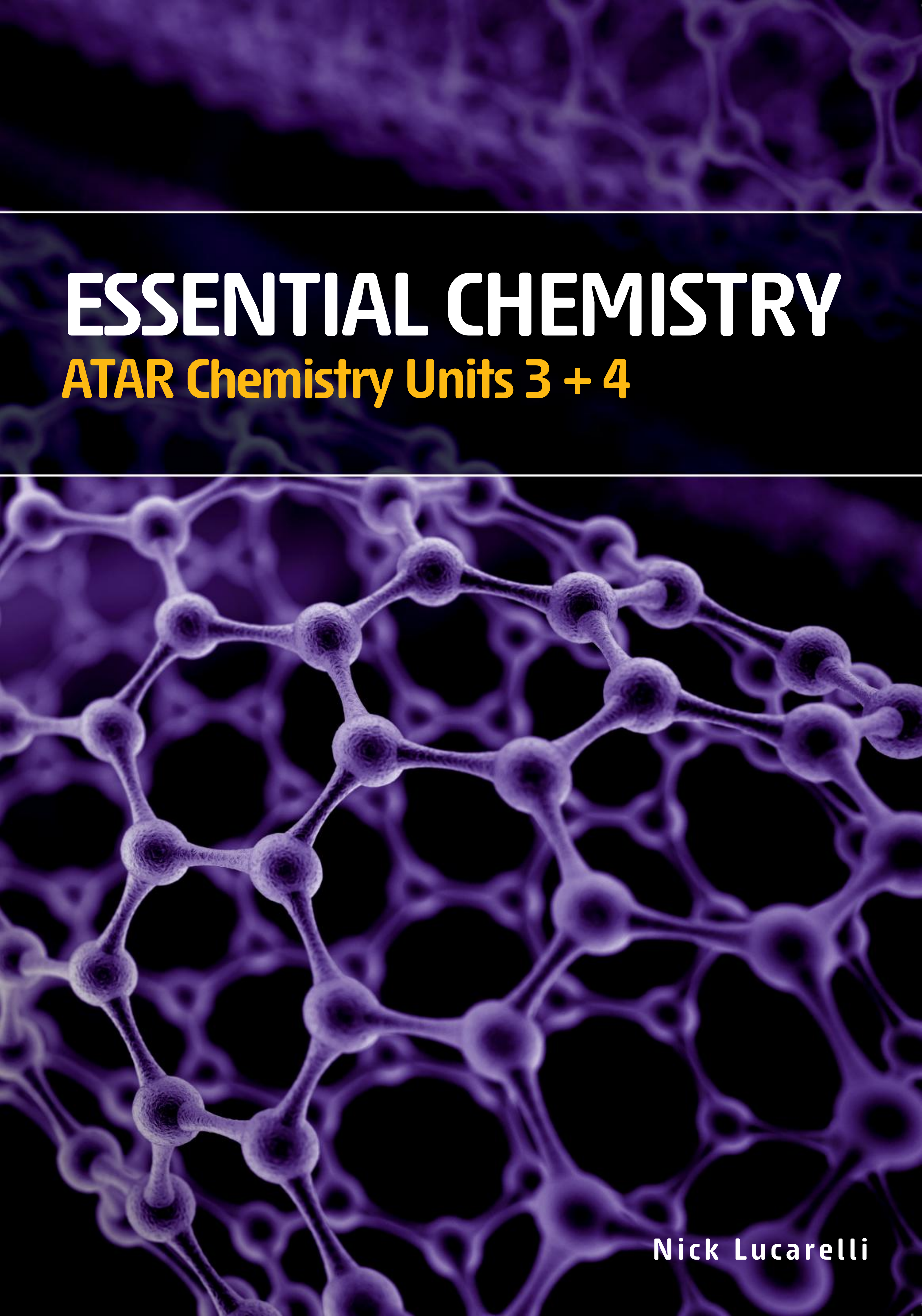

ESSENTIAL CHEMISTRY

ATAR Chemistry Units 3 + 4

Nick Lucarelli

ESSENTIAL CHEMISTRY

ATAR CHEMISTRY
UNITS 3 + 4

NICK LUCARELLI

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Lucas Publications
10 Davie Court
Willetton WA 6155
Telephone/Facsimile: (08) 9457 6521
Mobile: 0438200854
E-mail: niclucas@iinet.net.au
Web: http://www.lucaspublications.com.au/

First published: 10th August 2015

Reprinted: 20th October 2016, 10th October 2017, 15th October 2020

National Library of Australia: ISBN 978-0-9585253-4-3

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Printed in Western Australia:
Quality Press
8 Babel Road
Welshpool WA 6106
Phone: (08) 6254 9999

About this book

Essential Chemistry covers the West Australian ATAR Chemistry Course Units 3 and 4 as outlined by the School Curriculum and Standards Authority of Western Australia. It provides a complete coverage of the Science Understanding and Science as a Human Endeavour strands and includes aspects of the Science Inquiry Skills strand.

Great care has been taken to ensure the depth and breadth of chemistry content within this text accurately reflects the course outlined by the School Curriculum and Standards Authority. There are however, some inclusions that review content from the Chemistry Course Units 1 and 2. The author considers this desirable for developing a good understanding of the Chemistry Course Units 3 or 4. Their inclusion is for the convenience of teachers and students and is not intended to reflect content specific to the Chemistry Course Units 3 or 4.

Features

- Fifteen chapters conveniently sequenced to form a logical learning and teaching programme.
- Complete coverage and integration of the course strands: '**Science as a Human Endeavour**' and '**Science Understanding**' including aspects of '**Science Inquiry Skills**'.
- **Clear** and **easy to read** text that is **stimulating** and **concise**.
- Extensive use of **examples**, **illustrations**, **diagrams**, **tables** and **margin notes**.
- **Contextual situations** integrated into both the body of the text and study questions. These highlight the role of chemistry and chemists in society.
- **21 sets** of questions and problems with each question directly linked to a chapter section. Questions are carefully sequenced to allow mastery of single principles and concepts before leading into more challenging and complex tasks.
- A comprehensive **solutions manual** that provides students with detailed answers to all **written** and **calculation** questions as well as supplementary explanations and notes. These allow students to have greater control over their learning and progress.
- Fully **indexed** for convenient use.

Acknowledgements

In particular the author would like to acknowledge the meticulous efforts of Allan Knight, Norm Kingwell and Emily Chater in reviewing this publication. Their input has been invaluable in ensuring the content is both accurate and in line with the West Australian ATAR Chemistry Course Units 3 and 4.

A special thanks to Emily Chater for her article on the PDB and to Dana for assisting with data from NOAA's Earth System Research Laboratory and the Hawaii Ocean Time-Series program. I would also like to acknowledge Peter Tallent from the 'Ethanol Division' of The Manildra Group for his helpful information on the synthesis of ethanol from waste starch. To my wife Carolyn, thank you very much for your patience and contribution in proofing for grammar and ensuring the syntax in this book is as dependable as the chemistry.

Nick Lucarelli
August 2015

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CHAPTER1 | REVIEW: ENERGY AND REACTION RATE

1.1 Review: Understanding energy

Energy can be described as the capacity to do work or cause change. It is measured In **joules**. Some forms of energy are heat, chemical, electrical, light, kinetic and potential. The various forms of energy are interchangeable. However, the total amount of energy present is always constant. This means whenever one form of energy disappears or reduces in amount then another form of energy will appear or increase in amount so that the total quantity of energy present is unchanged. Thus, if the energy present in a given **system** falls then there will be a corresponding rise in the energy of its **surroundings** so that the total energy in the **system + surroundings** remains constant. (See Fig 1.) This idea is known as the **law of conservation of energy**.

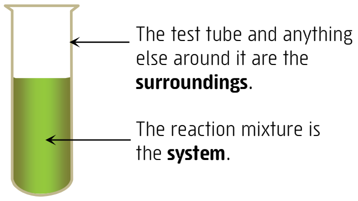

Figure 1 When analysing **energy** changes in a chemical reaction it is convenient to define the **reaction mixture** as the **system** and its container and everything else around it as the **surroundings**.

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Attempt Set 1 # 1.

1.2 Review: Energy changes in chemical reactions

During a chemical change, energy in the form of heat, light or electrical energy can be produced or consumed. Sometimes, for example, a reacting system and its surroundings is seen to heat or cool simply because of the chemical change taking place. These heating or cooling effects result from a difference in the **enthalpy** of the **products** of a reaction compared to what was originally present in the **reactants**. Enthalpy being a measure of the **energy** present in a substance. It includes (but is not limited to) the energy stored in chemical bonds, known as **chemical potential energy** plus the energy of particle motion, ie particle **kinetic energy**. Although it may seem odd, it is important to remember that weak bonds hold more chemical potential energy than do strong bonds.

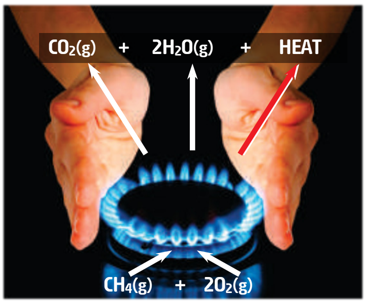
During a chemical change some bonds are broken and new ones are formed and so there will inevitably be a change (increase or decrease) in the amount of stored chemical potential energy (bond energy). As energy must be conserved, any change in chemical potential energy must be balanced by an opposite change in some other form of energy, usually particle kinetic energy ('heat'). This means the **temperature** of a reaction system will rise or fall and cause **heat** energy to flow into or out of the reaction system. (See Fig 2.) Remember, heat always flows from hot regions to cooler ones. This flow of heat (into or out of a reacting system) changes the enthalpy (total energy) of the reacting system. The resulting **enthalpy change**, **ΔH** is defined as:

$$\Delta H = H_{(products)} - H_{(reactants)}$$

where: **H** = enthalpy
ΔH = change in enthalpy

For chemical changes that happen at constant pressure, such as in an **open** beaker or test tube, the heat gain or loss of the system equals its change in enthalpy (**ΔH**). In these situations ΔH is also referred to as the **heat of reaction**.

Figure 2 A combustion reaction like that in a gas burner releases heat to the surroundings. This happens as the total energy stored in the bonds of the products is less than that of the reactants. The energy difference appears as heat in the reacting system causing its temperature to rise. Heat then flows out of the hot reacting system (gas flame) and into the cooler surroundings (air and hands). Overall **energy is conserved**.



$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

weak bonds, ie **high** chemical potential energy → strong bonds, ie **low** chemical potential energy

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Attempt Set 1 # 2.

1.3 Review: Endothermic and exothermic reactions

Reactions that **lose heat to the surroundings** (eg combustion, see Fig 2) are called **exothermic** reactions. These have a **negative** value for **ΔH**, ie enthalpy **decreases** during the course of the reaction. In an exothermic reaction some of the chemical potential energy stored in bonds is converted to particle kinetic energy. This causes an increase in the system's temperature. Overall energy is conserved with chemical potential energy becoming 'heat' energy. However, as this change raises the reacting system's temperature heat then flows out of the hot system and into the cooler surroundings. (See Fig 2.) The loss of heat energy from the system to the surroundings then means the system's enthalpy (total energy) has reduced and hence **ΔH is negative**.

Reactions that **gain heat from the surroundings** are called **endothermic** reactions. These reactions have a **positive** value for **ΔH**, ie enthalpy **increases** during the course of the reaction. This will happen if some of the particle kinetic energy in the reacting system is converted into chemical potential energy stored in bonds.

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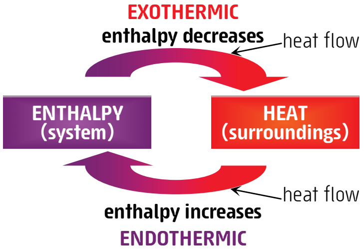
Overall there is **initially** no change in enthalpy. However, as a consequence of the reduced particle kinetic energy the reacting system's temperature will fall. Heat then flows from the warmer surroundings into the cooler reacting system. This now increases the reacting system's total energy, ie increases its enthalpy and hence **ΔH is positive**. (See Fig 3.)

Figure 3 Exothermic reactions convert chemical potential energy (**purple**), into increased particle kinetic energy (**red**). This means the temperature of the system (reaction mixture) rises and consequently **heat flows out of** the system (hot) to the surroundings (cool). Overall, the reacting system loses energy to the surroundings thus its **enthalpy decreases**.



Endothermic reactions convert particle kinetic energy ('heat') into stored chemical potential energy. The loss of particle kinetic energy within the reacting system (converted to chemical potential energy) causes the system's temperature to fall. As the system cools, **heat then flows into** it from the warmer surroundings. Thus the system gains energy from the surroundings and its **enthalpy increases**.

The enthalpy change, ΔH (or heat of reaction) for a chemical reaction can be shown graphically using an **energy profile diagram** (Fig 4) or it can be written along with the chemical equation. Sometimes the heat absorbed or released during the reaction is written into the equation rather than giving the enthalpy change. (See below.)

(A) Exothermic reaction
In this reaction **enthalpy reduces** by 572 kJ, ie ΔH= -572 kJ and so 572 kJ of heat is released to the surroundings.

(B) Endothermic reaction
In this reaction **enthalpy increases** by 394 kJ, ie ΔH=+394 kJ and so 394 kJ of heat is absorbed from the surroundings.

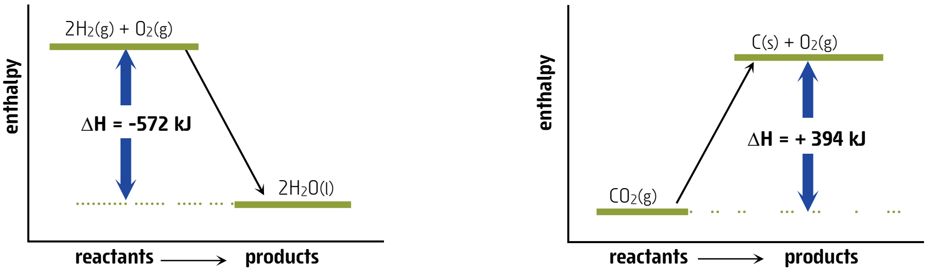


Figure 4 The energy profile diagram **(A)** shows the reduction in enthalpy for an **exothermic** reaction. In the **endothermic** reaction **(B)** there is an increase in enthalpy as products have more enthalpy than reactants.

For convenience **ΔH** is can be written along with the balanced equation, as shown for ① and ② (at left). Alternatively the **heat** absorbed or released in the reaction is written into the equation, as shown for ③ and ④.

Equation showing **enthalpy change**, **ΔH**

$2H_2(g) + O_2(g) \rightarrow$ O(l) Δ ①

heat released

$2H_2(g) + O_2(g) \rightarrow$ O(l) + **572 kJ**............... ③

Equation showing **enthalpy change**, **ΔH**

$CO_2(g) \rightarrow$ + $O_2(g)$ Δ **kJ** ②

Equation showing **heat absorbed**

(g) + **394 kJ** → + $O_2(g)$ .... ④

The above equations show how the energy change involved in a chemical reaction can be written along with the equation in terms of the **enthalpy change** (ie ΔH, see ① ② **heat flow** (see ③ ④

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Attempt Set 1 # 3 and 4.

1.4 Review: Collision theory and reaction rate

Adding a strip of zinc metal to a **dilute** hydrochloric acid solution results in a moderately fast reaction. Using **concentrated** hydrochloric acid makes this reaction much faster. (See Fig 10.) By comparison, under normal conditions, the rate of reaction between the reagents in a sparkler (Fig 5) is so slow that it appears as if no reaction is occurring at all. If however, the sparkler is lit, then an extremely rapid, almost explosive reaction is seen.

Figure 5 The reagents in a sparkler consist of a **heterogeneous mixture** of solid particles including: magnesium, aluminium, potassium chlorate and barium nitrate. Maximising the **surface area** or state of subdivision of these solid particles ensures a fast reaction rate. Also, once the reaction starts, its **exothermic** nature ensures it then continues rapidly due to the large amount of heat released.

Chemical **reaction rate** is a measure of the rate at which reactants are consumed or products are formed. Typically the rate or speed of chemical reactions increase with increasing **temperature**, **concentration**, **pressure** and **state of sub-division**. As well as these factors, the presence of a **catalyst** in a reaction mixture will also increase the rate of reaction. Catalysts are unique substances which are involved in a reaction without appearing to be consumed by the reaction. Thus the amount of catalyst present in a reaction mixture does not change as the reaction proceeds.

The way in which reactions occur and the reason why these conditions affect rate can be understood and explained in terms of the **collision theory**. This theory describes chemical reactions in terms of individual **particle collisions**. According to the collision theory, for a reaction to occur, all of the following conditions must be met.

- The reacting particles; atoms, molecules or ions must **collide**. (See Fig 6.)
- The collision energy must equal or exceed a certain minimum amount known as the **activation energy**, **E_a**. (See Fig 8.)
- The reacting particles must collide with a suitable **orientation**. (See Fig 7.)

Figure 6 The **collision theory** tells us that for a chemical reaction to occur there must be a **collision** between the reacting substances at the particle level. Here we see how the formation of HBr depends upon a collision between a **H_2 molecule** and a **Br_2 molecule**.

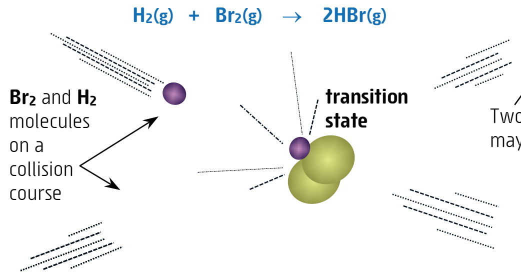
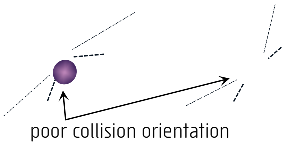
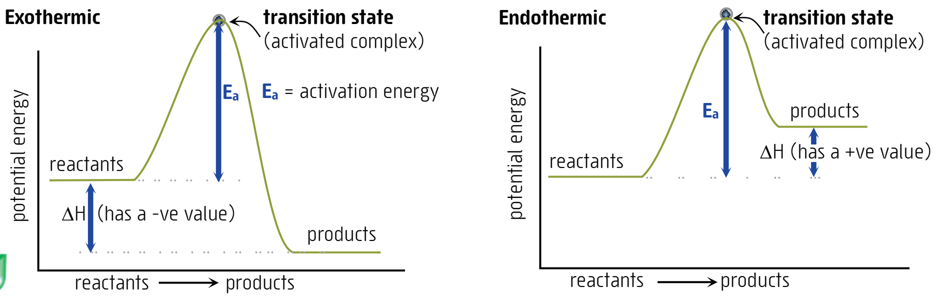


Figure 7 The transition state in Fig 6 shows a **suitable orientation** that can lead to a reaction between the colliding particles. The collision orientations shown below are not likely to be successful.



As reacting particles approach each other, repulsive forces between their electron clouds cause them to slow down and lose kinetic energy. This lost kinetic energy converts to increased potential energy of the colliding particles. If the colliding particles have sufficient kinetic energy they will approach close enough (collide) to form a **transition state**, (Fig 6) also known as the **activated complex**, the highest potential energy state for the reaction. The transition state is a point in the reaction where new bonds are forming and the original bonds are breaking. It is an unstable arrangement that decomposes quickly to form either the original reactants or new products. The minimum collision energy required to form the transition state is known as the **activation energy**, **E_a**. (See Fig 8.)

Figure 8 Energy profile diagrams show the change in potential energy for reacting particles as they approach and form an activated complex. If the colliding particles have too little kinetic energy they will rebound before the activated complex forms and so there would be no reaction. The minimum collision energy needed to form an activated complex is the **activation energy**. This is labelled **E_a**.



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Attempt Set 1 # 5 and 6.

1.5 Review: Factors that affect reaction rate

The collision theory gives us a basis for **understanding** and **explaining** the effects of concentration, temperature, pressure, state of sub-division and catalysts on reaction rate.

Concentration: Raising the concentration of an aqueous reagent increases the reaction rate. Typically doubling the concentration of a reagent will usually (but not always) double the reaction rate. The collision theory provides an explanation for this observation in terms of **collision rate**; also know as collision frequency. A higher concentration of reacting particles causes an increase in the rate (ie frequency) of collisions between these particles. This greater rate of collisions is the reason for the observed increase in reaction rate. (See Fig 9.)

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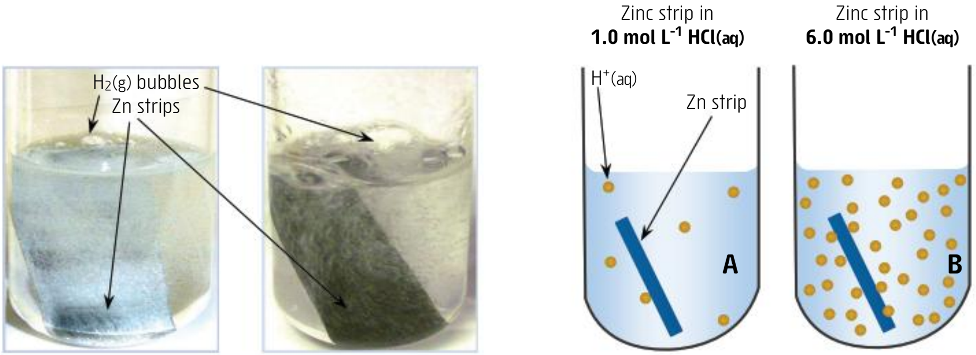
Figure 9 Concentration affects the rate of reaction between Zn(s) and HCl(aq).

$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$

Notice the rate of evolution of hydrogen gas is much greater in the right hand test tube with the higher concentration of HCl(aq). According to the collision theory, this is due to a greater rate of collisions between HCl(aq) [specifically $H^+(aq)$] and Zn atoms on the zinc surface in the more concentrated solution. This is visualised at the particle level by **Diagram A**, low $H^+(aq)$ concentration and **Diagram B**, high $H^+(aq)$ concentration.



Zinc strip in **1.0 mol L^{-1} HCl(aq)**

Zinc strip in **6.0 mol L^{-1} HCl(aq)**

A greater rate of collisions of $H^+(aq)$ ions with the Zn surface (6x greater) will occur in the **6.0 mol L^{-1} HCl(aq)**.

