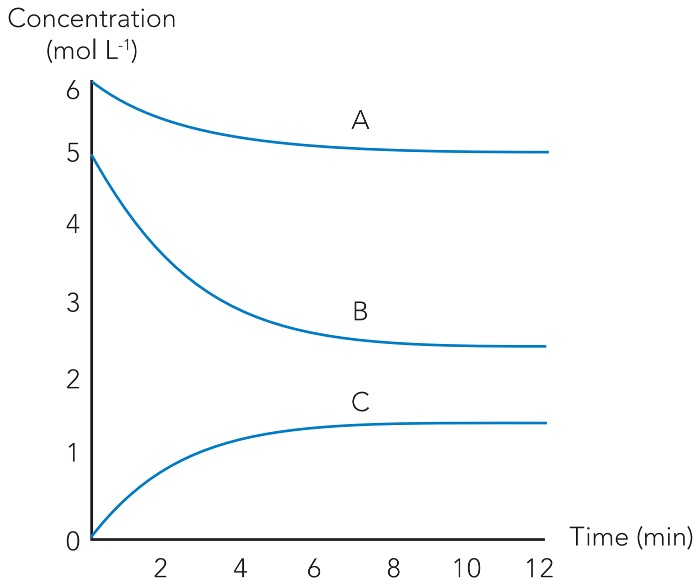
Include the following labels.

(a)	enthalpy	(b)	reaction coordinates	(c)	ΔH
(d)	activation energy	(e)	activated complex	(f)	reactants
(g)	products	(h)	a catalysed reaction pathway.		



[8 marks]

13. The gases nitrogen and hydrogen will react to form ammonia gas. In an experiment some hydrogen and nitrogen were placed in a flask and allowed to react. The concentrations of the gases present in the flask were monitored for a few minutes and the data graphed as shown below.



(a) Name the gases represented by lines B and C on the graph

Line B ____________________________

Line C ____________________________

(b) Write the equation for the reaction between the gases N_2, H_2 and NH_3.

____

(c) Compare the forward and reverse reaction rates for this reaction at:

(i) t = 2 ____

(ii) t = 10 ____

(d) Some ammonia gas is removed from the container at t = 10. How will this initially effect the:

(i) forward reaction rate ____________________________________

(ii) reverse reaction rate ____________________________________

[8 marks]

14. Ammonia can be used to produce HNO_3 through a series of reactions culminating in the following step:

$$3NO_{2(g)} + H_2O_{(l)} \rightleftharpoons 2HNO_{3(aq)} + NO_{(g)}$$

(a) State what effect the following changes will have on the equilibrium yield of nitric acid (increase, decrease or no change) and explain why this occurs.

(i) Increasing the pressure on the system.

(ii) Removing NO_2 from the system.

(iii) Adding NO to the system.

(b) Write the expression for the equilibrium constant K for this system.

[8 marks]

15. In a closed system the reaction between $CaCO_3$ and 2 mol L^{-1} HCl will reach equilibrium and K will have a very large value.

$$CaCO_{3(s)} + 2H^+_{(aq)} \rightleftharpoons Ca^{2+}_{(aq)} + CO_{2(g)} + H_2O_{(l)}$$

State what effect the following changes will have on the position of equilibrium.
Give a reason for your answer.

(a) Add another 10 mL of 2 mol L^{-1} HCl.

(b) Grind the $CaCO_3$ into smaller pieces.

(c) Add a large amount of H_2O to the system.

[6 marks]

16. When $BiCl_3$ is placed in water, the equation representing the equilibrium is:

$$BiCl_{3(aq)} + Cl^{-}_{(aq)} + H_2O_{(l)} \rightleftharpoons BiOCl_{(s)} + 2H^{+}_{(g)} + 3Cl^{-}_{(g)}$$

colourless *white precipitate*

(a) State how the following changes alter the position of the equilibrium (to the right, to the left, unchanged) and give a probable observation.

(i) More powdered $BiOCl_{(s)}$ was added.

____

(ii) Several drops of concentrated HCl were added.

____

(iii) Several drops of concentrated sodium hydroxide solution.

____

(b) Gentle warming caused the white solid to dissolve. Is the reaction, as represented by the equation above, exothermic or endothermic? Explain your prediction.

____

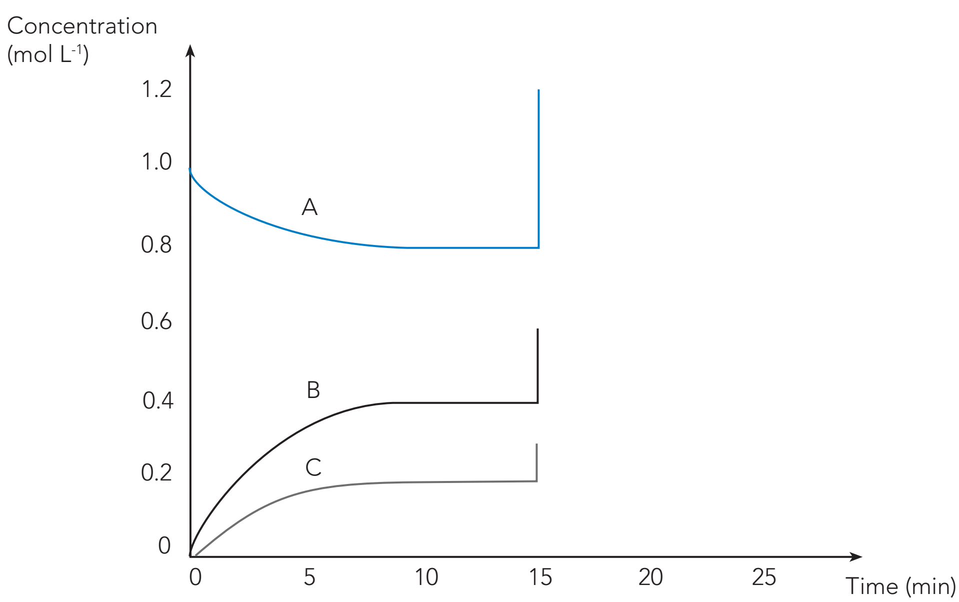
____

____

[8 marks]

17. Consider the following equilibrium reaction:

$$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$$



(a) What happened at t = 10 min?

____

(b) Name the components of the reaction represented on the graph.

A ____________, B ____________, C ____________

(c) Write an expression for the equilibrium constant for the reaction and calculate its value.

(d) What change was made to the system at t = 15 min?

(e) Complete the graph to show what is likely to happen after t = 15 min.

(f) Explain why the system is likely to behave in the way you have indicated and in particular why the concentration of each reactant changes in the way you have shown.

[16 marks]

END OF TEST (80 MARKS)

TRIAL TEST 2: ACIDS AND BASES

Time allowed:	**70 minutes**	**Section 1 –** Multiple Choice	20 marks
Total marks:	**80**	**Section 2 –** Short & Extended Answer	60 marks

SECTION 1 – MULTIPLE CHOICE (20 MARKS)

1. Which one of the following equations shows water behaving as a base?

   (a) $CO_{(g)} + H_2O_{(g)} \rightarrow CO_{2(g)} + H_{2(g)}$
   (b) $2Na_{(s)} + 2H_2O_{(l)} \rightarrow 2Na^+_{(aq)} + 2OH^-_{(aq)} + H_{2(g)}$
   (c) $O^{2-}_{(aq)} + H_2O_{(l)} \rightarrow 2OH^-_{(aq)}$
   (d) $NH_4^+{}_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + NH_{3(aq)}$

2. When phenolphthalein was added to a solution, a pink colour resulted. Which of the following statements could be correct for that solution?
   (a) The solution was formed when 50.0 mL of 2.00 mol L^{-1} nitric acid was added to 50.0 mL of 2.00 mol L^{-1} sodium hydroxide.
   (b) The solution was formed by the addition of 50.0 mL of 2.00 mol L^{-1} ethanoic acid to 50.0 mL of 2.00 mol L^{-1} potassium hydroxide.
   (c) The solution was formed at the end point of a titration between a strong acid and a weak base.
   (d) The solution was formed when 3.75g of ammonium chloride was dissolved in 20.0 mL of water.

3. Which one of the following statements is true?
   (a) The hydrogen ion concentration of a neutral solution is dependent on the temperature of the solution.
   (b) The equivalence point of a titration occurs when equal numbers of moles of acid and base have been mixed.
   (c) A buffer solution can be produced by mixing equal quantities of a strong acid and strong base to ensure a plentiful supply of H^+ ions and OH^- ions.
   (d) The salt produced when hydrochloric acid is reacted with sodium carbonate is weakly acidic.

4. A 2.50×10^{-2} mol L^{-1} ethanoic acid solution will have a pH of:
   (a) 1.60
   (b) -2.50
   (c) more than 1.60 but less than 7.00
   (d) dependent on the temperature of the water but always more than the pH of a hydrochloric acid solution with the same hydrogen ion concentration

5. Which of the following lists contains one acidic, one basic, and one neutral salt?

(a)	ammonium chloride	sodium hydrogensulfate	barium chloride
(b)	calcium nitrate	sodium chloride	ammonium chloride
(c)	barium nitrate	sodium phosphate	ammonium nitrate
(d)	barium sulfide	sodium fluoride	ammonium chloride

6. A buffer solution with a pH of approximately 4.7 was made by mixing 500 mL of 0.500 mol L^{-1} CH_3COOH with 500 mL of 0.500 mol L^{-1} $NaCH_3COO$.

$$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$$

(a) The addition of a 10 mL of 0.01 mol L^{-1} $NaOH_{(aq)}$ would raise the pH of the buffer solution by consuming the H_3O^+ ions.

(b) The additional of small quantities of hydrochloric acid will force the equilibrium to shift to the left by favouring the reaction that partially counteracts the increased pH.

(c) The addition of any amount of sodium hydroxide solution will not greatly change the pH because this is a buffer solution.

(d) The addition of 10.0 mL of 0.01 mol L^{-1} HNO_3 would not greatly alter the pH of the solution but the concentration of the CH_3COO^- ions would decrease.

7. Sulfuric acid is not suitable for use as a primary standard because:

(a) In its manufacture, there is uncertainty about how much SO_3 is dissolved in each litre of water.

(b) It is a strong acid and so will react too rapidly.

(c) It does not have a sufficiently high molar mass.

(d) It produces sulfate salts which are sometimes insoluble.

8. A solution was produced by blending 500 g of celery, boiling it for 20 minutes in water and then straining the mixture. Analysis found it to have a pH of 4.2. The hydroxide ion concentration of this solution would be closest to which value stated below?

(a) 3×10^{8} mol L^{-1}

(b) 2×10^{-10} mol L^{-1}

(c) 4×10^{-12} mol L^{-1}

(d) 5×10^{-13} mol L^{-1}

9. A student prepared a sodium hydroxide solution by dissolving 1.15 g of sodium hydroxide pellets in enough water to make exactly 50.0 mL of solution. This 50.0 mL of solution was then titrated against a 0.995 mol L^{-1} HCl solution. The end point of the titration was noted when 22.5 mL of the acid had been added instead of the expected 28.9 mL. The most likely cause of this lower then expected result would be:

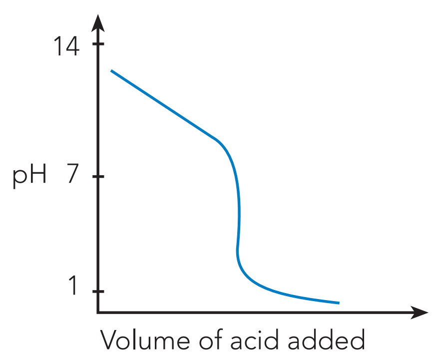
(a) the student chose methyl orange as an indicator instead of phenolphthalein.

(b) the sodium hydroxide pellets had absorbed water from the atmosphere prior to weighing.

(c) the student rinsed the burette with a small quantity of HCl solution before filling it with HCl solution.

(d) the 50.0 mL volumetric flash was rinsed with distilled water before the sodium hydroxide pellets were added.

10. The results of an acid base titration are shown in the graph to the right. Which of the following statements would be true about the titration?



(a) The titration was between 0.01 mol L^{-1} NaOH and 0.01 mol L^{-1} HCl.

(b) Phenolphthalein could be used as an indicator.

(c) Phenolphthalein or methyl orange could be used as an indicator.

(d) The titration involved a strong acid.

SECTION 2 – SHORT AND EXTENDED ANSWER (60 MARKS)

Answer each question in the space provided.

11. Give a chemical test and subsequent observations that could be used to distinguish between the following pairs of substances. You must clearly state the expected observation for each substance tested. No equations need to be given.

(a) 1 mol L^{-1} H_2SO_4 and 1 mol L^{-1} HNO_3

TEST ______________________________

OBSERVATION ______________________________

____

(b) Two white powders: magnesium carbonate and magnesium hydroxide

TEST ______________________________

OBSERVATION ______________________________

____

(c) Two colourless solutions: potassium ethanoate and potassium chloride

TEST ______________________________

OBSERVATION ______________________________

____

[12 marks]

12. Write balanced ionic equations for the following:

(a) $Ba(OH)_{2(aq)} + H_2SO_{4(aq)}$

____

(b) $KOH_{(aq)} + H_3PO_{4(aq)}$

____

(c) $CaCO_{3(s)} + HCl_{(aq)}$

____

[6 marks]

13. Use equations to help explain why a 0.01 mol L^{-1} HCl solution has a lower pH than a 0.01 mol L^{-1} CH_3COOH solution

____

____

____

[4 marks]

14. Write ionic equations for the process that occurs when the following acids are dissolved in water.

(a) carbonic acid: ____________________

(b) phosphoric acid: ____________________

(c) sulfuric acid: ____________________

[6 marks]

15. (a) Explain what hydrolysis of a salt is.

(b) Write equations to show the hydrolysis of the following salts. State if the result is an acidic, basic or neutral solution

(i) Na_2CO_3 ____________________

(ii) $(CH_3COO)_2Ca$ ____________________

(iii) NH_4NO_3 ____________________

[8 marks]

16. (a) State four characteristics of a primary standard.

(b) NaOH is deliquescent. Explain what this means.

(c) Explain the difference between the end point and the equivalence point of a titration.

[8 marks]

17. A solution was prepared by mixing 800 mL of 0.150 mol L^{-1} NaH_2PO_4 with 800 mL of 0.650 mol L^{-1} Na_2HPO_4. The solution was found to have a pH of approximately 7.2.

(a) Write the equation for the equilibrium that would be established between the $H_2PO_4^-$ and HPO_4^{2-} ions.

____

[1 mark]

(b) Use Le Châtelier's Principle to predict what would happen to the pH of the solution if 30 mL of 0.01 mol L^{-1} sodium hydroxide solution was added.

____

____

[3 marks]

(c) Explain (qualitatively) what would happen to the pH of the solution if 200 mL of 2 mol L^{-1} hydrochloric acid solution were added.

____

[2 marks]

18. In an experiment, a student was required to standardise a solution of hydrochloric acid using the primary standard, sodium carbonate. The sodium carbonate solution was prepared by dissolving 2.23 g of anhydrous sodium carbonate in enough distilled water to correctly fill a 500.0 mL volumetric flask. 20.0 mL aliquots of this solution were then titrated against a solution of hydrochloric acid. The volume of HCl used in the titrations is shown in the table below:

Titration	1	2	3	4	5
Initial reading (mL of HCl)	0.00	3.10	4.00	2.60	1.90
Final reading (mL of HCl)	42.50	44.80	45.30	44.00	43.20
Volume added					

Determine the concentration of the hydrochloric acid solution.

____

____

____

____

____

____

[10 marks]

END OF TEST (80 MARKS)

TRIAL TEST 3: OXIDATION AND REDUCTION

Time allowed: **70 minutes** **Section 1 –** Multiple Choice 20 marks
Total marks: **80** **Section 2 –** Short & Extended Answer 60 marks

SECTION 1 – MULTIPLE CHOICE (20 MARKS)

1. A test for nitrates is given by the equation below.

$$4Zn_{(s)} + NO_3^-{}_{(aq)} + 7OH^-{}_{(aq)} + 6H_2O_{(l)} \rightarrow 4[Zn(OH)_4]^{2-}{}_{(aq)} + NH_{3(g)}$$

The element that has been reduced in this process has experienced a change in oxidation number of:
(a) 2
(b) 4
(c) 6
(d) 8

2. I. $Zn^{2+}{}_{(aq)} + 4NH_{3(aq)} \rightarrow [Zn(NH_3)_4]^{2+}{}_{(aq)}$

II. $4H^+{}_{(aq)} + 2VO_2^+{}_{(aq)} + Sn^{2+}{}_{(aq)} \rightarrow Sn^{4+}{}_{(aq)} + 2VO^{2+}{}_{(aq)} + 2H_2O_{(l)}$

III. $Zn^{2+}{}_{(aq)} + 2Cl^-{}_{(aq)} \rightarrow Zn_{(s)} + Cl_{2(g)}$

IV. $BaCO_{3(s)} + 2H^+{}_{(aq)} + SO_4^{2-}{}_{(aq)} \rightarrow BaSO_{4(s)} + CO_{2(g)} + H_2O_{(l)}$

Which of the equations above show the **reduction** of a metal ion?
(a) I and II only.
(b) I and IV only.
(c) II and III only.
(d) II and IV only.

3. The equation for the addition of liquid bromine to a hot, concentrated solution of sodium hydroxide is:

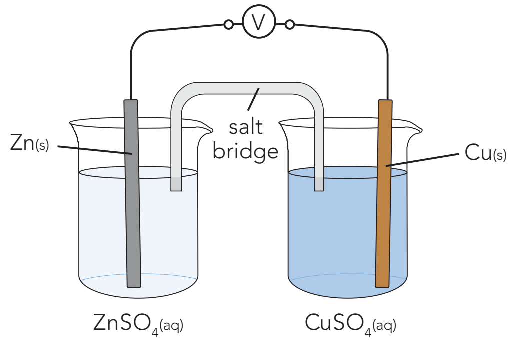
$$3Br_{2(l)} + 6OH^-{}_{(aq)} \rightarrow 5Br^-{}_{(aq)} + BrO_3^-{}_{(aq)} + 3H_2O_{(l)}$$

For this process, which of the following statements is correct?
I. the hydrogen is reduced.
II. the bromine is oxidised.
III. the oxygen is the reducing agent.
IV. the bromine is the oxidising agent.

(a) I and II only.
(b) II and III only.
(c) I, II and IV only.
(d) II and IV only.

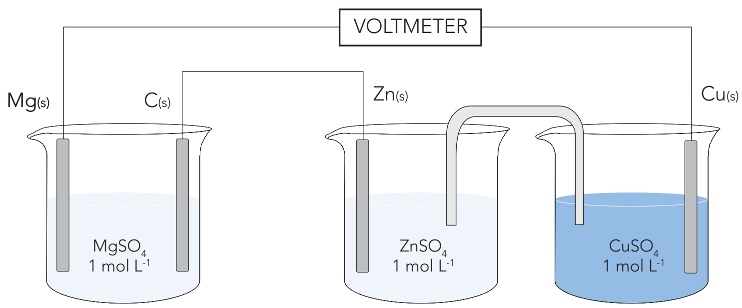
4. The $E°_{TOTAL}$ or emf value for the “reaction” between 1 mol L^{-1} H_2O_2 and 1 mol L^{-1} $H_2C_2O_4$ solutions is +2.27 V. Upon mixing 1 mol L^{-1} solutions of these two chemicals a student failed to observe any signs of a chemical reaction. A possible reason for this is:
(a) the $E°_{TOTAL}$ value for the reaction is not a predictor of reaction rate.
(b) the $H_2C_2O_4$ solution needs to be acidified.
(c) the reaction will only occur if a potential of greater than 2.27 V is applied to the reacting solutions.
(d) the reaction is endothermic and so needs energy to be added.

5.



Consider the galvanic cell shown above which is made up of Zn/Zn^{2+} and Cu/Cu^{2+} half cells. It would be correct to say that the reading on the voltmeter:
(a) is 1.10V
(b) is dependent on the surface area of the electrodes and the volume of the electrolyes
(c) is dependent on the temperature and concentration of the electrolyte solutions
(d) will become zero when Cu^{2+} ions stop moving through the salt bridge.

6. The diagram below shows two galvanic cells connected in series. The total emf for cells connected in series is the arithmetic addition of the each individual cell’s emf.

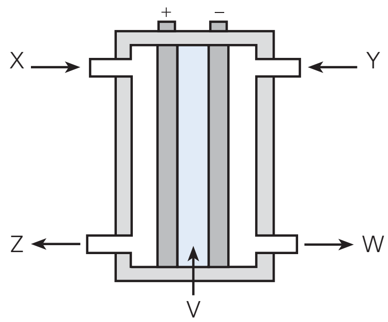


The standard reduction potentials are given below:

$Mg^{2+}_{(aq)} + 2e^- \rightarrow Mg_{(s)}$	E°	=	–2.36 V
$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$	E°	=	–0.76 V
$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$	E°	=	0.00 V
$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$	E°	=	+0.34 V

The reading on the voltmeter:
(a) cannot be calculated as the reduction potential for graphite ($C_{(s)}$) has not been provided.
(b) would be +3.12 V
(c) would be +1.26 V
(d) would be +3.46 V

7. The diagram below shows a basic structure for a hydrogen/oxygen fuel cell.



Which of the following statements is correct?

(a) Label V refers to a solution of electrolyte.

(b) Label W refers to the oxygen gas outlet.

(c) Label X refers to the water inlet.

(d) Label Y refers to the electrolyte inlet.

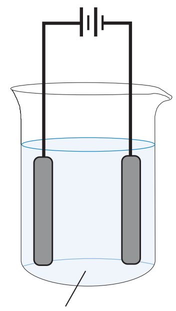
8. A 1.0 mol L^{-1} solution of $KCl_{(aq)}$ is to be electrolysed using inert electrodes as shown. Which of the following is correct?

(a) Hydrogen gas is produced at the cathode.

(b) Potassium metal is produced at the anode.

(c) Oxygen gas is produced at the cathode.

(d) Potassium metal is produced at the cathode.



9. An industrial chemist was experimenting with the electrolysis of a sample of sea water using inert platinum electrodes. Which one of the following statements concerning the experiment is incorrect?

(a) The chemist needs to be careful not to produce sparks as hydrogen gas is produced at the cathode.

(b) The chemist could use this process to collect sodium metal that would deposit onto the cathode.

(c) With some further experimenting, the chemist could develop this process to produce sodium hydroxide.

(d) The chemist could increase the rate of the electrolytic process by adding NaCl(s) to the sea water.

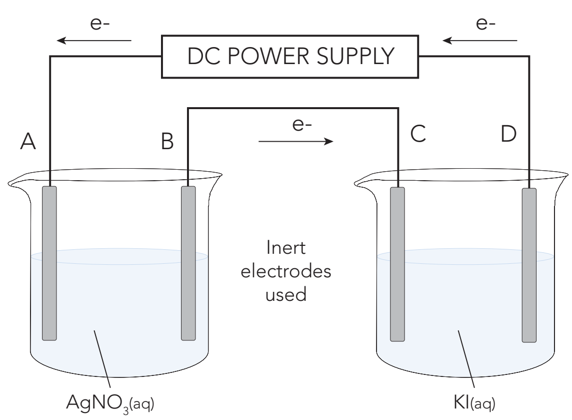
10. An experiment was conducted using two electrolytic cells connected in series as shown. An external voltage of approximately 2.0V was applied and the aqueous solutions are both 1.0 M. The electrodes, labelled A, B, C and D, are all inert. Which one of the following statements concerning this experiment is correct?

(a) Anodic reactions will occur at both electrodes B and D.

(b) Oxygen gas is produced at electrode B.

(c) Potassium metal will form on electrode C.

(d) Silver metal will form on electrode B.



11. Write balanced, ionic equations for any reaction that occurs in the following experiments. In each case state all observations that would result from the chemical reaction.

(a) A bromine water solution is added to a sodium iodide solution.

EQUATION ______________________________

OBSERVATION ______________________________

____

(b) A zinc strip is placed into a solution of copper(II) sulfate.

EQUATION ______________________________

OBSERVATION ______________________________

____

(c) A piece of sodium is placed into a beaker of water.

EQUATION ______________________________

OBSERVATION ______________________________

____

(d) An acidified $KMnO_4$ solution is added dropwise to a H_2O_2 solution.

EQUATION ______________________________

OBSERVATION ______________________________

____

[12 marks]

12. (a) Rewrite the two redox equations shown below as oxidation and reduction half equations.

(i) $Zn_{(s)} + 2H^{+}_{(aq)} \rightarrow Zn^{+2}_{(aq)} + H_{2(g)}$

Oxidation half equation ______________________________

Reduction half equation ______________________________

(ii) $Mg_{(s)} + 2H_2O_{(l)} \rightarrow Mg(OH)_{2(aq)} + H_{2(g)}$

Oxidation half equation ______________________________

Reduction half equation ______________________________

(b) Write the oxidation and reduction half equations for the reactions indicated below. Also give the overall redox equation.

(i) A strip of zinc metal placed in a solution of silver nitrate begins to dissolve and a silvery deposit forms.

Oxidation half equation ______________________________

Reduction half equation ______________________________

Redox equation ______________________________

(ii) Magnesium metal reacts with chlorine gas to produce magnesium chloride.