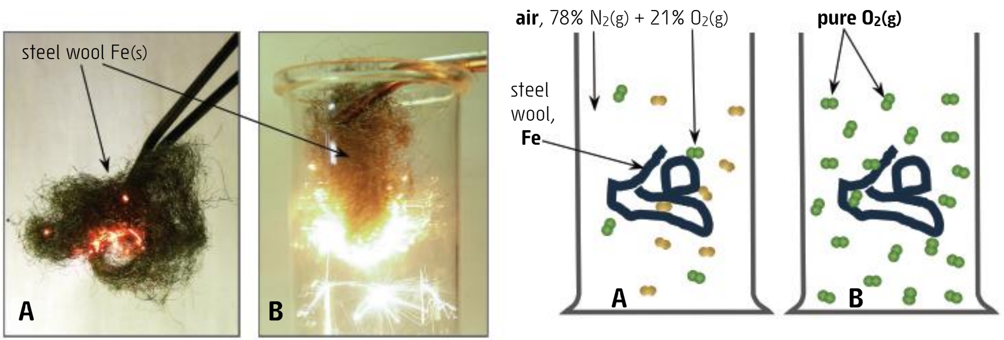
Gas pressure: Raising the pressure, by reducing volume or adding more gas to the same container, creates a greater concentration of reacting gas molecules. This causes an increase in the rate of collisions between these molecules, hence an increase in rate of reaction. Typically doubling the pressure of a gaseous reagent will usually (but not always) double the reaction rate. As with concentration in aqueous solutions the collision theory can explain the rate change in terms of **collision rate** of the reacting particles. (See Fig 10.)

Figure 10 Iron, in the form of steel wool, burns slowly in air as it reacts with $O_2(g)$ to produce $Fe_3O_4(s)$.

$3Fe(s) + 2O_2(g) \rightarrow Fe_3O_4(s)$

The $O_2(g)$ pressure in air is around 21 kPa. A gas jar of pure oxygen, however, contains $O_2(g)$ at a pressure of around 101 kPa. Here the same reaction is much more vigorous. The increased rate is due to the higher $O_2(g)$ pressure which gives rise to a greater rate of collisions between O_2 molecules and Fe atoms on the steel wool surface.

This is visualised at the particle level by **Diagram A**, low $O_2(g)$ pressure (air) and **Diagram B**, high $O_2(g)$ pressure (pure oxygen).



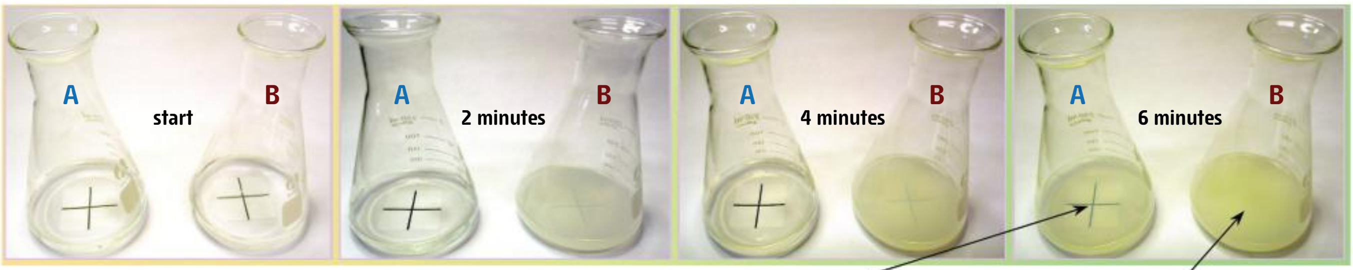
Steel wool burns slowly in **air**, ie **$O_2(g)$ at ≈ 21 kPa**.

Steel wool burns rapidly in **pure** $O_2(g)$, ie **$O_2(g)$** at **≈101 kPa**.

A greater rate of collisions of $O_2(g)$ molecules with the Fe surface (≈5x greater) will occur in pure oxygen (**B**) than air (**A**).

Temperature: Raising the temperature of a reaction mixture always increases the reaction rate. (See Fig 11.) This is true for both endothermic and exothermic reactions.

Figure 11 The series of images below show the reaction between **sodium thiosulfate** ($Na_2S_2O_3$) and **hydrochloric acid**: $S_2O_3^{2-}(aq) + 2H^+(aq) \rightarrow$ **S(s)** $+ SO_2(aq) + H_2O(l)$ at **15 °C** (Flask **A**) and **65 °C** (Flask **B**). The speed of this reaction can be visually monitored as it produces elemental sulfur, **S(s)** which turns the clear mixture cloudy yellow. Notice how the black cross disappears much more quickly in Flask B, the warmer flask. The rate of this reaction is much greater at the higher temperature as a greater percentage of the collisions between thiosulfate ions, **$S_2O_3^{2-}(aq)$** and hydrogen ions, **$H^+(aq)$** have a collision energy equal to or greater than the activation energy.



Flask **A** is at **15 °C**

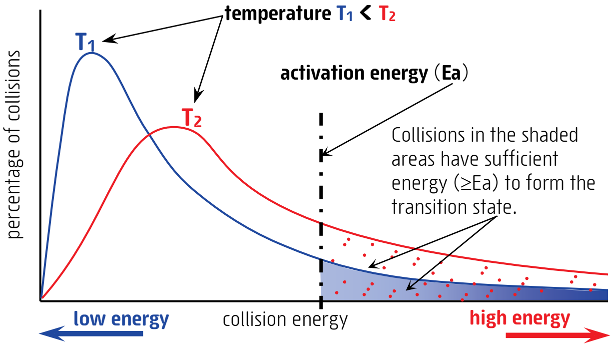
Flask **B** is at **65 °C**

After 6 minutes the black cross beneath Flask **A** is still visible while that beneath Flask **B** is no longer visible.

Using the collision theory it is possible to explain this in terms of **successful collisions**. At a higher temperature, particles on average have a **greater kinetic energy**. Remember, temperature is a measure of the **average kinetic energy** ($E_k = \frac{1}{2}mv^2$) of the particles of a substance. As the temperature of a substance rises so does the average kinetic energy of its particles.

Thus at a higher temperature the average **collision energy** of reacting particles in a reaction mixture increases (Fig 12) and a greater percentage of collisions will have sufficient energy, **≥ activation energy**, to form the activated complex. Thus a **greater percentage** of collisions are successful and hence reaction rate increases with increasing temperature.

Figure 12 The distribution of collision energies for the particles in a reaction mixture depends upon its temperature. At the higher temperature T a greater percentage of collisions have collision energy greater than activation energy, E area (red). The blue shaded area shows a smaller percentage of collisions have **collision energy** ≥ at the lower temperature T



It is also true, that higher temperatures mean an increased rate of collision between reacting particles. While this does contribute very slightly to an increased rate of reaction, its effect is known to be **minor** compared to the effect of increased collision energy.

State of subdivision: Heterogeneous reactions involve reactants that are in two separate phases, eg solid-solid, solid-liquid, solid-gas, liquid-gas or two immiscible liquids. In these reactions the reacting particles can only collide at the **surface boundary** where the separate phases make contact. Increasing the surface area (ie state of subdivision) of either of the reactants exposes a greater number of reacting particles to the possibility of a collision. This results in an increased **rate of collision** between the reacting particles and hence increases the reaction rate. (See Fig 13.)

Figure 13 Car engine fuel injectors spray liquid fuel into the combustion chambers (cylinders) forming a fine mist of fuel (high surface area). This increases the rate of collision between oxygen molecules (gas phase) and the fuel molecules (liquid phase), thus increasing the rate of fuel combustion.

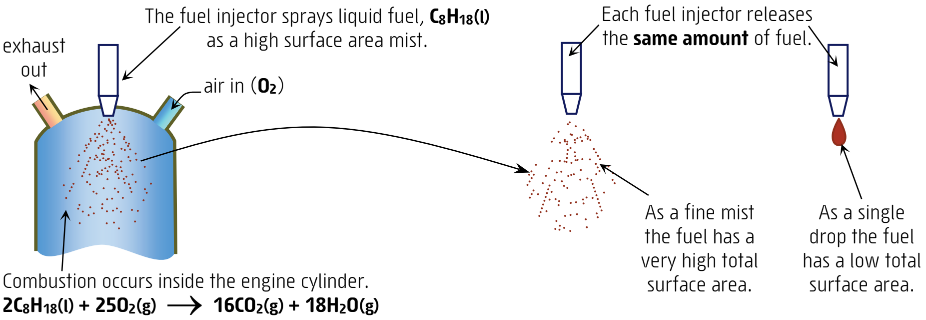
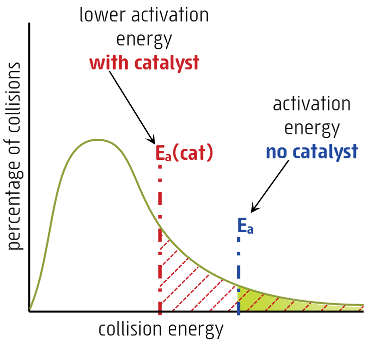


Figure 14 With a catalyst present the activation energy is lower. The shaded areas (red hatched and green) show a greater percentage of collisions have energy ≥Ea (activation energy) when a catalyst is present.



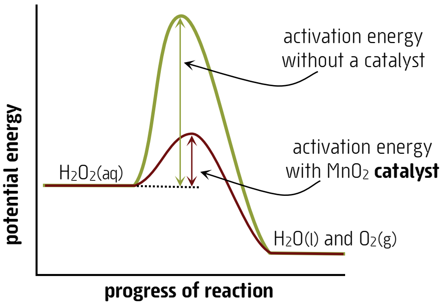
Catalysts: Certain substances, known as catalysts, have the ability to speed up chemical reactions while they remain chemically unchanged at the end of the reaction. Even though the catalyst might take part in the reaction there is no net consumption of the catalyst at the end of the reaction. Many transition metal elements like Mn, Pt, Pd, Au, Rh and their compounds show strong catalytic effects in certain reactions. The presence of a small amount of manganese dioxide, $MnO_2(s)$ for example, rapidly increases the rate of decomposition of hydrogen peroxide to oxygen and water. (See Fig 15.)

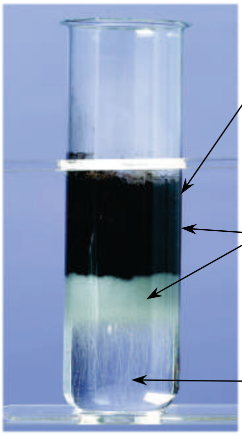
Catalysts increase the rate of reaction by providing a reaction pathway; a series of changes by which reactants change to products; with a **lower activation energy**. Thus when a catalyst is present a **greater percentage of collisions** will have energy equal to or greater than the activation energy. (See Fig 14.) As a result a greater percentage of collisions are successful and so the rate of reaction increases.

Figure 15 The **uncatalysed** and **catalysed** energy profile diagram for the decomposition of $H_2O_2(aq)$.

$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

A high activation energy makes this reaction slow under normal laboratory conditions. Adding a catalyst like $MnO_2(s)$ provides the reaction with a pathway of lower activation energy. Thus with the catalyst present a greater percentage of collisions between H_2O_2 molecules have sufficient energy to form the activated complex. Such collisions may go on to produce $H_2O(l)$ and $O_2(g)$. As a result the rate of decomposition of $H_2O_2(aq)$ is much greater with a catalyst present.





The economic synthesis of many valuable chemical substances involves the use of inorganic catalysts (eg Pt, Rh, MnO_2, V_2O_5) or enzymes (biological catalysts) to speed up otherwise slow reactions. Even though high temperatures and pressures can be effective they require the use of large amounts of energy which has associated economic costs, environmental costs and sustainability issues. Catalysts can offer a solution which is **sustainable**, has **lower energy input** and **minimises environmental impact**. The use of enzymes can be particularly advantageous as they are usually very fast acting, extremely specific in the reactions they catalyse and tend to be non-toxic to people or the environment. Their specificity helps to avoid unwanted side reactions and the formation of potentially harmful or wasteful by-products. (See Chapter 15.)

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Complete Set 1.

Set 1 Review: Energy change and reaction rate

Figure 16 Silver depositing on a copper coil.
$2Ag^{+}(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + 2Ag(s)$

1. Figure 16 shows the chemical change that occurs when a copper coil is placed into a silver nitrate solution. The reaction produces a deposit of pure silver and a solution of copper nitrate (pale blue). Use this example to show your understanding of the terms **system** and **surroundings** in the context of this chemical reaction.

2. The reaction mixture shown in Fig 16 shows a slight **temperature rise** as the reaction progresses. With this in mind answer the following questions.
   a. **Compare** the enthalpy of the reactants and products of this reaction.
   b. **Describe** the energy changes occurring in this situation that lead to the temperature rise. Your answer should refer to the reactants, products, enthalpy, chemical potential energy, heat, system and surroundings.
   c. On average which bonds are stronger, those of the reactants or products? **Justify** your answer.

3. Consider the reactions described here and **classify** them as endothermic or exothermic. In each case **describe** what happens to the temperature of the reacting system and give a brief **explanation** of why its temperature changes.
   a. $2H_2(g) + O_2(g) \rightarrow 2H_2O(l) + 572\text{ kJ}$
   b. $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) \quad \Delta H = -2870\text{ kJ}$
   c. $H_2O(s) \rightarrow H_2O(l) \quad \Delta H = 6.0\text{ kJ}$
   d. $C_2H_5OH(l) + 43\text{ kJ} \rightarrow C_2H_5OH(g)$

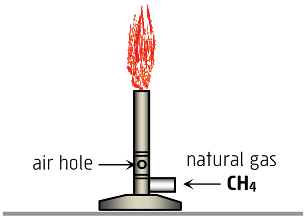


Figure 17 The heat produced from a Bunsen burner comes from the **combustion** of natural gas (essentially methane, CH_4). A collar surrounding the air hole can be adjusted to vary the amount of air mixing with methane.

4. A **Bunsen burner** (Fig 17) utilises the combustion of gaseous hydrocarbons like methane, $CH_4(g)$ as a means of producing high temperatures. Typically the reaction products are carbon dioxide gas and water vapour.
   a. Is this reaction endothermic or exothermic? **Explain**.
   b. Write an **equation** for the complete combustion of methane in air as described above.
   c. Write the equation to include **heat** given that each mole of methane releases 802 kilojoules of heat energy when burnt this way.
   d. Write the equation to show the enthalpy change, **ΔH**.
   e. Draw an **energy profile diagram** for this reaction. Label the axes, reactants, products, enthalpy of reactants, enthalpy of products and ΔH.

breaking
collide
repel
reactants
orientation
hydrogen bromide
kinetic energy
activation energy
randomly
activated complex
forming
electron clouds
molecules
decompose

5. The following passage describes the events taking place at the particle level when **hydrogen gas**, $H_2(g)$ and **bromine gas**, $Br_2(g)$ are mixed in a sealed container and react to form **hydrogen bromide**, $HBr(g)$. Use the terms listed to complete the passage. Some terms may be used more than once.

   Hydrogen and bromine (a) ____________ move (b) ____________ within the mixture of two gases. Occasionally a molecule of hydrogen gas will (c) ____________ with a molecule of bromine gas. When they collide the negatively charged (d) ____________ of the two molecules will partially overlap causing the molecules to (e) ____________ one another and slow down. If the molecules collide with sufficient (f) ____________ so that the collision energy is greater than or equal to the (g) ____________ and the collision has a favourable (h) ____________ then a reaction may occur.

   Once the molecules of hydrogen and bromine have collided with sufficient energy they form a single but unstable unit called an (i) ____________. In this structure the original bonds present within the hydrogen molecules and bromine molecules are (j) ____________ while new bonds between bromine atoms and hydrogen atoms are (k) ____________. This activated complex or transition state is a short lived arrangement of loosely bonded atoms that will rapidly (l) ____________ to form either the original (m) ____________ or (n) ____________.

6. The commonly used sports cold pack (Fig 18) contains $NH_4Cl(s)$ and water in separate compartments. When struck sharply the two substances mix allowing water to dissolve the solid NH_4Cl, resulting in a cooling effect.
   a. Is this reaction endothermic or exothermic? **Explain**.
   b. Write an **equation** for this reaction.
   c. Include **heat** in the equation given the dissolving of one mole of $NH_4Cl(s)$ absorbs 1.4 kilojoules of heat energy when dissolved.
   d. Show the enthalpy change, **ΔH** in your equation.
   e. **Draw** an **energy profile diagram** for this reaction. Label the axes, reactants, products, ΔH and activation energy (E_a).


Figure 18 Instant sports cold packs use an **endothermic** reaction to produce freezing temperatures. Sports hot packs use an **exothermic** reaction to produce a heating effect.

7. A student investigated the reaction rate of the **exothermic** reaction between calcium carbonate and hydrochloric acid. She used a 3.5 g piece of $CaCO_3(s)$ placed into 40 mL of 2.5 mol L^{-1} $HCl(aq)$ initially at 19 °C. As the reaction proceeded carbon dioxide was formed and collected by the downward displacement of water. The total volume of gas produced was noted every 30 seconds for a four minute period. Her results are graphed in Fig 19. The equation for this reaction is shown here.

   $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g)\ \ H_2O(g)$

   As can be seen in Fig 19 the rate of formation of $CO_2(g)$ is initially low ①
   ② ③
   to **account** for these changes in rate.

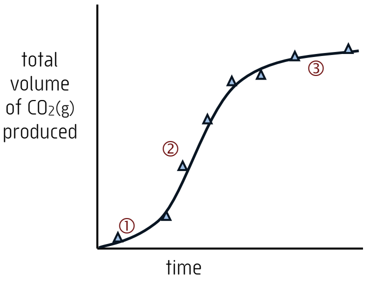


Figure 19 Shows how the rate of formation of carbon dioxide gas changes during the course of the reaction.

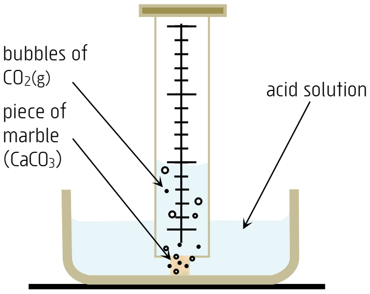
8. Hydrogen is an extremely flammable gas. Mixed with oxygen it can react explosively to produce water and a considerable amount of heat energy.

   $2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \quad \Delta H = -572\ kJ$

   At room temperature, however, there is no evidence of a reaction between these gases and at these conditions a mixture of hydrogen and oxygen can exist indefinitely. If however, a room temperature mixture of hydrogen and oxygen is passed over a **platinum** wire mesh the mixture will instantly ignite without the mesh itself showing any signs of chemical change.
   a. **Describe** how the presence of **platinum** mesh allows hydrogen and oxygen to react rapidly at room temperature.
   b. Use the information given to sketch an **energy profile diagram** for the reaction of $H_2(g)$ and $O_2(g)$ with and without the presence of platinum. On the profile label reactants, products, ΔH and activation energy.
   c. The **Hindenburg airship** disaster of 1937 (Fig 20) was the result of the combustion of on-board hydrogen gas used for the airship's buoyancy. The cause of the disaster has never been clearly established. One theory suggests lightning or an electrical spark, due to static electricity forming on the hull of the airship, may have been the cause. In either case, for the hydrogen gas to burn, it must have somehow leaked out of one or more of the buoyancy cells inside the airship hull.
      i. Use your knowledge of the **collision theory** to **explain** how lightning or a spark from a static discharge could ignite hydrogen gas from the Hindenburg.
      ii. 'A spark inside any one of the airship's buoyancy cells (filled with pure hydrogen gas) cannot cause the hydrogen it contains to ignite.' **Justify** this statement with reference to the collision theory.


Figure 20 The Hindenburg hits the ground in flames in Lakehurst, N.J. on May 6, 1937.

Figure 21 Apparatus for producing and collecting carbon dioxide gas.



The **rate of formation** of a substance in a chemical reaction can be calculated using:

$$\text{rate} = \frac{\text{amount produced}}{\text{time taken}}$$

Rate can be expressed in a variety of units, for example:

moles per second............... mol s^{-1}
grams per second .... g s^{-1}
millilitres per second.......... mL s^{-1}

9. The presence of certain gases in the atmosphere (like SO_2, SO_3 and NO_2) can cause the deterioration of metal, concrete and some types of stone structures. This happens as these gases dissolve in rain water producing various types of acidic solutions [eg respectively for the gases mentioned above: $H_2SO_3(aq)$, $H_2SO_4(aq)$, $HNO_2(aq)$ and $HNO_3(aq)$]. Rainfall that has been made acidic in this way is known as **acid rain**.

   Laura, a Chemistry student, decided to investigate what factors might alter the rate of deterioration of a marble statue affected by acid rain. She decided to focus on the heterogeneous reaction of marble, ie calcium carbonate, with a nitric acid solution.

   $$CaCO_3(s) + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + H_2O(l) + CO_2(g)$$

   She performed her reactions in a 500 mL open beaker at 25 °C and atmospheric pressure of 101 kPa. Her initial reaction involved using a single **2 cm cube of marble**, $CaCO_3$ in **200 mL** of **0.010 mol L^{-1} $HNO_3(aq)$.** The carbon dioxide produced by the reaction was collected in an inverted 50 mL measuring cylinder (Fig 21) initially full of the same acid solution.

   a. What **measurements** should Laura take in order to calculate the rate of reaction between marble, $CaCO_3$ and the nitric acid solution. (See border note.)

   b. She repeated her experiment several times being careful to change only one reaction variable for each new experiment. The alterations to reaction conditions used are described in the table below. Complete the table stating the **independent variable** that was altered and any **rate changes** you might expect Laura to observe. In the final column state how the collision theory **supports your predictions**.

Alteration to conditions (other conditions unaltered)	**Independent variable** (ie the one being altered)	**Predicted effect on the dependent variable** (ie reaction rate)	**Use the collision theory to justify your prediction**
i. Heat the reaction mixture to 55 °C.			
ii. Use 0.10 mol L^{-1} HNO_3.			
iii. Break the 2 cm cube of $CaCO_3(s)$ into ten smaller pieces.			
iv. Refrigerate the mixture to 2 °C.			

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10. **Chlorofluorocarbons**, CFCs are a very stable non toxic group of compounds that are now known to cause damage to the Earth's **ozone layer**. (See Fig 22.) When these pollutant gases reach the Earth's upper atmosphere they become decomposed through exposure to sunlight and form among other things free chlorine atoms, Cl.

$CFCl_3(g) \rightarrow CFCl_2(g) + Cl(g)$ (CFC decomposes in the upper atmosphere.)

It is the **free chlorine atoms** (free radicals) that are responsible for the depletion of **ozone molecules (O_3)**. These two reactions show one way that CFCs can deplete ozone.