Oxidation half equation ______________________________

Reduction half equation ______________________________

Redox equation ______________________________

[10 marks]

13. Complete the diagram below to illustrate a galvanic cell that uses magnesium and tin for the electrodes. Your diagram needs to clearly indicate each of the following:

(i) Direction of electron flow

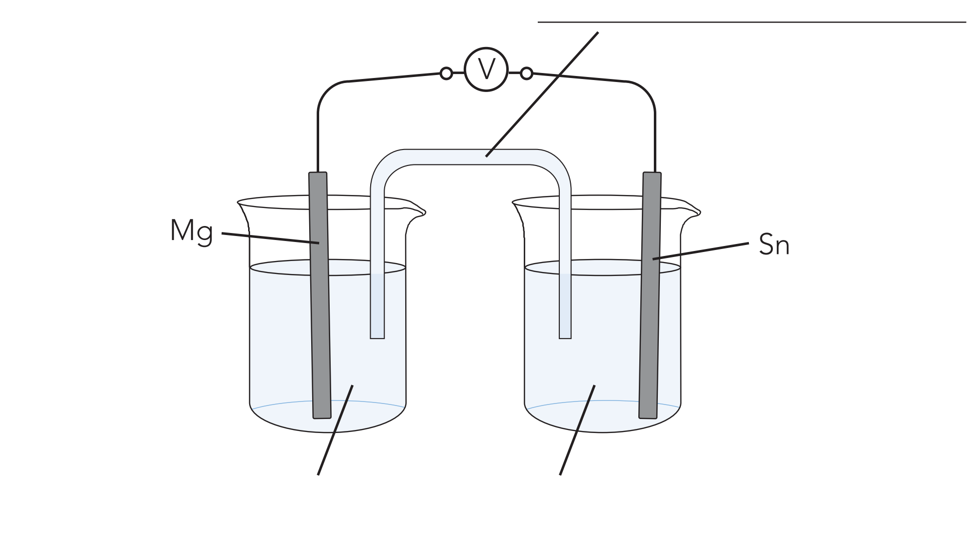
(iii) Direction of motion of –ve ions in the salt bridge

(v) The reading on the voltmeter (assume standard conditions)

(ii) Direction of motion of +ve ions in the Mg half cell

(iv) Name of suitable solutions to use in the salt bridge and each half cell

(vi) The equations for the reactions occurring at the anode and cathode



[12 marks]

14. A hobby farmer decided to restore a windmill that was used to pump ground water into a trough for stock to drink. After examining the steel support tower, the farmer found some evidence of rust.

(a) Write the anode and cathode half equations for the corrosion of the iron and the formation of rust.

Anode: ____________________

Cathode: ____________________

Rust formation: ____________________

(b) Describe two procedures that the farmer could follow to prevent further corrosion of the iron tower. Explain in each case how the action taken prevents further corrosion.

(i) ____________________

____

____

(ii) ____________________

____

____

[12 marks]

15. The corrosion of iron to form rust is caused by the action of oxygen and water in the air. The process occurs as a series of reactions.

(a) Give relevant equations for each of the following:

(i) The initial oxidation of the iron to form $Fe(OH)_{2(s)}$. Give the anodic, cathodic and overall reaction.

____

____

____

(ii) The further oxidation of the $Fe(OH)_{2(s)}$ to $Fe(OH)_{3(s)}$.

____

____

(iii) The partial dehydration to one of the forms of rust, $FeO_3.H_2O_{(s)}$.

____

____

(b) Briefly outline two means of reducing the corrosion of iron. In each case explain why the method is effective.

(i)

(ii)

[14 marks]

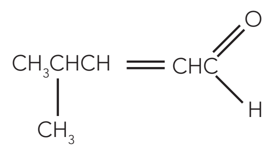
END OF TEST (80 MARKS)

TRIAL TEST 4: ORGANIC CHEMISTRY

Time allowed:	**70 minutes**	**Section 1 –** Multiple Choice	20 marks
Total marks:	**80**	**Section 2 –** Short & Extended Answer	60 marks

SECTION 1 – MULTIPLE CHOICE (20 MARKS)

1. Consider the compound whose structural formula is drawn below:



The IUPAC name for this molecule would need to indicate that the functional groups it contained included:

(a) a double bond and an aldehyde group.
(b) an alkyl group and an alcohol group.
(c) an alkyl group and a carboxyl group.
(d) a double bond and a carboxyl group.

2. From the list of 5 names below, pick the combination that are isomers of each other.

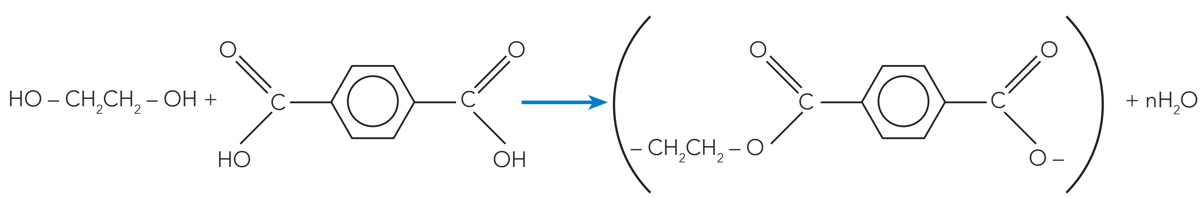
I	butanoic acid	II	butan-2-ol	III	ethyl ethanoate
IV	butanal	V	butanone		

(a) I and II
(b) II and III
(c) III and IV
(d) IV and V

3. Three important types of chemical reaction are:

I Condensation polymerisation
II Addition polymerisation
III Esterification

The equation for the production of terylene is:



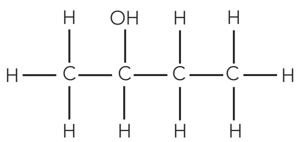
This reaction could be classified as a type:

(a) I reaction only.
(b) II reaction only.
(c) I and III reaction.
(d) II and III reaction.

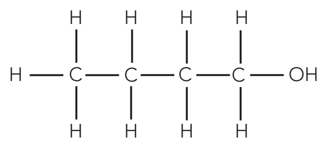
4. Which of the following lists contains empirical formulae **only**.

(a)	C_2H_6	$CuSO_4$	Mn_2O_3
(b)	HO	C_2H_3O	$N_2H_8SO_4$
(c)	OF_2	CCl_4	C_6H_6
(d)	$Pt_2N_2H_6Cl_2$	AgN_2H_6	CaO_2H_2

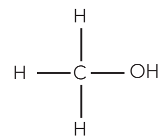
Use the structural formulae drawn below to answer questions 5 to 7.



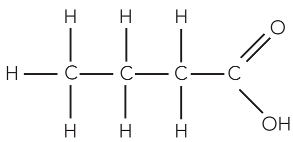
I



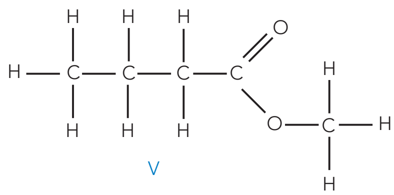
II



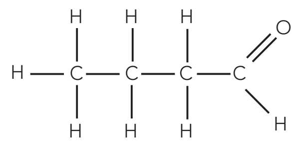
III



IV



V



VI

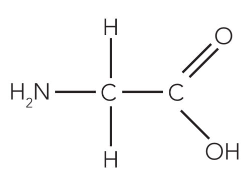
5. The substances which are polar but **do not** exhibit hydrogen bonding are:
   (a) IV & VI
   (b) I, IV, V & VI
   (c) IV & V
   (d) V & VI

6. The substance that would react with acidified $KMnO_4$ to form an isomer of VI is:
   (a) I
   (b) II
   (c) III
   (d) IV

7. The two substances that could be used to produce a third from the list are:
   (a) III & VI
   (b) II & IV
   (c) III & IV
   (d) V & VI

8. A compound containing only C, H and O was found to be composed of 77.38% oxygen and 19.36% carbon.
   (a) The compound would be carboxylic acid as it contains carbon, oxygen and a very small amount of hydrogen.
   (b) To determine the molecular formula of the compound, it would be necessary to vaporise a known mass of the compound to determine the percentage of hydrogen present.
   (c) The compound would be a carboxylic acid or an ester, more information would be needed to determine which.
   (d) The compound has an empirical formula O_3CH_2.

9. Consider the molecule shown.



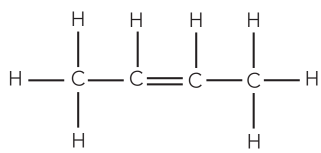
   This molecule would be best identified as:
   (a) a carboxylic acid
   (b) a primary amine
   (c) an α-amino acid
   (d) an amino aldehyde

10. Which of the following compounds would you expect to be most soluble in water?
(a) propane
(b) propanal
(c) propanone
(d) propan-1-ol

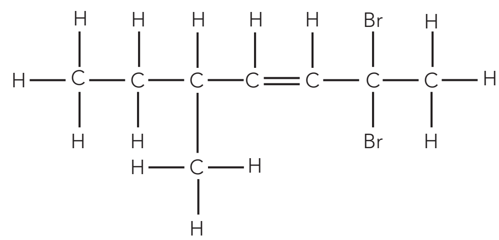
SECTION 2 – SHORT AND EXTENDED ANSWER (60 MARKS)

11. Use IUPAC rules to name the following compounds.

(a)



(b)



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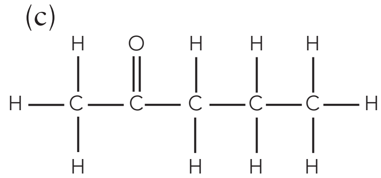

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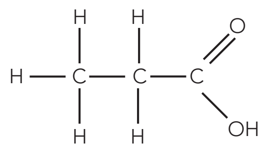

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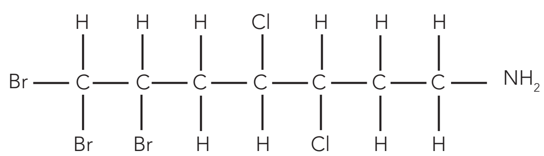

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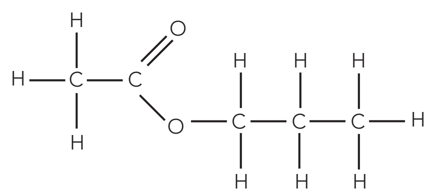


[12 marks]

12. Draw the structural formula for each of the following compounds.

(a) 1,2-dichloroethane

(b) *trans*-but-2-ene

(c) *cis*-2,3-diiodopent-2-ene

(d) pentan-1-amine (or pentanamine)

(e) 3,4-dimethylheptanal

(f) propyl butanoate

[12 marks]

13. Write the balanced equation for each of the following reactions:

(a) propene + chlorine gas

____

(b) butane + excess oxygen gas

____

(c) ethane + bromine (in presence of suitable catalyst)

____

[6 marks]

14. Use half equations to write balanced equations for the following reactions and name the organic product produced.

(a) Acidified potassium dichromate and propanal

OXIDATION: ______________________________

REDUCTION: ______________________________

REDOX: ______________________________

NAME: ______________________________

(b) Acidified potassium permanganate and butan-2-ol

OXIDATION: ______________________________

REDUCTION: ______________________________

REDOX: ______________________________

NAME: ______________________________

[8 marks]

15. Draw the structural formula and name the organic product of the following reactions:

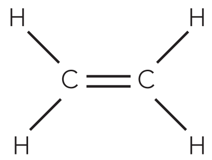
(a) ethanol + propanoic acid
(with concentrated H_2SO_4 as catalyst)

(b) heptan-1-ol + butanoic acid
(with concentrated H_2SO_4 as catalyst)

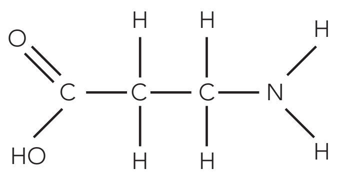
[4 marks]

16. Draw a section of the polymer chain formed when the following monomers are polymerised. You need to draw at least 4 monomer units in your polymer.

(a)

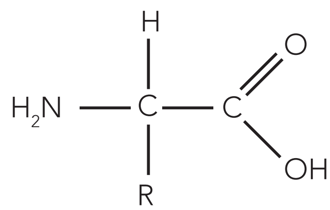


(b)



[4 marks]

17. The general formula of an a-amino acid can be written as:



Write the formula to show the ions formed when:

(a) It is dissolved in an acidic solution

(b) It is dissolved in a basic solution

[4 marks]

18. A 0.467 g sample of nicotine was burnt in excess oxygen to produce 1.266 g of carbon dioxide and 0.3589 g of water vapour.

A second sample of the nicotine, weighing 0.362 g was analysed and found to contain 0.06263 g of nitrogen.

A third sample of the nicotine, weighing 0.964 g was vaporised in a 0.0500 L container and found to exert a pressure of 544 kPa at a temperature of 277°C.

Determine the empirical and molecular formulae of the nicotine.

[10 marks]

END OF TEST – TOTAL 80 MARKS

TRIAL TEST 5: CHEMICAL SYNTHESIS

Time allowed:	**70 minutes**	**Section 1 –** Multiple Choice	20 marks
Total marks:	**80**	**Section 2 –** Short & Extended Answer	60 marks

SECTION 1 – MULTIPLE CHOICE (20 MARKS)

1. Which of the following compounds would be best to mix with warm water to help remove cooking oil from a fry pan?
   (a) C_7H_{16}
   (b) CH_3CHO
   (c) CH_3COOCH_3
   (d) $C_{16}H_{33}COONa$

2. The cleansing action of soaps is decreased when water contains which of the following ions:
   I. Na^+ ions
   II. Ca^{2+} ions
   III. NO^{3-} ions
   IV. Mg^{2+} ions
   (a) I only
   (b) II only
   (c) II, III and IV
   (d) II and IV

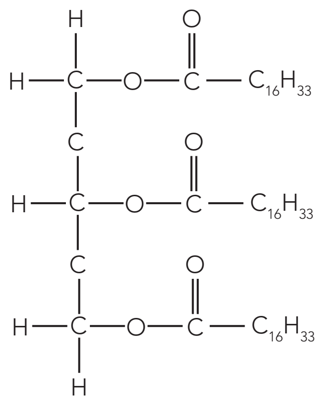
3. Which of the following statements about soaps is true?
   (a) Soaps dissolve oils by forming hydrogen bonds with the hydrophilic section of the oil
   (b) Soaps are unable to lather in hard water as scum forms when the stearate ion forms a polymerised precipitate with divalent anions in the water.
   (c) Soaps dissolving oils involves the alkyl region of soap ions being attracted to and then surround small globules of oil molecules.
   (d) Soaps are sulfonated esters of long chain fatty acids.

4. Which of the following statements about the production of alcohol by fermentation is **not** true?
   (a) Fermentation involves biological catalysts aiding the breakdown of the starch polymer into its monomer units.
   (b) Carbon dioxide is formed when the enzymes in yeast catalyse the breakdown of glucose.
   (c) To be pure enough for use as a biofuel, the yeast and starch must be distilled.
   (d) The alcohol to be used is purified by passing it through a molecular sieve.

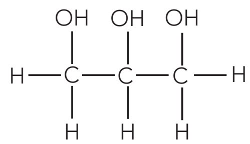
5. For use as a supplement to petrol, alcohol can be produced by fermentation or by:
   (a) The reduction of ethanoic acid obtained from the oxidation of grape vinegar.
   (b) The hydrolysis of ethene obtained from the cracking of hydrocarbons produced in the petroleum industry.
   (c) The bi-product of the base catalysed esterification of triglycerides.
   (d) The de-poylermisation of polyethene.

6. Which of the following molecules would be suitable for use as a biofuel?

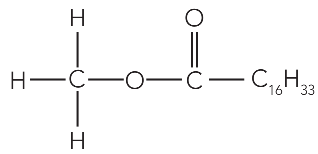
(a)



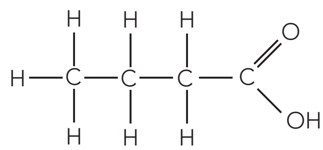
(b)



(c)



(d)



Questions 7 and 8 refer to the following stages in the production of sulfuric acid:

$S(s) + O_2(g) \rightarrow SO_2(g) + 297\ kJ\ mol^{-1}$

$2SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g) + 198\ kJ\ mol^{-1}$

$SO_3(g) + H_2SO_4(l) \rightarrow H_2S_2O_7(l)$

$H_2S_2O_7(l) + H_2O(l) \rightarrow 2\ H_2SO_4(l)$

7. Which of the following statements is most correct?
   (a) The production of sulfur trioxide is carried out at the moderately high temperature of 450ºC due to reaction rate considerations rather than yield considerations.
   (b) The equilibrium yield of sulfur trioxide is favoured by a high pressure in the reaction vessel however the cost of building high-pressure reaction vessels means that a high temperature is used instead.
   (c) Sulfur trioxide is dissolved in sulfuric acid rather than water because the product $H_2S_2O_7$ is much more soluble in water and consequently this additional step increases the yield of sulfuric acid.
   (d) The burning of the sulfur to produce sulfur dioxide must be carried out at a low temperature to ensure that the sulfur is not liquefied before combustion as liquid sulfur will inhibit the action of the vanadium catalyst.

8. When 32 g of sulfur is burnt in 32 g of oxygen
   (a) 196 g of sulfuric is produced
   (b) 64 g of sulfur dioxide is produced
   (c) 80 g of sulfur trioxide would be produced
   (d) 32 g of water is consumed to produce the sulfuric acid.

9. A 25.0 g sample of lead ore, predominantly PbS, was reduced to pure lead by the following process:

$2\ PbS + 3\ O_2 \rightarrow 2\ PbO + 2\ SO_2$

$2\ PbO + C \rightarrow 2\ Pb + CO_2$

If the lead ore was 63.5% PbS the mass of pure lead that could be obtained from the 25.0 g sample is:

(a) 15.9 g
(b) 6.74 g
(c) 13.7 g
(d) 27.4 g

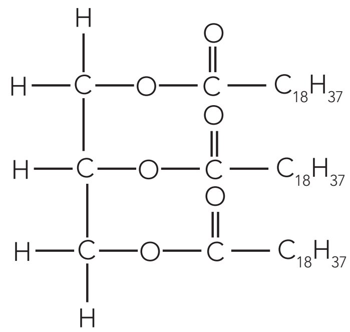
10. What mass of ammonia could be collected when 14.7 g of ammonium chloride mixed with 24.5 g of calcium hydroxide and heated?

$2\ NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2\ NH_3 + 2\ H_2O$

(a) 14.7 g
(b) 5.6 g
(c) 11.2 g
(d) 4.7 g

SECTION 2 – SHORT AND EXTENDED ANSWER (60 MARKS)

11. A soap is to be made from a fat with the formula as shown below:



(a) Write the equation for the reaction of this tristearate with NaOH to form soap.

____

____

____

____

[4 marks]

(b) With the aid of a diagram explain how soap can clean a dirty plate.

[4 marks]

(c) Briefly explain why a sample of water would be classified as hard, include the names of chemical species causing this.

____

____

____

____

[2 marks]

(d) Draw the structure of a typical detergent and explain what advantages detergents have over soaps.

[4 marks]

12. Two biofuels that are used around the world are ethanol, as an additive to petrol, and biodiesel as a replacement for "standard" diesel.

(a) Write the equation for the production of ethanol from ethene.

[3 marks]

(b) Write an equation for the production of a biodiesel from a fat or oil (tristearate).

[3 marks]

(c) What is the most common source of ethene and "standard" diesel?

[2 marks]

(d) Why are motorists encouraged to use biofuels over “standard” fuels in their motor vehicle?

[2 marks]

(e) Name two types of catalyst that are used in the production of biodiesel.

[2 marks]

13. Ammonia can be produced by the Haber Process.

(a) Write the equation for production of ammonia by this process.

[2 marks]

(b) This process should be carried out at a high pressure. Explain why.

[2 marks]

(c) Predict the effect an increase of temperature would have on the equilibrium yield of ammonia.

[2 marks]

(d) At what temperature is the Haber Process carried out. Justify the use of this temperature.

[3 marks]

(e) What catalyst is used in the Haber process? What effect does it have on the equilibrium yield of ammonia and why is it used?

______

______

______

[3 marks]

14. The North-West Shelf in Western Australia has large reserves of natural gas. The major component of natural gas is methane, which is used, primarily as fuel for heating and the generation of electricity. One possible use of methane is to convert it to methanol that will then be used as a petrol substitute.

The first stage in the conversion of the methane in natural gas to methanol is to remove impurities from the natural gas. These impurities often include ethane, propane, carbon dioxide, sulfur compounds, nitrogen and water.

The second stage in the production of methanol is to react methane with steam

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3\ H_2(g)$$

In the third stage, carbon monoxide and hydrogen are mixed at high temperature and pressure over an iron catalyst.

$$CO(g) + 2\ H_2(g) \rightarrow CH_3OH(g)$$

If a 1 tonne sample of natural gas was 85.0% methane, calculate:

(a) The mass of hydrogen gas that could be produced from this sample.

______

______

______

______

[4 marks]

(b) The mass of methanol that could be recovered from the 1 tonne sample if the reaction process was 92.5% efficient.

______

______

______

______

______

[6 marks]

15. Sea water contains approximately 0.13% magnesium by mass. The magnesium can be extracted from the sea water by the following steps:

A: Mg^{2+} ions are removed from the sea water by precipitation:

$$Mg^{2+}(aq) + Ca(OH)_2(s) \rightarrow Mg(OH)_2(s) + Ca^{2+}(aq)$$

B: The magnesium precipitate is then converted to a magnesium chloride solution by the addition of hydrochloric acid.

$$Mg(OH)_2(s) + 2\,H^+(aq) + 2\,Cl^-(aq) \rightarrow Mg^{2+}(aq) + 2\,Cl^-(aq) + 2\,H_2O(l)$$

C: The magnesium chloride is crystallised from solution and heated to form magnesium oxide

$$MgCl_2.6H_2O(s) \rightarrow MgO(s) + 2\,HCl(g) + 5\,H_2O(g)$$

D: Molten magnesium oxide is electrolysed to form pure Mg

Anode: $Mg^{2+}(l) + 2\,e^- \rightarrow Mg(l)$
Cathode: $2\,Cl^- \rightarrow Cl_2(g) + 2\,e^-$

(a) To initiate the extraction process, 1480 kg of calcium hydroxide was added to excess sea water. After a full cycle of the extraction process, 1120 kg of chlorine gas was collected at the cathode. Calculate the efficiency of the extraction process.

(b) Given this level of efficiency calculate the mass of sea water required per kilogram of magnesium produced.

[12 marks]

END OF TEST – TOTAL 80 MARKS

ANSWERS TO CHAPTER AND REVIEW QUESTIONS

CHP 1: CHEMICAL EQUILIBRIUM

Chapter Questions

1.1 *Example 3 is likely to be slowest since many more bonds have to break.*

1.2

(a) *2 single + 1 double (4).*

(b) *4 (4 H–O bonds).*

1.3 *When a bond is broken or formd- energy greater than minimum required and orientation is appropriate.*

1.4 *As the reaction proceeds, H^+ ions are converted to H_2 molecules, hence there are less H^+ ions per unit volume to react with the Zn (concentration decreases). So collisions decrease.*

1.5

(a) *24 cm^2* (b) *48 cm^2*

(c) *Surface area has doubled – chance of a successful collision increased.*

1.6 *To increase their surface area and so increase their rate of participation with more collisions.*

1.7 *A shift of 10°C will markedly increase the number of particles with a high energy ($E > E_a$). Hence collisions are more forceful and more frequent.*

1.8

(a) *Initially $[N_2]$ and $[H_2]$ are at their greatest and ∴ so is reaction rate, $[N_2]$ and $[H_2]$ will decrease rapidly causing decrease in reaction rate.*

(b) *H_2 is consumed at 3 times the rate of N_2 - refer to mole ratio in the equation.*

1.9

(a) $K = \frac{[NO_2]^2}{[N_2O_4]}$ (b) $K = \frac{[H_2][I_2]}{[HI]^2}$

(c) $K = [H^+][OH^-]$ (d) $K = [Ag^+][I^-]$

(e) $K = \frac{[SO_3]^2}{[SO_2]^2 . [O_2]}$

1.10

(a)

- *$[PCl_3]$ and $[Cl_2]$ is not initially affected hence forward reaction rate is not affected.*
- *$[PCl_5]$ has been reduced, hence reverse reaction rate is lower.*
  NOTE: This means that the net effect is a shift in equilibrium to the left.

(b) *System will partially compensate.*

Suppose $[PCl_5]$ goes from 2.00 → 2.10

then $[PCl_3]$ goes from 0.585 → 0.485
$[Cl_2]$ goes from 1.785 → 1.685
Hence 'K' = 2.57 (a little high).
By trial and error, can show –
$[PCl_5]$ = 2.06 mol L^{-1}
$[PCl_3]$ = 0.489 mol L^{-1}
$[Cl_2]$ = 1.689 mol L^{-1}

1.11

Initial change to		Direction
→ R/R	← R/R	favoured
nil	inc	←
nil	inc	←
inc	nil	→
nil	dec	→
nil	nil	nil

1.12

Consequent pressure change	Direction favoured
decrease	nil
decrease	→
increase	←
decrease	←
increase	→

1.13

(a) $N_2O_4 \rightleftharpoons 2NO_2$

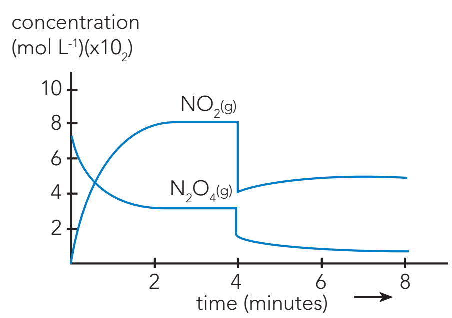
(b) $K = \frac{[NO_2]^2}{[N_2O_4]}$

(c) N_2O_4

(d) *At t = 2 minutes.*

(e) *It was reduced; volume of system was increased.*

(f)



1.14

Temperature change	Direction favoured
increase	→
decrease	←
increase	←
decrease	←

1.15

→ R/R	← R/R	[NO]	$[Br_2]$	[NOBr]	→,← or U
nil	dec	dec	dec	dec	→
inc	inc	inc	inc	inc	→

1.16

→ R/R	← R/R	$[H_2O]$	[CO]	$[H_2]$	→,← or U
nil	dec	nil	inc	dec	→
inc	inc	nil	nil	nil	U
inc	inc	nil	inc	inc	→
inc	inc	nil	inc	inc	←

1. Review Questions

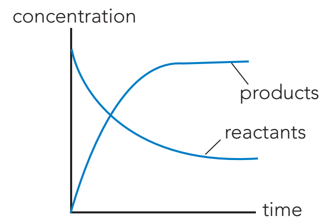
1.
(a) True
(b) True
(c) False. Chemical equilibrium only exists if the forward and reverse reaction rates are equal.
(d) False. For a chemical system in equilibrium the forward reaction rate will initially remain unaffected if some of the product is removed from the system. In actual fact the reverse reaction rate will decrease as there is less product.
(e) True. This is essentially Le Chatelier's Principle.

2.
(a) Nature of reactants, concentration, state of subdivision, temperature and catalyst.
(b) The minimum energy needed to reach an activated state.

3.
(a) No change, concentration of NaOH is not being altered.
(b) Rate increases, increased surface area of $Al_{(s)}$ increasing the number of Al atoms being exposed to other reactants.
(c) Rate decreases, temperature is decreased causing fewer collisions to have the activation energy.
(d) Rate increases, $[OH^-]$ has increased.

4.
(a) Higher temperature increases reaction rates; i.e. rate of activity of bacteria increases.
(b) If sandwiches are to be pre-made, they will need to be kept in a refrigerated area to reduce the activity of the bacteria.

5.
(a) Solution will lose its brown colour due to $I_{2(aq)}$ and become colourless.
(b) Reaction rate decreases because reactants become less concentrated.



(insufficient information to give accurate concentrations)

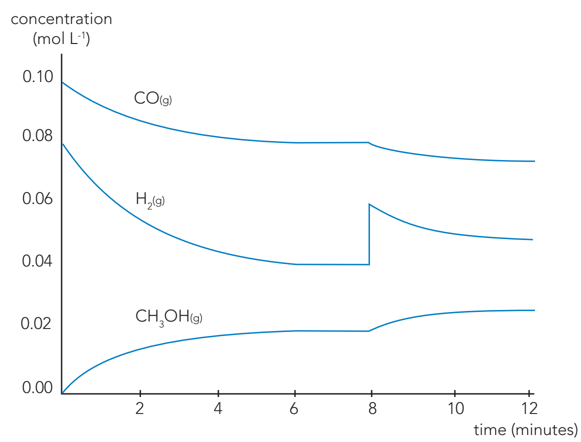
6.
(a) Catalysts do speed up chemical reactions (possibly involved in intermediate compounds between reactants and products) and they are re-usable. They DO react but are not permanently consumed.
(b) Providing an alternative reaction pathway with a lower activation energy.

7. (i) Constancy of macroscopic properties.
(ii) Rate of forward reaction equals the rate of the reverse reaction.

8.
(a) CrO_4^{2-} : yellow ; $Cr_2O_7^{2-}$: orange ; $H^+$and H_2O: colourless.
(b) Observe no changes in the system, especially changes in colour.
(c) $K = \dfrac{[Cr_2O_7^{2-}]}{[Cr_2O_4^{2-}]^2.\ [H^+]^2}$

9. If a chemical system that is at equilibrium is subject to a change, the chemical system will adjust to re-establish equilibrium. The adjustments will be in such a way as to partially counteract the imposed change.

10.
(a) $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$
(b) t = 6 min
(c)



(d) ***Experts only***
Estimate by trial and error to find concentration values that give K ≈ 156 e.g. if $H_{2\ (g)}$ loses half of its extra concentration to achieve equilibrium then we would have:
$[H_2]$ = 0.05 mol L^{-1}
[CO] = 0.075 mol L^{-1}

$[CH_3OH]$ = 0.025 mol L^{-1}
These give a K ≈ 133 (too low)
A close estimate will be final [CO] = 0.074 mol L^{-1}

11.
(a) *Forward reaction favoured, solution turns a deeper red.*
(b) *Concentration of all species decreased, reaction favoured which increases concentration (by producing more particles) – solution loses red colour.*
(c) *decreases because of production of precipitate. Reverse reaction favoured, solution loses red colour.*

12.
(a) *No change in concentration of the solid, no effect on yield of CO_2.*
(b) *No change in concentration, no effect on yield of CO_2.*
(c) *No change in concentration of CaO, no effect on yield of CO_2.*
(d) *CO_2 is removed, forward reaction favoured, yield of CO_2 increases.*

13.
(a) *No effect on the equilibrium yield.*
(b) *To ensure an economic reaction rate – a high yield at a slow rate is not necessarily economical.*

14.

Change made to equilibrium mixture	Effect on total gas pressure	Effect on $[O_2(g)]$	Effect on equilibrium position	Effect on value of K
Temp reduced to 50°C	decrease	increase	←	lower
More O_2 gas at 100°C is added	increase	increase	→	none
Some Ar gas at 100°C is added	increase	none	none	none
Volume of reaction vessel is reduced to 1.5 L	increase	increase	→	none
Small pellets of a catalyst are added	none	none	none	none

15.
(a) $K = \dfrac{[H_2]^4}{[H_2O]^4}$
(b) *Constant removal of H_2 will favour the forward reaction ($H_2O_{(g)}$ would be injected over the iron at the bottom of the reaction vessel).*
(c) *Using the iron in mesh form will increase the reaction rate. It will not increase the equilibrium yield of H_2 but it will increase the rate of production.*

16.
(a) $CO_{2\,(g)} + 394\ kJ \rightleftharpoons C_{(s)} + O_{2\,(g)}$
(b) *Equilibrium constant will not be affected.*
(c) *Forward reaction is favoured so as to (partially) consume the added energy.*

17.
(a) *Carbon dioxide in water forms carbonic acid, $H_2CO_{3(aq)}$.*
The carbonic acid, partially dissociates to form hydrogen
ions ($H_3O^+_{(aq)}$) which increase acidity. Equations are:

$$CO_{2(g)} \rightleftharpoons CO_{2(aq)}$$

$$CO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)}$$

$$H_2CO_{3(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + HCO_3^-{}_{(aq)}$$

(b) *Any increase in concentration of $CO_{2(g)}$ will, according to Le Châtelier's Principle, favour an increase in the concentration of $CO_{2(aq)}$. Similarly this will lead to more $H_2CO_{3(aq)}$ being formed and more $H_3O^+{}_{(aq)}$. Hence acidity will increase.*
(c) *An increase in the concentration of hydrogen ions in sea water will cause more of the carbonate ions in the water form bicarbonate ions to maintain the following equilibrium.*

$$H_3O^+_{(aq)} + CO_3^{2-}{}_{(aq)} \rightleftharpoons HCO_3^-{}_{(aq)} + H_2O_{(l)}$$

This makes calcification as indicated by the following equilibrium less favourable since there are less carbonate ions available.

$$Ca^{+2}_{(aq)} + CO_3^{2-}{}_{(aq)} \rightleftharpoons CaCO_{3(s)}$$

18.
(a) *$[H_3O^+]$ would increase*
(b) *$[H_3O^+]$ would decrease, but the equilibrium would shift to increase it again.*
(c) *$[H_3O^+]$ would decrease, but the equilibrium would shift to increase it again.*

For the Experts

19.
(a) *K = $(SO_3)^2 / (SO_2)^2(O_2)$*
(b) *The graph is horizontal between t = 4 and t = 6 indicating no change in concentration and that equilibrium has been reached.*
(c) *The equation for the reaction and initial concentrations of the gases are shown below. Values for t = 6 are also shown, determined as discussed below.*

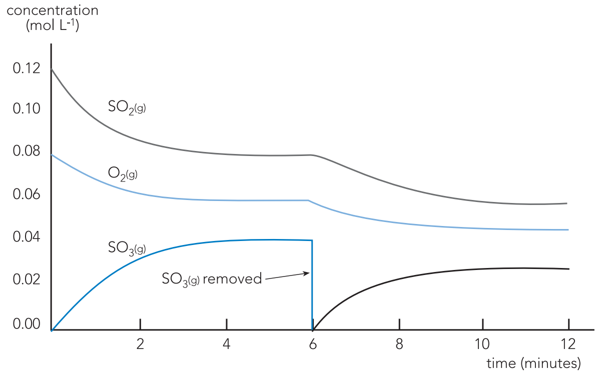
$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

Initial values 0.12 mol L^{-1} 0.08 mol L^{-1} 0.00

Values at t = 6 0.08 mol L^{-1} 0.06 mol L^{-1} 0.04 mol L^{-1}

From the graph we can see that the concentration of the $SO_{2(g)}$ has been reduced by 0.04 mol L^{-1} to 0.08 mol L^{-1}. Similarly, using the mole ratios from the equation we can see that the $O_{2(g)}$ concentration will be reduced by 0.02 mol L^{-1} to 0.06 mol L^{-1}. The concentration of the $SO_{3(g)}$ will increase from 0.0 to 0.04 mol L^{-1}.

(d) *See graph below for t = 0 to t = 6*



(e) *With all $SO_{3(g)}$ removed a new equilibrium will re-establish and some $SO_{3(g)}$ will form.*

CHP 2: ACIDS AND BASES

Chapter Questions

2.1 $n(Mg(OH)_2) = \frac{m}{M} = \frac{0.0500}{58.326} = 8.57 \times 10^{-4}$

$c(OH^-) = \frac{2 \times 8.57 \times 10^{-4}}{1.00} = 1.71 \times 10^{-3}$ M

$c(H^+) = \frac{1 \times 10^{-14}}{1.71 \times 10^{-3}} = 5.83 \times 10^{-12}$ M

$pH = \log[H^+] = 11.2$

2.2

(a) $pH = 3.60$

$\therefore [H^+] = 10^{-3.60}$

$\therefore [H^+] = 2.51 \times 10^{-4}$ mol L^{-1}

$[OH^-] = \frac{1.0 \times 10^{-14}}{2.51 \times 10^{-4}}$

$= 3.98 \times 10^{-11}$ mol L^{-1}

(b) $[H^+] = \frac{2.51 \times 10^{-4}}{2}$

$= 1.26 \times 10^{-4}$ mol L^{-1}

$[OH^+] = \frac{3.98 \times 10^{-11}}{2}$

$= 1.99 \times 10^{-11}$ mol L^{-1}

2.3 $[H^+] = \sqrt{K_w} = 2.34 \times 10^{-7}$

$pH = 6.63$

2.4 At 50°C $K_w = 5.48 \times 10^{-14}$ (rather than 1.00×10^{-14})

$[OH^-] = \frac{K_w}{[H^+]}$

$[H^+] = \text{inv} \log (-2.50)$ (OR $10^{-2.50}$)

$= 3.16 \times 10^{-3}$ M

$[OH^-] = \frac{5.48 \times 10^{-14}}{3.16 \times 10^{-3}} = 1.73 \times 10^{-11}$ mol L^{-1}

2.5 $H^+ + OH^- \rightarrow H_2O$

$n(HNO_3) = c.V. = 0.540 \times 0.0475$

$= 0.02565$ mol

$n(NaOH) = c.V. = 0.444 \times 0.0555$

$= 0.02464$ mol

$n(HNO_3)$ not consumed

$= 0.02565 - 0.02464 = 1.008 \times 10^{-3}$ mol

$[H^+] = n/V = 1.008 \times 10^{-3}/(0.0475 + 0.0555)$

$[H^+] = 9.79 \times 10^{-3}$ M

$pH = 2.01$

2.6

(a) $HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$

(b) $HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$

2.7 (a)

H_2SO_4	HSO_4^-
HF	F^-
H_2S	HS^-
HCO_3^-	CO_3^{2-}

(b)

NH_3	NH_4^+
$H_2PO_4^-$	H_3PO_4
F^-	HF
HSO_4^-	H_2SO_4

2.8

(a) NH_4^+/NH_3 ; H_2O/H_3O^+

(b) NH_3/NH_2^- ; PO_4^{3-}/HPO_4^{2-}

2.9

(a) $HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$

Solution becomes slightly acidic.

(b) $CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-$

Solution becomes slightly basic.

(c) $F^-(aq) + H_2O(l) \rightleftharpoons HF(aq) + OH^-(aq)$

Solution becomes slightly basic.

(d) $HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$

Solution becomes slightly acidic.

(e) $ClO^-(aq) + H_2O(l) \rightleftharpoons HClO(aq) + OH^-(aq)$

Solution becomes slightly basic.

2.10

$NaCl_{(aq)}$	strong base/strong acid	neutral
$Na_2CO_{3(aq)}$	strong base/weak acid	basic
$KH_2PO_{4(aq)}$	*strong base/weak acid	acidic
$MgF_{2(aq)}$	strong base/weak acid	basic
$Ca(ClO)_{2(aq)}$	strong base/weak acid	basic
$K_2SO_{4(aq)}$	strong base/weak acid	basic

* $H_2PO_4^{-1}$ *derived from polyprotic acid*

2.11

conjugate pair

(a)+(b)

$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$

acid *base* *base* *acid*

conjugate pair

(c) Addition of OH^- *would reduce* $[H_3O^+]$*. Forward reaction favoured to partially counteract this imposed change and pH of blood remains relatively constant.*

2.12

WEAK ACID	CONJUGATE BASE	EQUATION
CH_3COOH	CH_3COO^-	$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$
H_3PO_4	$H_2PO_4^-$	$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + H_3O^+(aq)$
NH_4^+	NH_3	$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$

2.13

(a) $V = 50{,}000\ L$, $pH = 7.6$, $[H^+] = 2.51 \times 10^{-8}$

$n(H^+) = cV = 50{,}000 \times 2.51 \times 10^{-8}$

$= 1.26 \times 10^{-3}$

$n(H^+)$ *added* $= 0.1 \times 12.0 = 1.20$

new $[H^+] = n/V = (1.20 + 1.26 \times 10^{-3})/50{,}000$

new $[H^+] = 2.40 \times 10^{-5}$

new $pH = 4.62$

(b) The pH did not change as predicted – the pool water must contain a buffer solution.

(c) A weak base such as $NaHCO_3$

$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CO_3^{2-}(aq)$

The buffer should not be harmful to humans or damaging to the pool and its fittings.

2.14

(a) It is deliquescent.

(b) It is not pure – it results from dissolving an approximate amount of gas in water.

2.15

(a) No.

(b) Neutralisation reaction produces an acidic (and soluble) salt NH_4Cl*. This salt will cause the solution to be acidic at the equivalence point.*

Phenolphthalein is not suitable as its colour change is in the basic region (methyl orange would be suitable).

2.16

(a) Phenolphthalein.

(b) $NaOH + CH_3COOH \rightarrow NaCH_3COO + H_2O$

$n(NaOH) = cV = 8.96 \times 10^{-4}$

$n(CH_3COOH)$ *dilute* $= 8.96 \times 10^{-4}$

$n(CH_3COOH)$ *in 250 mL* $= 1.120 \times 10^{-2}$

$m(CH_3COOH)$ *in 250 mL* $= nM$

$= 1.120 \times 10^{-2}$

$= 6.73 \times 10^{-1}\ g$

$$\%\ mass = \frac{6.73 \times 10^{-1}}{15.50} \times \frac{100}{1}$$

$= 4.34\ \%$

(c) $n(CH_3COOH) = n(CH_3COOH)$

in 250 mL dilute in 15.50 mL commercial

$= 1.120 \times 10^{-2}$

$$c(CH_3COOH) = \frac{1.120 \times 10^{-2}}{0.01550}$$

(i) $= 7.23 \times 10^{-1}\ mol\ L^{-1}$ *(ii)* $= 43.4\ g\ L^{-1}$

2.17

(a) $M(H_2C_2O_4.2H_2O) = 126\ g\ mol^{-1}$

$$n(H_2C_2O_4.2H_2O) = \frac{m}{M} = \frac{0.554}{126}$$

$= 4.40 \times 10^{-3}$

$$c(H_2C_2O_4(aq)) = \frac{n}{V} = \frac{4.40 \times 10^{-3}}{0.500}$$

$= 8.79 \times 10^{-3}\ mol\ L^{-1}$

(b) (i) phenolphthalein

(ii) pink → colourless

(iii) $2NaOH(aq) + H_2C_2O_4(aq) \rightarrow 2H_2O(l) + Na_2C_2O_4(aq)$

n(oxalic acid) $= cV$

$= 8.79 \times 10^{-3} \times 0.01965$

$= 1.73 \times 10^{-4}\ mol\ L^{-1}$

$n(NaOH) = 2n(H_2C_2O_4) = 3.45 \times 10^{-4}$

$$c(NaOH) = \frac{n}{V} = \frac{3.45 \times 10^{-4}}{0.0200}$$

$= 1.73 \times 10^{-2}\ mol\ L^{-1}$

(c) (i) phenolphthalein

(ii) pink → colourless

(iii) $n(NaOH) = c \times V$

$= 1.73 \times 10^{-2} \times 0.0200$

$= 3.46 \times 10^{-4}\ mol$

$c(CH_3COOH) = n(NaOH)$

$= 3.46 \times 10^{-4}\ mol$

$$c(CH_3COOH) = \frac{n}{V} = \frac{3.46 \times 10^{-4}}{0.03250}$$

$= 1.06 \times 10^{-2}\ mol\ L^{-1}$

2. Review Questions

1.

(a) True

(b) False. Acetic acid is a weak electrolyte.

(c) True

(d) False. A buffer solution can be a mixture of a weak base and its conjugate acid.

(e) True.

2. Test the electrical conductivity of each solution. Comparatively, the strong electrolyte will be the best conductor, then the weak electrolyte and the non-electrolyte should not conduct.

3.

STRONG	WEAK	NON
Na_2CO_3	NH_3	CH_3CH_2OH
HCl	CH_3COOH	$C_{12}H_{22}O_{11}$
NaCl	SO_2	

4.

(a) $[H^+] = 1.00 \times 10^{-4}$ mol L^{-1}
$[OH^-] = 1.00 \times 10^{-10}$ mol L^{-1}

(b) $[H^+] = 1.00 \times 10^{-10}$ mol L^{-1}
$[OH^-] = 1.00 \times 10^{-4}$ mol L^{-1}

(c) $[H^+] = 3.50 \times 10^{-6}$ mol L^{-1}
$[OH^-] = 2.86 \times 10^{-9}$ mol L^{-1}

(d) $[H^+] = 1.05 \times 10^{-13}$ mol L^{-1}
$[OH^-] = 9.50 \times 10^{-2}$ mol L^{-1}

5. (a) 3 (b) 5 (c) 12.6 (d) 3.52 (e) 9.18

6.

Material	pH	[H⁺] (mol L⁻¹)	[OH⁻] (mol L⁻¹)
vinegar	3.00	1.00×10^{-3}	1.00×10^{-11}
toothpaste	6.80	1.58×10^{-7}	6.30×10^{-8}
oven cleaner	13.5	3.16×10^{-14}	0.316
window cleaner	9.75	1.79×10^{-10}	5.6×10^{-5}

7. $c(HCl) = 3.16 \times 10^{-5}$ mol L^{-1}
$V(HCl) = 0.120$ L
$n(HCl) = 3.795 \times 10^{-6}$

$c(NaOH) = 1.58 \times 10^{-4}$ mol L^{-1}
$V(NaOH) = 0.075$ L
$n(NaOH) = 1.189 \times 10^{-5}$

HCl completely consumed;
n(NaOH) remaining
$= 1.18 \times 10^{-5} - 3.792 \times 10^{-6}$
$= 8.092 \times 10^{-6}$ mol

i.e. $[OH^-] = \dfrac{8.092 \times 10^{-6}}{(0.120 + 0.075)}$
$= 4.15 \times 10^{-5}$ mol L^{-1}

$[H^+] = \dfrac{1.00 \times 10^{-14}}{4.15 \times 10^{-5}}$
$= 2.41 \times 10^{-10}$ mol L^{-1}
pH = 9.62

8. CH_3COOH is a weak acid and will only partially ionise in solution (producing H_3O^+) and so will produce a solution with a higher pH than HNO_3 or HCl which are strong acids.

9.

(a) It will be considered neutral if $[H^+]=[OH^-]$. In this example $[H^+]\ [OH^-] \neq 1 \times 10^{-14}$ – a possible explanation is that the temperature of the solution was not at 25°C

(b) The temperature would be less than 25°C

(c) If neutral $K_w = [H^+]^2 = 2.86 \times 10^{-15}$

(d) For solution temperatures greater than 25°C.

10.

(a) Original pH = 7.8, V = 45,000 L
$[H^+] = 1.58 \times 10^{-8}$ mol L^{-1}
original $n(H^+) = c.V = 1.58 \times 10^{-8} \times 45{,}000 = 7.13 \times 10^{-4}$
m(HCl) added $= 0.900 \times 320 = 288$ g
n(HCl) added = m/M = 288/(1.008 + 35.45) = 7.90
new conc $= \dfrac{n\ old + n\ added}{V\ old + V\ added} = 7.13 \times 10^{-4} + 7.90$
45,000
$c(HCl) = 1.76 \times 10^{-14}$
pH = 3.76

(b) The pool contained a large amount of buffer solution compared to amount of HCl added.

11.

(a) NH_4^+ and NH_3 OH^- and H_2O

(b) HPO_4^{2-} and $H_2PO_4^-$ H_2CO_3 and HCO_3^-

(c) HCO_3^- and H_2CO_3 H_3O^+ and H_2O

(d) CH_3COOH and CH_3COO^-
NH_3 and NH_4^+

12.

Reactants	Salt Formed	Nature of the salt
$HCl + NH_3$	NH_4Cl	acidic
$H_2SO_4 + KOH$	K_2SO_4	slightly basic
CH_3COOH + NaOH	$NaCH_3COO$	basic
$HNO_3 + Mg(OH)_2$	$Mg(NO_3)_2$	neutral
H_3PO_4 + NaOH	Na_3PO_4	basic

13.

(a) acidic: $NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$

(b) neutral

(c) basic: $S^{2-}(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HS^-(aq)$

(d) basic: $CH_3COO^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + CH_3COOH(aq)$

14. $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$ ($Na_2CO_{3(s)} + 2H^+(aq) \rightarrow 2Na^+(aq) + H_2O(l) + CO_{2(g)}$)

The resulting solution is acidic because CO_2 dissolves in water to form solution of the weak acid H_2CO_3

$CO_{2(g)} + H_2O(l) \rightarrow H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$

15.

(a) *Add $H_2SO_4(aq)$ to both: the solution which produced a white precipitate would be the $Ba(OH)_2$.*

(b) *Dissolve both in water and test pH (with an indicator or a meter), the neutral solution would be the NaCl; the slightly basic solution would be the sodium ethanoate.*

(c) *Add $Ba(NO_3)_2(aq)$ to both: a white precipitate will form in the sulfuric acid.*

16. *HCl, NH_4Cl, NaCl, $NaCH_3COO$, NaOH.*

17.

(a) *pH of solution A < 7; hydrolysis of $NH_4^+(aq)$*
$NH_4^+(aq) + H_2O(l) \prod NH_3(aq) + H_3O^+(aq)$
pH of solution B > 7; NH_3 is a weak base
$NH_3(aq) + H_2O(l) \prod NH_4^+(aq) + OH^-(aq)$

(b) *Not expected to separate $[NH_3]$ and $[NH_4^+]$; but their concentrations will be greatest and concentration of H_3O^+ and OH^- will be least.*

(c) *$[NH_3] > [OH^-]$, therefore H^+ ions more likely to collide and react with NH_3.*

(d) *(i) H^+ ions would react with OH^- ions, forward reaction is favoured to partially counteract the reduced $[OH^-]$.*
(ii) The $[OH^-]$ will increase and the reverse reaction will be favoured to partially counteract this change.
In both cases, the pH will remain very close to 9.

(e) *The buffer capacity could be exceeded by adding sufficiently large amounts of H^+ or OH^- ions that the buffer could not counteract.*

18.

(a) *Primary Standard: substance that can be used to produce a pure solution of accurately known concentration.*

(b) *Standardisation: when a solution of known concentration is used to accurately determine the concentration of another solution.*

(c) *End Point: point at which the titration is stopped because the desired colour change is observed.*

(d) *Equivalence Point: point at which stoichiometrically equivalent amounts of reactants have been added to the reaction vessel.*

(e) *Indicator: substance which has a definite colour change when subject to different pH's.*

(f) *Rough Titration: first titration that is done quickly to get an approximate quantity of reactant needed to reach the end point.*

19.

(a) *Should be obtained in a very pure form.*

(b) *Have a known formula.*

(c) *Have a high molar mass.*

(d) *Should not react with air or absorb moisture from the air.*

20. *It is difficult to obtain pure as it is deliquescent, i.e. it absorbs moisture from the air and can form a solution in this moisture.*

21.

Reactant	Salt Produced	Nature of soln at equiv. point	Suitable indicator	Expected colour change
Na_2CO_3 + HCl	NaCl	acidic (due to CO_2)	methyl orange	yellow to red
NH_3 + HCl	NH_4Cl	acidic	methyl orange	yellow to red
NaOH + CH_3COOH	$NaCH_3COO$	basic	phenolph-thalein	pink to colourless

22. *Titration 1: should be a rough titration only. Titration 3: result is outside range of precision of ± 0.10 mL titrations 2, 4 and 5.*

23. *HCl + NH_3: end point will be in acidic region. Methyl orange should be used as an indicator. If phenolphthalein is used then the volume of HCl added will be less as the phenolphthalein will change at a pH of approximately 8 rather than 4.*

24. *Graph indicates an equivalence point in the basic region, indicative of a titration involving a strong base and a weak acid.*

25. *No as it has not changed the number of moles of solution in the conical flask.*

26. *Indicator changes colour more slowly and larger volumes are used which give smaller percentage errors. Burette would not need to be continually refilled.*

27.