$Cl(g) + O_3(g) \rightarrow ClO(g) + O_2(g)$ .... $_3$.)

$ClO(g) + O(g) \rightarrow Cl(g) + O_2(g)$ .... $_3$ formation.)

a. Write the **overall equation** for the depletion of ozone, O_3 in the presence of chlorine atoms, Cl. (You will need to add reaction ① ②

oxygen, as shown in your net reaction (from 10a above), is normally very slow. What is the general **name** for substances like these chlorine atoms which increase reaction rate this way? **Justify** your answer.

c. With reference to the collision theory briefly **explain** the role of chlorine atoms in increasing the rate of ozone depletion.

Figure 22 Ozone, O_3 is an allotrope of oxygen, O_2 occurring naturally in a region of the Earth's upper atmosphere known as the ozone layer. Both the formation and presence of ozone result in the absorption of harmful **UV radiation** from the sun.
The depletion of ozone by chlorofluorocarbons (CFCs) was first recognised during the mid-1970s. Peak production of CFCs occurred in 1977 and since then their use has diminished to the point where their use has now largely ceased. The substitution of chlorofluorocarbons with safer alternatives is a direct result of international protocols.

11. Transport vehicles like the motor car use an **internal combustion engine** to produce movement. These engines operate by burning fuels like petrol, diesel or LPG in air. The major products of the combustion reaction are carbon dioxide gas and water vapour. Heat energy from this reaction is ultimately converted to movement energy within the engine. This movement energy is then transferred to rotational movement of the vehicle's wheels.

a. The combustion of petrol (eg C_8H_{18}) in air (O_2) is **exothermic** and **extremely slow** at room temperature. Sketch an **energy profile diagram** for this reaction. On the profile label reactants, products, ΔH and activation energy. **Justify** the size of the activation energy shown on your sketch.

b. In the internal combustion petrol engine the rate of fuel combustion is increased by converting **liquid** petrol into a **fine mist** of petrol droplets. This is achieved by spraying the fuel into combustion cylinders using a device called a fuel injector. (See Fig 13 and 24.) Why should this technique increase the rate of combustion?

c. The combustion rate of petrol in the internal combustion petrol engine is further increased by compressing the reaction mixture. A moving piston (Fig 24) within the combustion cylinder reduces the fuel/air volume by a factor of around 10 times. Why does **compression** of the reaction mixture increase the rate of combustion?

d. Despite the use of high pressure and subdividing the liquid petrol to form a mist, the rate of combustion in a petrol engine remains insignificant until a spark plug (Fig 23) produces a small but high temperature spark within the petrol air mixture.

   i. Use your knowledge of the **collision theory** to **account** for the effect of the high temperature spark on the rate of combustion within the fuel/air mixture in the immediate vicinity of the spark.

   ii. The spark is only able to cause heating within the very small volume of the reaction mixture that is in direct contact with the spark itself. What causes the remaining gas mixture (outside the spark area) to also rapidly burn?

e. One unwanted reaction occurring in the internal combustion engine is the reaction of nitrogen gas, N_2 with oxygen gas, O_2 to produce nitric oxide (nitrogen monoxide gas, NO). Nitric oxide is a harmful substance to both the environment and human health. It also becomes involved in a series of atmospheric reactions producing harmful substances generally known as photochemical smog.

The rate of formation of NO gas in the atmosphere (78% N_2 and 21% O_2) is negligible compared to the rate of its formation inside the combustion cylinders (Fig 24) of a motor car engine. **Account** for the difference in rate of formation of NO in the engine cylinders compared to the atmosphere.

Figure 23 A view of a **spark plug** used to ignite the fuel air mixture inside an internal combustion engine.

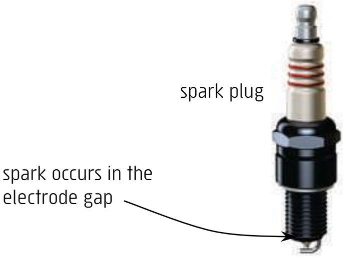
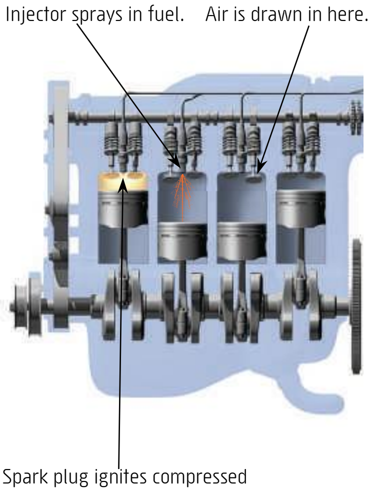


Figure 24 A side view of a **fuel injected** petrol engine.



Spark plug ignites compressed fuel air mixture inside the combustion cylinders.

CHAPTER 2 | CHEMICAL EQUILIBRIUM

2.1 Reversible reactions

'Diamonds are forever', or so they say? Interestingly though, graphite is actually the preferred or more stable form of carbon. Despite this, under normal conditions, once formed, a diamond shows no sign of changing back into graphite. Just as well!

Figure 1 Diamond and graphite are two interchangeable **allotropes** of carbon.

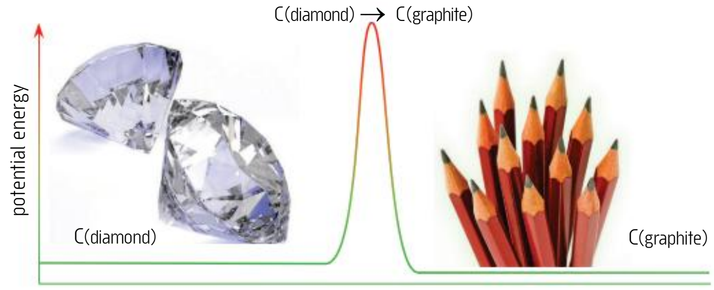
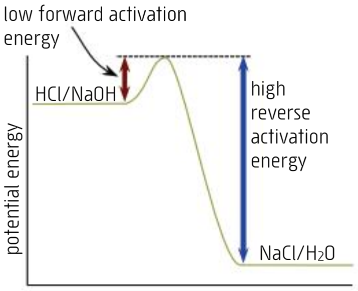


Figure 2 Potential energy profile for the reaction of NaOH(aq) with HCl(aq).

$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$



This apparently **non-reversible** reaction is due to a very **high activation energy** (Fig 1) for both the formation of diamond and its conversion back to graphite. Other reactions, like the formation of salt and water from sodium hydroxide and hydrochloric acid, have a very low activation energy in one direction but a high activation energy in the reverse direction. (Fig 2.) Here the products, ie NaCl and H_2O, form rapidly but the reverse reaction, ie the formation of NaOH and HCl, does not appear to occur under normal conditions. **Reversible reactions** however, have a **low activation energy** for both the forward and reverse reaction.

Non-reversible reactions tend to be the exception. Most chemical reactions and physical changes are reversible, at least to some extent. **Reversible** reactions do not go to completion as once the products form they react together to reform reactants. This is most easily seen in physical processes like evaporation and condensation or dissolving and crystallising. If reversible processes like these are confined to a **closed system**, ie one where **energy** can enter or leave but not **matter**, then the forward and reverse reactions compete with one another preventing the reaction from going to completion in either direction.

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Attempt Set 2 # 1.

2.2 Evaporation of water - a physical equilibrium

A small amount of water left in an open flask on the laboratory shelf will over a period of weeks disappear. An unsealed flask such as this is an **open system**. It allows water vapour (ie matter) to diffuse into the surrounding air and escape from the flask. (See Fig 3.) Once all of the water has evaporated and escaped, the flask is left dry. However, if the same amount of water is left in a stoppered flask, ie a **closed system**, then evaporation can still occur but the vapour is unable to escape. (See Fig 4.) Under these conditions the confined water vapour can condense and revert to the liquid phase within the flask. Thus in a closed system like this, evaporation ① and its reverse process, condensation ②, can both occur. The equations for these opposing changes can be shown separately or written together ③ using a double arrow, $\rightleftharpoons$.

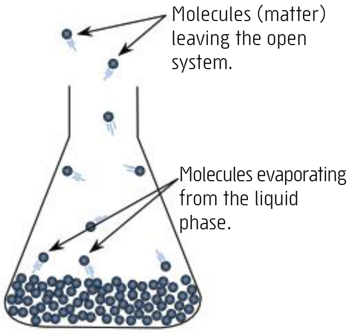

Figure 3 An **open system** (above) allows both matter and energy to flow in or out of the system.

A **closed system** (Fig 4) is one where matter can not enter or leave but energy can.

evaporation: $H_2O(l) \longrightarrow H_2O(g)$ ....①

condensation: $H_2O(g) \longrightarrow H_2O(l)$ ......②

or $H_2O(l) \overset{①}{\underset{②}{\rightleftharpoons}} H_2O(g)$ .... ③

Initially there is minimal vapour in the stoppered flask (Fig 4) and the rate of vapour condensation ② will be much less than the rate of liquid evaporation ①. Over time the concentration of water vapour in the air above the liquid steadily rises. The increasing vapour concentration leads to an increasing rate of vapour condensation. Eventually the rate of condensation will equal the rate of evaporation. At this point the liquid water and the confined water vapour are said to be in a state of **dynamic equilibrium**.
Even though water continues to evaporate there will be no further increase in its vapour concentration as the vapour is condensing as fast as it is forming. A consequence of this is the pressure due to water vapour inside the flask will become **constant** over time. This constant vapour pressure is referred to as the **equilibrium vapour pressure**. (See Fig 5.)

A system that has achieved equilibrium always appears static, ie it appears as though the reactions within the system have stopped. However, at a particle level both the **forward** and **reverse** reactions are still proceeding, albeit at the **same rate**. This is why a chemical or physical equilibrium is said to be **dynamic** rather than **static**.

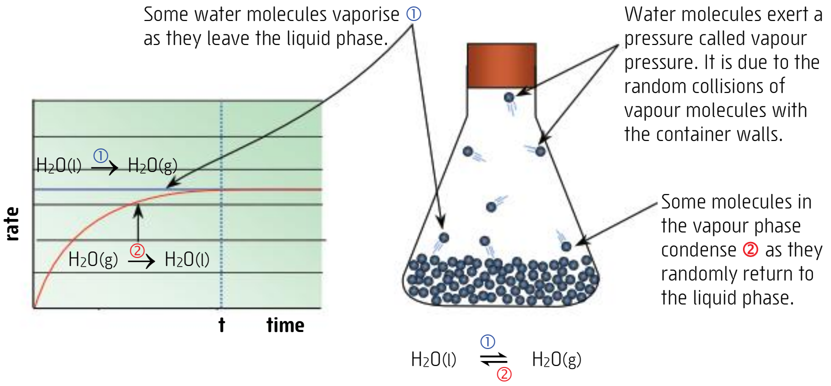

Figure 4 At a given temperature the rate of evaporation ① of water in the flask is constant. The graph shows this as a horizontal blue line. At first, the rate of condensation ② (red line) of $H_2O(g)$ is negligible as the concentration of $H_2O(g)$ is initially negligible.

As the $H_2O(g)$ concentration rises (due to the steady rate of evaporation) so does the rate of its condensation. Eventually the rate of condensation equals the rate of evaporation. At this point, **t** in the graph, the system is said to be in a state of **dynamic equilibrium** and the water vapour pressure reaches a steady value called the **equilibrium vapour pressure**.

The position of this equilibrium describes the extent to which water is in the vapour phase. The greater the vapour pressure, the more the equilibrium position favours the vapour phase (products). For this system the tendency to exist in the vapour phase increases with increasing temperature but it also depends upon the nature of the liquid involved. (See Fig 5.) In particular it depends upon the strength of the intermolecular forces present within the liquid. Where these are stronger, the equilibrium vapour pressure is correspondingly lower and the vapour phase is less favoured.

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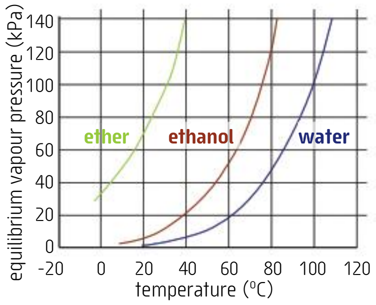

Figure 5 These graphs show how vapour pressure increases with temperature. The low vapour pressure of water is due to its strong intermolecular forces.

2.3 Reversible reactions and chemical equilibrium

Many chemical reactions are known to be **reversible**. When confined to a **closed system**, reversible reactions can reach a point where they are said to be in **equilibrium**. For a chemical reaction at equilibrium, two equal but **opposing** reactions are proceeding at the **same rate**.

Example 1 Reversible reactions in the $NO_2(g)/N_2O_4(g)$ equilibrium. (See Fig 6.)

$2NO_2(g) \rightarrow N_2O_4(g)$ .... ①   Note: NO_2 is **brown** while N_2O_4 is **colourless**

$N_2O_4(g) \rightarrow 2NO_2(g)$........ ②

Notice the products of reaction ① are the same as the reactants for reaction ② and vice versa. Thus reaction ① and ② are said to be **reversible** or opposing reactions. If a sample of $NO_2(g)$ is placed into a sealed container, its molecules will combine by reaction ① to form $N_2O_4(g)$ molecules. Over time this reduces the concentration of $NO_2(g)$ and hence reduces the rate of reaction ①. Also, as $N_2O_4(g)$ begins to form it can then decompose by reaction ② reforming the original $NO_2(g)$. At some point the concentrations of $NO_2(g)$ and $N_2O_4(g)$ are such that the rate of the opposing reactions ① and ② are equal. At this point the system is said to be at **equilibrium**.

Figure 6 Matter can not enter or leave a **closed system**. An open beaker could serve as a closed system for an equilibrium involving only condensed phases of matter like solids, liquids or aqueous solutions. The sealed glass tubes shown here form a closed system for the gaseous **$NO_2(g)/N_2O_4(g)$** equilibrium. (See Example 1.)

The two vials, **B** and **C** originally contained an identical equilibrium mixture of $NO_2(g)$ (**brown**) and $N_2O_4(g)$ (**colourless**), as seen in vial A. Placing vial A into water at different temperatures causes the equilibrium to change, re-establishing itself with a new ratio of $NO_2(g)$:$N_2O_4(g)$.

If vial **A** is placed into hot water, **B** it becomes darker brown, indicating the concentration of $NO_2(g)$ has increased. The lighter coloured vial in the cold water, **C** has a higher concentration of colourless $N_2O_4(g)$.

This ability of chemical equilibrium systems to respond to changes, such as temperature changes, is a reminder of the **dynamic** nature of chemical equilibrium.

Double arrows $\rightleftharpoons$ are used to show reactions like those in the $NO_2(g)/N_2O_4(g)$ system are reversible.

$$\underset{\textbf{brown}}{2NO_2(g)} \quad \underset{②}{\overset{①}{\rightleftharpoons}} \quad \underset{\textbf{colourless}}{N_2O_4(g)} \qquad \Delta H = -57\text{ kJ}$$

Written this way reaction ① is referred to as the **forward reaction** and reaction ② as the **reverse reaction**. For a system like this to be at equilibrium, the rate of the forward reaction ① must equal the rate of the reverse reaction ②. Thus, at equilibrium in the NO_2/N_2O_4 system, NO_2 is being consumed by reaction ① as fast as it's being produced by reaction ②. Similarly N_2O_4 is being formed by reaction ① as fast as it's being consumed by reaction ②. Consequently the effects of forward and reverse reactions cancel one another out. So at equilibrium the concentration of both NO_2 and N_2O_4 remains constant over time. This **constancy** of **concentrations** for all the reactants and products is the hallmark of a chemical system that has reached equilibrium. Because of this constancy of concentrations, other features of a system at equilibrium, like its **colour**, **pressure** or **temperature** (known as **macroscopic properties**) also remain constant over time.

Despite the static appearance of a system at equilibrium, ie nothing seems to be changing, it is still active as both the forward and reverse reactions are still occurring, albeit at the same rate. For this reason a chemical system at equilibrium is said to be **dynamic** as opposed to static, which would incorrectly imply the forward and reverse reactions have stopped.

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Attempt Set 2 # 5 and 6.

2.4 Equilibrium position: Reactants versus products

While the concentration of all reactants and products remains constant at equilibrium, the **relative concentrations** of reactants compared to products is different for different systems. Some systems naturally favour a high concentration of products at equilibrium while in other systems reactants may be favoured. The **equilibrium constant**, **K_c** gives a numerical value relating the concentration of all species in a system at equilibrium. The overall expression for K_c is known as the **equilibrium constant expression**.

For the general reaction: $aA + bB \rightleftharpoons cC + dD$

$$K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

where: **K_c** is the equilibrium constant
a, b, c and d are coefficients of the substances A, B, C and D.
$[A]^a$ is the equilibrium concentration of A raised to the power of a and so on for $[B]^b$, $[C]^c$ and $[D]^d$.

Table 1 The equilibrium constant, **K_w** for the ionisation of water at different temperatures.

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

Temperature (°C)	**$K_w = [H^+][OH^-]$**
0	0.144×10^{-14}
10	0.292×10^{-14}
20	0.681×10^{-14}
25	1.008×10^{-14}
30	1.47×10^{-14}
40	2.92×10^{-14}
50	5.5×10^{-14}
100	55×10^{-14}

Points to note about the equilibrium constant **expression**:

- Only **gases** and **aqueous** species, those subscripted **(aq)** or **(g)**, appear in the expression. **Solids** and **liquids** [eg $CaCO_3(s)$ and $H_2O(l)$] have a fixed concentration and so they are not included in the equilibrium constant expression.
- The concentrations of each of the different species are the concentrations at **equilibrium** in mol L^{-1} but the equilibrium constant, K_c has no units.
- While K_c has a **constant value** for all conditions of concentration and pressure its value does change if temperature changes. (See Table 1.)

The **magnitude** of **K_c** gives an indication of the equilibrium composition of a reaction mixture, ie it indicates the relative concentrations of products compared to reactants.

- **Large** values of **K_c** imply the equilibrium **favours products**.
- **Small** values of **K_c** imply equilibrium **favours reactants**.
- Values of **K_c close to 1** imply significant concentrations of both reactants and products are present at equilibrium. (See Table 2.)

Table 2 Equilibrium position and equilibrium constant. Square brackets, [ ] are used as an abbreviation for concentration.

Reaction	**Equilibrium constant**	**K_c (at 25 °C)**	**Equilibrium composition**
$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$	$K_c = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$	**1.7×10^{-5}**	Reactants are favoured as K_c is small.
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$	**5.1×10^5**	Products are favoured as K_c is large.
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$	$K_c = \frac{[NO_2]^2}{[N_2O_4]}$	**0.21**	Neither reactants nor products are favoured as K_c is close to 1.

Although the equilibrium constant, K_c has a set value (for a given temperature) there are many possible combinations of reagent concentration that will give it. Also, irrespective of the reagent concentrations initially placed into a closed system, a chemical equilibrium will always readjust itself so that the combination of reagent concentrations at equilibrium gives the same constant value of K_c for the given reaction and temperature. (See Table 3.)

Notice the **reaction quotient**, **Q_c** (see left) in table 3, is not constant. Its value simply depends upon the concentration of reagents currently present in the chemical system. The equilibrium constant expression though reflects the concentrations present when the system has reached equilibrium, ie when the rate of the forward and reverse reactions are equal. Notice how **K_c** has a constant value but the individual reagent concentrations do not.

The reaction quotient expression has a similar appearance to the equilibrium constant expression.

$$Q_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

However, the concentration values for this expression are for a system not necessarily at equilibrium. If the reaction quotient, **$Q_c = K_c$** then the system is at equilibrium.

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Table 3 Initial reagent concentration and resulting equilibrium concentration (**at 100 °C**) for the equilibrium: $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

Initial concentration (mol L^{-1})		$Q_c = \frac{[NO_2]^2}{[N_2O_4]}$	**Resulting equilibrium concentration**		$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.21$
$[N_2O_4]$	$[NO_2]$		$[N_2O_4]$	$[NO_2]$	
0.0333	0.0499	$\frac{[0.0499]^2}{0.0333} = 0.0748$	0.0233	0.0699	$\frac{[0.0699]^2}{0.0233} = 0.21$
0.1052	0.0657	$\frac{[0.0657]^2}{0.1052} = 0.0410$	0.0752	0.1257	$\frac{[0.1257]^2}{0.0752} = 0.21$
0.2560	0.2220	$\frac{[0.2220]^2}{0.2560} = 0.1925$	0.2520	0.2300	$\frac{[0.2300]^2}{0.2520} = 0.21$

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Attempt Set 2 # 7 and 8.

2.5 Shifting the equilibrium position

A very important feature of chemical equilibrium systems is their ability to return to a state of equilibrium after alterations, called **imposed changes**, have been made to the system. The following imposed changes will affect an equilibrium system.

- Changing the **concentration** of any one species in the system, ie by selectively adding it to the system or removing it from the system.
- Changing the **total pressure** in a gaseous system, ie by raising or lowering its volume.
- Changing the **temperature** of the system, ie by adding or removing heat from the system.

Le Chatelier's principle predicts (but does not explain) how an equilibrium system will respond to these imposed changes. It states, "If a system is at equilibrium and a change in conditions is imposed on the system then the system will readjust to establish a new equilibrium that **partially counteracts** the imposed change." The principles of **reaction rate** and **collision theory** can further be used to **explain** such changes.

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2.6 Le Chatelier's principle and concentration changes

If the **concentration** of any one species in an equilibrium system is altered (raised or lowered) by a change imposed on the system, then by Le Chatelier's principle a new equilibrium will form in such a way that **partially counteracts** this imposed change. In doing this a system will consume some of the added reagent or replace some of the consumed reagent. While these changes are happening the system is temporarily out of equilibrium and the rate of the forward and reverse reactions will not be equal. At some point the system returns to equilibrium when the rates of forward and reverse reactions are again equal. When it does, the concentrations and amounts of all the reagents will have altered in such a way that has **partially minimised** (counteracted) the imposed change in concentration as predicted in Le Chatelier's principle. (See Fig 7.)