(a) $n(\text{conc. } H_2SO_4) = n(\text{dilute } H_2SO_4)$

$c_1V_1 = c_2V_2$

$$V_1 = \frac{c_2V_2}{c_1} = \frac{0.250 \times 2.00}{18.0}$$

$= 0.0278$ L

V_1 (conc. H_2SO_4) = 27.8 mL

(b) V(conc. HNO_3)

$$= \frac{c_2V_2}{c_1} = \frac{0.500 \times 0.100}{14.0} = 0.00357 \text{ L}$$

V(conc. HNO_3) = 3.57 mL

(c) V(conc. HCl)

$$= \frac{c_2V_2}{c_1} = \frac{0.750 \times 0.500}{12.0} = 0.0312 \text{ L}$$

V(conc. HCl) = 31.2 mL

28.

(a) m(battery acid) = D × V
= 1.224 × 2.00 × 10^3 = 2440 g
m(H_2SO_4) = 35.0% of m(battery acid)

$$= 2440 \times \frac{35.0}{100} = 854 \text{ g}$$

$$n(H_2SO_4) = \frac{m}{M} = \frac{854}{98.086} = 8.71 \text{ mol}$$

n(H_2SO_4) per cell = 8.71 ÷ 6 = 1.45 mol

29.

(a) min [H^+] = inv log (–7.8)
= 1.58 × 10^{-8} mol L^{-1}

(b) no. H_3O^+ ions = c × V × 6.022 × 10^{23}
=1.58 × 10^{-8} × 3.50 × 10^4 × 6.022 × 10^{23}
= 3.34 × 10^{20} ions

(c) If pH = 7.2, [H^+] = inv log (–7.2)
= 6.31 × 10^{-8} mol L^{-1}
n(acid) in pool if pH = 7.8 = cV
= 1.58 × 10^{-8} × 3.50 × 10^4 = 5.53 × 10^{-4} mol
n(acid) in pool if pH = 7.2 = cV
= 6.31 × 10^{-8} × 3.50 × 10^4 = 2.21 × 10^{-3} mol
n(HCl) to be added
= 2.21 × 10^{-3} – 5.53 × 10^{-4}
= 1.657 × 10^{-3} mol

(d) $$V(\text{conc. HCl}) = \frac{n}{c} = \frac{1.657 \times 10^{-3}}{12}$$

= 1.38 × 10^{-4} L (0.138 mL)

30. $$n(Mg(OH)_2) = \frac{m}{M} = \frac{30.0}{58.316} = 0.514; \text{ mol}$$

n(OH^-) = 2 × 0.514 = 1.029

$$n(Al(OH)_3) = \frac{m}{M} = \frac{30.0}{78.004} = 0.385; \text{ mol}$$

n(OH^-) = 3 × 0.385 = 1.154 mol
n(OH^-) in 375 mL = 1.029 + 1.154 = 2.18 mol

$$n(OH^-) \text{ in 10.0 mL} = 2.18 \times \frac{10}{375} = 0.0582 \text{ mol}$$

∴ n(HCl) neutralised = n(OH^-) in 10.0 mL
= 0.0582
V(HCl) neutralised

$$= \frac{n}{c} = \frac{0.0582}{\text{inv log }(-0.9)} = 0.462 \text{ L}$$

31. $2NaOH_{(aq)} + MgCl_{2(aq)} \rightarrow$
$2NaCl_{(aq)} + Mg(OH)_{2(s)}$

$$n(NaOH) = \frac{m}{M} = \frac{25.3}{39.998} = 0.633 \text{ mol}$$

$$n(MgCl_2) = \frac{m}{M} = \frac{9.60}{95.2} = 0.101 \text{ mol}$$
(Limiting Reagent)
n(OH^-) consumed = 2n($MgCl_2$) = 0.202 mol

(a) n(OH^-) remaining in solution
= 0.633 – 0.202 = 0.431 mol
c (OH^-) remaining in solution

$$= \frac{n}{V} = \frac{0.431}{8.45} = 0.0510 \text{ mol L}^{-1}$$

(b) $$c(H^+) = \frac{1.00 \times 10^{-14}}{c(OH^-)} = \frac{1.00 \times 10^{-14}}{0.0510}$$

= 1.96 × 10^{-13} mol L^{-1}

(c) pH = –log [H^+] = 12.7

32.

(a) $2HCl + Na_2CO_3 \rightarrow 2NaCl + CO_2 + H_2O$

(b) n(Na_2CO_3) = cV = 0.997 × 0.0200
= 1.994 × 10^{-3} mol

(c) average V(HCl) =
(titration 2 + titration 3 + titration 4) ÷ 3
= 41.4 mL

(d) n(HCl) = 2n(Na_2CO_3) = 3.988 × 10^{-3} mol

$$c(HCl) = \frac{n}{V} = \frac{3.99 \times 10^{-3}}{0.0414}$$

=0.0963 mol L^{-1}

33.

(a) $NaOH + HCl \rightarrow NaCl + H_2O$
n(HCl) = cV = 0.107 × 0.0298
n(HCl) = 3.189 × 10^{-3} mol
n(NaOH) = n(HCl) = 3.189 × 10^{-3} mol

$$c(\text{dilute NaOH}) = \frac{n}{V} = \frac{3.189 \times 10^{-3}}{0.0200}$$

= 0.159 mol L^{-1}

(b) (Oven cleaner was diluted twice: in steps II and III)
$n(NaOH)$ in 250 mL of dilute solution from step III
$= cV = 0.159 \times 0.250$
$n(NaOH)$ in 250 mL from step III
$= 0.0399$ mol
$\therefore n(NaOH)$ in 24.0 mL from step II
$= 0.0399$ mol

$c(NaOH)$ from step II $= \frac{0.0399}{0.0240}$
$= 1.66$ mol L^{-1}
$\therefore n(NaOH)$ in all of solution in step II
$= cV = 1.66 \times 0.250 = 0.415$ mol
$m(NaOH)$ in all of solution in step II
$= nM = 0.415 \times 39.998 = 16.6$ g
% NaOH in drain cleaner

$$= \frac{16.6}{25.0} \times \frac{100}{1} = 66.4\% \ (w/w)$$

34. $H_2SO_4 + Na_2CO_3 \rightarrow Na_2SO_4 + CO_2 + H_2O$
$n(Na_2CO_3) = cV = 0.0939 \times 0.025 = 2.35 \times 10^{-3}$
$\therefore n(\text{dilute } H_2SO_4) = n(Na_2CO_3) = 2.35 \times 10^{-3}$
$c(\text{dilute } H_2SO_4) = \frac{n}{V} = \frac{2.35 \times 10^{-3}}{0.0247}$
$= 0.0950$ mol L^{-1}
$n(\text{dilute } H_2SO_4)$ in 1.00 L $= cV$
$= 0.0950 \times 1.00 = 0.0950$ mol
$\therefore n(\text{conc. } H_2SO_4)$ in 20.0 mL
$= n(\text{dilute } H_2SO_4)$ in 1.00 L
$= 0.0950$ mol
$c(\text{battery acid}) = \frac{n}{V} = \frac{0.0950}{0.0200}$
$= 4.75$ mol L^{-1}

35. At equivalence point the solution is neutral
i.e. $[H^+] = 1.00 \times 10^{-7}$ mol L^{-1}
$V(\text{solution}) = 0.0249 + 0.0200 = 0.0449$ L
$\therefore n(H^+)$ at equivalence point $= cV$
$= 1.00\times 10^{-7} \times 0.0449 = 4.49 \times 10^{-9}$ mol
$n(H^+)$ in 1 drop $= cV = 0.100 \times 0.0001$
$= 1.00\times 10^{-5}$ mol
$\therefore n(H^+)$ in solution after 1 drop added
$= 4.49 \times 10^{-9} + 1.00\times 10^{-5} = 1.00\times 10^{-5}$ mol

$$c(H^+) = \frac{n}{V} = \frac{1.00 \times 10^{-5}}{0.0449}$$

$= 2.23 \times 10^{-4}$ mol L^{-1}
new pH $= -\log(2.23\times 10^{-4}) = 3.65$
$\therefore$ change in pH $= 7.00 - 3.65 = 3.35$

For the Experts

36.
(a) $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$
(b) $n(HCl) = cV = 0.136 \times 0.0226$
$= 3.07 \times 10^{-3}$ mol
(c) $n(Na_2CO_3)$ in 20 mL = 1/2$n(HCl)$
$= 1.54 \times 10^{-3}$ mol
(d) $n(Na_2CO_3)$ in 500 mL of solution

$$= \frac{500}{20} \times 1.54 \times 10^{-3} = 3.84 \times 10^{-2} \text{ mol}$$

$m(Na_2CO_3)$ in 500 mL of solution
$= nM = 3.84 \times 10^{-2} \times 105.99$
$= 4.07$ g
$\therefore m(H_2O)$ in $Na_2CO_3.xH_2O$
$= m(Na_2CO_3.xH_2O) - m(Na_2CO_3)$
$= 10.96 - 4.07 = 6.89$ g
(e) $n(H_2O)$ in $Na_2CO_3.xH_2O$

$$= \frac{6.89}{18.016} = 0.382 \rightarrow \frac{n(H_2O)}{n(Na_2CO_3)} = \frac{0.382}{3.84 \times 10^{-2}} \text{ mol}$$

i.e. $n(H_2O) = 10 \times n(Na_2CO_3)$
$\therefore$ correct formula $= Na_2CO_3.10H_2O$

CHP 3: OXIDATION AND REDUCTION

Chapter Questions

3.1
(a) $Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$
(b) Mg (c) Mg (d) Cl_2

3.2 True: oxidant removes electrons from reductant, e.g. $2Fe + O_2 \rightarrow 2FeO$
O_2 removes electrons from Fe to form O^{2-} and Fe^{2+}.

3.3
(a) (+6) (-2) (b) (+6) (-2)
(c) (+5) (-2) (d) (-3) (+1) (-1)
(e) (+1) (+4) (-2) (f) (+2) (+4) (-2)

3.4
(a) Redox (b) Not Redox
(c) Not Redox (d) Redox

3.5
(a) oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
reduction: $2H^+(aq) + 2e^- \rightarrow H_2(g)$
(b) oxidation: $Mg(s) \rightarrow Mg^{2+}(s) + 2e^-$
reduction: $S(s) + 2e^- \rightarrow S^{2-}(s)$

3.6
(a) $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$
(b) $H_2C_2O_4(aq) \rightarrow 2CO_2(g) + 2H^+(aq) + 2e^-$
(c) $CH_3CH_2OH(l) \rightarrow CH_3CHO(l) + 2H^+(aq) + 2e^-$

3.7
(a) $(MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)) \times 2$
$(H_2S(g) \rightarrow S(s) + 2H^+(aq) + 2e^-) \times 5$
$2MnO_4^-(aq) + 5H_2S(g) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5S(s) + 8H_2O(l)$

(b) $ClO^- + 2H^+ + 2e^- \rightarrow Cl^- + H_2O$
$SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$
$ClO^-(aq) + SO_2(g) + H_2O(l) \rightarrow$
$Cl^-(aq) + SO_4^{2-}(aq) + 2H^+(aq)$

3.8

(a) $5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightarrow$
$5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$

(b) $Sn^{2+}(aq) + 2H^+(aq) + OCl^-(aq) \rightarrow$
$Cl^-(aq) + Sn^{4+}(aq) + H_2O(l)$

3.9

$2ClO_3^- + 12H^+ + 10e^- \rightarrow Cl_2 + 6H_2O$
$(ClO_3^- + H_2O \rightarrow ClO_4^- + 2H^+ + 2e^-) \times 5$
$7ClO_3^-(aq)+2H^+(aq) \rightarrow Cl_2(g)+5ClO_4^-(aq)+H_2O(l)$

3.10

$4OH^- + Cl_2 \rightarrow 2OCl^- + 2e^-$
$Cl_2 + 2e^- \rightarrow 2Cl^-$
$4OH^- + 2Cl_2 \rightarrow 2Cl^-(aq)+2OCl^-(aq)+2H_2O(l)$

3.11

$(Cu \rightarrow Cu^{2+} + 2e^-) \times 3$ −0.34 V
$(NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O) \times 2$ +0.96 V
$2NO_3^- + 3Cu + 8H^+ \rightarrow 3Cu^{2+} + 2NO + 4H_2O$ +0.62 V

3.12

$Fe \rightarrow Fe^{2+} + 2e^-$ $E° = +0.44$ V
$Cu^{2+} + 2e^- \rightarrow Cu$ $E° = +0.34$ V
$Cu^{2+} + Fe \rightarrow Fe^{2+} + Cu$ $E°_{TOT} = +0.78$ V
Not feasible → the steel tank will react. Alloying alters likely reactions.

3.13

(a) $Fe \rightarrow Fe^{2+} + 2e^-$ +0.44 V
$Zn^{2+} + 2e^- \rightarrow Zn$ −0.76 V
No reaction −0.32 V

(b) $Cu \rightarrow Cu^{2+} + 2e^-$ +0.44 V
$NO_3^- + 4H+ + 3e^- \rightarrow NO + 2H_2O$ +0.96 V
+1.40 V
Reaction will occur.

(c) $Br_2 + 2e^- \rightarrow 2Br^-(aq)$ +1.08 V
$2Cl^- \rightarrow Cl_2 + 2e^-$ −1.36 V
Reaction will not occur. −0.32 V

(d) $Cl_2 + 2e^- \rightarrow 2Cl^-$ +1.36 V
$H_2S \rightarrow S + 2H^+ + 2e^-$ −0.17 V
Reaction does occur. +1.25 V

(e) $2I^- \rightarrow I_2 + 2e^-$ −0.54 V
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ +1.51 V
Reaction does occur. +0.97 V

(f) $Ca \rightarrow Ca^{2+} + 2e^-$ +2.87 V
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ −0.83 V
Reaction does occur. +2.04 V

(g) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ +1.51 V
$Fe^{2+} \rightarrow Fe^{3+} + 2e^-$ −0.77 V
Reaction does occur. +0.74 V

3.14

Common Oxidising Agents	Name	Reduction Half Equation	E°
Cl_2	chlorine	$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36V
MnO_4^-	permanganate ion	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	+1.51V
$Cr_2O_7^{2-}$	dichromate ion	$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	+1.36V
ClO^-	hypochlorite ion	$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$	+0.90V
H^+	hydrogen ion	$2H^+ + 2e^- \rightarrow H_2$	0.00V

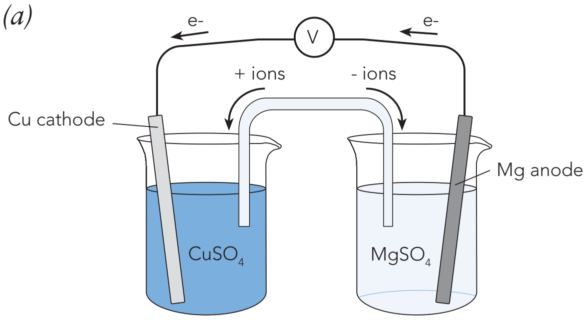
3.15

Common Reducing Agents	Name	Reduction Half Equation	E°
Mg	magnesium	$Mg \rightarrow Mg^{2+} + 2e^-$	+2.36
Zn	zinc	$Zn \rightarrow Zn^{2+} + 2e^-$	+0.76V
$C_2O_4^{2-}$	oxalate ion	$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$	+0.43V
H_2	hydrogen gas	$H_2 \rightarrow 2H^+ + 2e^-$	0.00V
Fe^{2+}	iron (II) ion	$Fe^{2+} \rightarrow Fe^{3+} + e^-$	-0.77V

3.16
(a) $Zn \rightarrow Zn^{2+} + 2e^-$
(b) (i) *Zn strip will be blackened, dull salmon pink solid growing on it.*
(ii) *Solution loses blue colour.*
(c) (i) Cu^{2+}
(ii) Zn

3.17
(a) *To allow a flow of ions to complete the circuit.*
(b) (i) Zn^{2+}, NH_4^+ *ions move away from Zn/ Zn^{2+} half cell.*
(ii) SO_4^{2-}, NO_3^- *ions move away from Cu/ Cu^{2+} half cell.*
(c) • *slowly dissolves*
• *slowly gains mass*
• *no change*
• *loses blue colour*

3.18
(a)



(b) $Mg \rightarrow Mg^{2+} + 2e^-$
$Cu^{2+} + 2e^- \rightarrow Cu$
$Mg(s) + Cu^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cu(s)$
(c) 2.71 V
(d) (i) *Chemical equilibrium has been reached.*
(ii) *Reactants are consumed.*

Dry Cell – Overall Reaction

$2MnO_2(s) + Zn(s) + 2H^+(aq) \rightarrow Mn_2O_3(s) + Zn^{2+}(aq) + H_2O(l)$

3.19
(a) $NH_4^+(aq) \rightarrow NH_3(aq) + H^+(aq)$
(b) *Once it has been discharged it cannot be recharged.*
(c) *Advantages: cheap, transportable.*
Disadvantages: relatively short life, cheap casing can dissolve, hence allowing leakage.

3.20
$Zn \rightarrow Zn^{2+} + 2e^-$
$Ag_2O + H_2O + 2e^- \rightarrow 2Ag(s) + 2OH^-(aq)$

Lead-Acid Accumulator – Overall Reaction for Discharge

$Pb + PbO_2 + 2SO_4^{2-} + 4H^+ \rightarrow 2PbSO_4 + 2H_2O$

3.21
$2PbSO_4(s) + 2H_2O(l) \rightarrow Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq)$

3.22
(i) *Electrodes are same substance – no reaction to produce transfer of e^-.*
(ii) *Density of electrolyte decreases.*

Fuel Cell – Overall Reaction

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

3.23
(a) 1.23 V
(b) $H_2 + 2OH^- \rightarrow 2H_2O + 2e^-$
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
(c) $2H_2 + O_2 \rightarrow 2H_2O$
(d) *Same reaction but hydrogen combustion is explosive.*

3.24
$CH_4 + 2H_2O \rightarrow CO_2 + 8H^+ + 8e^-$
$(O_2 + 2H_2O + 4e^- \rightarrow 2H_2O) \times 2$
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

3.25
(a) *Possible cathode reactions*
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ -0.26 V
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ -0.83 V

Possible anode reactions
$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ -0.34 V
$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ -1.36 V
$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ -1.23 V

Overall reaction
$Ni^{2+}(aq) + Cu(s) \rightarrow Ni(s) + Cu^{2+}(aq)$

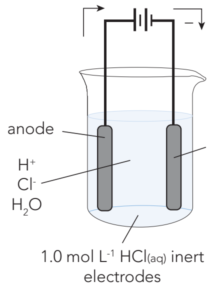
(b) *Concentration of Ni^{+2} ions in solution will decrease while that of Cu^{+2} ions will increase. As this occurs Cu^{+2} ions will be preferentially reduced at the cathode (more positive E° than Ni^{+2} or H_2O)*

3.26
(a) *Aqueous NaCl (1.0 mol L^{-1})*
anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$
Products are O_2 and H_2.
(b) *Aqueous NaCl (concentrated)*
anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$
cathode: $H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

Products are Cl_2, H_2 and NaOH solution.

3.27

(a)



(b) anode:

$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$	-1.36 V
$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$	-1.23 V

cathode:

$2H^+(aq) + 2e^-$	0.00 V
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^+(aq)$	-0.83 V

Overall reaction

$2H_2O(l) \rightarrow O_2(g) + 2H_2(g)$

3.28

(a) Molten NaCl
anode: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$
cathode: $Na^+(l) + e^- \rightarrow Na(l)$
Products are Cl_2 and Na.

(a) Molten PbI_2
anode: $2I^-(l) \rightarrow I_2(l)$
cathode: $Pb^{2+}(l)$ + 2e- $\rightarrow$ Pb
Products are I_2 and Pb.

3.29

anode: $Ag(s) \rightarrow Ag^+(aq)$ + e-
cathode: $Ag^+(aq)$ + e- $\rightarrow Ag(s)$
Overall reaction
$Ag(s)$ anode $\rightarrow Ag(s)$ cathode

3.30

The equilibrium reaction keeps the concentration of Ag^+ ions in solution low but fairly constant. As Ag^+ ions are deposited at the cathode more of the $Ag(CN)_2^-$ dissociates to maintain equilibrium. This keeps the Ag^+ ions in solution fairly constant.

3.31

(a) anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$
Overall reaction

(b) (i) E° for their oxidation is much higher than Cu.
(ii) These valuable metals are recovered from the anode mud for profit.

(c) (i) Only a small voltage is used which is not high enough to reduce these ions.
(ii) The Pb^{+2} ions react with the sulphate ions and are recovered as lead sulphate residue. The electrolyte solution is periodically replaced as the Ni^{+2} ion concentration increases. The Ni^{+2} ions are removed as nickel sulphate solution.

3.32 Au, Ag, Cu, Pb, Fe, Al, Mg, Na

3. Review Questions

1.

(a) True

(b) True

(c) False. Standard reduction potentials (E0 values) are measured using a hydrogen half-cell as a reference cell.

(d) False. The salt bridge in a simple Daniell electrochemical cell allows ions to migrate through it so that each half-cell remains electrically neutral

(e) True.

2. (a) +2 (b) +6 (c) -1 (d) +3
(e) +1 (f) +3 (g) +2

3. (a) H (b) Na (c) Cl
(d) nil (e) C

4. (a) O (b) N (c) O (d) nil

5.

Oxidising Agents	Reducing Agents
oxygen gas, chlorine gas, acidified potassium permanganate, concentrated sulfuric acid, potassium dichromate (acidified), concentrated nitric acid, hydronium ion	zinc, hydrogen gas, carbon, iron (II) ions oxalic acid

6.

Equation	Colour of Reactants	Colour of Products
$Br_2(aq) + 2I^-(aq) \rightarrow 2Br^-(aq) + I^2(aq)$	straw brown	red brown
$2Br^-(aq) + Cl_2(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$	colourless	straw brown
$Cl_2(aq) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I^2(aq)$	colourless	red brown
$2Ag^+(aq) + Cu(s) \rightarrow 2Ag(s) + Cu^{2+}(aq)$	colourless solution, reddish metal	light blue solution, silvery black crystals
$Mg(s) + Cu^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cu(s)$	blue solution	soln loses colour, brown black crystals grow

7.

(a) $2S_2O_3^{2-}(aq) + I_2(s) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$

(b) $2Br^-(aq) + SO_4^{2-}(aq) + 4H^+(aq) \rightarrow Br_2(l) + SO_2(g) + 2H_2O(l)$

(c) $3Ag_2S(s) + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 6Ag^+(aq) + 3S(s) + 2NO(g) + 4H_2O(l)$

(d) $2CrO_4^{2-}(aq) + 6Cl^-(aq) + 16H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3Cl_2(g) + 8H_2O(l)$

(e) $MnCl_2(s) + Br_2(aq) + 4OH^-(aq) \rightarrow MnO_2(s) + 2Br^-(aq) + 2Cl^-(aq) + 2H_2O(l)$

8.

(a) $Ag(s) + 2H^+(aq) + NO_3^-(aq) \rightarrow Ag^+(aq) + NO_2(g) + H_2O(l)$

(b) $S_{(s)} + Cr_2O_7^{2-}{}_{(aq)} \rightarrow SO_4^{2-}{}_{(aq)} + Cr_2O_{3(s)}$

(c) $3H_2S_{(s)} + 2NO_3^-{}_{(aq)} + 2H^+{}_{(aq)} \rightarrow 3S_{(s)} + 2NO_{(g)} + 4H_2O_{(l)}$

(d) $2ClO^-{}_{(aq)} + 4H^+{}_{(aq)} + 2Cl^-{}_{(aq)} \rightarrow 2Cl_{2\,(g)} + 2H_2O_{(l)}$

(e) $5Fe^{2+}{}_{(aq)} + MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} \rightarrow 5Fe^{3+}{}_{(aq)} + Mn^{2+}{}_{(aq)} + 4H_2O_{(l)}$

(f) $Cr_2O_7^{2-}{}_{(aq)} + 14H^+{}_{(aq)} + 6I^-{}_{(aq)} \rightarrow 2Cr^{3+}{}_{(aq)} + 3I_{2(aq)} + 7H_2O_{(l)}$

(g) $2MnO_4^-{}_{(aq)} + 5H_2O_{2(aq)} + 6H^+{}_{(aq)} \rightarrow 2Mn^{2+}{}_{(aq)} + 5O_{2(g)} + 8H_2O_{(l)}$

9. When an element is simultaneously oxidised and reduced, disproportionation is said to occur, e.g.

$H_2O_{2(aq)} + 2H^+{}_{(aq)} + 2e^- \rightarrow 2H_2O_{2\,(l)}$

$H_2O_{2(aq)} \rightarrow O_{2(g)} + 2H^+{}_{(aq)} + 2e^-$

$2H_2O_2 \rightarrow O_2 + 2H_2O$

(-1) (0) (-2)

i.e. the oxygen in hydrogen peroxide has been oxidised to form O_2 and reduced in forming H_2O.

10. May be used as bleaches or for sterilising swimming pool water and drinking water

11. Chlorine, gold, silver, hydrogen, lead, calcium.

12. Br^- and I^-.

13. K^+, Cr^{3+}, Br_2, $Cr_2O_7^{2-}$, Au^{3+}, MnO_4^-, H_2O_2.

14.

(a) All oxidising agents above $Sn^{4+} + 2e^- \rightarrow Sn^{2+}$ in a table of a standard reduction potentials.

(b) All reducing agents below $Fe^{2+} + Fe^{3+} \rightarrow e^-$ in a table of standard reduction potentials.

(c) Acidified MnO_4^- (only just), HClO, H_2O_2 or F_2 (by use of a table of standard reduction potentials).

(d) Acidified NO_3^-, Hg^{2+}, Br_2.

15. A galvanic cell may be established and the Al oxidises causing the rivets to break.

16.

(a) The standard electrode potential is the potential acquired if a chemical (eg. $Al_{(s)}$) is immersed in a solution of its ions (e.g. Al^{3+} ions) of concentration 1.00 mol L^{-1} at 25°C. E° values are a comparison between the standard reduction potential of a substance and the H_2/H^+ reference cell.

(b) No – if reduction is occurring, oxidation must occur simultaneously.

(c) Mg, Na.

17.

(a) No reaction.

(b) $(Cu^+ \rightarrow Cu^{2+} + e^-) \times 2$

$I_2 + 2e^- \rightarrow 2I^-$

$2Cu^+{}_{(aq)} + I_{2\,(aq)} \rightarrow 2Cu^{2+}{}_{(aq)} + 2I^-{}_{(aq)}$

(c) $(MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O) \times 2$

$(H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-) \times 5$

$2MnO_4^-{}_{(aq)} + 5H_2O_2 + 6H^+{}_{(aq)} \rightarrow 2Mn^{2+}{}_{(aq)} + 5O_{2\,(g)} + 8H_2O_{(l)}$

(d) $Cu \rightarrow Cu^{2+} + 2e^-$

$(NO_3^- + 2H^+ + e^- \rightarrow NO_{2(g)} + H_2O_{(l)}) \times 2$

$Cu_{(s)} + 2NO_3^-{}_{(aq)} + 4H^+{}_{(aq)} \rightarrow Cu^{2+}{}_{(aq)} + 2NO_{2(g)} + 2H_2O_{(l)}$

(e) $(Na \rightarrow Na^+ + e^-) \times 2$

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

$2Na_{(s)} + 2H_2O_{(l)} \rightarrow 2Na^+{}_{(aq)} + H_{2\,(g)} + 2OH^-{}_{(aq)}$

(f) $(MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O) \times 2$

$(2Cl^- + Cl_2 + 2e^-) \times 5$

$2MnO_4^-{}_{(aq)} + 10Cl^-{}_{(aq)} + 16H^+{}_{(aq)} \rightarrow 2Mn^{2+}{}_{(aq)} + 5Cl_{2(g)} + 8H_2O_{(l)}$

(g) No reaction.

(h) Boiling removes O_2; iron will not corrode.

$Fe + Fe^{2+} \rightarrow 2e^-$ +0.44 V

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ –0.41 V

+0.03 V potential, will occur very slowly.

18. They do initially – but once an oxide layer is formed it will protect the metal beneath from further oxidation. This oxide layer is a coherent coating.

19. (a) oxidation (b) reduction (c) negative (d) positive

20.

(a) From Mg → Pb (b) electrons

(c) ions (Mg^{2+}, Pb^{2+}, NO_3^-) (d) KNO_3

(e) $Mg_{(s)} \rightarrow Mg^{2+}{}_{(aq)} + 2e^-$

(f) $Pb^{2+}{}_{(aq)} + 2e^- \rightarrow Pb_{(s)}$ (g) +2.24 V

(h) To complete the circuit by allowing the movement of ions.

21.

(a) Yes

(b) Yes, but no current would flow in the external circuit, reading on meter = 0.

22.

(a) Anode: $Zn_{(s)} \rightarrow Zn^{2+} + 2e^-$ (0.76)
Cathode: $Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$ (0.34)
E° = 1.10 V

(b) Anode: $Fe_{(s)} \rightarrow Fe^{2+} + 2e^-$ (0.44)
Cathode: $Ag^+ + e^- \rightarrow Ag_{(s)}$ (0.80)
E° = 1.24 V

(c) Anode: $Al_{(s)} \rightarrow Al^{3+} + 3e^-$ (1.68)
Cathode: $I_{2\,(aq)} + 2e^- \rightarrow 2I^-$ (0.54)
E° = 2.22 V

(d) Anode: $2Br \rightarrow Br_2 + 2e^-$ (–1.08)
Cathode: $F_{2(g)} + 2e^- \rightarrow 2F^-$ (2.89)
E° = 1.81 V

(e) Anode: $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$ (–0.70)
Cathode: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ (1.51)
$E° = 0.81$ V

23.

Electrochemical Cells	Electrolytic Cells
Spontaneous chemical reaction	Forced chemical reaction
oxidation occurs at the anode	oxidation occurs at the anode
anode is negative	anode is positive
electrical energy is created by a chemical change	a chemical change is caused by electrical energy

24.
(a) $Na^+(l) + e^- \rightarrow Na^+(l)$
$2Cl^-(l) \rightarrow Cl(g) + 2e^-$ min volts = 4.07 V
(b) $Zn^{2+}(l) + 2e^- \rightarrow Zn(l)$
$2Br^-(l) \rightarrow Br_2(g) + 2e^-$ min volts = 1.84 V
(c) $Pb^{2+}(l) + 2e^- \rightarrow Zn(l)$
$2I^-(l) \rightarrow I_2(g) + 2e^-$ min volts = 0.67 V
(d) $K^+(l) + e^- \rightarrow K(l)$
$2F^-(l) \rightarrow F_2(g) + 2e^-$ min volts = 5.83 V

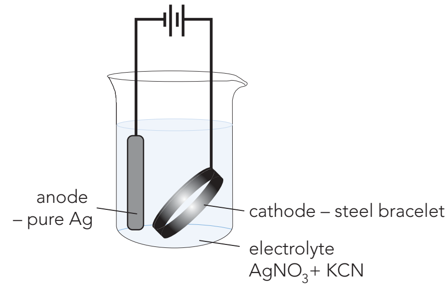
25.
(a) Na^+, Cl^-, H_2O (b) Cl^- and H_2O
(c) H_2O
(d) Na^+ and H_2O; H_2O most likely
(e) $(2H_2O) + 2e- \rightarrow H_2 + 2OH^-) \times 2$
$E° = -.083V$ (-0.41 V at pH=7)
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$
$E° = -1.23V$ (-0.82 V at pH=7)
$2H_2O(l) \rightarrow O_2(g) + 2H_2(g)$

(f) 2.06 V minimum (-1.23 V at pH=7)

26. (c) H_2O is oxidised (d) H_2O is reduced

27.
(a) oxidation: $2I^-(aq) \rightarrow I_2(s) + 2e^-$ $E° = -0.54$ V
reduction: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$ $E° = -0.26$ V
$2I^-(aq) + Ni^{2+}(aq) \rightarrow I_2(s) + Ni(s)$ $E° = -0.80$ V
(b) oxidation: $Pb(s) \rightarrow Pb^{2+} + 2e^-$ $E° = +0.13$ V
reduction: $Pb^{2+} + 2e^- \rightarrow Pb(s)$ $E° = -0.13$ V
$Pb(s) \rightarrow Pb(s)$ $E° = 0.0$ V
Lead is effectively being transferred from the anode to the cathode.Very small positive voltage needed.
(c) oxidation:
$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $E° = -1.23$ V
$(2H^+(aq) + 2e^- \rightarrow H_2) \times 2$ $E° = 0.00$ V
$2H_2O(l) \rightarrow O_2(g) + 2H_2(g)$
(d) anode:
$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ $E° = -0.34$ V
$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E° = -0.83$ V
$Cu^{2+}(aq) + H_2(g) + 2OH^-(aq)$ $E° = -1.17$ V

28. Make the steel the cathode:
$Ag^+(aq) + e^- \rightarrow Ag(s)$
The steel will be coated with Ag.



29. H_2SO_4: $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$
NaOH: $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$

30.
- reduced
- cathode, $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
- iron (II) hydroxide
- $Fe_2O_3.H_2O$ or FeO(OH)

31. The reduction process is:
$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-$
By having an alkaline environment the reverse reaction is favoured and reduction process is less likely to occur.

32.
(a) It coats the iron and stops contact with O_2 and H_2O, hence stopping the iron from corroding.
(b) $Fe \rightarrow Fe^{2+} + 2e^-$, $E° = +0.44$ V
$Sn(s) \rightarrow Sn^{2+} + 2e^-$, $E° = +0.14$ V
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$, $E° = +0.82$ V
Once the Fe is exposed to O_2 and H_2O it will oxidise in preference to the Sn; i.e. the Fe will protect the Sn from oxidation.
(c) $Fe \rightarrow Fe^{2+} + 2e^-$, $E° = +0.44$ V
$Zn \rightarrow Zn^{2+} + 2e^-$, $E° = +0.76$ V
The Zn will oxidise before the Fe, protecting the Fe.

33. The Mg (or Zn) has a higher oxidation potential than the Fe and so will be oxidised before the Fe.

34. Add coating of oil: prevents O_2 and H_2O coming in contact with the Fe and so reduces the likelihood of corrosion.
Clean drain holes: stops H_2O build up which could promote rusting.

35.
(a) Oxidation occurs at the anode; by making the pipe the cathode the likelihood of it corroding is reduced.
(b) The metals that are connected as the anode will oxidise and need replacement at some stage.

36. *By the oxidation of C and CO_2.*

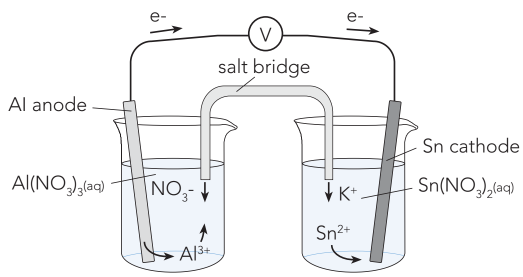
$C(s) + O_2(g) \rightarrow CO_2(g)$

$C(s) + CO_2(g) \rightarrow 2CO(g)$

(b) $Fe_2O_3(s) + 3CO_2(g) \rightarrow 2Fe(l) + 3CO_2(g)$

For the Experts

37. *(a), (d)*



(b) *Anode:* $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$

Cathode: $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$

(c) $E° = +1.54$ V

(d) *See diagram at (a).*

(e)

- *The concentration of the reactant ions in solution will have reduced.*
- *The electrode surfaces become pitted or coated and reduce reaction rate.*

(f) *The Sn electrode would have gained mass as the Sn^{2+} ions form $Sn(s)$ on its surface.*

CHP 4: ORGANIC CHEMISTRY

Chapter Questions

4.1 (a) *alkene (=)* (b) *alkene (=)*

(c) *-oic acid(-COOH)* (d) *halide (-Cl)*

(e) *ester* $\overset{O}{\overset{\|}{-C-O-}}$ (f) *ketone* $\overset{O}{\overset{\|}{-C-}}$

(g) *secondary alcohol (–OH)*

(h) *amine* $(-NH_2)$

4.2

3	propene	propyl
4	1-butene	butyl
5	2-pentene	pentyl
6	1-hexene	hexyl
7	3-heptene	heptyl
8	3-octene	octyl

4.3

(a) *butane*

(b) *but-1-ene*

(c) *chloromethane*

(d) *3-methylbut-1-ene*

(e) *4-ethyl-2-methylheptane*

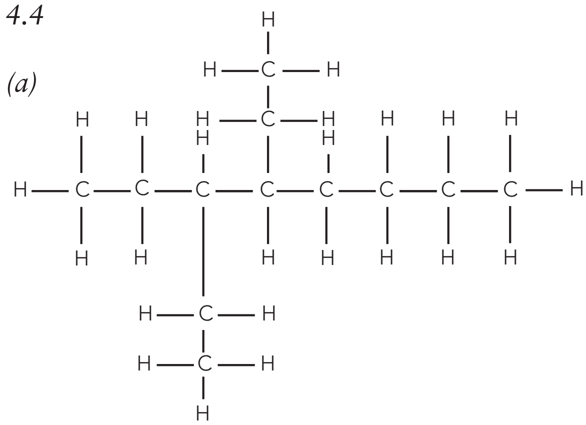
(f) *3-methylpentane*

(g) *1,2-difluoro-2-methylhex-3-ene*

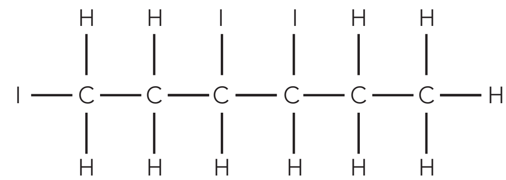
(h) *4-chloro-1,3,4-trifluorobut-1-ene*

4.4

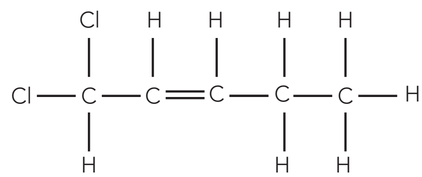
(a)



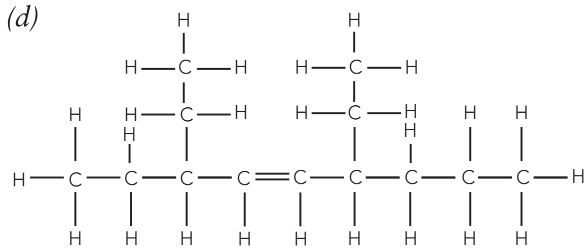
(b)



(c)



(d)



4.5

(a) *incorrect numbering – should be but-2-ene*

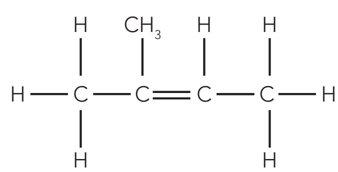
(b) *longest chain is butane not propene*

(c) *incorrect numbering – should be pent-1-ene*

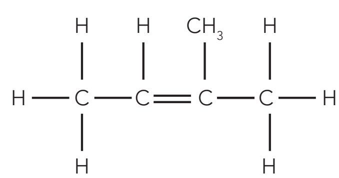
(d) *incorrect numbering – should be 2,3-dimethylpent-1-ene*

4.6

(a)

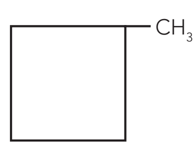


(b)

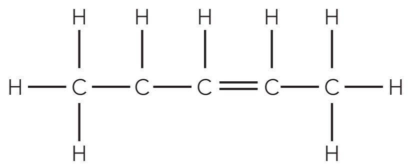


Not an isomer – incorrectly numbered – same as (a).

(c)



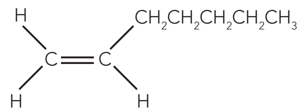
(d)



Wrong name - pent-2-ene - so same as Isomer 2.

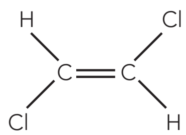
4.7 (a) cis-*3-chlorohex-3-ene*
(b) cis-*2,3-dichlorobut-2-ene*
(c) trans-*1,4-dichlorobut-2-ene*
(d) cis-*1,2-dibromobut-1-ene*

4.8
(a)

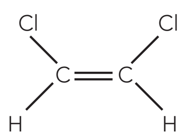


Not a geometric isomer.

(b)

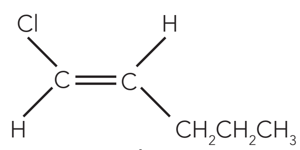


trans

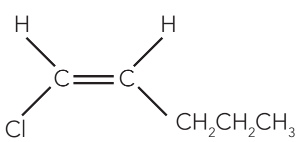


cis

(c)



trans

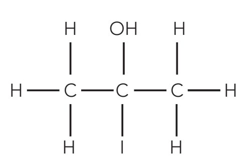


cis

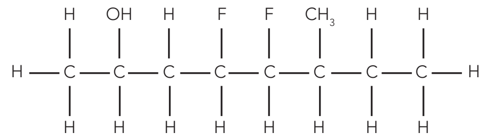
4.9
(a) *3-methylpentan-1-ol*
(b) *5-bromo-1,1,1-trifluoro-3,4-dimethylpentan-2-ol*

4.10
(a) *heptan-2-ol*
(b) *3-chloro-1,1-diiodopentan-2-ol*
(c) *5,5,5-trichloro-3-methylpentan-1-ol*
(d) *2-chloro-2,3-dimethylbutan-1-ol*

4.11
(a)



(b)



4.12
(a) $(CH_3CH_2CH_2CH_2OH \rightarrow$
$CH_3CH_2CH_2C\overset{O}{\underset{H}{\lessgtr}} + 2H^+ + 2e^-) \times 3$
$Cr_2O_7 + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$3CH_3CH_2CH_2CH_2OH + Cr_2O_7^{2-} + 8H^+ \rightarrow$
$3CH_3CH_2CH_2C\overset{O}{\underset{H}{\lessgtr}} + 7H_2O + 2Cr^{3+}$

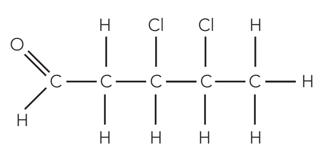
(b) $(CH_3CH_2\overset{OH}{\overset{|}{C}}HCH_2CH_3 \rightarrow$

$CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3 + 2H^+ + 2e^-) \times 5$
$(MnO_4^- + 8H^+ + 5e^- \rightarrow$
$Mn^{2+} + 4H_2O) \times 2$
$5CH_3CH_2\overset{OH}{\overset{\|}{C}}CH_2CH_3 + 2MnO_4^- + 6H^+ \rightarrow$
$5CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3 + 2Mn^{2+} + 8H_2O$

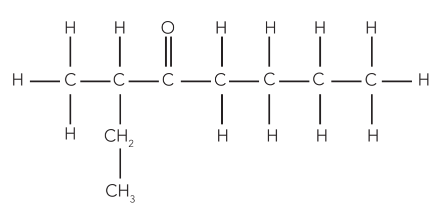
(c) $C_4H_{10}O + 6O_2 \rightarrow 4CO_2 + 5H_2O$

4.13
(a) *3,5-dibromo-5-iodopentanal*
(b) *3,3-dimethylbutanone*
(c) *3,3,3-trichloropropanoic acid*
(d) *3-chloro-3-methylbutanal*
(e) *4,4,4-trifluoro-3,3-diiodobutanone*
(f) *3-methylheptanal*

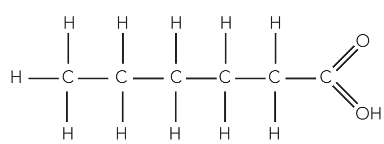
4.14
(a)



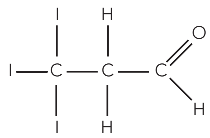
(b)



(c)

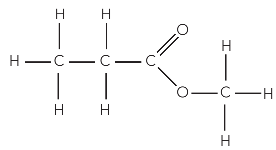


(d)

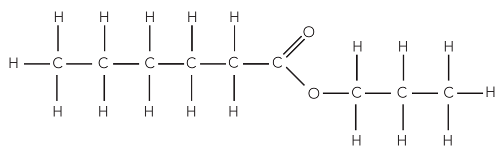


4.15

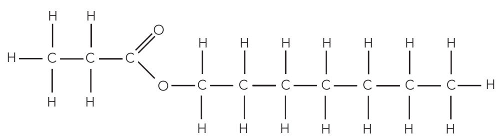
(a) methyl propanoate



(b) propyl hexanoate



(c) heptyl ethanoate



4.16

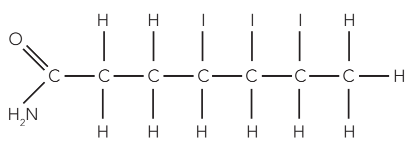
(a) ethanol + propanoic acid
(b) 1-octanol + butanoic acid
(c) 1-propanol + methanoic acid

4.17

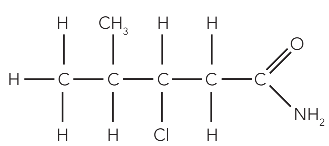
(a) 7,7,7-trifluoro-3-methylheptanamide
(b) 2,5-dibromohexanamide

4.18

(a)



(b)



4.19

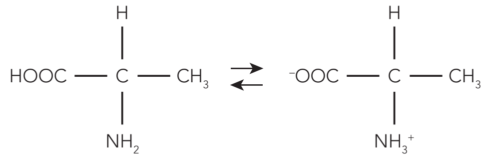
(a) 2-methylpentan-1-amine
(b) 2,5-dichloro-3,4-dimethylhexan-1-amine

4.20

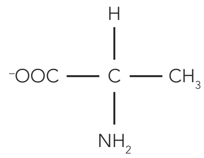
As the R chain of alanine is a methyl group, alanine would be non-polar and neutral.

4.21

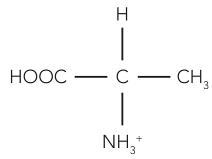
(a)



(b)



(c)

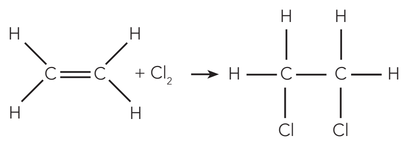


4.22

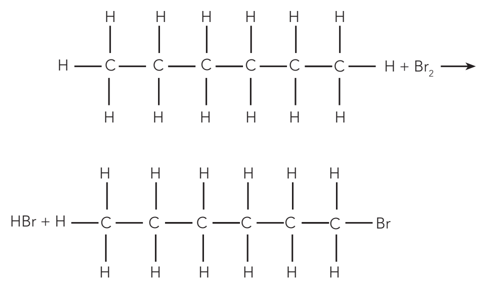
Isoleucine would have the more hydrophobic side chain as it has a larger hydrocarbon.

4.23

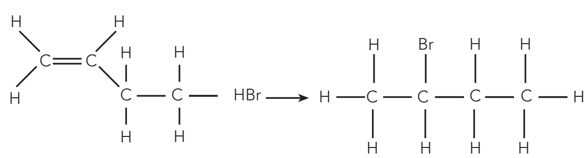
(a)



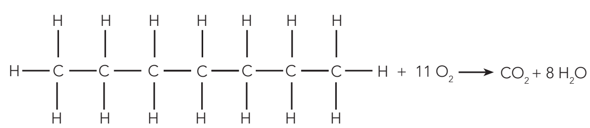
(b)



(c)

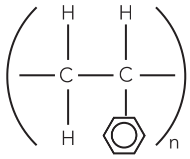


(d)



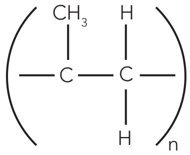
4.24

(a)



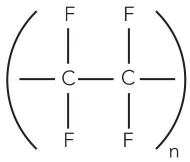
polymer = polystyrene

(c)

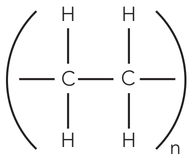


polymer = polypropene

(b)



(d)



polymer = polyethene or polythene

4.25 *Four monomer units are drawn.*

4.26

(a) *No because the NH_2 group is not attached to the alpha carbon*

(b) *The sequence of alpha amino acids is the primary structure while the effect of the dispersion forces is the tertiary structure.*

4.27

Motor oil is non-polar - use a non-polar solvent, such as petrol, to dissolve it. Use a detergent to clean up residue.

4.28

Methylated spirits is polar and so will not be a very good solvent for non-polar materials. Tends not to leave streaks because it evaporates so quickly.