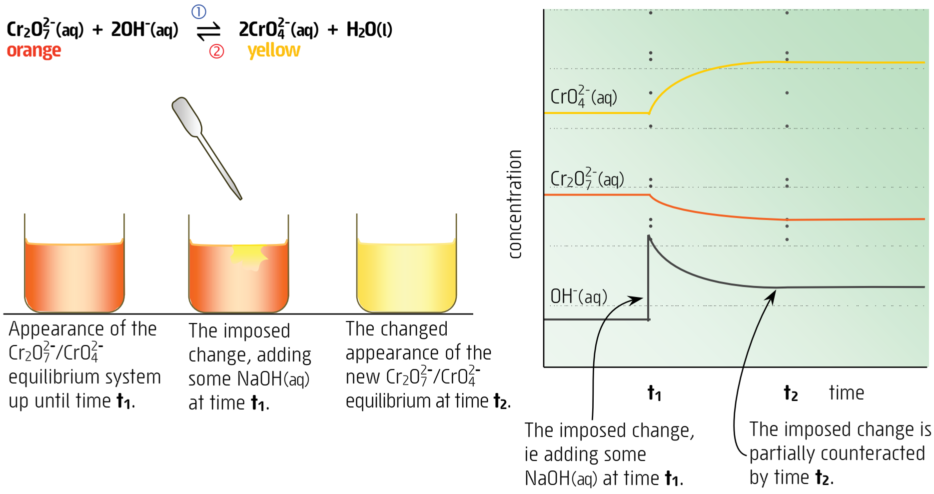

Figure 7 A **concentration time** graph for the $Cr_2O_7^{2-}/CrO_4^{2-}$ equilibrium system.

In this example, the $Cr_2O_7^{2-}/CrO_4^{2-}$ system is at equilibrium up until time t_1 when a small amount of concentrated NaOH(aq) is added to the system. This **imposed change** selectively raises the $[OH^-]$. Thus the system is now temporarily out of equilibrium as the higher $[OH^-]$ means the forward reaction rate, ① increases while the reverse reaction rate, ② remains unchanged (remember rate rises with concentration).

This change temporarily favours the formation of products and consumption of reactants. Consequently all concentrations change during the time interval t_1 to t_2 until a new equilibrium is established at t_2.

When the new equilibrium is established the $[OH^-]$ returns part way back to its original concentration prior to the imposed change, as predicted by **Le Chatelier's principle**.

Example 2 Use **Le Chatelier's principle** (LCP) to **predict** how the listed changes will affect the concentration of each species in this equilibrium system. Describe how the colour of the system changes when equilibrium is re-established. Originally the solution is **yellow**. Use **[ ]** for concentration.

$$\underset{\text{orange}}{Cr_2O_7^{2-}(aq)} + 2OH^-(aq) \rightleftharpoons \underset{\text{yellow}}{2CrO_4^{2-}(aq)} + H_2O(l)$$

Change	**Imposed change**	**Prediction using LCP**	**Concentration changes**			**amount of $H_2O(l)^{*1}$**	**Colour change**
			$[Cr_2O_7^{2-}]$	**$[OH^-]$**	**$[CrO_4^{2-}]$**		
Adding NaOH(aq)	$[OH^-]$ is raised	favours products	decreases	Initially $[OH^-]$ increases, due to the added OH^-. It then partially reduces but remains higher than the original $[OH^-]$.	increases	Water forms but its concentration is unchanged^{*1}.	yellow to deeper yellow
Adding HCl(aq) [consumes OH^-]	$[OH^-]$ is lowered	favours reactants	increases	First it decreases, due to the added acid. It then increases but remains lower than the original concentration^{*2}.	decreases	Water is consumed but its concentration is unchanged^{*1}.	yellow to orange
Add some $Pb(NO_3)_2(aq)$ [precipitates insoluble $PbCrO_4$]	$[CrO_4^{2-}]$ is lowered	favours products	decreases	decreases	First it decreases, as it is precipitated by the added Pb^{2+}. It then increases, but remains lower than the original concentration^{*2}.	Water forms but its concentration is unchanged^{*1}.	yellow to orange but the colour is lighter

^{*1} The concentration of water in an aqueous solution is essentially constant at ≈55.5 mol L^{-1}, even if some is added, removed, consumed or produced.

^{*2} The original concentration refers to the concentration just prior to the imposed change.

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Attempt Set 2 # 9 and 10.

2.7 Collision theory and concentration changes

Changes that occur in an equilibrium system when the concentration of one species is selectively altered can be **explained** in terms of the **collision theory** and **reaction rates**. If the concentration of a **reactant** has been **increased**, as with the OH^- ion concentration in the $Cr_2O_7^{2-}/CrO_4^{2-}$ equilibrium in Fig 7, then this selectively increases the rate of the forward reaction ①

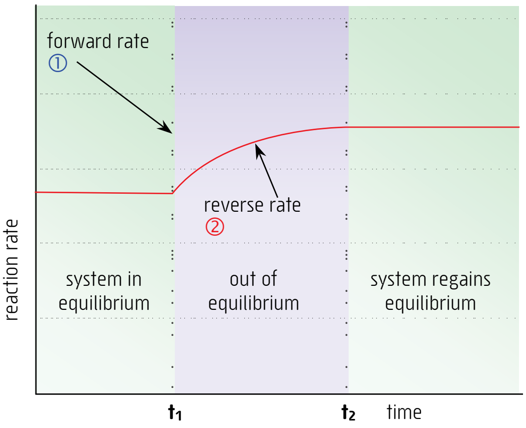
Over time this leads to a reduction in the concentration of the reactants, $Cr_2O_7^{2-}(aq)$ and $OH^-(aq)$, as these are temporarily used faster than they are produced. Also a corresponding increase occurs in the concentration of the product $CrO_4^{2-}(aq)$ as it is temporarily produced faster than it is used. (See Fig 7 and 8.) As a result of these concentration changes, the forward reaction rate slowly decreases, due to falling reactant concentrations and collision rates, while the reverse reaction rate slowly increases (the $CrO_4^{2-}(aq)$ concentration is rising).

These concentration changes continue until the rate of the forward reaction is once again equal to the rate of the reverse reaction and the system is again in equilibrium. These concentration and rate changes are shown graphically in Fig 7 and 8. The net effect of these changes is a **partial reduction** of the imposed change as **predicted** by Le Chatelier.

Figure 8 The rate of the forward and reverse reactions in the $Cr_2O_7^{2-}/CrO_4^{2-}$ equilibrium system change when some NaOH(aq) is added to it at time **t_1**.

$$Cr_2O_7^{2-}(aq) + 2OH^-(aq) \underset{②}{\overset{①}{\rightleftharpoons}} 2CrO_4^{2-}(aq) + H_2O(l)$$

The system is at equilibrium until **t_1** as rate ① equals rate ② $_1$ and **t_2** the system is out of equilibrium as rate ① ②
products to change until **t_2** when the rate of the forward reaction is once again equal to the rate of the reverse reaction and the system is once again in equilibrium.



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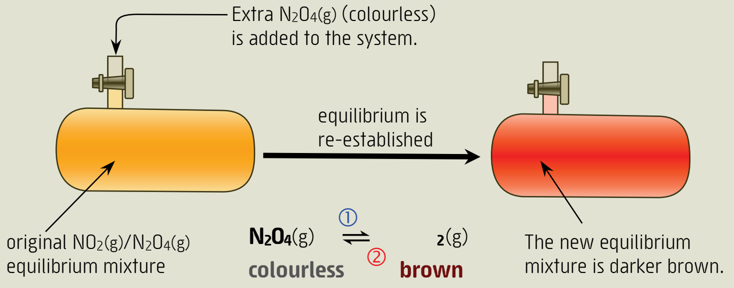
Changes that occur in a gaseous equilibrium system when the concentration of a single species is selectively raised or lowered can also be **explained** in terms of the **collision theory** and **reaction rates**. (See Example 3 and Fig 9.)

Example 3 A sealed vial (right) contains a pale yellow equilibrium mixture of NO_2(g)/N_2O_4(g). Some colourless N_2O_4(g) was then injected into the vial. The mixture soon becomes a darker brown colour.

Use the **collision theory** and your knowledge of **reaction rates** to **explain** how the addition of N_2O_4(g) affects the equilibrium system from just before the extra N_2O_4(g) was added until after equilibrium is re-established. Remember, N_2O_4(g) is **colourless** while NO_2(g) is a **brown**.



Solution:

Before the addition of extra N_2O_4: The system is at equilibrium and therefore the rate of the forward reaction ①) equals the rate of the reverse reaction ② O_4). Thus the concentration of NO_2(g) and N_2O_4(g) remain constant as does the pale yellow colour.

At the point of adding extra N_2O_4: Selectively adding N_2O_4 to the system increases its concentration (**partial pressure**). According to the collision theory this will increase the rate of collisions between N_2O_4 molecules and hence increase the rate of the forward reaction ① ② is initially unaffected as the concentration of NO_2 has not been altered. Thus immediately upon the addition of N_2O_4 the rate of production of NO_2 becomes greater than its rate of consumption.

After adding extra N_2O_4: The increased forward reaction rate ① to increase while the concentration of N_2O_4 decreases. The falling N_2O_4 concentration leads to a decreasing rate of collisions between these molecules and hence by the collision theory, the rate of the forward reaction ①
concentration.

At some point the concentration of N_2O_4 will have decreased sufficiently and that of NO_2 will have increased sufficiently so that the rate of the forward reaction ① ②
this point the concentration of NO_2 will be higher than it initially was (brown colour has intensified) and the concentration of N_2O_4 will also be higher than it initially was but lower than immediately after the imposed change. (See Fig 9.)

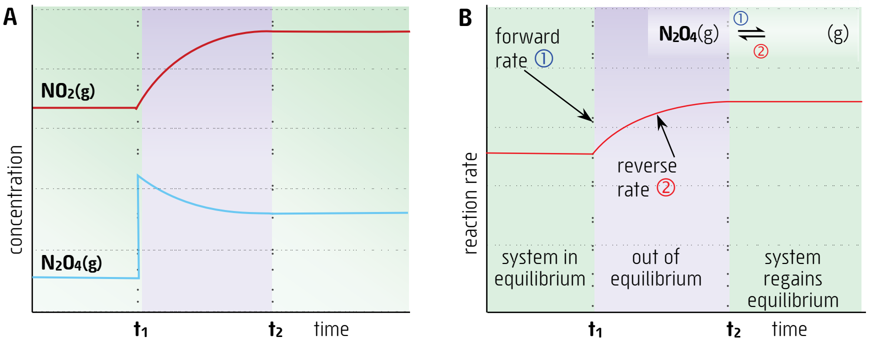


Figure 9 Graph A shows the concentration changes in the NO_2(g)/N_2O_4(g) system described in Example 3.

Some N_2O_4(g) is introduced into the system at time t_1 and the system regains equilibrium at time t_2.

Graph B shows how the initial imposed change in N_2O_4(g) concentration causes the forward reaction rate ① 1. Subsequent changes in concentration cause the forward and reverse reaction rates to slowly alter until they are once again equal at time t_2.

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Attempt Set 2 # 11.

2.8 Le Chatelier's principle: Changing the total pressure

An equilibrium system involving **gases** requires a sealed container (a closed system) for it to achieve equilibrium. If the container **volume** of such a system is altered then this will cause an imposed change to its **total pressure**. (See Fig 10.) Increasing the system's volume will decrease pressure within the system. Conversely reducing the system's volume will cause an increase in total pressure.

In either case, if a pressure change is imposed on a system at equilibrium (by altering its volume) then by Le Chatelier's principle the equilibrium will re-establish itself in such a way as to **minimise** the pressure change. Since pressure within a system is due solely to **gases** within the system then the system can readjust pressure by altering the **total moles of gas** present within the system, thus:

- **Increasing** the **pressure** inside a system (by reducing volume) will favour the side of the equilibrium reaction with fewer moles of gas. (See Fig 11.) Fewer moles of gas mean less pressure within the system thus partially counteracting the imposed change.
- **Decreasing** the **pressure** inside a system (by increasing volume) will favour the side of the equilibrium reaction with the greater moles of gas. More moles of gas means more pressure thus partially counteracting the imposed change.

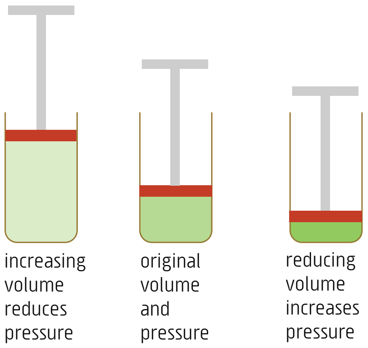
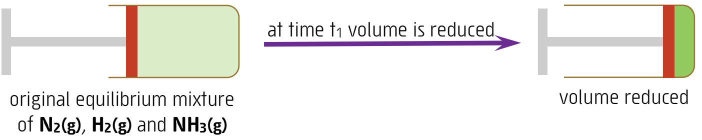
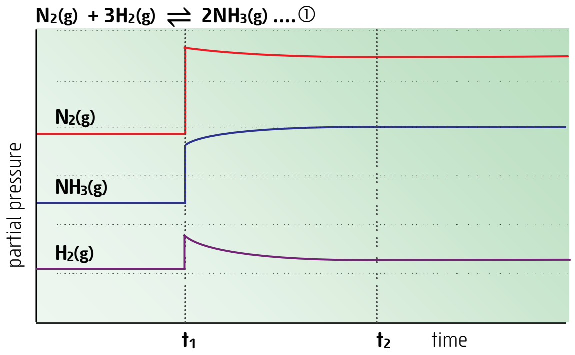


Figure 10 The **pressure** of an equilibrium system can be altered by changing its **volume**. This causes the pressure (and hence concentration) of all of the gases in the system to change by the same factor.

Figure 11 The system at right is at equilibrium up until time **t_1**. At **t_1** the volume of the system is reduced causing the pressure of all gases within the system to rise by the same **factor**. The system then readjusts until a new equilibrium is established at time **t_2**.





By Le Chatelier's principle, the system will re-establish a new equilibrium such that the imposed change, ie the higher total pressure is partially minimised. Thus in this system products will be favoured as this reduces the total moles of gas in the system (4 moles of gas are consumed for every 2 moles of gas formed) thus reducing the total pressure.

Note: The initial partial pressures of N_2, H_2 and NH_3 in **Fig 11** are randomly chosen. They are not intended to bear any relationship to the coefficients of equation ① However, the changes in partial pressure of these gases after t_2 are in proportion to the coefficients of reaction ①

If both sides of the equilibrium reaction have the same number of moles of gas, then changing the pressure has no effect on the equilibrium position. It must be noted that increasing pressure by adding an **inert gas** (one that does not react with the substances in the equilibrium system) has **no effect** on the equilibrium position. Also, changing pressure by selectively adding or removing one of the gaseous reactants or products is equivalent to altering the concentration of that substance only. Here the equilibrium readjusts as described previously in sections 2.6 and 2.7.

Example 4 The following examples show how **Le Chatelier's** principle can be used to **predict** the effect of pressure changes [by altering volume] on the equilibrium position of several equilibrium systems.

Equilibrium system	Alteration	Imposed change	Effect on the equilibrium position
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ 4 moles of gas — 2 moles of gas	volume increased	reduced pressure	This favours the formation of reactants. In this way there is a net increase in the moles of gas (2 mol of gas to 4 mol of gas) thus partially counteracting the reduced pressure.
$2C(s) + O_2(g) \rightleftharpoons 2CO(g)$ 1 mole of gas — 2 moles of gas	volume reduced	increased pressure	This favours the formation of reactants. In this way there is a net decrease in the moles of gas (2 mol of gas to 1 mol of gas) and thus a partial reduction of the increased pressure.
$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ 0 moles of gas — 1 mole of gas	volume increased	reduced pressure	This favours the formation of products. In this way there is a net increase in the moles of gas (0 mol of gas to 1 mol of gas) and thus a partial increase of the reduced pressure.
$I_2(g) + H_2(g) \rightleftharpoons 2HI(g)$ 2 moles gas — 2 moles gas	volume reduced	increased pressure	No effect. There are equal moles of gas on both sides of the equation. Neither side of the equilibrium can counteract the imposed change.

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Attempt Set 2 # 12.

2.9 Le Chatelier's principle and temperature change

The **temperature** of an equilibrium system can be changed by simply heating or cooling it. Adding heat to the system from an outside source, ie heating it will cause its temperature to rise. Conversely, removing heat from the system, ie cooling it will cause its temperature to fall. Le Chatelier's principle can be used to **predict** how an equilibrium system will respond to such a change. Using this principle, if the temperature of a system at equilibrium is altered, the system changes in a way that minimises (counteracts) the imposed temperature change.

- If the **temperature** of an equilibrium system is **raised** (Fig 12) by heating, then a new equilibrium is established **favouring** the **endothermic** process. By doing this, the system converts some of the added heat to chemical potential energy (bond energy), thus causing its temperature to fall, ie partially counteracting the imposed change.
- If the **temperature** of an equilibrium system is **lowered** by cooling, then a new equilibrium is established **favouring** the **exothermic** process. By doing this, the system converts some chemical potential energy (bond energy) to heat (see p1-2), thus causing its temperature to rise, ie partially counteracting the imposed change.

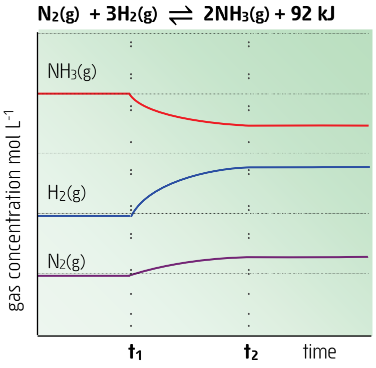

Figure 12 The **temperature** of this equilibrium system (above left) was raised at **t_1**. As predicted by Le Chatelier, this will result in a new equilibrium favouring the endothermic process (reverse reaction). In this way the system changes heat to chemical potential energy thus partially counteracting the imposed change, ie the raised temperature. Notice how the concentration changes are proportional to the stoichiometric coefficients of the equilibrium equation.

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Example 5 The following examples show how Le Chatelier's principle can be used to **predict** the effect of a temperature change on the equilibrium position of several equilibrium systems. (See margin note, points to remember, at bottom right)

Equilibrium system	Alteration	Imposed change	Effect on equilibrium position
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ + **92 kJ** left to right (→ right to left (←	reaction mixture is **heated**	temperature raised	Favours the endothermic reaction, ie formation of **N_2** and **H_2** as this changes heat to potential energy thus partially opposing the raised temperature.
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ **ΔH = -198 kJ** left to right (→ right to left (←	reaction mixture is **cooled**	temperature lowered	Favours the exothermic reaction, ie **SO_3** as this changes some potential energy to heat thus partially opposing the lowered temperature.
$C(s) + H_2O(g)$ + **131 kJ** $\rightleftharpoons CO(g) + H_2(g)$ left to right (→ right to left (←	reaction mixture is **heated**	temperature raised	Favours the endothermic reaction, ie **CO** and **H_2** as this converts heat to potential energy thus partially decreasing the raised temperature.
$I_2(g) + H_2(g) \rightleftharpoons 2HI(g)$ **ΔH = +26 kJ** left to right (→ right to left (←	reaction mixture is **cooled**	temperature lowered	Favours the exothermic reaction, ie **I_2** and **H_2** as this produces heat and so partially counteracts the lowered temperature.

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Attempt Set 2 # 13.

Points to remember:

Temperature: Increases with increasing particle kinetic energy.

Heat: Energy that naturally flows from a hot system (high temperature) to a cooler one.

Chemical potential energy: Energy stored by the chemical bonds in a substance.

Enthalpy: A measure of the total energy in a chemical system. It includes chemical potential energy and particle kinetic energy.

Exothermic: These reactions have a -ve ΔH and cause a temperature rise as some chemical potential energy is converted into particle kinetic energy.

Endothermic: These reactions have a +ve ΔH and cause temperature to fall as some particle kinetic energy is converted into chemical potential energy.

See 1.1 to 1.3 p 1-2 for a full review.

2.10 Understanding the effect of temperature change

According to the collision theory a temperature rise will increase particle collision energy and thus increase reaction rate. However, not all reactions are affected equally. **Endothermic** reaction rates are much more sensitive to temperature change than exothermic reactions. Thus in an equilibrium system a temperature change affects the endothermic reaction rate more than the exothermic reaction rate. Raising the temperature of an equilibrium system increases the rate of the endothermic reaction more than the exothermic reaction. Conversely, lowering temperature lowers the endothermic reaction rate more than the exothermic reaction rate. This differential effect on exothermic and endothermic reaction rates explains why (as Le Chatelier predicted) an increasing temperature favours the endothermic process while a decreasing temperature favours the exothermic process.

Furthermore, unlike changes in concentration and pressure, a change in temperature causes a change in the value of the equilibrium constant K_c. For an endothermic reaction K_c increases as temperature increases while for an exothermic reaction K_c decreases with increasing temperature. (See Fig 13.)

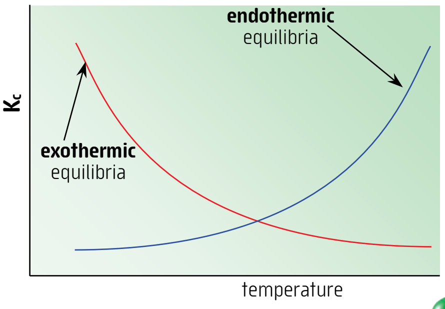
Figure 13 The equilibrium equation shown here is exothermic as written, ie **left to right**.

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ **ΔH = -198 kJ**

Thus the value of the equilibrium constant (below) for this reaction decreases as temperature increases.

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$

The graph at right shows the general change of K_c with temperature for **endothermic** and **exothermic** reactions.



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Attempt Set 2 # 14.

2.11 Other alterations

The presence of a **catalyst** in an equilibrium system has no effect on the equilibrium position. However, a catalyst will speed up the rate of attainment of equilibrium. This happens as the catalyst increases the rate of both the forward and reverse reactions equally. Also the addition or removal of reactants or products which are present as **solids**, (s) or **liquids**, (l) does not alter the equilibrium concentration or the amount of any other species.

(See Example 6.)

Example 6 Imposed changes that have no effect on equilibrium position.

Equilibrium system	**Alteration to system**	**Effect on equilibrium concentrations**
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$	adding the catalyst Fe/Fe_3O_4	No effect as the forward and reverse reaction rate increase equally.
$2C(s) + O_2(g) \rightleftharpoons 2CO(g)$	carbon is finely powdered	No effect as substances in the solid phase have a fixed concentration.
$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$	removing some CaO(s)	No effect as solids have a fixed concentration.
$2H_2O(l) \rightleftharpoons 2H_2(g) + O_2(g)$	removing some $H_2O(l)$	No effect as substances in the liquid phase have fixed concentration.

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Attempt Set 2 # 15 to 19.