4.29

Func. Group	Gen. Formula	Name ends in	Solubility	Produced by
–Cl –I –Br	R – X	has the prefix matching the alkene	usually low - increases as molecule becomes more polar	substitution –C–C– + Br_2 → –C–C– Br + HBr addition C=C + Br_2 → –C–C–
>C=C< (alkene)	R1–C=C–R_2	–ene	not soluble	not applicable
–NH_2 (primary amine)	R–C–NH_2	–amine	soluble	not applicable
–OH (alcohols)	R–OH	–ol	soluble	hydration of an alkene
–CHO (aldehydes)	R–CHO	–al	soluble	oxidation of a primary alcohol
O ‖ –C– (ketones)	R_1–C–R_2 O	–one	soluble	oxidation of a secondary alcohol
–COOH (carboxylic acids)	R–C	–oic acid	soluble	oxidation of a primary alcohol or of an aldehyde
O ‖ –C–O – (esters)	R–C	–oate	not soluble	alcohol and carboxylic acid

4.30

Primary alcohol + $KMnO_4$	aldehyde or carboxylic acid	loss of purple colour, odour produced
Secondary alcohol + $K_2Cr_2O_7$	ketone	orange solution turns green, odour produced
Tertiary alcohol + $KMnO_4$	NR	NR
Alkane + Cl_2	chloroalkane	faint yellow/ green colour disappears
Alkene + Cl_2	dichloroalkane	as above

4.31

COMBUSTION
Hydrocarbons
Alcohols
Aldehydes, ketones
Esters
Carboxylic acids
$+ O_2 \rightarrow CO_2 + H_2O$

SUBSTITUTION
Alkane + Halogen → haloalkane + hydrogen halide
Alkene + Halogen → dihaloalkane

OXIDATION OF ALCOHOLS

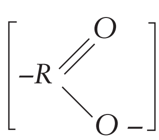
Primary Alcohol + $KMnO_4$ or $K_2Cr_2O_7$ $\xrightarrow{\text{Oxidising agent}}$ aldehyde → carboxylic acid

Secondary Alcohols + $KMnO_4$ or $K_2Cr_2O_7$ (Oxidising agent) → ketone

Tertiary Alcohols + $KMnO_4$ or $K_2Cr_2O_7$ (Oxidising agent) → no reaction

REACTIONS OF ESTERS

IN ACIDIC CONDITIONS:
Ester + Water → carboxylic acid + alcohol

** Ester + Hydroxide →*  *+ alcohol*

** Soap making is an example of the hydrolysis of an ester.*
e.g. CH_2OOCR
|
$CHOOCR$ + 3NaOH → *soap + glycerol*
|
CH_2OOCR

Table 4.3

glucose	$C_6H_{12}O_6$	$C_6H_{12}O_6$	CH_2O
ethyne	CHCH	C_2H_2	CH
benzene	C_6H_6	C_6H_6	CH

4.32

	C	H	O
mass	40.0	6.67	53.3
moles	40.0/12.01 = 3.33	6.67/1.008 = 6.62	53.5/16.00 = 3.33
mole ratio	1	2	1
simple ratio	1	2	1

Empirical formula = CH_2O
EF mass = 30
MF mass = 60
∴ MF mass = 2 × EF mass
∴ MF = 2 × EF = $C_2H_4O_2$

Worked Example 4.4

	C	H	O
mass	2.008	0.337	4.015
moles	2.008/12.01 = 0.167	0.337/1.008 = 0.334	4.015/16.00 = 0.251
mole ratio	1	1.9996	1.5009
simple ratio	2	4	3

EF = $C_2H_4O_3$
EF mass = 76
MF mass = 228
∴ MF = 3 × EF = $C_6H_{12}O_9$

Worked Example 4.5
(a) sample 1 mass of H =
= 0.05093 g
sample 2 mass of S =
= 0.2702 g
∴ mass of O
= 0.6578 – 0.2023 – 0.05093 – 0.2702
= 0.1344 g

	C	H	S	O
mass	0.2023	0.05093	0.2702	0.1344
moles	0.01684	0.05052	0.00842	0.00840
mole ratio	2.005	6.014	1.003	1
simple ratio	2	6	1	1

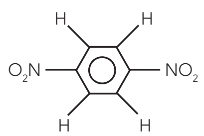
Hence EF = C_2H_6SO

(b) *molecular mass = 78.21 g*
EF mass = 78.14, MF mass = EF mass
MF = C_2H_6SO

Worked Example 4.6

	C	H	N	O
moles	3.571	2.383	1.1906	2.377
mole ratio	3.000	2.001	1	1.996
simple ratio	3	2	1	2

(a) *EF =* $C_3H_2NO_2$
(b) *EF mass = 84*
$\therefore$ *MF = 2 × EF =* $C_6H_4N_2O_4$
(c)

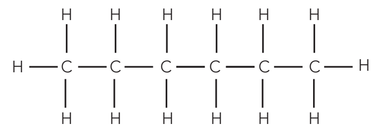


4. Review Questions

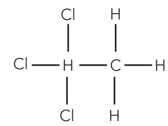
1.
(a) *False. The IUPAC name for* $CH_3COCH_2CCl_3$ *is 4,4,4-trichlorobutanone.*
(b) *True*
(c) *False. Alcohols and aldehydes can be oxidised by acidified potassium permanganate solutions to form carboxylic acids.*
(d) *True*
(e) *False, Cysteine is the only α-amino acid that forms disulfide bridges which affects the secondary structure of the protein.*

2. (a) *pentane*
(b) *3-bromo-1,1,1-triiodopentane*
(c) *but-1-ene*
(d) *ethanamine*
(e) *4-ethylhept-1-ene*
(f) *3,6-dibromo-7,7,8-trifluorooct-2-ene*
(g) *3,3,4-trichlorobutan-1-amine*
(h) *1,4-dichlorobenzene*
(i) trans*-1,2-difluoroethene*
(j) trans*-hex-3-ene*
(k) *propan-1-ol*
(l) *5,5-dichloro-3,3-dimethylheptanal*
(m) *4,4,4-triiodobutanone*
(n) *propan-1-amine*
(o) *2,2,4-trichloropentanal*
(p) *methanal*
(q) *α-amino acid (glycine)*
(r) *butanoic acid*
(s) *8,8,8-trichloro-6-ethyl-5-methyloct-2-ene*
(t) *3-fluorobutanal*
(u) *1-chlorobutanal*
(v) *propyl propanoate*
(w) *methyl butanoate*
(x) *pentyl methanoate*

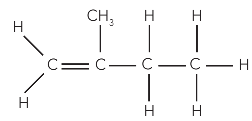
3. (a)



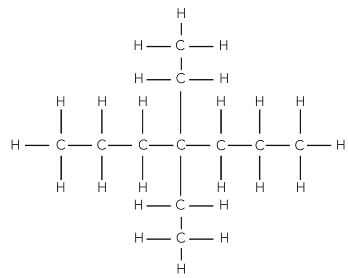
(b)



(c)



(d)



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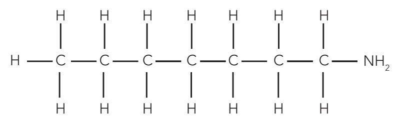
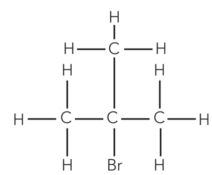


(f)



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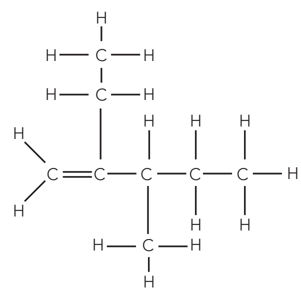

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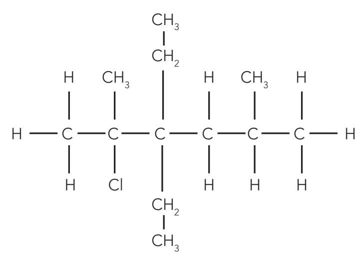
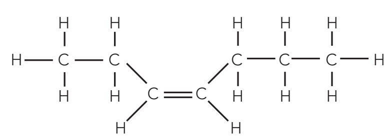


(i)



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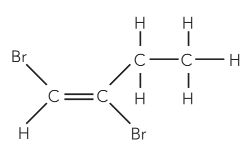
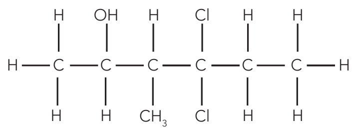
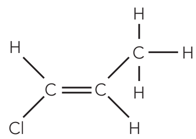


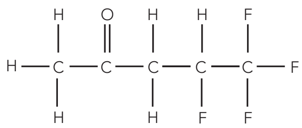
(k)



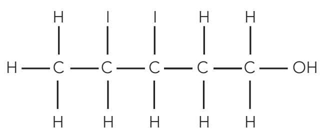
(l)



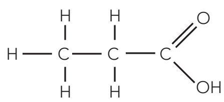
(m)



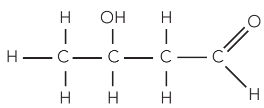
(n)



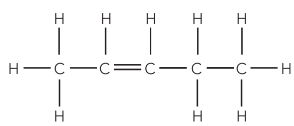
(o)



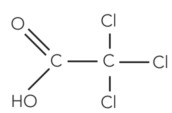
(p)



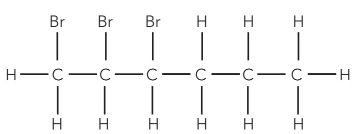
(q)



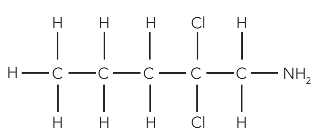
(r)



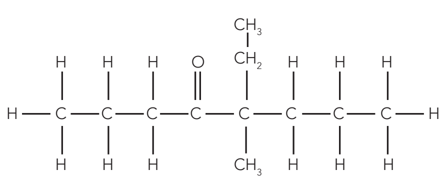
(s)



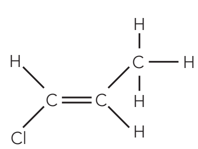
(t)



(u)



(v)



4.

(a) *Add several drops of acidified* $KMnO_4$ *solution to both. The butanal will decolourise the* $KMnO_4$ *while the butanone will not*

(b) *Add several drops of acidified* $KMnO_4$ *solution to both. The butanal will decolourise the* $KMnO_4$ *while the hexane will not (or check solubility in water - butanal is more soluble than hexane).*

(c) *As (c) to (e) above - ethanol decolourises* $KMnO_4$ *while propanone does not.*

(d) *Add a small piece of sodium to both. The sodium reacts more vigorously with 1-butanol than it does with 2-methylpropan-2-ol.*

(f) *Check solubilities, methanol is much more soluble in water than 1-pentanol. (Check boiling points - methanol has a lower boiling point than 1-pentanol.)*

5.

(a) *(i) oxidation*

$(CH_3CH_2OH \rightarrow CH_3CHO + 2H^+ + 2e^-) \times 3$

reduction

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

(ii) nett

$3CH_3CH_2OH + Cr_2O_7^{2-} + 8H^+$
$\rightarrow 3CH_3CHO + 2Cr^{3+} + 7H_2O$

(iii) orange solution turns green when mixed with colourless solution

(b) *(i) oxidation*

$(H_2O + CH_3OH \rightarrow HCOOH + 4H^+ + 4e^-)$
$\times 5$

reduction

$(MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O) \times 4$

(ii) nett

$5CH_3OH + 4MnO_4^- + 12H^+$
$\rightarrow 5HCOOH + 4Mn^{2+} + 11H_2O$

(iii) purple solution becomes colourless on mixing with colourless liquid

(c) *(i) oxidation*

$(CH_3CH(OH)CH_2CH_3 \rightarrow CH_3C(=O)CH_2CH_3 + 2H^+ + 2e^-) \times 5$

reduction

$(MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O) \times 2$

(ii) nett

$5CH_3CH(OH)CH_2CH_3 \rightarrow 2MnO_4^- + 6H^+$

$\rightarrow 5CH_3C(=O)CH_2CH_3 \rightarrow 2Mn^{2+} + 8H_2O$

(iii) purple solution becomes colourless on mixing with colourless liquid

(d) (i) *oxidation*

$(CH_3CH_2CH_2CH_2CHO + H_2O \rightarrow CH_3CH_2CH_2CH_2COOH + 2H^+ + 2e^-) \times 5$

reduction

$(MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O) \times 2$

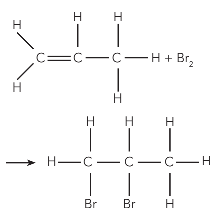
(ii) *nett*

$5CH_3CH_2CH_2CH_2CHO + 2MnO_4^- + 6H^+ \rightarrow 5CH_3CH_2CH_2CH_2COOH + 2Mn^{2+} + 3H_2O$

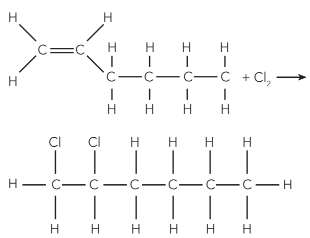
(iii) *purple solution becomes colourless on mixing with colourless liquid*

6. (a) cis-*but-2-ene*
   (b) trans-*1-chorohex-l-ene*
   (c) cis-*1,2-dibromobut-l-ene*
   (d) *1,1-dibromobut-l-ene*

7. (a)

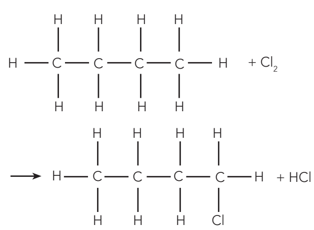


(b)

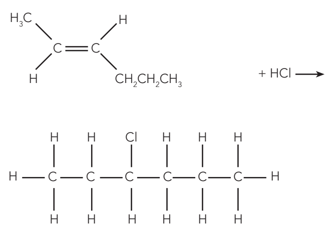


(c) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

(d)



(e)



(f) $2C_8H_{18} + 17O_2 \rightarrow 8CO_2 + 18H_2O$

8. (a) *ester*
   (b) *carboxylic acid*
   (c) *alcohol*
   (d) *alkene*

9. (a) *methyl methanoate*
   (b) *butyl ethanoate*
   (c) *hexyl heptanoate*
   (d) *ethyl pentanoate*

10. (a) $CH_3CH_2CH_2CH_2OH + C_6H_{13}COOH$

$\rightarrow C_6H_{13}C(=O)O-CH_2\,CH_2\,CH_2CH_3$

(b) $CH_3OH + C_4H_9COOH$

$\rightarrow C_4H_9C(=O)O-CH_3$

(c) $CH_3CH_2OH + HCOOH$

$\rightarrow H-C(=O)O-CH_2CH_3$

(d) $CH_3CH_2OH + CH_3COOH$

$\rightarrow CH_3C(=O)O-CH_2CH_3$

11.

(a)

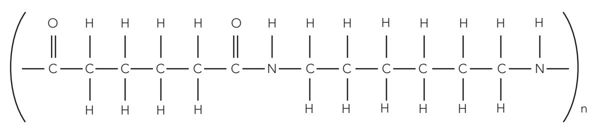
(i) $CH_3CH_2COOCH_3 + H_2O \rightarrow CH_3CH_2COOH + CH_3OH$

(ii) $CH_3CH_2COOCH_3 + OH^- \rightarrow CH_3CH_2COO^- + CH_3OH$

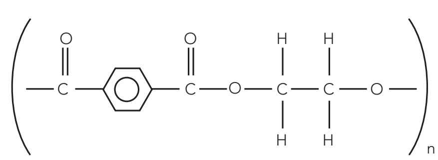
(b) *Soap.*

12.

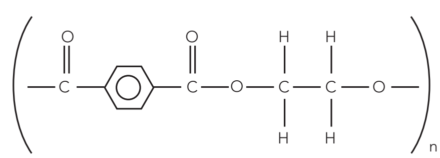
(a) *Nylon "6,6"*



(b) *Terylene*

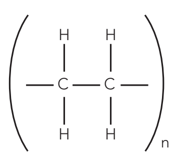


(c) *Dacron*

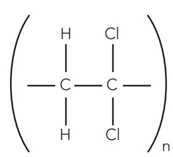


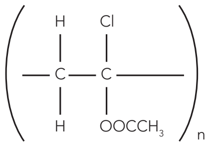
(d) H_2O

13. (a)



(b)

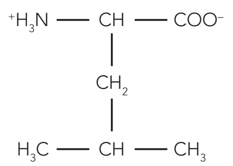


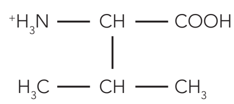
(c) 

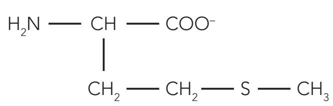
14.

(a) The -COOH group and the $-NH_2$ group are connected to the first carbon in the chain.

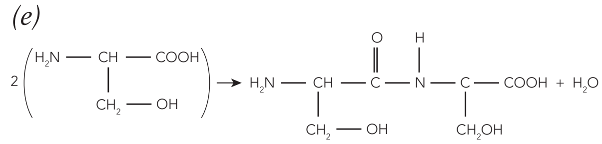
(b) A zwitterion is a neutral molecule that contains a positive ion and a negative ion. When leucine dissolves in water a zwitterion is formed as shown below



(c) 

(d) 

(e)



This is condensation polymerisation.

15. Phenylalanine

16. (a) The α-helix shape is created when hydrogen bonds occur between the carbonyl O of one amino acid and the amino H of an amino acid that is 4 positions down the chain.

(b) The secondary structure of a protein is because of hydrogen bonding between amide and carbonyl groups in the protein polymer chain. The tertiary structure is because bonding between the side chains in the protein molecule, the bonding may be hydrogen bonding, dipole-dipole interactions, dispersion forces, covalent bonds or ionic interactions.

17. $C_xH_yO_z + O_2 \rightarrow CO_2 + H_2O$

9.994 g   14.65 g   5.979 g

(a) $n(C) = n(CO_2) = \dfrac{14.65}{44.01} = 0.3329$ mol

$m(C) = 0.3329 \times 12.01 = 3.998$ g

$n(H) = 2n(H_2O) = \dfrac{2 \times 5.997}{18.016}$

$= 0.6657$ mol

$m(H) = 0.6657 \times 1.008 = 0.6711$ g

$m(O) = m(sample) - [m(C) + m(H)]$

$= 9.994 - [3.998 + 0.6711] = 5.325$ g

$n(O) = \dfrac{m}{M} = 0.3329$

C	H	O
0.3329	0.6657	0.3329
1	2	1

$EF = CH_2O$

(b) $H + OH^- \rightarrow H_2O$

$n(NaOH) = cV = 0.986 \times 0.0375$

$= 0.0370$

$\therefore n(H^+) = 0.0370$

If monoprotic then n(compound)

$= n(H^+) = 0.0370$

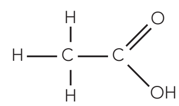
$M(compound) = \dfrac{m}{M} = \dfrac{2.22}{0.0370}$

$= 60.04$ g mol^{-1}

mass of EF = 30, MF = 2 × EF

Molecular formula = $C_2H_4O_2$

(c)



(ethanoic acid)

18. $C_xH_yO_z + O_2 \rightarrow CO_2 + H_2O$

0.392 g   0.320 g

(a) $n(C) = n(CO_2) = \dfrac{PV}{RT} = \dfrac{101.3 \times 0.547}{8.315 \times 373.1}$

$= 1.79 \times 10^{-2}$ mol

$m(C) = 1.79 \times 10^{-2} \times 12.01 = 0.215$ g

$n(H) = 2n(H_2O) = \dfrac{2 \times m}{M} = \dfrac{2 \times 0.320}{18.016}$

$= 3.55 \times 10^{-2}$

$m(H) = 3.58 \times 10^{-2}$ g mol

$m(O) = m(sample) - [m(C) + m(H)]$

$= 0.392 - [0.215 + 0.0358] = 0.141$ g

$n(O) = \dfrac{m}{M} = 8.84 \times 10^{-3}$

C	H	O
$\dfrac{0.0179}{0.00884}$	$\dfrac{0.0355}{0.00884}$	$\dfrac{0.00884}{0.00884}$
2.02	4.02	1

$\therefore EF = C_2H_4O$

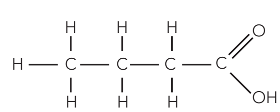
(b) $n = \dfrac{PV}{RT} = \dfrac{194 \times 0.100}{8.315 \times 523.1} = 4.46 \times 10^{-3}$ mol

$M = \dfrac{m}{n} = \dfrac{0.392}{4.46 \times 10^{-3}} = 87.9$ g mol^{-1}

mass of EF = 44,

mass of MF = 2 × mass of EF

∴ Molecular formula = $C_4H_8O_2$

(c) (i) 

(ii) methyl butanoate

19. (a)

	Cu	S	O	H
mass	5.945 × 25.45%	5.945 × 12.84%	5.945 × 57.67%	5.945 × 4.04%
moles	$\frac{1.513\ g}{63.55}$	$\frac{0.7633g}{32.07}$	$\frac{3.428\ g}{16.00}$	$\frac{0.240\ g}{1.008}$
	$\frac{0.02381}{0.02380}$	$\frac{0.02380}{0.02380}$	$\frac{0.2142}{0.02380}$	$\frac{0.2383}{0.02380}$
	1	1	9	10

EF = $CuSO_9H_{10}$

(b) $m(H_2O)$ lost = 2.145 g
$n(H_2O)$ lost = = = 0.1191 mol
mole ratio of H_2O lost = =5.00
MF = $CuSO_4.5H_2O$

20.

(a) $C_xH_yO_z + O_2 \rightarrow CO_2 + H_2O$

11.61 g 26.41 g 10.81 g

$n(C) = \frac{26.41}{44.01} = 0.6001$ mol

$m(C) = 0.6001 \times 12.01 = 7.207$ g

$n(H) = \frac{2 \times 10.81}{18.016} = 1.200$ mol

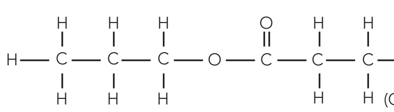
$m(H) = 1.200 \times 1.008 = 1.2096$ g
$m(O) = 11.61 - (7.207 + 1.2096)$
$= 3.193$ g

$n(O) = \frac{3.193}{16.00} = 0.1996$ mol

C	H	O
$\frac{0.6001}{0.1996}$	$\frac{1.200}{0.1996}$	$\frac{0.1996}{0.1996}$
3.006	6.01	1

EF = C_3H_6O

(b) Information suggests Z is an ester made from an alcohol and carboxylic acid of equal length and less than 5 carbons each.
i.e.



($C_6H_{12}O_2$)

21.

(a) $C_xH_yN_z + O_2 \rightarrow CO_2 + H_2O + NO_2$

3.990 g ~~8.927 g~~ ~~5.478 g~~ 3.111 g

$n(C) = \frac{8.927}{44.01} = 0.2028$ mol

$n(H) = \frac{2 \times 5.478}{18.016} = 0.6081$ mol

$n(N) = \frac{3.111}{46.01} = 0.0676$ mol

C	H	N
$\frac{0.2028}{0.0676}$	$\frac{0.6081}{0.0676}$	$\frac{0.0676}{0.0676}$
2.999	8.993	1

EF = C_3H_9N

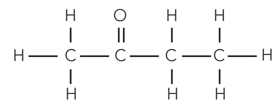
(b) $n = \frac{PV}{RT} = \frac{101.3 \times 2.680}{8.315 \times 483.1} = 0.0676$

$M = \frac{m}{n} = \frac{3.990}{0.0676} = 58.99$

molar mass of EF = 59 = molar mass of MF

∴ Molecular formula = C_3H_9N

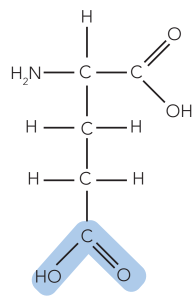
(c)



propanamine

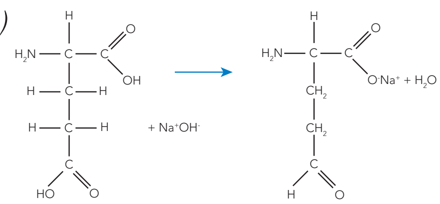
22. **For the Experts**

(a)

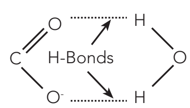


(b) acidic COOH group, polar.

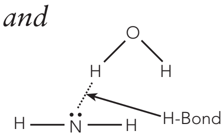
(c)



(d) Soluble in H_2O owing to



and



CHP 5: CHEMICAL SYNTHESIS

Chapter Questions

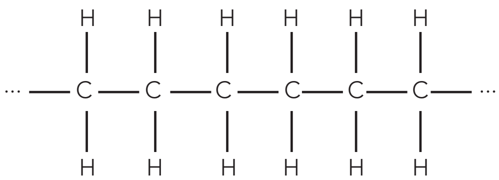
5.1 $C_2H_4(g) + H_2O(g) \rightarrow CH_3CH_2OH(g)$ + 45 kJ mol^{-1}

5.2 **Temperauture:** As the forward reaction is exothermic, a low temperature favours the formation of the products and consequently a high yield of ethanol.
Pressure: A high pressure would favour a high yield of ethanol as a high pressure favours the forward reaction as it produces fewer particles which helps reduced the imposed increase in pressure.

5.3 Increasing the concentration of the reactants would favour the forward reaction as an increase in the rate of the forward reaction would partially counteract the imposed change by reducing the concentration of the reactants.

5.4 The yield of ethanol is favoured by a low temperature, however to have an economical rate of production of ethanol a compromise between rate and yield requires the moderately high temperature of 300 ¬∞C to be used.

5.5



5.6 $CH_3CH_2OH + CH_3COOH \rightarrow CH_3COOCH_2CH_3 + H_2O$

5.7 The statement is not valid, a catalyst will not alter the relative proportion of product as compared to reactant as it favours both forward and reverse reactions equally. A catalyst is used because it gives a greater reaction rate.

5.8 As the reaction $2\ SO_2 + O_2 \rightarrow 2\ SO_3$ is exothermic, the equilibrium yield of SO_3 is favoured by a low temperature but the low temperature gives an uneconomical rate of production of SO_3. A compromise between yield and rate leads to the choice of reaction vessel temperatures of 400ºC to 450ºC. Increasing the pressure, effectively increases the concentration of all gaseous molecules present. The forward reaction is favoured in this case as it partially opposes this increase pressure by reducing the pressure because less particles are being formed.

5.9

STEP 1: $2NaOH + H_2SO_4 \rightarrow 2H_2O + Na_2SO_4$

3.200 g 1.125 g x g

STEP 2: $n(NaOH) = \dfrac{3.200}{40.0} = 0.080$

$n(H_2SO_4) = \dfrac{1.125}{98.08} = 0.0115$

Stoic. ratio of $\dfrac{NaOH}{H_2SO_4} = \dfrac{2}{1} = 2$

Actual ratio $= \dfrac{0.0800}{0.0115} = 6.98$

$\therefore H_2SO_4$ is the limiting reagent.

STEP 3: $n(Na_2SO_4) = n(H_2SO_4) = 0.0115$ mol

$m(Na_2SO_4) = nM = 0.0115 \times 142.05$

$m(Na_2SO_4) = 1.63$ g

STEP 4: n(NaOH) remaining

$= n(NaOH) - 2n(H_2SO_4)$

$= 0.0800 - 0.0229 = 0.0571$

m(NaOH) remaining = nM

$= 0.0571 \times 40.0 = 2.28$ g

5.10

(a) $n(NaOH) = cV = 0.0200 \times 0.450 = 9.00 \times 10^{-3}$

$n(MgCl_2) = 0.030 \times 0.540 = 0.0162$

NaOH is the limiting reagent.

$n(Mg(OH)_2) = \dfrac{1}{2} n(NaOH) = 4.50 \times 10^{-3}$ mol

$m(Mg(OH)_2) = nM = (4.50 \times 10^{-3})\ 58.316$

$= 0.262$ g

(b) $c(Na^+)$ ions $= \dfrac{n}{V} = \dfrac{9.00 \times 10^{-3}}{0.0500}$

$= 0.180$ mol L^{-1}

$c(Cl^-)$ ions $= \dfrac{n}{V} = \dfrac{2 \times 0.0162}{0.0500}$

$= 0.648$ mol L^{-1}

$c(Mg^{2+})$ ions $= \dfrac{n}{V} = \dfrac{(0.0162 - 0.00450)}{0.0500}$

$= 0.234$ mol L^{-1}

5.11

$n(Cu) = \dfrac{m}{M} = \dfrac{12.25}{63.55} = 0.193$ mol

$n(Cu_2S)$ in ore $= \dfrac{1}{2}\ n(Cu) = 0.193 \times \dfrac{1}{2}$

$= 0.0964$

$m(Cu_2S)$ in ore $= nM = 0.0964 \times 159.17$

$= 15.3$ g

$\therefore$ % Cu_2S in ore $= \dfrac{15.3}{154.5} \times \dfrac{100}{1}$

$= 9.93\%$

5.12

STEP 1: $2NH_3 \rightarrow 2NH_4HCO_3 \rightarrow 2NaHCO_3 \rightarrow Na_2CO_3 \rightarrow Na_2CO_3 . 10H_2O$

$m(Na_2CO_3 . 10H_2O)$

$= 1000 \times \dfrac{100}{90} = 1111$ kg

(allowing for 90% efficiency)

STEPS 2,3,4:

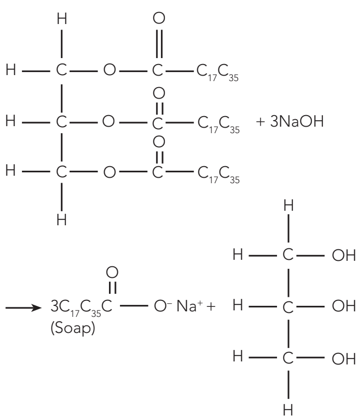
$n(Na_2CO_3 . 10H_2O)$

$= \frac{m}{M} = \frac{1111000}{286.15} = 3883$ moles

$n(NH_3) = 2n(Na_2CO_3 . 10H_2O)$
$= 2 \times 3883 = 7766$
$m(NH_3)$ required $= nM = 7766 \times 17.034$
$= 1.32 \times 10^5$ g = 132 kg
$n(NaCl) = 2n(Na_2CO_3 . 10H_2O) = 7766$ mol
$m(NaCl) = nM = 7766 \times 58.44$
$= 4.54 \times 10^5$ g = 454 kg

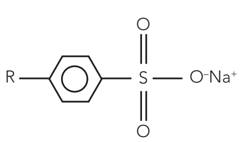
5. Review Questions

1.
(a)



(b) *The soap is able to dissolve in water because the Na^+ ions dissociate from the soap leaving a negative region around the O. The interactions between the highly polar water molecules and this region of the soap molecules allows the soap to dissolve.*
(c) *The long hydrocarbon chain end is responsible for the soap being able to dissolve in or attract to non-polar fat and oil stains.*

2.
(a) Ca^{2+} and Mg^{2+} ions
(b) *Because they combine with the soap to form insoluble substances, i.e.* $Mg(C_{17}H_{35}COO)_2$ *and* $Ca(C_{17}H_{35}COO)_2$. *These precipitate out and remove soap from the solution. A 'scum' forms.*
(c) *Smaller amounts of detergents are required to clean the same amount of dirty materials plus they do not form insoluble substances when used in water containing* Ca^{2+} *or* Mg^{2+} *ions.*
(d)



where R is a hydrocarbon chain of at least 10 carbons in length.

3.
(a) *A zwitterion is a neutral ion that has both a negative and a positive charge.*
(b) *A surfactant, such as a soap or detergent, lowers the surface tension of liquids and allows for greater interaction or mixing between the liquids.*
(c) *(i) is the zwitterion, with the positive region being one of the* CH_3 *groups joined to the N and the negative regions is O atom that is joined to the C with a single bond.*
(d) *The section labeled R is a non-polar hydrocarbon region of the zwitterion. This non-polar section is attracted to the oils on the skin. It helps break the oil down into small globules or micelles that are suspended in the water.*

4.
(a) *propan-1-ol and propan-2-ol*
(b) $CH_3CH = CH_{2(g)} + H_2O_{(g)} \rightarrow CH_3CHOHCH_{3(g)}$
(c) *High pressure as the forward reaction would be favoured as it would produce less particles, decreasing the pressure and partially counteract the imposed change.*
(d) *This would indicate that at low temperatures the reaction rate would be too slow to be economically viable. A compromise is found between yield of product, favoured by low temperatures and rate of production as favoiured by high temperatures.*

5. *The production of ethanol by the acid catalysed hydrolysis of ethene requires temperatures in the region of 300°C. The fermentation of alcohol is best at temperatures of about 25°C. The lower temperature in part is due to the reactions involved being catalysed by enzymes.*

6. $H_2C = CH_2 + H_2O \rightleftharpoons CH_3CH_2OH$

(Ethanol can be oxidised to ethanoic acid by O_2 *as per the equation:*

$CH_3CH_2OH + O_2 \rightarrow CH_3COOH + H_2O)$

$CH_3CH_2OH + CH_3COOH \rightarrow CH_3COOCCH_3$

7. *These conditions would be based on ensuring that the rate of production of the ethanoic acid was at high as possible within the economic constraints of building reaction vessels and ongoing energy consumption to produce and maintain these pressure and temperature conditions. 20 C and 1 atm would be far cheaper to build and run but the rate of production of the CH3COOH would be too slow to be economically viable.*

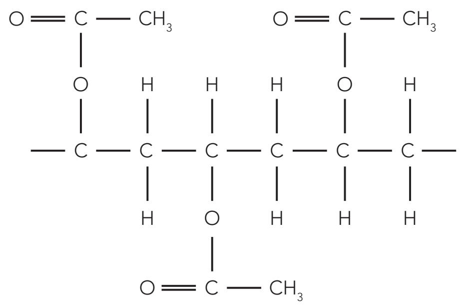
8. $n(CH_3OH) = \frac{m}{M} = \frac{9.44 \times 10^6}{32.042} = 295\ 000$

$n(CO) = \frac{n}{M} = \frac{6.38 \times 10^6}{28.01} = 228\ 000$

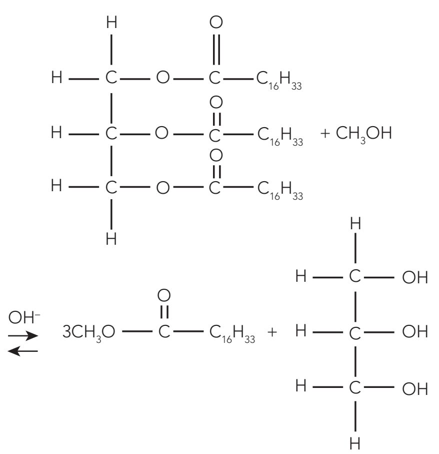
CO is the limiting reagent

$n(CH_3COOH) = n(CO)$
$m(CH_3COOH) = n.M = 228000 \times (24.02 + 32.00 + 4.032)$
$m(CH_3COOH) = 1.37 \times 10^7\ g$

9.



10.
(a)



(b) *The use of a biological enzyme may allow the production of the biodiesel to occur at temperatures and pressures much closer to standard conditions. This will reduce costs to build the plant and also the ongoing run costs to maintain the higher temperatures and pressures as required by the base catalysed process.*

(c) *Using biodiesel rather than petro-diesel is using a renewable energy source, the CO_2 released when burning biodiesel is offset against CO_2 absorbed when plant that is the source of the biodiesel is grown, if biodiesel is spilt it is far less of an environmental hazard as compared to petro-diesel.*

11.
(a) $Zn_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + H_{2(g)}$

(b) $n(Zn) = \frac{m}{M} = \frac{7.34}{65.38} = 0.112\ mol$

$n(HCl) = cV = (1.50)\ (0.120) = 0.180\ mol$

To find L.R. consider Zn. 0.112 mol of Zn would require (2) (.112) = 0.224 mol of HCl (from equation).
There is only 0.18 mol of HCl available ∴ HCl is LR.

(c) $n(H_2)$ *collected* = (½) (0.18) = 0.090 mol

$V(H_2) = \frac{nRT}{P} = \frac{(0.090)(8.315)(291.1)}{105}$

= 2.07 L

(d) *To find excess zinc, first determine mass of zinc consumed.*
n(Zn) that react = (½) (0.18)
∴ m(Zn) that react = (0.090)(65.38)
= 5.88 g
∴ m(Zn) remaining = 7.34 – 5.88
= 1.46 g

12.
(a) $Na_2CO_{3(s)} + 2HNO_{3(aq)} \rightarrow 2NaNO_{3(aq)} + CO_{2(g)} + H_2O_{(l)}$

(b) $n(Na_2CO_3) = \frac{15.5}{106} = 0.146\ mol$

$n(HNO_3) = cV = (2.42)\ (0.100) = 0.242\ mol$

To determine LR, consider Na_2CO_3 0.146 mol of HNO_3 would require (2) (0.146) = O.292 mol of HNO_3 (from equation).
There is only 0.242 mol of HNO_3 available ∴ HHO_3 is LR.

(i) $n(CO_2)$ *produced* = (½)(0.242) = 0.121 mol
∴ $V(CO_2)$ *STP* = (n) (22.41) = 2.71 L

(ii) *All ions are still in solution except those that reacted to form CO_2 and H_2O*

$c(Na^+) = \frac{n}{V} = \frac{(0.146)(2)}{0.100} = 2.92\ mol\ L^{-1}$

$c(NO_3^-) = \frac{n}{V} = \frac{(0.242)}{0.100} = 2.42\ mol\ L^{-1}$

For CO_3^{-2} determine how many reacted

$n(CO_3^{-2})$ *reacted* = (½) (0.242) = 0.121 mol
$n(CO_3^{-2})$ *left over* = 0.146 – 0.121 = 0.0250 mol

$c(CO_3^{-2}) = \frac{n}{V} = \frac{0.025}{0.100} = 0.250\ mol\ L^{-1}$

For H^+ they are all consumed

∴ $c(H^+) = 0$ *[Note for a neutral solution the $[H^+]$ would still be $1 \times 10^{-7}\ mol\ L^{-1}$]*

13.

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$
200 ml 500 ml
All gas volumes at same condition hence from equation
1 Vol (CH_3H_8) + 5 Vol (O_2) → 3 Vol (CO_2) + 4 Vol (H_2O)
To find Limiting Reagent, consider C_3H_8
200 mL C_3H_8 would require (5)(200) = 1000 mL of O_2
Since there is only 500 mL of O_2, it is the LR
Hence final volumes of gases remaining

- *Vol of O_2 = 0 all O_2 consumed*
- *Vol of C_3H_8 = 100 mL (1/5 (500) consumed)*
- *Vol of CO_2 = 300 mL (3/5) (500) produced)*
- *Vol of H_2O = 400 mL (4/5) (500) produced)*

14.

(a) $Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$

(b) *n(NaI) available = cV*
= (1.15) (0.050)
= 5.75×10^{-2} mol
n(KI) available = cV
= (0.50) (0.100)
= 5.00×10^{-2} mol
$n(I^-)$ total available = 10.75×10^{-2} mol
$n(Pb(NO^3)^2)$ added = 20.0 = 6.04×10^{-2} mol
331.22
6.04×10^{-2} mol of $Pb(NO^3)^2$ would require $2(6.04 \times 10^{-2})$ mol of I^-
i.e. 12.08×10^{-2} mol I^-
But we have only 10.75×10^{-2} mol I^-
Hence I^- is the limiting reagent.
$n(PbI^2)$ formed = ½ × $n(I)^-$
= (½)(10.75×10^{-2})
= 5.375×10^{-2}
∴ $m(PbI^2) = (5.375 \times 10^{-2})(461) = 24.8$ g

(c) *$I^-(aq)$ is all consumed*
i.e. $c(I^-) = 0$
$Pb^{2+}(aq)$ is in excess
$n(Pb^{2+}(aq))$ in excess = 6.04×10^{-2} - ½(10.75×10^{-2})
= 6.65×10^{-3}

$$c(Pb^2+(aq)) = \frac{6.65 \times 10^{-3}}{0.150}$$

$c(Pb^2+(aq)) = 4.43 \times 10^{-2}$ mol L^{-1}

$$c(Na^+(aq)) = \frac{5.75 \times 10^{-2}}{0.150}$$

= 3.83×10^{-1} mol L^{-1}

$$c(K^+) = \frac{5.00 \times 10^{-2}}{0.150}$$

= 3.33×10^{-1} mol L^{-1}

$$c(NO^{3-}) = \frac{2(6.04 \times 10^{-2})}{0.150}$$

= 0.805 mol L^{-1}

15. *From the equations for the reactions, 1 mol S(s) produces 1 mol H_2SO_4*

$$n(S) = \frac{m}{M} = \frac{3.25 \times 10^6}{32.06} = 101372$$

$n(H_2SO_4) = n(S) = 101372$

$m(H_2SO_4)$ pure = n.M = 101372 × 98.076 = 9.94×10^6 g

$$m(acid) = \frac{9.94 \times 10^6 \times 100}{98.5}$$

= 1.10×10^7 g = 11.0 tonnes

16. *From the equations, 1 mol of P_4 will produce 4 mol of H_3PO_4*

$m(H_3PO_4)$ in final acid solution

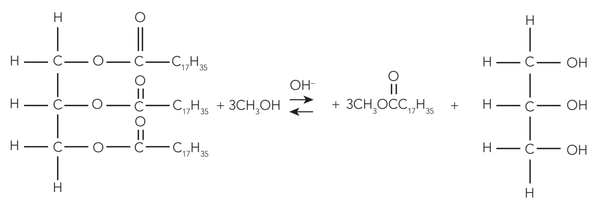
$$= \frac{1500000 \times 85.0}{100} = 1.275 \times 10^6 \text{ g}$$

$$n(H_3PO_4) \frac{m}{M} = \frac{1.275 \times 10^6}{97.994} = 13011$$

$$n(P_4) = \frac{n(H_3PO_4)}{4} = \frac{13011}{4} = 3253$$

$m(P_4)$ = n.M = 3253 × (30.97 × 4) = 4.03×10^5 g or 403 kg.

17.



molecular formula of palm oil - $C_{57}O_6H_{110}$

$$n(\text{palm oil}) = \frac{m}{M}$$

$$= \frac{1000}{((57 \times 12.01) + (6 \times 16.00) + (110 \times 1.008))}$$

= 1.12

n(biodiesel) = 3 × n(palm oil) = 3.37

molecular formula for biodiesel ester = $C_{19}O_2H_{38}$

m(biodiesel) = n.M = 3.37 × ((19 × 12.01) + 32.00 = (38 × 1.008)) = 1.00 kg

Process is 85% efficient, therefore the mass of bioidiesel = 850 g/kg of triglyceride.

18. $m(\text{iron ore}) = m(Fe_2O_3) = \frac{33.3}{100 \times 1.40 \times 10^9}$

$= 4.66 \times 10^8$ tonnes

Assumption from question: Steel is 99% Fe and 1% C

$n(Fe_2O_3) = \frac{m}{M} = \frac{4.66 \times 10^{14}}{((2 \times 55.85)\ 3 \times 16.00))}$

$= 2.92 \times 10^{12}$

$n(Fe) = 2 \times n(Fe_2O_3) = 5.84 \times 10^{12}$

$m(Fe) = n.M = 5.84 \times 10^{12} \times 55.85$

$= 3.26 \times 10^{14}$ g

m (plain steel) $m(Fe) \times \frac{100}{99} = 3.29 \times 10^{14}$ g

m(plain steel) $= 3.29 \times 10^8$ tonnes

$2\ C + O_2 \rightarrow 2\ CO \times 3$

$$\frac{Fe_2O_3 + 3\ CO \rightarrow 2\ Fe + 3\ CO_2 \times 2}{6\ C + 3\ O_2 + 2\ Fe_2O_3 \rightarrow 4\ Fe + 6\ CO_2}$$

$n(Fe_2O_3) = \frac{m}{M} = 1.40 \times \frac{1015}{159.7}$

$= 8.77 \times 10^{12}$

$n(CO_2) = 3 \times n(Fe_2O_3) = 2.63 \times 10^{13}$

$m(CO_2) = n.M = 2.63 \times 10^{13} \times (12.01 + 32.00) = 1.16 \times 10^{15}$ g

$m(CO_2) = 1.16$ billion tonnes of CO_2 produced

19. $2\ ZnS + 3\ O_2 \rightarrow 2\ ZnO + 2\ SO_2$

$$\frac{ZnO + C \rightarrow Zn + CO \times 2}{2\ ZnS \rightarrow 2\ Zn}$$

$m(ZnS) = 235000 \times \frac{65.0}{100} = 1.53 \times 10^5$ g

$n(ZnS) = \frac{m}{M} = \frac{1.53 \times 10^5}{(65.38 + 32.06)} = 1568$

$n(Zn) = n(ZnS) = 1568$

$m(Zn) = n.M = 1568 \times 65.38 = 1.02 \times 10^5$ g

$m(Zn) = 10^2$ kg

20. $n(Al) = \frac{m}{M} = \frac{3500000}{26.98} = 1.297 \times 10^5$

$n(Al_2O_3) = \frac{n(Al)}{2} = 6.49 \times 10^4$

$m(Al2O3) = n.M = 6.94 \times 10^4 \times ((2 \times 26.98) + (3 \times 16.00))$

$m(Al_2O_3) = 6.61 \times 10^6$ g

$m(\text{Bauxite}) = m(Al_2O_3) \times \frac{100}{60.0} = 1.10 \times 10^7$ g

m(Bauxite) $= 11.0$ tonnes

For the Experts

21.

(a) $4NH_3\ .... \rightarrow 4HNO_3$

$n(NH_3) = \frac{m}{M} = \frac{1.50 \times 10^6}{17.034} = 8.81 \times 10^4$ mol

$n(HNO_3) = n(NH_3) = 8.81 \times 10^4$ mol

$m(HNO_3) = nM = 8.81 \times 10^4 \times (1.008 + 14.01 + 48.00)$

$m(HNO_3) = 5.55 \times 10^6$g (5.55 tonnes)

(b) $n(HCl) = cV = 0.2725 \times 0.0396 = 0.0108$ mol

$n(NH_3) = n(HCl) = 0.0108$

$n(NO_3^-)$ in 25 ml aliquot $= n(NH_3) = 0.0108$ mol

$n(NO_3^-)$ in 500 ml $= 0.0108 \times \frac{500}{25} = 0.2158$

$\therefore n(HNO_3)$ in original 20.0 g $= 0.2158$ mol

$m(HNO_3)$ in original 20.0 g $= nM$

$= 0.2158 \times (1.008 + 14.01 + 48.00) = 13.6$ g

% mass $HNO_3 = \frac{13.6}{20.0} \times \frac{100}{1} = 68.0\%$

(c) density $= 1.41$g cm^{-3} $V = \frac{mass}{density} = \frac{20.0}{1.41}$

$= 14.2$ mL

mass $= 20.0$g

$c(HNO_3) = \frac{n}{V} = \frac{0.2158}{0.0142} = 15.2$ mol L^{-1}

ANSWERS TO TRIAL TESTS

TRIAL TEST 1:
Reaction Rates and Equilibrium

Section 1

1. *d*	6. *d*
2. *c*	7. *b*
3. *a*	8. *c*
4. *a*	9. *d*
5. *b*	10. *b*

[20]

Section 2

11.

(a) Increase pressure - concentration of the O_2 is increased, this will increase the likelihood of a successful collision between reactant particles as there are more O_2 particles per unit volume.

(b) Increase the surface area of the C_8H_{18} - make it into a fine spray. Reactions occur on the surface of solids and liquids - by increasing the surface area the chance of a successful collision is increased.

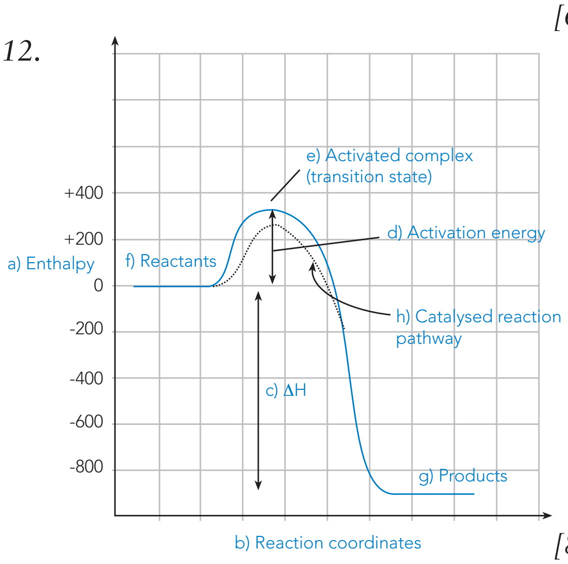
(c) Increase the temperature - reactant particles will be moving more rapidly - collisions will be more frequent and more energetic. The number of successful collisions occurring will increase.

or/and:

Add a Catalyst: an alternative reaction pathway exists that requires less energy – hence more of the collisions will now have an energy greater than the activation energy.

[6]

12.



[8]

13.

(a) Line B is H_2 while line C is NH_3

(b) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

(c) At t = 2 the forward reaction rate is greater than the reverse reaction rate. At t = 10 the forward and reverse reaction rates are equal.

(d) (i) Forward RR no change since no change to concentrations of the reactants.

(ii) Reverse RR will initially be lower as the concentration of the products is lower.

[8]

14.

*(a) (i) **increase,** since extra pressure favours the side with less gaseous molecules (there are 3 on the left and only 1 on the right)*

*(ii) **decrease,** the equilibrium position shifts to the left to partially counteract the imposed change*

*(iii) **decrease,** the equilibrium position shifts to the left to partially counteract the imposed change*

(b) $K = \dfrac{[HNO_3]^2[NO]}{[NO_2]^3}$

[8]

15.

(a) No change – the concentration of the H_2SO_4 has not been changed.

(b) No change – the concentration of the $CaCO_3$ is not altered.

(c) Reverse reaction favoured – concentrations decreased equally – reverse reaction favoured to partially counteract this.

[6]

16.

(a) (i) Unchanged – white powder will settle on the bottom.

(ii) To the left – white precipitate dissolves.

(iii) To the right – more white precipitate produced.

(b) Exothermic – on warming the reaction is favoured that tries to oppose this warming, ie. reaction that consumes energy is favoured which is the reverse reaction.

[8]

17.

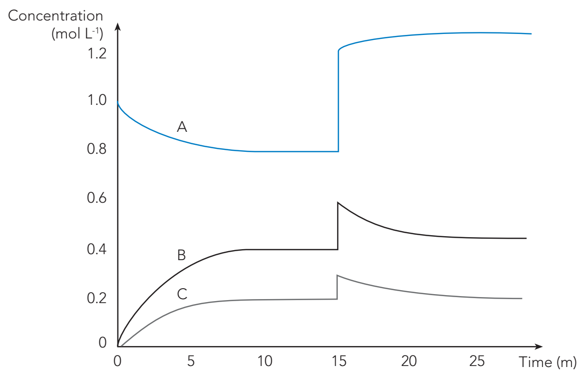
(a) Equilibrium was reached.

(b) A is CH_3OH, B is H_2, C is CO

(c) $K = \dfrac{[CH_3OH]}{[CO][H_2]^2} = \dfrac{(0.8)}{(0.2)(0.4)^2} = 2.5$

(d) Pressure was increased by reducing volume of the containing vessel.

(e)



(f) The equilibrium will shift so as to compensate for the greater imposed pressure. Moves right as there are less molecules. Concentration of the H_2 affected most as there are two molecules of it. The other reactants affected equally (one molecule of each) but in opposite directions.

[16]

TRIAL TEST 2: Acids and Bases

Section 1

1. d	6. d
2. b	7. a
3. a	8. b
4. c	9. b
5. c	10. d

[20]

Section 2

11.

(a) Test: Add $Ba(NO_3)_2(aq)$ to both solutions
Observation: white precipitate forms in the H_2SO_4, no change in the HNO_3

(b) Test:Add powders to HCl solutions
Observation: $MgCO_3$ will fizz as bubbles of gas are produced, $Mg(OH)_2$ will simply dissolve

(c) Test: Add universal indicator to both
Observation: KCl solution will turn green, KCH_3COO will form orange/yellow.

[12]

12.

(a) $Ba^{2+}(aq) + 2OH^-(aq) + 2H^+(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s) + 2H_2O(l)$

(b) $3OH^-(aq) + H_3PO_4(aq) \rightarrow PO_4^{3-}(aq) + 3H_2O(l)$

(c) $CaCO_3(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + CO_2(g) + H_2O(l)$

[6]

13. HCl is a strong acid and is completely ionized when in solution
$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$
For HCl, the $[H^+] = [HCl]$
CH_3COOH is a weak acid and so only a small percentage of molecules ionise
$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$

For CH_3COOH, the $[H^+] < [CH_3COOH]$
Therefore, $[H^+]$ in HCl is > $[H^+]$ in CH_3COOH and pH of 0.01 mol L^{-1} HCl is less

[4]

14. (a) $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$
(b) $H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq)$
(c) $H_2SO_4(aq) \rightleftharpoons H^+(aq) + HSO_4^-(aq)$

[6]

15.

(a) Hydrolysis is the reaction between a salt and water to produce either H_3O^+ ions or OH^- ions.

(b)

(i) $CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$; basic

(ii) $CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH(aq)$; basic

(iii) $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$; acidic

[8]

16.