2.12 Ocean equilibria and atmospheric CO_2

Human activity, such as burning carbon based fuels, is thought to be the main cause of the currently observed rising atmospheric $CO_2(g)$ concentration. (See Fig 14.) This is a significant issue as carbon dioxide is a **greenhouse gas**. Its presence in the atmosphere contributes to warmer temperatures by its ability to reabsorb heat that would otherwise radiate from the Earth's surface and out into space. This helps prevent the Earth's surface temperature from plunging to below zero. However, it is now understood that the rising atmospheric $CO_2(g)$ concentration is causing a steady rise in average global temperatures. This in turn is driving **climate change**.

Figure 14 The graph at right shows the atmospheric concentration of CO_2 in parts per million by volume (**ppmv**). Data from 1910 till 1953 is from the **Siple Station ice core** in Antarctica. Data from 1953 onwards is from **Mauna Loa** in Hawaii.

A clear trend is evident showing an increased rate of growth in the atmospheric CO_2 concentration. The current rate of increase is around **2 ppmv per year**, equivalent to 2 x 10^{10} tons of CO_2 per year!

Note: The y axis starts at 290 ppmv. For the latest data see: http://www.esrl.noaa.gov/gmd/ccgg/trends/

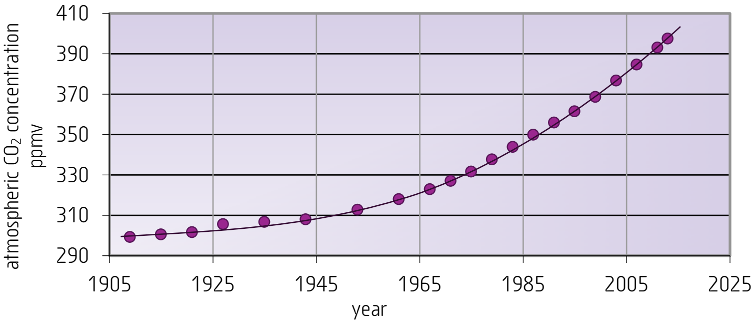

Figure 15 A table coral showing the effects of bleaching.

Ocean temperatures: Rising average atmospheric temperatures can also have a negative impact on marine life. Most marine organisms are ectothermic (cold-blooded), ie their internal body temperature is the same as their surrounding environment. Typically, their metabolic processes have evolved to work efficiently over a narrow temperature range. Temperatures outside of that range significantly alter the rate of these reactions and can impact the survival of these marine organisms. **Coral** for example, relies on a symbiotic relationship with an algae (zooxanthellae) that live inside coral's tissue and are very efficient food producers. These algae provide up to 90% of the energy (food) coral requires to grow and reproduce. **Coral bleaching** (Fig 15) is an example where warmer water can cause coral to expel the algae living in their tissues. This causes the coral to turn completely white, hence the term bleaching. While some corals are able to feed themselves, most corals struggle to survive without their symbiotic algae.

Mass bleaching events of this type have occurred on the Great Barrier Reef in 1998 and 2002. The 2002 event was the largest coral bleaching event on record with 60% of reefs affected and a further 5% severely damaged. This bleaching event was preceded by two periods of hot weather that resulted in sea surface temperatures a few degrees Celsius higher than the long-term summer maxima.

The ocean as a 'carbon sink': An important chemical equilibrium exists between atmospheric gases like N_2, O_2 and CO_2 and their presence in sea water. This equilibrium helps to **moderate** any changes in the atmospheric concentration of these gases. Importantly, the ocean plays a major role in moderating the human induced, ie **anthropogenic**, rising atmospheric carbon dioxide concentration.

Acting as a 'carbon sink' the ocean absorbs around one third of humankind's current annual emissions of CO_2. In this way the ocean plays a vital role in regulating the extent of CO_2 induced climate change. However, this comes at a cost as it is causing an effect known as **ocean acidification**. This decrease in ocean pH can directly impact the health and population of many calcifying species, including oysters, clams, sea urchins, coral and calcareous plankton. Changing populations of these organisms will impact many aspects of the wider marine environment.

Atmospheric CO_2 and ocean equilibria: The two major effects of ocean acidification on sea water are to:

- **increase** its **hydrogen ion** concentration.
- **decrease** its **carbonate ion** concentration.

The concentration of these two ions and others are connected to the presence of atmospheric carbon dioxide through several chemical equilibria.

First, wind and wave action allow atmospheric carbon dioxide to dissolve in seawater ①

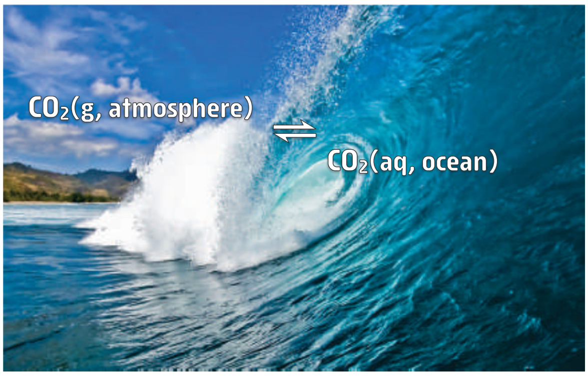

Figure 16 Wind and wave action help to maintain a responsive CO_2 concentration equilibrium between the atmosphere and ocean.

$CO_2(g, atmosphere) \rightleftharpoons CO_2(aq, ocean)$ ①

$_2$ then becomes involved in a further series of equilibrium reactions where it initially forms carbonic acid, H_2CO_3 ② ③ ④

$_2$ concentration can result in an increased $H^+(aq)$ concentration and thus lower ocean pH.

$CO_2(aq, ocean) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$ ②

$_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$ ③

$_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$ ④

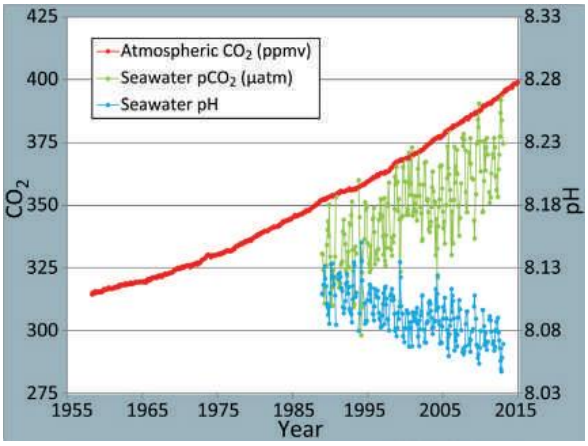

Figure 17 Data series of the atmospheric CO_2 concentration at **Mauna Loa Observatory** in Hawaii along with the ocean pH and CO_2 concentration at the nearby **Station Aloha**. The graph shows the compelling relationship between atmospheric and oceanic CO_2 concentration and the resulting ocean pH.

(Note: ppmv = parts per million by volume, 1 μatm = 1×10^{-6} atm.)

Figure from National Oceanic and Atmospheric Administration's (NOAA) Pacific Marine Environmental Laboratory Carbon Program; http://www.pmel.noaa.gov/co2/. Data from NOAA's Earth System Research Laboratory and the Hawaii Ocean Time-Series program.

structures can potentially counteract the increased $H^+(aq)$ concentration by reacting with it to form free calcium ions and hydrogencarbonate ions ⑤

equilibrium process.

$CaCO_3(s, sediments\ and\ shells) + H^+(aq) \rightleftharpoons Ca^{2+}(aq) + HCO_3^-(aq)$ ⑤

$_2$ and ocean acidification: Ocean acidification is the term used to describe the lowering of the ocean pH due to increased atmospheric carbon dioxide. (See Fig 17.) Studies show that seawater has maintained a steady pH of 8.2 for many millions of years. However, over the last 250 years since the industrial era, the average ocean pH has fallen by 0.1 to a current average pH of 8.1. While this is a small fall in pH it represents a 30% increase in the oceans $H^+(aq)$ ion concentration. Remember, pH is a **logarithmic** function, 1 unit of pH represents a 10 times change in $H^+(aq)$ ion concentration. pH shifts of this size would normally be expected to take thousands of years rather than a few hundred as has occurred. Furthermore, computer modelling predicts a further 0.4 fall in pH could be expected by 2100.

The process of ocean acidification can be understood using the principles of chemical equilibrium. This reveals how a rising atmospheric CO_2 concentration has lead to a falling ocean pH. Initially an increasing atmospheric $CO_2(g)$ concentration causes an increase in the rate of CO_2 dissolving. This shifts equilibria ① $_2$(aq, ocean) concentration. A higher CO_2(aq, ocean) concentration then increases the rate of formation of $H_2CO_3(aq)$ by reaction ② $_2CO_3(aq)$ concentration. The raised $H_2CO_3(aq)$ concentration has a flow on effect causing equilibria ③ to shift to the right thus raising the concentration of both $H^+(aq)$ and $HCO_3^-(aq)$.

Although the extra H_2CO_3(aq) produces the **same molar amount** of H^+(aq) and HCO_3^-(aq) the actual **factor increase** in the H^+(aq) concentration is much greater than for HCO_3^-(aq). This happens as the H^+(aq) concentration is initially extremely low ($\approx 6.3 \times 10^{-9}$ mol L^{-1}), much lower than the HCO_3^-(aq) concentration ($\approx 1.9 \times 10^{-3}$ mol L^{-1}). The net effect of this is to cause the equilibrium reaction ④

$^+$(aq) has increased by a greater factor than the HCO_3^-(aq) concentration.] This change partially negates the increased H^+(aq) concentration while also reducing the normal CO_3^{2-}(aq) concentration.

Thus the overall effect of ocean acidification, ie adding extra CO_2 to the oceanic system is to slightly increase the concentration of both HCO_3^-(aq) and H^+(aq) while reducing the concentration of CO_3^{2-}(aq). Both the increase in H^+(aq) concentration and the reduced carbonate ion concentration are very significant issues for **calcifying species**.

Impact of ocean acidification: Ocean acidification, ie a decreasing ocean pH and decreasing CO_3^{2-}(aq) concentration, is predicted to have negative effects on marine ecosystems and organisms. Initially this will directly affect the health of calcifying species, like oysters, clams, sea urchins, coral and calcareous plankton. These rely on a **constant pH** and **carbonate ion** concentration to maintain the integrity of their shells and skeletons. They absorb Ca^{2+}(aq) ions and CO_3^{2-}(aq) ions from sea water to produce their calcium carbonate based shells and skeletons. However, as ocean acidification reduces carbonate ion concentration, so these organisms become stressed. They must expend more energy to absorb the necessary CO_3^{2-}(aq) needed to grow their shells and skeletons. This in turn impacts their survival and population. Furthermore, the elevated H^+(aq) concentration has the potential to **dissolve calcium carbonate** already present in the shells and skeletons of these organisms. (See reaction ⑤

uncertain.

Figure 18 A healthy reef system owes its presence to a great variety of calcifying species, like oysters, clams, sea urchins, corals, and calcareous plankton.

Populations of plankton species that have calcium carbonate based shells could be affected by more acidic environments as would the populations of the many marine organisms that rely on them as a food source. Weaker (or non-existent) coral reefs could fail to protect coastlines from harsh ocean waves. Coral reefs (Fig 18) also provide habitats for many fish species, so without reef systems there would be loss of marine life. Finally, a weakening of the reefs would make them more susceptible to further damage from storms and predators.

The future of our oceans: When pH changes in the ocean have occurred over a very long period of time, the ocean has been able to **compensate**. This happens because large collections of sediment at the bottom of the ocean contain large amounts of calcium carbonate, mostly from the shells of deceased marine creatures. Over long time periods, these sediments dissolve to decrease the H^+(aq) ion concentration and replenish the carbonate ion lost to reaction with excess H^+(aq). However, the changes we are seeing today in the ocean's pH levels have happened **rapidly** in terms of the geological time scale. Because the acidification is occurring over a short time frame and in water close to the surface the sediment reserve on the ocean floor has not had the chance to dissolve and counteract the effects of the added acidity.

Research on the impacts of ocean acidification on marine organisms and ecosystems is still in its infancy. Efforts to monitor ocean acidification worldwide are just beginning, so it is difficult to predict exactly how the impacts will cascade throughout the marine food chain and affect the overall structure of marine ecosystems. It appears the most effective way of preventing ocean acidification and rising ocean temperatures is to stabilise and reduce the level of greenhouse gases in the atmosphere, particularly of CO_2, the main driver of climate change and the major cause of ocean acidification. This aim is reflected in the ultimate goal of the **United Nations Framework Convention on Climate Change** (UNFCCC) and all affiliated bodies to achieve 'stabilisation of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system'.

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Complete Set 2.

Set 2 Chemical equilibrium

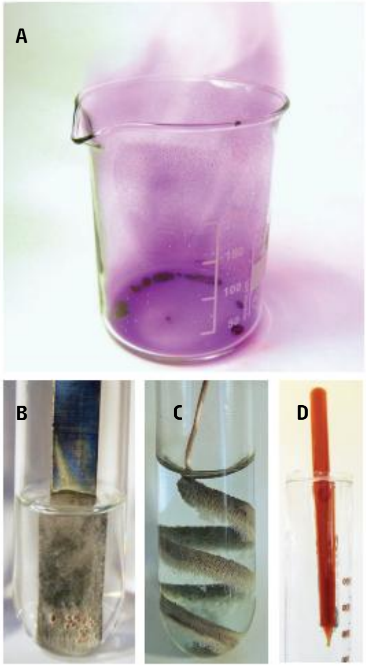
1. Equation ① (below) is for the combustion of myricyl palmitate, $C_{46}H_{92}O_2$, a major component of bees wax used in some candles. Equation ② shows the formation of carbonic acid in soft drink. What is the **significance** of the **single** and **double** arrows used in these equations? Also, **account** for the reversibility (or otherwise) of these reactions in terms of activation energy.

   $C_{46}H_{92}O_2(s) + 68O_2(g) \rightarrow 46CO_2(g) + 46H_2O(g)$ .... ①

   $CO_2(g) + H_2O(g) \rightleftharpoons H_2CO_3(aq)$.................................. ②

2. Several chemical and physical changes described below are illustrated in Fig 19. Decide if these changes are shown occurring in an **open** or **closed system**. **Justify** your answer.
   a. Sublimation of iodine crystals:
      $I_2(s) \rightleftharpoons I_2(g)$
   b. A zinc strip reacting with a solution of hydrochloric acid in an unsealed test tube: $Zn(s) + 2H^+(aq) \rightleftharpoons H_2(g) + Zn^{2+}(aq)$
   c. A copper coil reacting with a silver nitrate solution in an unsealed test tube: $Cu(s) + 2Ag^+(aq) \rightleftharpoons 2Ag(s) + Cu^{2+}(aq)$
   d. A sealed vial of N_2O_4/NO_2 at 20 °C placed into a cylinder of hot water at 95 °C: $2NO_2(g) \rightleftharpoons N_2O_4(g)$

Figure 19 Images for Question 2. Both test tubes are unsealed (not stoppered) but the vial in D is sealed.



3. The following passage describes the formation of the **water/water vapour** equilibrium. Use the terms shown to complete the passage.

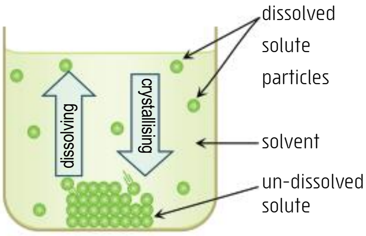
   Wet clothing left on a washing line will soon become dry due to (a) __________ of water from the clothing. However, a piece of wet cloth left inside a small sealed jar will most probably never become (b) __________. The sealed jar is a (c) __________ where water vapour that forms from evaporation cannot (d) __________ the container. When confined to a closed system, the resulting water vapour will (e) __________ to reform liquid water within the jar.

   In a situation like this, the (f) __________ of evaporation of water within the jar will eventually (g) __________ the rate of condensation of the resulting water vapour. When this happens, the water and water vapour are said to be in a state of (h) __________. The equilibrium is said to be dynamic because both the (i) __________ and (j) __________ reactions are still proceeding. Thus changes are occurring at a molecular level even though at a (k) __________ level no changes appear to be occurring and the system appears to be (l) __________.

static
evaporation
equal
escape
reverse
condense
forward
dry
dynamic equilibrium
closed system
rate
macroscopic

4. Soluble substances like sucrose, $C_{12}H_{22}O_{11}(s)$ (sugar) for example, will dissolve in water until the solution becomes **saturated**. At this point a state of dynamic equilibrium exists between the **dissolved** substance and its **undissolved** solid. The following questions refer to such an equilibrium system for sucrose. (See Fig 20.)
   a. The two physical changes that occur in this equilibrium system are the **dissolving** of sucrose and its **crystallising**. Write **separate equations** for each of these changes.
   b. Write a **single equation** to represent this solubility equilibrium.
   c. An **open beaker**, as shown in Fig 20, is a good approximation of a closed system for this solubility equilibrium when considering a short time frame (eg a few days) but not over a longer time frame (eg a few months). Explain.
   d. Another sugar called glucose, $C_6H_{12}O_6$ forms a saturated solution at 25 °C with a concentration of **4.0 mol L^{-1}**. Consider the following situations and compare the **rate** of glucose **dissolving** with the **rate** of glucose **crystallising**. Each solution contains excess undissolved **solid** glucose.
      i. A glucose solution at 25 °C with a glucose concentration of 4.0 mol L^{-1}.
      ii. A glucose solution at 25 °C with a glucose concentration of 3.2 mol L^{-1}.
      iii. A glucose solution with a concentration of 4.0 mol L^{-1} that is cooled to 5 °C.

Figure 20 Solubility equilibria involve an equilibrium between the two opposing processes of **dissolving** and **crystallising**.



reversible
reactants
constant
static
equal
$H_3O^+(aq)$ and $CH_3COO^-(aq)$
$CH_3COOH(aq)$ and $H_2O(l)$
reverse
forward
products
dynamic
rate
②
①
concentration

5. The following passage describes the concept of **equilibrium** in a chemical system. Use the list of terms to **complete** the passage. Some of the terms listed are **distractors** and will not be used.

All chemical reactions occur in a forward direction where (a) ____________ are consumed over time to form (b) ____________. In many chemical reactions the products of the forward reaction can also react in a (c) ____________ reaction to reform the original reactants. Reactions like this are said to be (d) ____________. When confined to a closed system, reversible reactions can reach a state of equilibrium where the (e) ____________ of the forward reaction is (f) ____________ to the rate of the reverse reaction. At equilibrium the system shows no change in appearance over time and seems to be inactive (static). However, as the forward and reverse reactions are still proceeding the equilibrium system is said to be (g) ____________

Ethanoic acid in water, for example, forms an equilibrium system as shown here:

$$CH_3COOH(aq) \quad + \quad H_2O(l) \quad \underset{②}{\overset{①}{\rightleftharpoons}} \quad H_3O^+(aq) \quad + \quad CH_3COO^-(aq)$$

The forward reaction is labelled (h) ____________ and produces (i) ____________. The reverse reaction, represented by (j) ____________ consumes these same substances so that at equilibrium the concentration of all species in the reaction become (k) ____________.

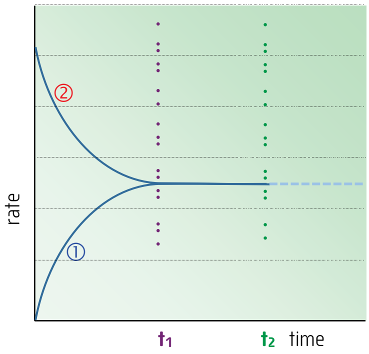


Figure 21 Rate of the forward and reverse reactions for the **N_2O_4/NO_2** equilibrium system.

$$N_2O_4(g) \underset{②}{\overset{①}{\rightleftharpoons}} \qquad (g)$$

6. The equilibrium reaction between $N_2O_4(g)$ and $NO_2(g)$ is shown here. The **forward** and **reverse** reactions are labelled ① ②

$${}_2O_4(g) \underset{②}{\overset{①}{\rightleftharpoons}} 2NO_2(g)$$

This equilibrium is established by adding a pure sample of **one** of the gases into a sealed vial. The graph at left shows how the rate of the forward and reverse reactions change over a period of time from when the gas is initially added to the sealed vial.

a. Which of the gases, $N_2O_4(g)$ or $NO_2(g)$ was initially added to the vial? **Justify** your answer with reference to the graph in Fig 21.

b. What is **significant** about the system from time t_1 onwards?

c. Some extra N_2O_4 gas is injected into the vial at time t_2. What immediate effect would this have on the **rate** of the forward and reverse reactions? **Justify** your answer with reference to the **collision theory** of reaction rates.

7. Write the **equilibrium constant expression** for the reactions shown here.

a. $HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$

b. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

c. $Pb^{2+}(aq) + 2I^-(aq) \rightleftharpoons PbI_2(s)$

d. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

e. $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$

f. $CaCO_{3(s)} + 2H^+_{(aq)} \rightleftharpoons H_2O_{(l)} + CO_{2(g)} + Ca^{2+}_{(aq)}$

8. Use your knowledge of the **equilibrium constant, K_c** to answer the following.

a. Which species are **favoured** in the following equilibrium systems? Answer **reactants**, **products** or **neither**.

i $2CO(g) + O_2(g) + \rightleftharpoons 2CO_2(g)$ $\quad K_c = 2.2 \times 10^{22}$

ii $NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$ $\quad K_c = 5.8 \times 10^{-10}$

iii $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ $\quad K_c = 0.21$

b. Ethanoic acid is known to be a **weak** acid. Account for this observation by referring to the equilibrium constant for the ionisation of ethanoic acid.

$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$ $\quad K_c = 1.74 \times 10^{-5}$

c. Which of the two acids, nitric acid or nitrous acid is likely to be the **strongest** acid? Explain your choice with reference to K_c.

$HNO_2(aq) \rightleftharpoons H^+(aq) + NO_2^-(aq)$ $\quad K_c = 5.1 \times 10^{-4}$

$HNO_3(aq) \rightleftharpoons H^+(aq) + NO_3^-(aq)$ $\quad K_c = 23$

d. What does the equilibrium constant for the dissociation of lead iodide indicate about its **solubility** in water?

$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$ $\quad K_c = 8 \times 10^{-9}$

9. Use the list of terms to **complete** the following passage about **equilibrium** and **Le Chatelier's principle**.

The macroscopic properties of a chemical system at equilibrium, such as pressure, temperature, concentration and (a) ____________ remain constant over time. This happens because the rate of the forward and reverse reactions occurring in the equilibrium system are occurring at the same rate and thus (b) ____________ each other's effect. If an alteration is made to an equilibrium system, such as changing its (c) ____________, or (d) ____________ or if the (e) ____________ of any one species in the equilibrium system is altered then the rates of the forward and reverse reactions are no longer equal and the system will (f) ____________ be in equilibrium. When this happens the composition of the system changes until the rates of the forward and reverse reactions are once again equal. Le Chatelier's principle allows the effect of such an (g) ____________ to be predicted. It states, 'When a change is (h) ____________ on a system at equilibrium, a new equilibrium position will be established such that it (i) ____________ the imposed change'.

pressure
partially counteracts
'cancel out'
imposed
concentration
no longer
imposed change
temperature
colour

10. The equilibrium reaction involving dichromate ion and chromate ion is shown here. The **forward** and **reverse** reactions are labelled ① ②

$$Cr_2O_7^{2-}(aq) + 2OH^-(aq) \underset{②}{\overset{①}{\rightleftharpoons}} 2CrO_4^{2-}(aq) + H_2O(l)$$

orange **yellow**

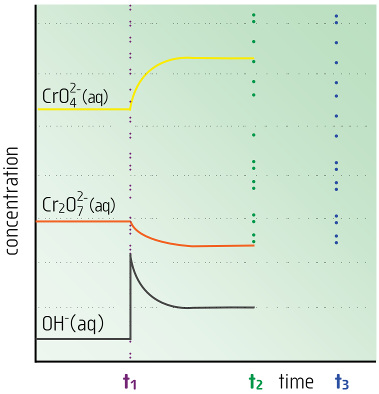


Figure 22 Changing concentrations for $Cr_2O_7^{2-}(aq)$, $OH^-(aq)$ and $CrO_4^{2-}(aq)$ in the chromate-dichromate equilibrium system.

a. At time t_1 (Fig 22) some concentrated sodium hydroxide solution, NaOH(aq) was added to the system. **Describe** how Le Chatelier's principle predicts the falling concentration of the dichromate ion as shown in the graph in Fig 22.

b. Use your knowledge of **stoichiometric principles** to explain why the resulting drop in the concentration of dichromate ions is only half that of the drop in concentration of the hydroxide ions.

c. At time t_2 a small amount of concentrated hydrochloric acid is mixed into this system. This causes an instant drop in the concentration of hydroxide ions to exactly half its current value. Show this on the graph in Fig 22.

d. Use Le Chatelier's principle to **predict** how this imposed change, from Part (c), causes all three substances to change concentration until equilibrium is again achieved at time t_3. Show these changes on the graph in Fig 22. Note, your concentration changes should be consistent with stoichiometric principles.

e. **Why** is the concentration of $H_2O(l)$ not included on the graph in Fig 22?

11. Many metallic ions have the ability to form **complex ions** with **ammonia**. Copper(II) ions react this way forming the deep blue copper(II) ammine complex ion as shown in Fig 23.

$$Cu^{2+}(aq) + 4NH_3(aq) \underset{②}{\overset{①}{\rightleftharpoons}} \qquad)_4]^{2+}(aq)$$

light blue **deep blue**

Figure 23 Try this! Add a small amount of concentrated ammonia solution to a copper sulfate solution. You will see a **blue gelatinous precipitate** form, this is due to the formation of $Cu(OH)_2(s)$. This happens as ammonia is a weak base and produces a low concentration of $OH^-(aq)$ in water. The presence of the $OH^-(aq)$ ions results in the precipitation of insoluble $Cu(OH)_2(s)$.

Now add excess ammonia solution to the precipitate. You will see it dissolve and the solution turn a clear dark blue colour. This change is due to the formation of the soluble complex ion $[Cu(NH_3)_4]^{2+}(aq)$. Three equilibrium reactions are involved in this situation.

$NH_3(aq) + H_2O(l) \rightleftharpoons \qquad ^+(aq) + OH^-(aq)$

$Cu^{2+}(aq) + 2OH^-(aq) \rightleftharpoons \qquad (s)$

$Cu(OH)_2 + 4NH_3 \rightleftharpoons \qquad)_4]^{2+} + 2OH^-$

When **excess ammonia** is present, no precipitate forms and the equilibrium can be simplified to:

$Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons \qquad)_4]^{2+}(aq)$

A beaker containing some 1.0 mol L^{-1} copper(II) sulfate solution has a light blue colour. A **large amount** of concentrated ammonia solution, $NH_3(aq)$ is then stirred into the copper(II) sulfate solution. The mixture eventually becomes a **constant** dark blue colour. Answer the following questions about this system.

a. Is the system at equilibrium after the addition of ammonia? **Justify** your answer.

b. More ammonia solution is now added to the beaker and the solution becomes even darker blue. **Describe** how Le Chatelier's principle predicts this change.

c. Use your knowledge of **collision theory** and **reaction rates** to **explain** why the addition of more ammonia solution causes the changes as predicted in Part (b).

Continued next page.

d. A small amount of concentrated HCl(aq) is added to the solution. This causes the conversion of some $NH_3(aq)$ to $NH_4^+(aq)$. **Describe** how the concentrations of $Cu^{2+}(aq)$, $NH_3(aq)$ and $[Cu(NH_3)_4]^{2+}(aq)$ change as a result of adding HCl(aq).

e. Use your knowledge of **collision theory** and **reaction rates** to **explain** why the addition of HCl(aq) solution causes the changes as predicted in Part (d).

12. Methanol, CH_3OH can be produced by the reaction of carbon monoxide gas, CO and hydrogen gas, H_2 as shown here:

$$CO(g) \; + \; 2H_2(g) \; \underset{②}{\overset{①}{\rightleftharpoons}} \; CH_3OH(g)$$

A system like this has reached equilibrium in a closed 2.0 L container. The **volume** of the system is then **halved** by **compressing** it.

a. What initially happens to the **total pressure** inside the container immediately after the **volume** is **halved**?

b. Are reactants or products favoured as equilibrium is re-established? **Describe** how Le Chatelier's principle is used to predict how the equilibrium readjusts.

c. The **CO(g)** had a partial pressure of **55 kPa** before the system was compressed. **Describe** what happens to its partial pressure immediately after compression and up until the point where equilibrium is re-established.

13. The following chemical systems have reached equilibrium in a closed system when an **alteration in temperature** is made to the system. Use your understanding of Le Chatelier's principle to complete the table.

Equilibrium system	**Imposed change** (Write heated or cooled.)	**Effect on equilibrium position** (Write favours reactants or favours products.)
a. $C_2H_5OH(l) \; + \; 43 \text{ kJ} \; \rightleftharpoons \; C_2H_5OH(g)$	heated	
b. $2H_2(g) \; + \; O_2(g) \; \rightleftharpoons \; 2H_2O(l) \; + \; 572 \text{ kJ}$	heated	
c. $N_2(g) \; + \; 3H_2(g) \; \rightleftharpoons \; 2NH_3(g) \quad \Delta H = -92 \text{ kJ}$	cooled	
d. $NH_4Cl(s) \; \rightleftharpoons \; NH_4^+(aq) \; + \; Cl^-(aq) \quad \Delta H = 26.4 \text{ kJ}$	heated	
e. $PCl_5(g) \; + 87.9 \text{ kJ} \; \rightleftharpoons \; PCl_3(g) \; + \; Cl_2(g)$		favours reactants
f. $2NO_2(g) \; \rightleftharpoons \; N_2O_4(g) \quad \Delta H = -57 \text{ kJ}$		favours products

Table 4 **K_w** for the ionisation of water at different temperatures.

Temperature (°C)	**$K_w = [H^+][OH^-]$**
0	0.144×10^{-14}
20	0.681×10^{-14}
40	2.92×10^{-14}
100	55×10^{-14}

14. The following equation shows the equilibrium process for the ionisation of water. The **forward** and **reverse** reactions are labelled ① ②

$$H_2O(l) \; \underset{②}{\overset{①}{\rightleftharpoons}} \; H^+(aq) \; + \; OH^-(aq)$$

The equilibrium constant for this reaction is specifically referred to as K_w. Table 4 lists K_w values for a variety of temperatures.

a. What is the **significance** of the very small values for K_w?

b. Is the ionisation process as written endothermic or exothermic? **Justify** your answer with reference to the effect of temperature on K_w.

c. The ionisation reaction has reached equilibrium in a beaker of water at 20 °C. The water is then heated to 50 °C. How does this temperature change affect:

i. the **concentration** of $H^+(aq)$ and $OH^-(aq)$ when equilibrium is re-established?

ii the **rate** of reaction ① ②

15. The following chemical systems have reached equilibrium when an alteration in conditions is made to the system. Determine the **imposed change** caused by the alteration and use your understanding of Le Chatelier's principle to predict how this affects the new equilibrium position. Answer **favours reactants**, **favours products** or **no effect** and give a brief **description** of how you applied Le Chatelier's principle (LCP) to determine the effect of the imposed change.

Equilibrium system and alteration	Imposed change	Describe how LCP predicts the effect on the equilibrium position
$HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$		
i. A small amount of concentrated HCl(aq) is added to the system.		
ii. Some concentrated NaOH(aq) is added to the equilibrium system.		
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 92\ kJ$		
i. The system volume is reduced.		
ii. The system is heated.		
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)\ \Delta H = -198\ kJ$		
i. The system volume is increased.		
ii. Some $O_2(g)$ is added to the system.		
iii. The system is cooled.		
$CaCO_3(s) + 179\ kJ \rightleftharpoons CaO(s) + CO_2(g)$		
i. Extra $CaCO_3(s)$ is added to the system.		
ii. The system is cooled.		
iii. Some CaO(s) is removed from the system.		

16. A sample of cobalt(II) chloride is dissolved in a small amount of concentrated hydrochloric acid solution HCl(aq) and the following reversible reaction occurs.

$$\underset{\text{pink}}{Co(H_2O)_6^{2+}(aq)} + 4Cl^-(aq) \rightleftharpoons \underset{\text{blue}}{CoCl_4^{2-}(aq)} + 6H_2O(l)$$

The ion $Co(H_2O)_6^{2+}(aq)$ is pink while $CoCl_4^{2-}(aq)$ is blue. All other species in the system are colourless. When the system reaches equilibrium it has a predominately blue colour.

a. Some concentrated silver nitrate solution is then added to the mixture causing the **precipitation** of **AgCl(s)**.
    (i) How will the **colour** change when equilibrium is re-established?
    (ii) Use your knowledge of collision theory and reaction rates to explain why the addition of $AgNO_3(aq)$ affects the **concentration** of each of the species from the moment it is added until when equilibrium is re-established.

b. A second sample of cobalt(II) chloride is prepared using less HCl(aq) thus giving the solution a **pink colour** at equilibrium. The pink solution, originally at 20 °C, is then heated to around 90 °C causing its colour to **turn blue**.
    (i) What is the favoured equilibrium position at the higher temperature?
    (ii) Is the forward reaction (as written above) endothermic or exothermic? Use your knowledge of the effect of temperature on the equilibrium constant for endothermic and exothermic reactions to **justify** your answer.

17. **Hydrogen** is an essential raw material in ammonia manufacture, preparation of saturated fats and oils, extraction of metals, synthesis of methanol and many other processes. While hydrogen gas does not occur naturally, it can be chemically synthesised from **natural gas** by the '**steam reforming process**' ①
reaction' ②

① $(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$ $\Delta H = 206$ kJ

② $+ H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ $\Delta H = -41$ kJ

a. What conditions of **temperature** and **pressure** would favour a high yield of hydrogen gas, ie favour the forward reaction, in the 'steam reforming process' and the 'water-gas shift reaction'?

b. Describe conditions that would favour a **high rate** of attainment of equilibrium, ie conditions that give the fastest possible reaction rates, in the 'steam reforming process' and the 'water-gas shift reaction'.

c. The industrial synthesis of many important compounds often involves the application of equilibrium reactions. The conditions used in these processes are often said to be a compromise. Refer to your answer from (a) and (b), for the 'steam reforming process' ① what is meant by a **compromise** of conditions used.

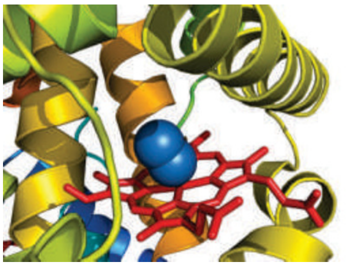
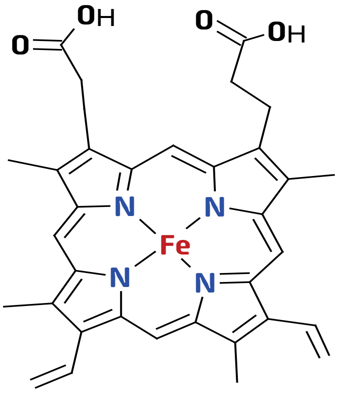


Figure 24 This computer generated model depicts part of the structure of a **haemoglobin** molecule. The section in red represents a **heme** group. A haemoglobin molecule has four heme groups and each one is capable of bonding to a single oxygen molecule, shown in blue. The full structure of a heme B group ($C_{34}H_{34}N_4O_4Fe$) is shown below.
Image courtesy of The Australian National University.



Oxygen transport around the body is largely due to the action of haemoglobin. Some 95 % of the oxygen absorbed into the bloodstream by the lungs is bound to haemoglobin molecules present in red blood cells. Each haemoglobin molecule can attach to 4 oxygen molecules and a single red blood cell may contain around 250 million haemoglobin molecules.

Although oxygen molecules are chemically bound to haemoglobin molecules, this is a weak bond. The weak bond easily allows oxygen to be released into cells where its concentration is low and reabsorbed in the lungs where its concentration is high. In this way oxygen is available for cellular

18. **Mount Kilimanjaro** in Tanzania is a popular tourist destination for recreational mountain climbers. It has an elevation of 5895 m and is a relatively easy 5 to 6 day climb. Despite this many climbers do not reach the summit as they suffer from nausea, headaches and excessive fatigue as they approach the summit. These symptoms are due to **hypoxia**, a disorder caused by a lack of oxygen reaching body tissues. Hypoxia can be fatal in serious cases. The effect can be attributed to **lower atmospheric oxygen concentrations** at high altitudes. At the summit of Mount Kilimanjaro the partial pressure of oxygen in the atmosphere is around **10 kPa** while at sea level oxygen has a partial pressure of **20 kPa**.

The uptake of oxygen by the lungs is largely due to the ability of **haemoglobin molecules** (abbreviated **Hb**, see Fig 24) to form a weak bond with **oxygen molecules**, **$O_2(g)$**, producing the unstable compound **oxyhaemoglobin $HbO_2(aq)$**. This process can be simply represented by an equilibrium reaction.

$$\text{Hb(aq, in blood)} + O_2\text{(g, air in lungs)} \rightleftharpoons HbO_2\text{(aq, in blood)}$$

Oxygen gas absorbed this way, ie as oxyhaemoglobin $HbO_2(aq)$ then moves around the body via the circulatory system releasing oxygen to body cells as needed.

a. Use Le Chatelier's principle and the equilibrium equation shown here to **account** for hypoxia occurring at high altitudes like that of Mount Kilimanjaro.

b. Sometimes, people can avoid hypoxia by spending a few weeks at high altitude. Again refer to the equilibrium equation shown to suggest how the body might adjust so that oxygen uptake can increase despite the low partial pressure of oxygen.

19. **Hydrogen fluoride** gas is extremely soluble in water producing a weakly acidic solution, HF(aq). Although HF is only a **weak** acid (K_c=6.8 x 10^{-7} for its aqueous ionisation) it is an **extremely hazardous** substance. Fatalities have been reported from skin exposure to as little as 2.5 % of body surface area.

HF(aq) exists mostly as a molecular substance and in this form is easily absorbed through skin contact. Once absorbed, HF molecules slowly diffuse through body tissue while remaining in its harmless molecular form. Over time HF **ionises** forming **fluoride ions** and **hydrogen ions**. This slow formation of $H^+(aq)$ results in deep tissue burns.

Continued next page.

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One effect of the raised fluoride ion concentration is the precipitation of blood serum soluble calcium ions, Ca^{2+} as **insoluble CaF_2**. This process encourages the further ionisation of HF molecules. Ultimately this results in the **complete ionisation** of HF and causes considerable loss of serum soluble calcium ions. As this happens, bodily metabolic processes try to replace the lost serum soluble calcium ions by extracting it from bone. This can quickly result in **hypocalcaemia** which involves destruction of bone by **decalcification**. The loss of bone calcium can be visualised by these two **simplified** equilibrium reactions.

Ca^{2+}(bone) $\rightleftharpoons$ Ca^{2+}(blood serum) .... ①

$^{2+}$(blood serum) + $2F^{-}$(aq) $\rightleftharpoons$ CaF_2(s) .... ②

a. Write an equation for the **ionisation** of HF and refer to **Kc** to **justify** the statement that it normally produces only very low concentrations of H^{+}(aq) and F^{-}(aq) ions.

b. Use your knowledge of **concentration** and **reaction rates** to **account** for the ability of HF to penetrate deeply into skin tissue before it then begins a slow process of complete ionisation to form hydrogen ions and fluoride ions.

c. Why can HF exposure ultimately cause **deep tissue burns**?

d. Refer to equations ① ② and **reaction rates** to account for **decalcification** in bones by the ionisation of HF.

20. Use the list of terms at right to **complete** the following passage about rising ocean temperature and ocean acidification.

The atmospheric concentration of certain greenhouse gases like methane and (a) __________ are known to be increasing due to (b) __________ causes, ie human induced. One effect these gases have on our environment is to cause a measureable rise in average atmospheric (c) __________ and subsequent climate change. Rising atmospheric temperature can also impact upon the ocean where effects such as massive (d) __________ events have been recorded on several occasions. The health of coral is an important issue as coral communities play a significant role in providing (e) __________ for many marine organisms.

The well documented rising atmospheric carbon dioxide concentration is also thought to be the cause of (f) __________. This is due to an (g) __________ between atmospheric CO_2(g) and (h) __________ present in the ocean. Because of this equilibrium, the rising atmospheric CO_2(g) concentration is causing a rise in the oceanic CO_2(aq) concentration. Thus the ocean behaves as (i) __________ minimising the extent of rising atmospheric CO_2(g) concentration and thus minimising potential climate change. However, the rising ocean concentration of CO_2(aq) is causing two subtle though very significant changes to some long standing ocean chemistry, rising (j) __________ and falling (k) __________. Both of these changes will impact upon the health and survival of (l) __________ marine species like oysters, clams, sea urchins, coral and (m) __________.

temperature
carbon dioxide
H^{+}(aq) concentration
CO_3^{2-}(aq) concentration
anthropogenic
carbon sink
calcifying
calcareous plankton
coral bleaching
food and habitat
ocean acidification
equilibrium
CO_2(aq)

21. The following equation shows the equilibrium that occurs between atmospheric and oceanic carbon dioxide.

CO_2(g, atmosphere) $\rightleftharpoons$ CO_2(g, ocean)

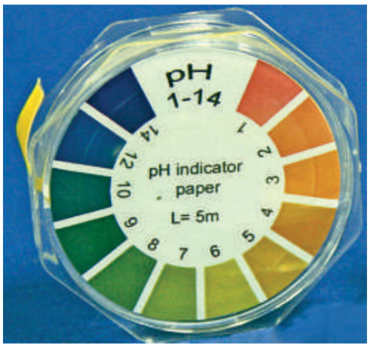
a. Use your knowledge of reaction **rates** and changing atmospheric CO_2(g) concentration to **account** for the currently rising ocean concentration of CO_2(aq).

b. Ocean pH is known to have changed from a pre-industrial pH of 8.2 to a current pH of 8.1. **Account** for this fall in pH with reference to appropriate equations and equilibrium principles.

22. Although more carbon dioxide than ever before is now dissolving in the ocean this is not resulting in a rise in carbonate ion, CO_3^{2-}(aq) concentration. Instead, CO_3^{2-}(aq) concentration is decreasing. **Account** for this fall in CO_3^{2-}(aq) concentration with reference to appropriate equation(s) and equilibrium principles.

CHAPTER 3 | REVIEW: ACID-BASE PROPERTIES

Figure 1 Universal indicator paper is impregnated with a mixture of several indicators (plant dyes). These produce a range of colours that gradually change with a solution's acidity or more specifically its pH.



A colour chart is used to identify solution pH.

3.1 Chemical and physical properties of acids and bases

Acids and bases are two distinct groups of compounds that are well known for their unique set of chemical and physical properties. **Acidic solutions** typically conduct an electric current, will turn blue litmus red and have a sour taste. Similarly **basic solutions** also conduct an electric current; however, these solutions will turn red litmus blue, have a bitter taste and a slippery soapy feel.

Some of the **chemical properties** of acidic and basic solutions are illustrated below. These are summarised with a general word equation and an example showing a chemical equation and a **net ionic equation** for the property.

- **Acidic** solutions dissolve most metals (Pb, Sn, Ni, Co, Cd, Fe, Cr, Zn, Mn, Al, Mg, Na, Ca, Sr, Ba, K, Li), forming a salt (see border note below) and hydrogen gas. The metals Au, Pt, Ag and Cu are unaffected by dilute acids.

ACID + METAL → SALT + $H_2(g)$

Example: Some hydrochloric acid solution is poured onto a strip of nickel metal.

$2HCl(aq) + Ni(s) \rightarrow NiCl_2(aq) + H_2(g)$

$2H^+(aq) + Ni(s) \rightarrow Ni^{2+}(aq) + H_2(g)$

- **Acidic** solutions react with **metal hydroxides** producing a salt and water.

ACID + METAL HYDROXIDE → SALT + H_2O

Example: A solution of nitric acid is poured onto some calcium hydroxide solid.

$2HNO_3(aq) + Ca(OH)_2(s) \rightarrow \quad)_2(aq) + 2H_2O(l)$

$2H^+(aq) + Ca(OH)_2(s) \rightarrow \quad (aq) + 2H_2O(l)$

- **Acidic** solutions react with **metal oxides** producing a salt and water. (Note the similarity to the reaction between acids and metal hydroxides.)

ACID + METAL OXIDE → SALT + H_2O

Example: A sulfuric acid solution is added to solid copper(II) oxide.

$H_2SO_4(aq) + CuO(s) \rightarrow CuSO_4(aq) + H_2O(l)$

$2H^+(aq) + CuO(s) \rightarrow Cu^{2+}(aq) + H_2O(l)$

- **Acidic** solutions react with **carbonate compounds** producing a salt, water and carbon dioxide gas.

ACID + CARBONATE → SALT + H_2O + $CO_2(g)$

Example: Hydrochloric acid solution is added to solid nickel carbonate.