(a) be obtained pure; have a known formula; not react with surroundings; have a high molar mass

(b) deliquescent: absorbs water from the atmosphere and dissolves in the water

(c) end point: the point at which the titration is stopped because the desired colour change is observed
equivalence point: reactants have been mixed in stoichiometrically equivalent amounts

[8]

17.

(a) $H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$

(b) The OH^- ions will reduce the concentration of the H_3O^+ ions. The forward reaction would be favoured to partially counteract this change and the pH would remain reasonably constant.

(c) The buffer capacity of the solution would be exceeded and the pH would drop considerably.

[6]

18. $2HCl + Na_2CO_3 \rightarrow 2NaCl + CO_2 + H_2O$
2 mol 1 mol
$M(Na_2CO_3)$ = 45.98 + 12.01 + 48.00 = 105.99

$n(Na_2CO_3)$ in 500 mL $= \frac{m}{M} = \frac{2.23}{105.99}$
$= 0.0210$ *mol*

$c(Na_2CO_3) = \frac{n}{V} = 0.0421 \text{ mol L}^{-1}$

$n(Na_2CO_3)$ used in titration $= cV$

$= 0.0421 \times 0.0200 = 8.42 \times 10^{-4}$ *mol*

$n(HCl) = 2n(Na_2CO_3)$

$= 2 \times 8.42 \times 10^{-4} = 1.68 \times 10^{-3}$

$c(HCl) = \frac{n}{V} = \frac{1.68 \times 10^{-3}}{0.0413}$

$= 4.08 \times 10^{-2} \text{ mol L}^{-1}$

TRIAL TEST 3:
Oxidation and Reduction

Section 1

1. d	6. d
2. c	7. a
3. d	8. a
4. a	9. b
5. c	10. a

[20]

Section 2

11.

(a) Equation: $Br_{2(aq)} + 2I^-_{(aq)} \rightarrow 2Br^-_{(aq)} + I_{2(aq)}$
Observation: straw yellow solution turns a red/brown colour

(b) Equation: $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$
Observation: metal turns black and then black coloured crystals grow on it.
Solution loses blue colour

(c) Equation: $2Na_{(s)} + 2H_2O_{(l)} \rightarrow 2Na^+_{(aq)} + 2OH^-_{(aq)} + H_{2(g)}$
Observation: silver coloured metal fizzes around on top of water, colourless, colourless gas produced

(d) Equation: $2MnO_4^-{}_{(aq)} + 5H_2O_{2(aq)} + 6H^+_{(aq)} \rightarrow 2Mn^{2+}_{(aq)} + 5O_{2(g)} + 8H_2O_{(l)}$
Observation: purple solution goes colourless and bubbles of colourless odourless gas produced

[12]

12.

(a)

(i) Oxidation $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$
Reduction $2H^+_{(aq)} + 2e^- \rightarrow H^2{}_{(g)}$

(ii) Oxidation $Mg_{(s)} \rightarrow Mg^{2+}_{(aq)} + 2e^-$
Reduction $2H_2O_{(l)} + 2e^- \rightarrow 2OH^-_{(aq)} + H_{2(g)}$

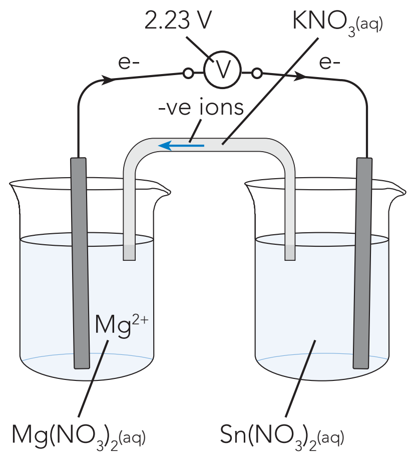
(b)

(i) Oxidation $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$
Reduction $(Ag^+_{(aq)} + e- \rightarrow Ag_{(s)}) \times 2$
Redox $Zn_{(s)} + 2Ag^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Ag_{(s)}$

(ii) Oxidation $Mg_{(s)} \rightarrow Mg^{2+}_{(s)} + 2e-$
Reduction $Cl_{2(g)} \rightarrow 2Cl^-_{(s)}$
Redox $Mg_{(s)} + Cl_{2(g)} \rightarrow MgCl_{2(s)}$

[10]

13.



ANODE: $Mg \rightarrow Mg^{2+} + 2e^-$
CATHODE: $Sn^{2+} + 2e^- \rightarrow Sn$

[12]

14.

(a) Anode: $Fe \rightarrow Fe^{2+} + 2e^-$
Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
Rust formation: $2Fe(OH)_3 \rightarrow Fe_2O_3.H_2O + 2H_2O$

(b) (i) Coat the windmill with a paint to stop the oxygen and water coming in contact with the iron. This will prevent the cathodic reaction.
(ii) Connect another metal of higher oxidation potential to the windmill so that the iron acts as a cathode and the other metal an anode. For example if the other metal is zinc it will oxidise instead of the iron.

[12]

15.

(a)

(i) $(Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^-) \times 2$ anodic reaction
$O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-{}_{(aq)}$ cathodic reaction

$2Fe_{(s)} + O_{2(g)} + 2H_2O_{(l)} \rightarrow 2Fe(OH)_{2(s)}$

(ii) $4Fe(OH)_{2(s)} + 2H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)}$
(iii) $2Fe(OH)_{3\ (s)} \rightarrow Fe_2O_3 . H_2O + 2H_2O_{(l)}$

(b) Any two of the following:

- Painting or plating the iron. This excludes air and/or water hence reaction prevented.
- Using a sacrificial anode such as galvanising

iron with zinc. The more reactive zinc will corrode in preference to the iron.

- *Using cathodic prevention by applying a low voltage to, say, a steel jetty. The power source provides a source of electrons in preference to the iron.*

[14]

TRIAL TEST 4: Organic Chemistry

Section 1

1. *a*	6. *a*
2. *d*	7. *c*
3. *c*	8. *d*
4. *b*	9. *c*
5. *d*	10. *d*

[20]

Section 2

11.

(a) cis-but-2-ene

(b) cis-2,2-dibromo-5-methylhept-3-ene

(c) pentan-2-one

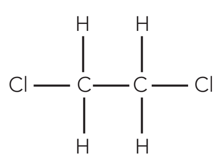
(d) propanoic acid

(e) 6,7,7-tribromo-3,4-dichloroheptan-1-amine

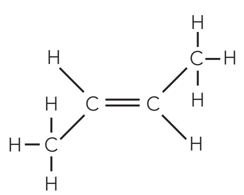
(f) propylethanoate

12.

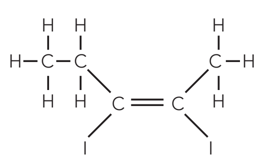
(a)



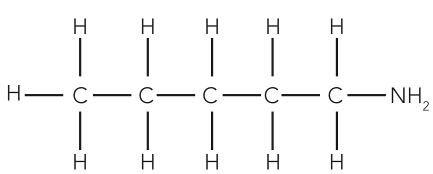
(b)



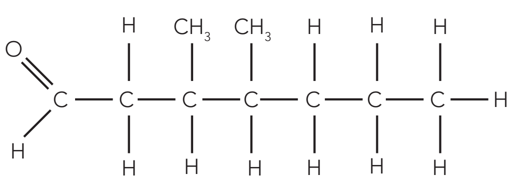
(c)



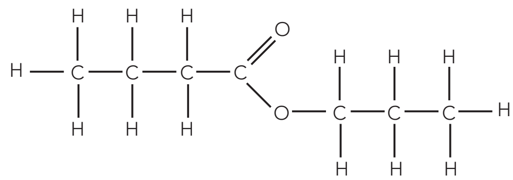
(d)



(e)

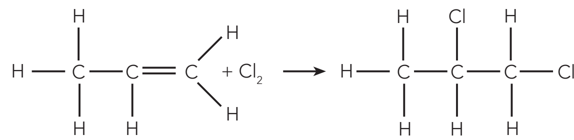


(f)



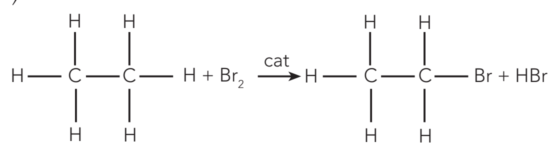
13.

(a)



(b) $2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O$

(c)



14.

(a) Oxidation: $CH_3CH_2CHO + H_2O \rightarrow CH_3CH_2COOH + 2H^+ + 2e^-$

Reduction: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

Redox: $3CH_3CH_2HO + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow 3CH_3CH_2COOH(aq) + 2Cr^{3+}(aq) + 4H_2O(l)$

Name: *propanoic acid*

(b) Oxidation: $CH_3CHOHCH_2CH_3 \rightarrow CH_3COCH_2CH_3 + 2H^+ + 2e$

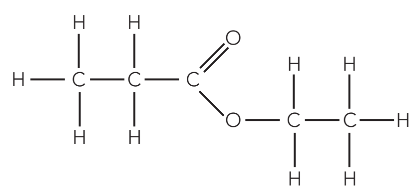
Reduction: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Redox: $5CH_3CHOHCH_2CH_3 + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 5CH_3COCH_2CH_3 + 2Mn^{2+}(aq) + 8H_2O(l)$

Name: *butanone*

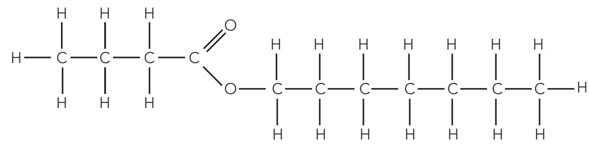
15.

(a)



ethyl propanoate

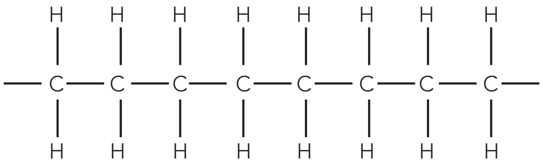
(b)



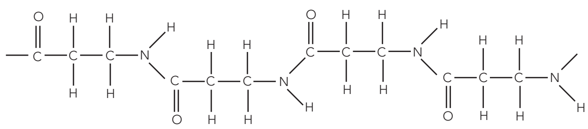
heptyl butanoate

16.

(a)

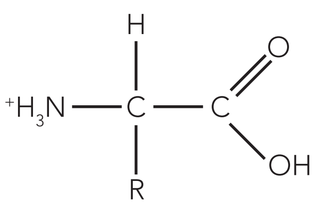


(b)

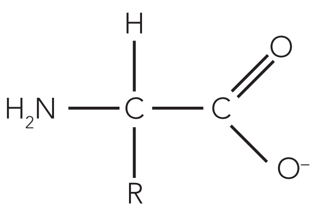


17.

(a)



(b)



18. *nicotine* + $O_2 \rightarrow CO_2 + H_2O$ + ?

0.467 g (nicotine)   *1.266 g* (CO_2)   *0.3589 g* (H_2O)

$$n(C) = n(CO_2) = \frac{1.266}{44.01} = 0.02877 \text{ mol}$$

$$m(C) = 0.02877 \times 12.01 = 0.34548 \text{ g}$$

$$n(H) = 2n(H_2O) = \frac{2 \times 0.3589}{18.016} = 0.03984 \text{ mol}$$

$$m(H) = 0.03984 \times 1.008 = 0.04016 \text{ g}$$

2^{nd} sample is different size to first sample but must contain the same proportion of N. i.e. proportion N in first sample

$$= 0.467 \times \frac{0.06263}{0.362}$$

$$= 0.0808 \text{ g}$$

$$n(N) \text{ in first sample} = \frac{0.0808}{14.01} = 5.767 \times 10^{-3} \text{ mol}$$

m(O) in nicotine = 0.467 – (0.3455 + 0.04016 + 0.0808) = 0.0 g

Nicotine contains C, H + N only

C	H	N
$\frac{0.02877}{0.005767}$	$\frac{0.03984}{0.005767}$	$\frac{0.005767}{0.005767}$
4.98	6.91	1

EF of Nicotine = C_5H_7N

Sample 3

$m = 0.964$ *g*

$$n = \frac{PV}{RT} = \frac{544 \times 0.0500}{8.315 \times 550} = 5.948 \times 10^{-3} \text{ mol}$$

$$M = \frac{m}{n} = \frac{0.964}{5.948 \times 10^{-3}} = 162.08 \text{ g mol}^{-1}$$

mass of EF = 81.116

mass of molecular formula = 2 × mass of EF

∴ molecular formula = 2 × EF

$= C_{10}H_{14}N_2$

TRIAL TEST 5: Chemical Synthesis

Section 1

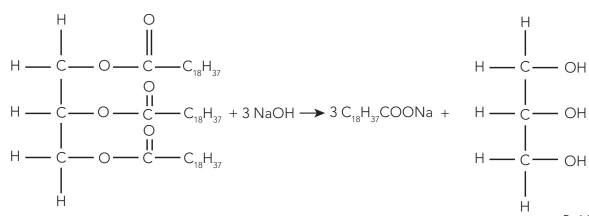
1. *d*
2. *d*
3. *c*
4. *c*
5. *b*
6. *c*
7. *a*
8. *b*
9. *c*
10. *d*

[20]

Section 2

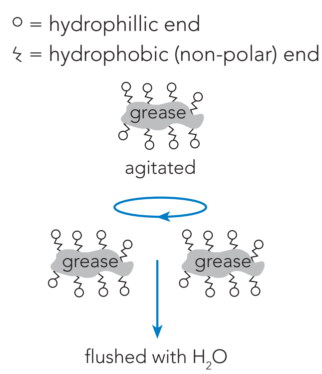
11.

(a)



[4]

(b)

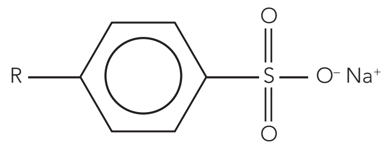


[4]

(c) *Water is classified as hard if soap will not lather in it. This is caused by the water containing Mg^{2+} and Ca^{2+} ions that form insoluble salts with soap anions.*

[2]

(d)

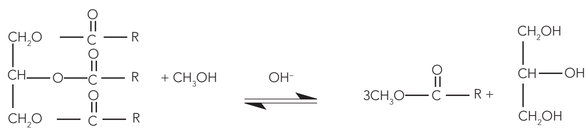


[4]

12.

(a) $C_2H_4 + H_2O \rightarrow CH_3CH_2OH$ [3]

(b)



[3]

(c) *The most common source of ethene and diesel is from crude oil.* [2]

(d) *Standard fuels are fossil fuels and so are not renewable. Biofuels are from renewable sources and the use of them will prolong the life of the fossil fuels.*

[2]

(e) *lipase and bases (such as sodium hydroxide).*

[2]

13.

(a) $3\ N_{2(g)} + 2\ H_{2(g)} \rightarrow 2\ NH_{3(g)} + 92\ kJ\ mol^{-1}$

[2]

(b) *At high pressure the concentration of all gaseous species is increased. The forward reaction is favoured as it reduces the number of particles and consequently partially counteracts the imposed pressure increase. The forward reaction being favoured leads to a higher yield of NH_3.*

[2]

(c) *As the forward reaction is exothermic, an increase in temperature will lead to the reverse reaction being favoured to partially counteract the imposed change. This would lead to a lower yield of ammonia.*

[2]

(d) *The Haber process is carried out at approximately 500 °C. This high temperture is required to ensure that the reaction rate is suffiently high to produce ammonia at a rte that is economically viable.*

[3]

(e) *An iron/iron oxide catalyst is used to increase the rate of production of ammonia. As it effects the forward and reverse reactions equally, a catalyst has no effect on the equilibrium yield of ammonia.*

[3]

14.

(a) $m(\text{methane}) = 850\ 000\ g$

$$n(CH_4) = \frac{n}{M} = \frac{850000}{16.042} = 5.299 \times 10^4$$

$n(H_2) = 3.n(CH_4) = 1.59 \times 10^5$

$m(H_2) = n.M = 1.59 \times 10^5 \times 2.016 = 3.20 \times 10^5\ g$

$m(H2) = 320\ kg$

[4]

(b) $n(CH_3OH) = n(CH_4) = 5.299 \times 10^4$

$m(CH_3OH)$ *if 100% efficient* $= n.M$

$m(CH_3OH) = 5.299 \times 10^4 \times (12.01 + 3.024 + 16.00 + 1.008)$

$m(CH_3OH) = 1.698 \times 10^6\ g$

$m(CH_3OH)$ *at 92.5% efficiency*

$$= 1.698 \times 10^6 \times \frac{92.5}{100}$$

$m(CH_3OH) = 1.57 \times 10^6\ g$ *(1.57 tonne)*

[6]

15.

(a) *By examining the reaction pathways, 1 mole of $Ca(OH)_2$ will lead to 1 mole of Cl_2 being produced.*

$$n(Ca(OH)_2) = \frac{m}{M} = \frac{1480000}{(40.08 + 32.00 + 2.016)}$$

$= 19974$

$$n(Cl_2) = \frac{m}{M} = \frac{1120000}{70.90} = 15796$$

If 100% efficient. 19974 mol of $Ca(OH)_2$ should produce 19974 mol of Cl_2.

Efficiency of process

$$= \frac{(n(Cl_2)}{n(Ca(OH)_2) \times \frac{100}{1}}$$

$$= (\frac{15796}{19974}) \times \frac{100}{1}$$

$= 79.1\%$

(b) If 100% efficient, 1kg of sea water would produce 0.0013 kg of Mg

i.e. $\frac{1}{0.0013} = \frac{x}{1}$

x = 7692 kg (7962 kg of sea water required to produce 1 kg of Mg)

However process is on 79.1% efficient, therefore

$m(\text{sea water}) = 7692 \times \frac{79.1}{100}$

m(sea water) = 9725 kg

[12]

INDEX

Table of relative atomic masses (atomic weights)

ELEMENT	SYMBOL	ATOMIC NUMBER	RELATIVE ATOMIC MASS	ELEMENT	SYMBOL	ATOMIC NUMBER	RELATIVE ATOMIC MASS
Actinium	Ac	89	[227]	Mendelevium	Md	101	[258]
Aluminium	Al	13	26.98	Mercury	Hg	80	200.59
Americium	Am	95	[243]	Molybdenum	Mo	42	95.95
Antimony	Sb	51	121.78	Moscovium	Mc	115	[289]
Argon	Ar	18	39.95	Neodymium	Nd	60	144.24
Arsenic	As	33	74.92	Neon	Ne	10	20.18
Astatine	At	85	[210]	Neptunium	Np	93	[237]
Barium	Ba	56	137.3	Nickel	Ni	28	58.69
Berkelium	Bk	97	[247]	Nihonium	Nh	113	[286]
Beryllium	Be	4	9.01	Niobium	Nb	41	92.91
Bismuth	Bi	83	209.00	Nitrogen	N	7	14.01
Bohrium	Bh	107	[272]	Nobelium	No	102	[259]
Boron	B	5	10.81	Oganesson	Og	118	[294]
Bromine	Br	35	79.90	Osmium	Os	76	190.23
Cadmium	Cd	48	112.4	Oxygen	O	8	16.00
Caesium	Cs	55	132.91	Palladium	Pd	46	106.42
Calcium	Ca	20	40.08	Phosphorus	P	15	30.97
Californium	Cf	98	[251]	Platinum	Pt	78	195.08
Carbon	C	6	12.01	Plutonium	Pu	94	[244]
Cerium	Ce	58	140.11	Polonium	Po	84	[209]
Chlorine	Cl	17	35.45	Potassium	K	19	39.10
Chromium	Cr	24	52.00	Praseodymium	Pr	59	140.91
Cobalt	Co	27	58.93	Promethium	Pm	61	[145]
Copernicium	Cn	112	[285]	Protactinium	Pa	91	231.04
Copper	Cu	29	63.55	Radium	Ra	88	[226]
Curium	Cm	96	[247]	Radon	Rn	86	[222]
Darmstadtium	Ds	110	[281]	Rhenium	Re	75	186.21
Dubnium	Db	105	[268]	Rhodium	Rh	45	102.91
Dysprosium	Dy	66	162.50	Roentgenium	Rg	111	[280]
Einsteinium	Es	99	[252]	Rubidium	Rb	37	85.47
Erbium	Er	68	167.30	Ruthenium	Ru	44	101.07
Europium	Eu	63	152.00	Rutherfordium	Rf	104	[267]
Fermium	Fm	100	[257]	Samarium	Sm	62	150.36
Flerovium	Fl	114	[289]	Scandium	Sc	21	44.96
Fluorine	F	9	19.00	Seaborgium	Sg	106	[271]
Francium	Fr	87	[223]	Selenium	Se	34	78.97
Gadolinium	Gd	64	157.30	Silicon	Si	14	28.09
Gallium	Ga	31	69.72	Silver	Ag	47	107.87
Germanium	Ge	32	72.63	Sodium	Na	11	22.99
Gold	Au	79	197.00	Strontium	Sr	38	87.62
Hafnium	Hf	72	178.50	Sulfur	S	16	32.06
Hassium	Hs	108	[270]	Tantalum	Ta	73	180.95
Helium	He	2	4.003	Technetium	Tc	43	[98]
Holmium	Ho	67	164.93	Tellurium	Te	52	127.60
Hydrogen	H	1	1.008	Tennessine	Ts	117	[294]
Indium	In	49	114.82	Terbium	Tb	65	158.92
Iodine	I	53	126.90	Thallium	Tl	81	204.38
Iridium	Ir	77	192.22	Thorium	Th	90	232.04
Iron	Fe	26	55.85	Thulium	Tm	69	168.93
Krypton	Kr	36	83.80	Tin	Sn	50	118.71
Lanthanum	La	57	138.91	Titanium	Ti	22	47.87
Lawrencium	Lr	103	[262]	Tungsten	W	74	183.8
Lead	Pb	82	207.2	Uranium	U	92	238.03
Lithium	Li	3	6.94	Vanadium	V	23	50.94
Livermorium	Lv	116	[292]	Xenon	Xe	54	131.29
Lutetium	Lu	71	175.00	Ytterbium	Yb	70	173.05
Magnesium	Mg	12	24.31	Yttrium	Y	39	88.91
Manganese	Mn	25	54.94	Zinc	Zn	30	65.38
Meitnerium	Mt	109	[276]	Zirconium	Zr	40	91.22

[ ] = mass number of the isotope with the longest half life   *Atomic weights from data published by IUPAC Commission on Atomic Weights 2013*

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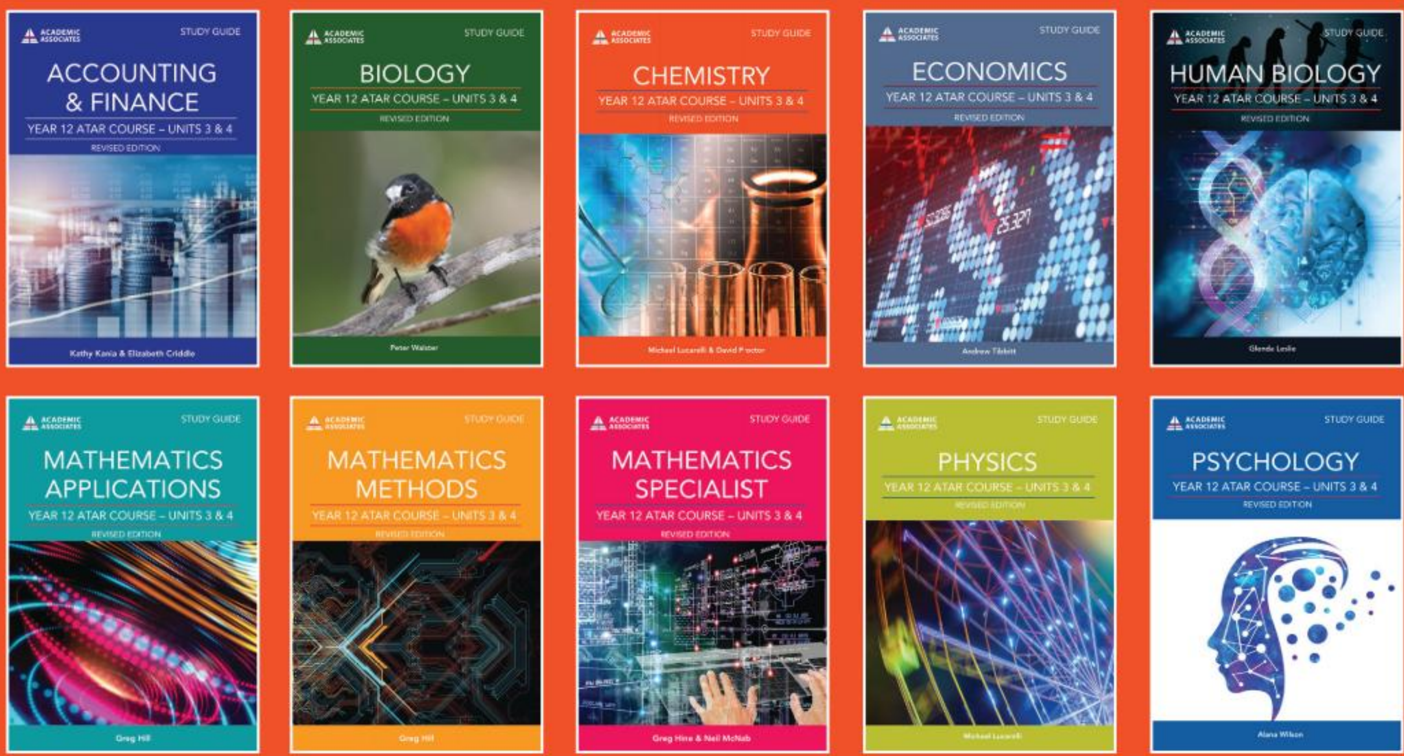

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