$2HCl(aq) + NiCO_3(s) \rightarrow NiCl_2(aq) + H_2O(l) + CO_2(g)$

$2H^+(aq) + NiCO_3(s) \rightarrow Ni^{2+}(aq) + H_2O(l) + CO_2(g)$

- **Acidic** solutions react with **hydrogencarbonate compounds** producing a salt, water and carbon dioxide gas.

ACID + HYDROGENCARBONATE → SALT + H_2O + $CO_2(g)$

Example: Hydrochloric acid solution is added to solid nickel hydrogencarbonate.

$2HCl(aq) + Ni(HCO_3)_2(s) \rightarrow NiCl_2(aq) + 2H_2O(l) + 2CO_2(g)$

$2H^+(aq) + Ni(HCO_3)_2(s) \rightarrow Ni^{2+}(aq) + 2H_2O(l) + 2CO_2(g)$

Salts are formed when one or more of the acidic hydrogen atoms from an acid have been replaced by a metal ion(s).

acid	**some of its salts**
HCl	$NaCl$, KCl, $MgCl_2$, $AlCl_3$
HNO_3	$NaNO_3$, $AgNO_3$, $Fe(NO_3)_3$
H_2SO_4	$KHSO_4$, $BaSO_4$, $Al_2(SO_4)_3$

The formula for the salts of organic acids, such as ethanoic acid, CH_3COOH can be written with the positive metal ion at the end or the start of the formula.

eg sodium ethanoate:

NaCH_3COO or CH_3COO**Na**

- **Acidic** solutions react with **metal sulfites** producing a salt, water and sulfur dioxide. (Note the similarity to the acid-carbonate reaction.)

$$\textbf{ACID} + \textbf{METAL SULFITE} \rightarrow \textbf{SALT} + H_2O + SO_2(g)$$

Example: Hydrochloric acid solution and sodium sulfite powder are mixed.

$$2HCl(aq) + Na_2SO_3(s) \rightarrow 2NaCl(aq) + H_2O(l) + SO_2(g)$$
$$2H^+(aq) + Na_2SO_3(s) \rightarrow 2Na^+(aq) + H_2O(l) + SO_2(g)$$

Sulfur dioxide is a poisonous colourless gas with a pungent choking odour.

- **Basic** solutions react with **ammonium salts** producing a salt, water and ammonia gas.

$$\textbf{BASE} + \textbf{AMMONIUM SALT} \rightarrow \textbf{SALT} + H_2O + NH_3(g)$$

Example: A potassium hydroxide solution is mixed with an ammonium chloride solution.

$$KOH(aq) + NH_4Cl(aq) \rightarrow KCl(aq) + H_2O(l) + NH_3(g)$$
$$OH^-(aq) + NH_4^+(aq) \rightarrow H_2O(l) + NH_3(g)$$

Ammonia is a toxic colourless gas that has a characteristic irritating pungent odour.

- **Basic** solutions react with **non-metal oxides** producing a salt and water. These reactions are best understood by visualising the acid that forms when the oxide dissolves in water. (See margin notes at right.)

$$\textbf{BASE} + \textbf{NON-METAL OXIDE} \rightarrow \textbf{SALT} + H_2O$$

Example: Sulfur dioxide gas is bubbled through a potassium hydroxide solution.

$$2KOH(aq) + SO_2(g) \rightarrow K_2SO_3(aq) + H_2O(l)$$
$$2OH^-(aq) + SO_2(g) \rightarrow SO_3^{2-}(aq) + H_2O(l)$$

Reactions like the one above are better visualised as a two part process. First the non-metal oxide dissolves in water to form an acid solution. The resulting acid is then neutralised by the base. (See below.)

initially $SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3(aq)$

then $H_2SO_3(aq) + 2OH^-(aq) \rightarrow 2H_2O(l) + SO_3^{2-}(aq)$

overall $SO_2(g) + 2OH^-(aq) \rightarrow H_2O(l) + SO_3^{2-}(aq)$

The margin notes at right show what acid is formed when some common non-metal oxides dissolve in water.

Non-metal oxide	**Acid** formed in water
CO_2 carbon dioxide	H_2CO_3 carbonic acid
SO_2 sulfur dioxide	H_2SO_3 sulfurous acid
SO_3 sulfur trioxide	H_2SO_4 sulfuric acid
NO_2 nitrogen dioxide	HNO_3 and HNO_2 nitric and nitrous acid
P_4O_{10} phosphorous (v) oxide	H_3PO_4 phosphoric acid

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Complete Set 3.

Set 3 Review: Acid-base properties

1. A student conducted several tests on the following solutions. From the results obtained, determine whether the solutions are **acidic**, **basic** or **neutral**. If the test is **inconclusive** state this and indicate which solutions (ie **acidic**, **basic** or **neutral**) are consistent with the result. Briefly justify your answer.

Solution	**Test results**
A	This solution turned universal indicator paper (Fig 1) a yellow-orange colour.
B	Solution B was found to be a good conductor of electricity.
C	When solid ammonium chloride was added to this solution it produced a strong pungent odour.
D	A strip of blue litmus paper added to this solution remained blue.
E	Red litmus remained red in this solution and the solution showed no reaction with a strip of magnesium metal.
F	Solution F produced a vigorous reaction and a colourless gas with $Na_2CO_3(s)$.

2. Write a **balanced chemical equation** (not ionic) for the chemical reaction that takes place when each of the following pairs of reagents is combined. For each reaction briefly note an **observation** you would expect.
   a. $HNO_3(aq)$ and $Fe(OH)_3(s)$
   b. $CaO(s)$ and $HCl(aq)$
   c. $KOH(aq)$ and $NH_4NO_3(aq)$
   d. $Ca(OH)_2(s)$ and $H_3PO_4(aq)$
   e. **aluminium** metal and excess **sulfuric acid**
   f. solid **potassium carbonate** and **hydrochloric acid**
   g. **copper(II) oxide** and **nitric acid** solution
   h. **carbon dioxide** gas and **potassium hydroxide** solution

Note: If any reagent in a reaction mixture is present as a **solution** then the reaction mixture must contain water. This means any soluble products will also be in solution. Solubility rules can be found in Appendix 5.

3. Write a balanced **net ionic equation** and give an **observation** that could be expected for the following experiments.
   a. Powdered copper oxide, **$CuO(s)$** is added to a sulfuric acid solution [**$H^+(aq)$** and **$SO_4^{2-}(aq)$**].
   b. A sodium hydrogencarbonate solution [**$Na^+(aq)$** and **$HCO_3^-(aq)$**] is added to a nitric acid solution [**$H^+(aq)$** and **$NO_3^-(aq)$**].
   c. Crystals of solid ammonium chloride, **$NH_4Cl(s)$** are added to a sodium hydroxide solution [**$Na^+(aq)$** and **$OH^-(aq)$**].
   d. A solution of ammonium chloride [**$NH_4^+(aq)$** and **$Cl^-(aq)$**] is added to a potassium hydroxide solution [**$K^+(aq)$** and **$OH^-(aq)$**].
   e. Granulated **zinc** is added to a **hydrochloric acid** solution.
   f. A **sulfuric acid** solution is added to a **copper(II) hydroxide** suspension (Fig 2).
   g. A **hydrochloric acid** solution is added to powdered **aluminium oxide**.
   h. **Carbon dioxide gas** is bubbled through a **sodium hydroxide** solution.
   i. A **sulfuric acid** solution is added to **marble chips**, $CaCO_3(s)$.
   j. **Ammonia** gas is bubbled through a **hydrochloric acid** solution.
   k. Solid **copper(II) carbonate** is added to a **nitric acid** solution.

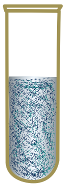

Figure 2 A **suspension** is a cloudy mixture consisting of fine particles of an insoluble solid spread throughout (suspended) in a liquid phase.

4. Both vinegar and lemon juice are suitable for removing insoluble lime scale (essentially a solid deposit of calcium carbonate) that can form inside a kettle. With the aid of an equation **explain** how vinegar is suitable for this use.

Figure 3 Phosphoric acid is a key ingredient in some rust converters. Photograph courtesy of Septone Products Pty Ltd.

5. **Rust converters** (Fig 3) are used for treating rusty iron surfaces before painting. One type of rust converter contains **phosphoric acid** as a major active ingredient. Given that the reddish-brown substance known as rust is essentially **iron(III) oxide**, **Fe_2O_3**, **explain** how the rust is chemically converted by a rust converter.

6. Farmers sometimes apply the compounds **ammonium nitrate** or **ammonium sulfate** to the soil as a nitrogen fertiliser that helps improve crop yield. Both ammonium ions and nitrate ions are a water soluble source of nitrogen able to be absorbed by plant roots.

   Another compound farmers often apply to their soil is **lime** (CaO). This is ideal for increasing soil pH. Why should the nitrogen fertilisers and lime not be mixed together and applied simultaneously?

Figure 4 Concrete swimming pools like the one shown here often have a plaster or **marbelite** finish on the inside surface. Excessively low pH water can slowly dissolve the plaster surface.

7. In **swimming pools** the pH should be kept between 7.2 and 7.8. If the pool pH gets too low this indicates the water has become quite acidic. Low pH is a particular problem in **marbelite** or **plaster** pools. It can result in the pool walls slowly dissolving and becoming slightly rough in texture (Fig 4.). The rough surface then becomes an ideal breeding ground for algae and pool maintenance becomes a problem. The major components in marbelite and plaster include **CaO**, **$CaCO_3$** and **$Ca(OH)_2$**, **Explain**, with the aid of **equations**, why low pH will affect plaster and marbelite pools as described.

CHAPTER 4 | UNDERSTANDING ACID-BASE PROPERTIES

Figure 1 Many of the distinctive properties of acids and bases were known long before the concept of acids and bases was clearly defined. Inhabitants of the Mediterranean regions in ancient times recognised substances for tastes like **sour** and **bitter** which today we recognise as properties of **acids** and **bases**.

The ability of certain substances to affect the vibrancy and colour of plant dyes was also known and used by sixteenth century textile dyers. Today we use this property as the basis of the simple analytical test, the **litmus test**, to identify acids and bases.

4.1 Science at work: Evolution of acid-base theories

The characterisation of acids and bases as we know them today was first outlined by **Robert Boyle** (1627-1691) who in 1661 summarised their known properties as:

Acids: Have a sour taste, are corrosive to metals, change the colour of certain vegetable dyes, such as litmus from blue to red and lose their acidity when they are mixed with bases.

Bases (Boyle used the term **alkalis**): Feel slippery, change the colour of litmus from red to blue and become less alkaline when they are combined with acids.

Boyle also develop the **litmus test** (still used today) for identifying acidic and basic solutions. However, despite Boyle's insight into the classification of acids and bases, a theory that could account for their properties would still be a century away.

Antoine Lavoisier (1743-1794) is credited with the first theory of acidity. In his extensive experimental work on combustion Lavoisier had observed the **oxides** of many **non-metal** elements like carbon, phosphorus and sulfur (eg CO_2, P_2O_5 and SO_2) dissolved in water to produce **acidic solutions**. In 1776 these observations led him to propose the acidity of a compound was due to the presence of **oxygen** in the compound. The existence of oxygen, as the highly reactive elementary substance present in air, had only just been discovered in 1774 through a series of experiments conducted by Joseph Priestley.

At this time experimentation on the composition of compounds and the isolation of elements was gaining momentum. **Alessandro Volta** had recently published, in 1800, his discovery of the voltaic pile, a chemical cell that produced a steady electric current. Over the next few years **Humphry Davy** (1778-1829) would use Volta's discovery and the process of electrolysis to separate many previously unknown elements from their compounds. (See Fig 2.) During the period 1807-8 Davy discovered many of the group 1 and 2 elements including Na, K, Mg, Ca, Sr and Ba. Through his experimental observations Davy realised the **strongly basic compounds** of group 1 and 2 elements were all **oxides**, eg Na_2O, CaO and MgO. This revelation contradicted Lavoisier's theory of acidity being due to the presence of oxygen.

Figure 2 A 19th century engraving of **Humphry Davy** using electrolysis to isolate the metallic element in alkalis and alkaline earths. He is shown experimenting at the Royal Institution in 1807. The Voltaic batteries he used are seen on the table in front of him.

Through his experimental observations on the electrolytic separation of elements from their compounds Davy was able to disprove Lavoisier's oxygen theory of acids. He also suggested that all acids contain hydrogen.

Davy's theory that acids are substances containing replaceable hydrogen would hold sway for most of the 19th century. It was not seriously improved upon until 1884 when **Svante Arrhenius** (below) proposed a radically new model of acid-base behaviour based on the formation of hydrogen ions and hydroxide ions.

Davy was also able to show the recently discovered strong acid called '**muriatic acid**' (he later named it **hydrochloric acid**) did not contain the element oxygen at all but only produced hydrogen gas and chlorine gas when electrolysed. Experimental observations by others at the time showed more acids (HCN, HBr and HI) did not contain oxygen but did contain hydrogen. These observations led Davy to theorise the presence of **hydrogen** in a compound would give it **acidic properties**.

Davy's theory was problematic as it could not account for the lack of acidic properties of some compounds that were known to contain hydrogen (eg CH_4). **Von Liebig** (1803-1873) had observed, as did many others, that metals reacted with acids to produce hydrogen gas. He concluded the metal was replacing some or all of the hydrogen contained in the acid to produce hydrogen gas and a salt. With this in mind, in 1838 he proposed an extended version of Davy's theory that acids contained **replaceable hydrogen**.

Even with Von Liebig's modification there remained problems with Davy's theory. Concentrated nitric acid for example produces **nitrogen dioxide gas** when reacting with metals, not hydrogen gas. A major new theory on acid-base behaviour was soon to be developed by the Swedish scientist **Svante Arrhenius** (1859-1927). Arrhenius had recently developed ground-breaking theories on electrolytes and the formation of ions in solution, work for which he was awarded the 1903 Nobel prize in Chemistry. It was **Arrhenius** who first proposed the role of **hydrogen ions** and **hydroxide ions** in acid-base behaviour.

In 1884 he described a theory of acid-base behaviour centred on the ability of certain substances that contain H or OH to produce hydrogen ions, **$H^+(aq)$** or hydroxide ions, **$OH^-(aq)$** when dissolved in water.

The **Arrhenius** theory states:

- An **acid** is a substance that will **ionise** in solution producing **$H^+(aq)$** ions, eg:

  $HNO_3(aq) \rightarrow$ **$H^+(aq)$** $+ NO_3^-(aq)$ .... ①
  hydrogen ions are produced by the acid HNO_3

  $CH_3COOH(aq) \rightleftharpoons$ **$H^+(aq)$** $+ CH_3COO^-(aq)$..... ②
  hydrogen ions are produced by the acid CH_3COOH

- A **base** is a substance that will **dissociate** in solution releasing **$OH^-(aq)$** ions, eg:

  $NaOH(s) \rightarrow$ **$OH^-(aq)$** $+ Na^+(aq)$ ....③
  hydroxide ions are released from the base NaOH

Thus according to Arrhenius, the acidic properties of a solution are due to the presence of hydrogen ions, **$H^+(aq)$** while basic properties result from the presence of hydroxide ions, **$OH^-(aq)$**. If a basic and acidic solution are mixed then the properties become **neutralised** as $H^+(aq)$ and $OH^-(aq)$ react to form water, $H_2O(l)$.

The Arrhenius theory also accounts for the varying strength of different acids. This is based upon the extent of the ionisation reaction. According to Arrhenius, a strong acid is more fully ionised in aqueous solution than a weak acid. A single arrow, → (see ①
⇌ (see ②

acid like HNO_3 produces a higher $H^+(aq)$ concentration and stronger acidic properties than a weak acid like CH_3COOH.

The Arrhenius theory gives a good account of the acid-base behaviour of some acids and ionic hydroxides and is still used today to account for acid-base behaviour. However, the theory is limited as it only applies to acid-base behaviour in **aqueous** solutions. Also it does not explain or predict the basic nature of many other compounds such as **carbonates** and **oxides** (eg Na_2CO_3 and MgO) and **salts** like Na_3PO_4 and KCH_3COO, none of which contain OH^-.

The **Brønsted-Lowry** theory is a more comprehensive model of acid-base behaviour which first appeared in 1923. This theory gives a broader and more satisfactory account of acid-base behaviour. It was independently developed by the Danish chemist, Johannes Brønsted (1879-1947) and the English chemist, Thomas Lowry (1874-1936).

Ionisation and **dissociation**:

Arrhenius had originally used the term dissociation to mean the formation of ions by acids such as HCl, H_2SO_4 and HNO_3. However, these acids have a **covalent molecular** structure and do not actually contain ions. When dissolved in water these acids produce ions in a reaction we now call **ionisation**, see ① ②
reaction that results in the formation of hydrogen ions not originally present in the acid.

The bases referred to by Arrhenius are all ionic hydroxide compounds, eg NaOH, KOH, $Ba(OH)_2$ and so on. These compounds actually do contain hydroxide ions which are simply released when dissolved in water, see reaction ②
dissociation.

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Attempt Set 4 # 1, 2 and 3.

4.2 The Brønsted-Lowry theory of acid-base behaviour

The **Brønsted-Lowry** theory explains acid-base behaviour in terms of **proton transfer** between two species, ie hydrogen ion transfer. (See Fig 3.) This theory has wide application and can account for the basic nature of species which do not themselves contain hydroxide ions, eg NH_3, HCO_3^-, PO_4^{3-} or S^{2-}. It does this by showing the role of the solvent, which is typically water, in the acid-base process. It states:

- An **acid** is a substance that **donates** a **proton** (ie a hydrogen ion, H^+
  A **base** is a substance that **accepts** a **proton** (ie a hydrogen ion, H^+

Brønsted-Lowry theory can be seen when a strong acid like $HNO_3(l)$ dissolves in water to produce a nitric acid solution.

H^+ ion (proton) transfer from HNO_3 to H_2O

$HNO_3(l) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$............ ④
base
hydrogen ions, $H_3O^+(aq)$ make the solution acidic

In reaction ④ is behaving as an acid as each HNO_3 molecule donates a proton (H^+ ion) to a water molecule. By accepting a hydrogen ion (proton) each water molecule behaves as a base. This Brønsted-Lowry proton transfer reaction requires both an acid and a base to be present for the reaction to occur. In this case the **solvent**, water, is behaving as a base.

Figure 3 The aqueous **hydrogen ion**, also known as a **proton** or **hydronium ion** can be represented as **$H^+(aq)$** or **$H_3O^+(aq)$**. The latter form shows that in water each hydrogen ion, H^+ is strongly attached to one water molecule, ie **$H^+ + H_2O = H_3O^+$.**

Chemists often use these terms, hydrogen ion, proton and hydronium ion interchangeably.

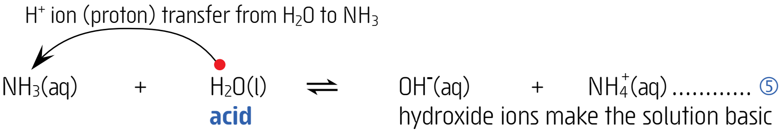
$H^+ + H_2O \rightarrow H_3O^+$

Remember, a hydrogen **atom** consists of a nucleus containing a single proton plus an electron cloud with a single electron. Since a hydrogen **ion** has lost its single electron then all that remains is a nucleus containing the single proton. Hence the term **proton** is synonymous for a **hydrogen ion**, H^+.

The very small size of a hydrogen ion (just a nucleus) gives it an enormous charge density. As a consequence it becomes very strongly attracted to the lone pair (and δ⁻) of the oxygen atom in a water molecule to form the **hydronium ion**, H_3O^+.

The following reaction, ⑤ acts as a Brønsted-Lowry base when dissolved in water. In this reaction each NH_3 molecule accepts a proton while each water molecule donates a proton. In this case the solvent, water, acts as an acid.

The **Brønsted-Lowry** theory also introduces the concept that acid-base behaviour is relative, ie it depends on the given situation. Thus a species like water may act as a base with a strong acid like nitric acid, eg in reaction ④, but then act as an acid with a weak base like ammonia as in reaction ⑤.


$$NH_3(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_4^+(aq) \text{ .... ⑤}$$

Brønsted-Lowry equations represent reversible equilibrium reactions. A double arrow, ⇌ (eg reaction ⑤

→ may be used if the reaction is considered to go to completion (ie essentially only products present at equilibrium) eg reaction ④

Lowry equations represent reversible equilibrium reactions.

Reactions ④ ⑤
④ ⑤

substance is identified as being an acid or base in the context of a particular reaction. As most reactions occur in an aqueous solution it is often convenient to describe acid-base strength with reference to how the substance behaves in the solvent water. (See Table 1.)

The **strength** of the acids and bases listed in Table 1 indicates the extent to which the Brønsted-Lowry proton transfer reaction goes to completion with the solvent water. This is sometimes referred to as the **degree of ionisation**.

Careful! Do not confuse strong and weak with concentrated and dilute.

Concentrated and **dilute** refer to the ratio of solute to solution. A dilute acid has a low ratio of acid to solution, eg 0.1 mol L^{-} (aq). A concentrated acid has a high ratio of acid to solution, eg 6.0 mol L^{-} (aq).

Table 1 Strength of common Brønsted-Lowry acids and bases compared to water. (See border note.)

Strong acids		**Strong bases**	
sulfuric acid	**H_2SO_4**	oxide ion	**O^{2-}**
hydrochloric acid	**HCl**	hydroxide ion	**OH^-**
nitric acid	**HNO_3**		
Weak acids (ranked with strongest at top)		**Weak bases (ranked with strongest at top)**	
sulfurous acid	**H_2SO_3**	sulfide ion	**S^{2-}**
hydrogensulfate ion	**HSO_4^-**	phosphate ion	**PO_4^{3-}**
phosphoric acid	**H_3PO_4**	methylamine	**CH_3NH_2**
ethanoic acid	**CH_3COOH**	carbonate ion	**CO_3^{2-}**
carbonic acid	**H_2CO_3**	ammonia	**NH_3**
hydrogensulfite ion	**HSO_3^-**	hydrogenphosphate	**HPO_4^{2-}**
dihydrogenphosphate ion	**$H_2PO_4^-$**	hydrogencarbonate ion	**HCO_3^-**
ammonium ion	**NH_4^+**	ethanoate ion	**CH_3COO^-**

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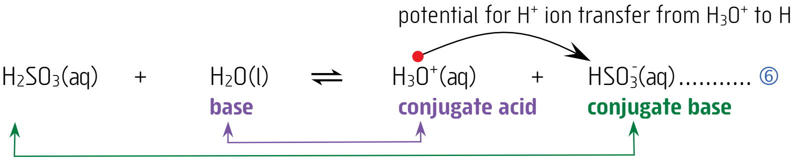
Attempt Set 4 # 4, 5, 6 and 7.

4.3 Conjugate acid-base pairs

The **Brønsted-Lowry** theory recognises the **reversibility** of proton transfer reactions, ie recognises their equilibrium nature. Thus once a base has gained a proton, its product could potentially donate back this gained proton, thus act as an acid. For this reason the product of a base is called the **conjugate acid** of that base. Similarly the product of an acid that has donated a proton, could potentially act as a base by regaining a proton and so is called the **conjugate base** of that acid.


$$H_2SO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HSO_3^-(aq) \text{ .... ⑥}$$

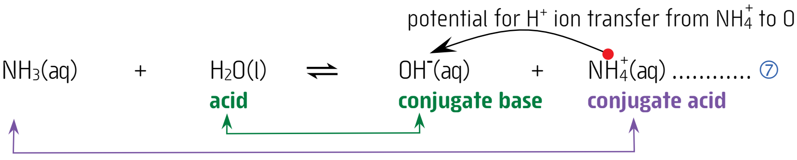

$$NH_3(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_4^+(aq) \text{ .... ⑦}$$

Table 2 Acid-bases conjugate pairs

Acid	**Conjugate base**	**difference**
HCl	Cl^-	H^+
H_2SO_4	HSO_4^-	H^+
HSO_4^-	SO_4^{2-}	H^+
Base	**Conjugate acid**	**difference**
O^{2-}	OH^-	H^+
OH^-	H_2O	H^+
HCO_3^-	H_2CO_3	H^+

In any acid-base conjugate pair the formula of the acid is always greater by the equivalent of H^+.

In reaction ⑥ $_2SO_3$(aq) is the acid and HSO_3^-(aq) is its **conjugate base** while H_2O(l) is the base and H_3O^+(aq) is its **conjugate acid**. Conjugate acid-base pairs always differ in their formula by one proton, H^+. The acid species of the pair always has the extra H^+ in its formula. It must be remembered that the Brønsted-Lowry model classifies substances as acids or bases in the context of a given reaction. Thus in reaction ⑥ $_3^-$(aq) is classified as a conjugate base; however, this same species acts as an acid when added to pure water. (See Table 1.)

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Attempt Set 4 # 8, 9, 10 and 11.

4.4 Acidity constant K_a and acid strength

An acid-base proton transfer reaction is an example of an **equilibrium** process. The equilibrium constant for such a reaction occurring in water is known as the **acidity constant**, **K_a** (or acid dissociation constant). **K_a** is a numerical measure of the extent to which the proton transfer reaction goes to completion, hence it is an indicator of acid strength.

HA(aq) + **H_2O(l)** $\rightarrow$ **H_3O^+(aq)** + **A^-(aq)** ....a general single proton transfer reaction*

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

where: **K_a** is the acidity constant of the acid **HA**

[**H_3O^+**] is the equilibrium concentration of **H_3O^+** and so on for [**A^-**] and [**HA**].

There are several important points to remember about the acidity constant, K_a.

- **HA** is a generic formula for a monoprotic acid such. (See border note above.)
- The proton transfer equation is for the transfer of a **single proton** from the acid HA to a water molecule.
- H_2O(l) has a **fixed** concentration ($\approx$ 55.5 mol L^{-1}) and so is not included in the acidity constant expression.

As with all equilibrium constants the **size** of K_a gives an indication of the tendency of the reaction to form products or remain as reactants. Thus the larger the K_a, the greater the tendency is for the acid to donate a proton to water. Hence the stronger the acid is and the greater is the degree of its ionisation.

Example 1 Consider the two acids, ethanoic acid, CH_3COOH and sodium hydrogensulfate*, $NaHSO_4$. The K_a for these acids is: $K_a(CH_3COOH) = 1.7 \times 10^{-5}$ and $K_a(HSO_4^-) = 1.0 \times 10^{-2}$.

a. Write a **proton transfer equation** for each of the acids in water and give its K_a expression.

b. What does the **magnitude** of K_a indicate about the **strength** of each acid. **Justify** your answer with reference to the K_a expression.

c. 20.0 mL of a 1.00 mol L^{-1} solution of each acid is added to a similar 5.00 g zinc granule. Which acid produces the **most vigorous** reaction? **Explain**.

a. $CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$ and $K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$

$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$ and $K_a = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]}$

b. The larger the value of K_a the more the equilibrium position favours products. Hence a larger value of K_a indicates a greater tendency for the acid to form hydrogen ions and so the stronger the acid is. Hence as HSO_4^- has the larger K_a value it is the stronger acid.

c. The acid with the higher H^+(aq) concentration will give the faster rate of reaction. As both acids have the same initial concentration then the acid with the greater K_a produces the solution with a higher H^+(aq) concentration. Thus the 1.00 mol L^{-1} $NaHSO_4$(aq) solution will show the most vigorous reaction with the zinc granule.

While the acidity constant indicates the ability of an acid to donate a proton to a water molecule it also indicates the **strength** of its **conjugate base** to accept a proton back from water, ie to act as a base. If K_a is very large (a strong acid) then its conjugate base is extremely weak (possibly neutral). As K_a is progressively smaller and the acid progressively weaker so the conjugate base becomes a progressively stronger base. (See Table 3.)

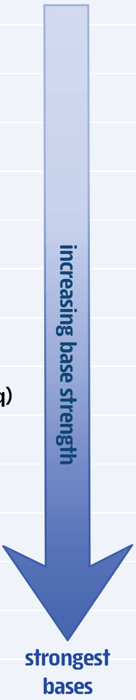
---

* **HA** is a general formula often used to represent a monoprotic acid, eg for HNO_3 or HCl the symbol **A^-** would represent NO_3^- or Cl^- respectively.

*When $NaHSO_4$ dissolves in water it dissociates to produce a solution of the weak acid hydrogensulfate, HSO_4^-.

Table 3 Brønsted-Lowry proton transfer equations and acidity constant, K_a for some common species

Acid	Acid					Conjugate base	K_a (25 °C)
sulfuric acid	**$H_2SO_4(aq)$**	+ $H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	**$HSO_4^-(aq)$**	$\approx 10^9$
hydrochloric acid	**$HCl(aq)$**	+ $H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	**$Cl^-(aq)$**	$\approx 10^7$
nitric acid	**$HNO_3(aq)$**	+ $H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	**$NO_3^-(aq)$**	2.0×10^1
oxalic acid	**$H_2C_2O_4(aq)$**	+ $H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	**$HC_2O_4^-(aq)$**	5.6×10^{-2}
sulfurous acid	**$H_2SO_3(aq)$**	+ $H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	**$HSO_3^-(aq)$**	1.4×10^{-2}
hydrogensulfate ion	**$HSO_4^-(aq)$**	+ $H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	**$SO_4^{2-}(aq)$**	1.0×10^{-2}
phosphoric acid	**$H_3PO_4(aq)$**	+ $H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	**$H_2PO_4^-(aq)$**	7.1×10^{-3}
hydrogenoxalate ion	**$HC_2O_4^-(aq)$**	+ $H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	**$C_2O_4^{2-}(aq)$**	5.4×10^{-5}
ethanoic acid	**$CH_3COOH(aq)$**	+ $H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	**$CH_3COO^-(aq)$**	1.7×10^{-5}
carbonic acid	**$H_2CO_3(aq)$**	+ $H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	**$HCO_3^-(aq)$**	4.5×10^{-7}
hydrogensulfite ion	**$HSO_3^-(aq)$**	+ $H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	**$SO_3^{2-}(aq)$**	6.5×10^{-8}
dihydrogenphosphate ion	**$H_2PO_4^-(aq)$**	+ $H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	**$HPO_4^{2-}(aq)$**	6.3×10^{-8}
ammonium ion	**$NH_4^+(aq)$**	+ $H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	**$NH_3(aq)$**	5.8×10^{-10}
hydrogenphosphate ion	**$HPO_4^{2-}(aq)$**	+ $H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	**$PO_4^{3-}(aq)$**	4.2×10^{-13}
water	**$H_2O(l)$**	+ $H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	**$OH^-(aq)$**	1.0×10^{-14}



Data source: G. Aylward & T. Findlay, *SI Chemical Data* (2008, 6th Edition) John Wiley & Sons Australia, LTD.

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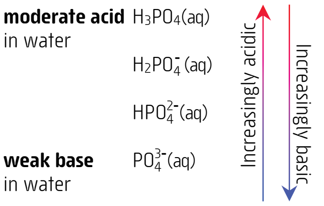
Attempt Set 4 # 12 and 13.

4.5 Polyprotic acids

Acids like HCl and HNO_3 are said to be **monoprotic**. These acids can donate only one proton per acid molecule. **Polyprotic** acids are able to donate more than one proton per molecule of acid. These include diprotic acids, ie those that have two acidic hydrogen atoms, eg H_2SO_4 and triprotic acids that have three acidic hydrogen atoms per molecule, eg H_3PO_4. The conjugate base of a polyprotic acid is usually (but not always) acidic in relation to water. However, its acid strength is always less than the original acid. (See border note.) This can be seen with the example of sulfuric acid where its first acidity constant, $K_{a,1}$ is much greater than its second acidity constant, $K_{a,2}$.

In any series of **polyprotic acids**, eg phosphoric acid, the acid strength decreases as more protons are successively removed.



$H_2SO_4(aq)$ + $H_2O(l)$ $\rightleftharpoons$ $H_3O^+(aq)$ + $HSO_4^-(aq)$.......... **first** proton transfer: $K_{a,1} \approx 10^9$

$HSO_4^-(aq)$ + $H_2O(l)$ $\rightleftharpoons$ $H_3O^+(aq)$ + $SO_4^{2-}(aq)$..........**second** proton transfer: $K_{a,2} = 1.0 \times 10^{-2}$

A general trend can be seen in any series of polyprotic acids where **subsequent acidity constants decrease** with each proton transfer. This trend is to be expected as each subsequent conjugate base of the original acid has an increasingly negative charge making it harder to donate (lose) a hydrogen ion (positive).

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Attempt Set 4 # 14 and 15.

4.6 Acid-base properties of salts

When an acid reacts with a base, a salt and water are always produced. Although this is called a **neutralisation** reaction, the **salt** formed in this reaction is not always neutral. Often a salt may be either acidic or basic. The acid-base properties of salts can be understood in terms of the Brønsted-Lowry theory. If one of the ions present in a salt, reacts with water acting as a proton donor (acid), then its solutions will be acidic. An ammonium chloride solution, $NH_4Cl(aq)$ for example is acidic. Its acidity is due to the ammonium ion, NH_4^+ which acts as a weak acid in water, see below. The chloride ion, $Cl^-(aq)$ is neutral. (See Table 1, 3 and 4.)

The reaction of a salt ion with water (at right) to form an acidic or basic solution is sometimes called **hydrolysis**. More generally though, this is just an example of a Brønsted-Lowry proton transfer reaction.

$NH_4^+(aq)$ + $H_2O(l)$ $\rightleftharpoons$ $H_3O^+(aq)$ + $NH_3(aq)$ ....⑧
formation of H_3O^+ gives an acidic salt solution

This reaction of an ion with water, as shown above ⑧ . As seen here, when an ion hydrolyses in water it causes a change in the solutions pH.

If a salt contains an ion that hydrolyses by acting as a proton acceptor (base) then its solution will be basic. A sodium ethanoate solution, $CH_3COONa(aq)$ for example, is basic as the ethanoate ion, CH_3COO^- is a weak base in water. The Na^+ ion is neutral. (See Table 1, 3 and 4.)

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + CH_3COOH(aq) \quad ⑨$$

formation of OH^- gives a basic salt solution

Some salts contain both an acidic and a basic ion. In this situation the salt solution may be neutral or its acidity is governed by the ion with the strongest acid or base characteristics. Table 1 lists and ranks the acid-base strength of some typical ions found in salts. Thus the acidity of a salt solution is found by analysing the ions it contains. (See Example 2.)

Table 4 Common neutral ions

Some common neutral ions	
lithium ion	Li^+
sodium ion	Na^+
potassium ion	K^+
magnesium ion	Mg^{2+}
calcium ion	Ca^{2+}
barium ion	Ba^{2+}
chloride ion	Cl^-
bromide ion	Br^-
iodide ion	I^-
nitrate ion	NO_3^-

Example 2 Determine the acidity of the following salt solutions and state the ion causing this.

salt solution	$NaCl(aq)$	$Mg(HSO_4)_2(aq)$	$KNO_3(aq)$	$NH_4Cl(aq)$	$K_2CO_3(aq)$	$Ca(HCO_3)_2(aq)$	$NaCH_3COO(aq)$	$NaH_2PO_4(aq)$
ion affecting acidity	nil	HSO_4^-	nil	NH_4^+	CO_3^{2-}	HCO_3^-	CH_3COO^-	$H_2PO_4^-$
acidity	neutral	acidic	neutral	acidic	basic	basic	basic	acidic

A useful generalisation for predicting the acid-base nature of a salt is to consider the relative strength of the acid and base that produced it. (See Table 5.)

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Complete Set 4

Table 5 The acid-base properties of a salt can be predicted from the strength of its parent acid and base.

	Strong base	**Weak base**
Strong acid	neutral salt	acidic salt
Weak acid	basic salt	neutral salt

Set 4 Theories of acid-base behaviour

1. The scientific method is an evidence based process. Scientists propose new models and theories to fit experimental observations. Theories may be modified or changed when experimentation yields new observations that do not agree with the current model or theory. With this in mind answer the following questions.
   a. What observations led Antoine Lavoisier to propose that it was the presence of oxygen in a compound that gave it acidic properties?
   b. What new observations by Humphry Davy led him to challenge Antoine Lavoisier's proposal that a compound's acidity was due to oxygen in the compound?
   c. Davy later proposed that acids were compounds that contained hydrogen, not oxygen, as Lavoisier had proposed. What observations by Davy and others led him to propose his new model of acidity?
   d. Although Davy's theory seemed to be heading in the right direction it did have some problems. What had Von Liebig and others noted about this theory which did not match current observations? How did Von Liebig modify Davy's theory to make it more consistent with what was known at the time?

2. Use the list of terms given to correctly **complete** the following passage.

   In 1884 a major new theory of acid-base behaviour was proposed by **Svante Arrhenius**. Arrhenius proposed that certain substances containing (a) ___________ in their formula could dissolve in water to produce (b) ___________. The acid-base properties of the resulting solution were then caused by the presence of these (c) ___________. Specifically, he states an acid is a substance that (d) ___________ in water releasing (e) ___________ into solution while a base is understood to be a substance that **dissociates** in water releasing (f) ___________.

   This theory has proved suitable for explaining the acid-base properties of many substances like HCl, HNO_3, NaOH and $Ba(OH)_2$ but is unable to explain the acidic properties of substances like (g) ___________ or the basic properties of substances like (h) ___________.

ions
Na_2CO_3
ionises
$H^+(aq)$ or $OH^-(aq)$
$FeCl_3$ or $Cr(NO_3)_3$
$H^+(aq)$
$OH^-(aq)$
H or OH

3. The Arrhenius model of acid-base behaviour was a significant improvement on Davy's proposal. This model gave a good account of the acid-base behaviour of many compounds in water and could also account for the varying strength of different acids and bases. The Arrhenius model was based on the ability of certain compounds to produce hydrogen ions or hydroxide ions in solution
   a. Use the Arrhenius model to account for the acid-base properties of HCl and $Ba(OH)_2$. You will need to include suitable equations as part of your answer.
   b. How does the Arrhenius model account for the varying strength of different acids like HCl and CH_3COOH? Include suitable equations as part of your answer.

4. One problem with the Arrhenius theory is its inability to account for the basic nature of substances like ammonia, NH_3. Briefly describe how the Brønsted-Lowry model is able to explain the basic nature of an ammonia, NH_3 solution. You will need to include a Brønsted-Lowry proton transfer equation as part of your answer.

5. Consider the following proton transfer reactions. Use your knowledge of the **Brønsted-Lowry** theory to classify the underlined substances as behaving as an **acid** or **base**. Write your answer in the spaces provided.
   a. $NH_3(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$
   __________ __________
   b. $H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq)$
   __________ __________
   c. $H_2O(l) + HNO_2(aq) \rightleftharpoons NO_2^-(aq) + H_3O^+(aq)$
   __________ __________
   d. $HCOO^-(aq) + H_2O(l) \rightleftharpoons HCOOH(aq) + OH^-(aq)$
   __________ __________

6. Write both a **Brønsted-Lowry** equation (ie proton transfer) and an **Arrhenius** equation (ie **ionisation**), **where possible**, for each of the following acids and bases when they dissolve in water. Show single proton transfer or single ionisation only. Use an appropriate arrow to show if the reaction is partial or complete. (See Table 1 and 4.)
   a. HCl c. NH_3 e. H_2SO_4 g. CH_3NH_2
   b. CH_3COOH d. H_3PO_4 f. H_2SO_3

7. Give an **answer** and a brief **explanation** for each of the following.
   a. Which of these solutions, 1.0 mol L^{-1} HNO_3 or 1.0 mol L^{-1} CH_3COOH, has the highest hydrogen ion concentration?
   b. Which solution is most basic, 1.0 mol L^{-1} $NH_3(aq)$ or 1.0 mol L^{-1} $NaOH(aq)$?
   c. Which solution is most acidic, 1.0 mol L^{-1} $HCl(aq)$ or 0.1 mol L^{-1} $HCl(aq)$?

ammonium ion
single arrow
partially
donates
products
proton acceptor
proton transfer
conjugate acid
reversible
proton
water
conjugate base

8. Use the list of terms given at left to **complete** the following passage.

   The **Brønsted-Lowry** model explains acid-base behaviour in terms of (a) __________. An acid is a substance that (b) __________ a proton while a base is the (c) __________. Using this model the basic nature of substances like Na_2CO_3 and NH_3 can be better understood. This equation shows how ammonia can act as base in water.

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

   When added to water, ammonia acts as a (d) __________ acceptor to form an (e) __________. In this process (f) __________ acts as the acid donating a hydrogen ion to ammonia. In this way hydroxide ions are formed and the solution becomes basic. Reactions like this are said to be (g) __________. In the reverse reaction the ammonium ion, NH_4^+ is said to be the (h) __________ of ammonia, NH_3 while the hydroxide ion, OH^- is said to be the (i) __________ of the acid water, H_2O. Using double arrows in the equation shows ammonia is a weak base (in water) only (j) __________ converting to $OH^-(aq)$ and $NH_4^+(aq)$ ions. When a strong acid or base reacts with water the equilibrium is said to lie to the right, ie (k) __________ are favoured and a (l) __________ is used to show this.

9. Classify the reaction **products** from Question 5 as **conjugate acids** or **conjugate bases**.

10. Write the formula for the **conjugate base** of the following species.

a. HCl b. HSO_4^- c. HPO_4^{2-} d. NH_4^+

11. Write the formula for the **conjugate acid** of the following species.

a. CH_3COO^- b. OH^- c. NH_3 d. HPO_4^{2-}

12. The proton transfer reaction referred to in the Brønsted-Lowry model of acid-base behaviour is an equilibrium process. The equilibrium constant for such a reaction is known as the acidity constant, K_a or sometimes called the acid dissociation constant. Refer to the following proton transfer reaction and the acidity constant for oxalic acid to answer the following questions.

$$H_2C_2O_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HC_2O_4^-(aq) \qquad K_a = 5.6 \times 10^{-2}$$

a. A 15 g sample of solid oxalic acid is dissolved in 150 mL of water. **Compare** the rate of the **forward** and **reverse** reactions (shown above) when the oxalic acid has just been added and again some time later when the system has reached equilibrium.

b. What does K_a imply about the **equilibrium position** for this reaction?

c. Would you describe oxalic acid as a strong or moderate acid? **Explain**.

d. Use your knowledge of **reaction rates** to **explain** how the concentration of $H_2C_2O_4(aq)$ and $HC_2O_4^-(aq)$ change when some concentrated sodium hydroxide solution is added to the system.

13. Consider the two acids, **nitric acid**, HNO_3 and **carbonic acid**, H_2CO_3.

a. Write the acid **dissociation constant** expression for each of these acids.

b. Refer to the K_a values for these acids (Table 3) and compare their acid strength. **Justify** your answer with reference to the K_a.

c. Solutions of each acid are prepared by dissolving the equivalent of one mole of each acid in 0.5 L of water. Which solution has the greater concentration of hydrogen ions? **Explain**.

14. **Classify** the acids, nitric acid HNO_3, ethanoic acid, CH_3COOH and sulfuric acid, H_2SO_4 as polyprotic, monoprotic or diprotic.

15. The triprotic acid phosphoric acid can undergo several proton transfer reactions as shown.

$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq)$$
$$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$$
$$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$$

a. **Rank** the three acids from strongest to weakest.

b. **Account** for the trend in acid strength stated above.

c. **Rank** the basic properties of the three conjugate bases from strongest to weakest.

$OH^-(aq)$
$SO_4^{2-}(aq)$
hydrolysis
$H_2CO_3(aq)$
proton
$H_3O^+(aq)$
water

16. **Complete** the following passage about the **acid-base properties** of **salt solutions**. Use the terms at left.

Salt solutions are sometimes acidic or basic in nature. This can happen if the ions in solution are themselves weak acids or bases and thus have a tendency to donate or accept protons from (a) ___________. Thus the basic nature of a $NaHCO_3$ salt solution is due to the hydrogencarbonate ion, HCO_3^- accepting a proton from water and thus causing water molecules to be converted to (b) ___________ ions. (See equation ①

$_3^-(aq)$ + $H_2O(l)$ $\rightleftharpoons$ $OH^-(aq)$ + (c) ___________..................... ①

(d) ___________ to water.
Thus the salt solution of $NaHSO_4$ is acidic as the hydrogensulfate ion, HSO_4^- will donate a proton to water thus causing water molecules to be converted to (e) ___________. (See equation ②

$_4^-(aq)$ + $H_2O(l)$ $\rightleftharpoons$ $H_3O^+(aq)$ + (f) ___________ .... ②

① ② (g) ___________ reactions.

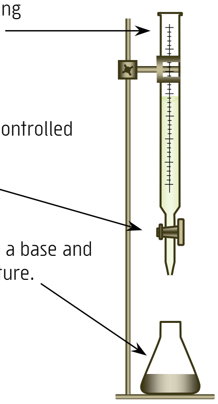
17. How do the following species affect the acidity of water? Classify each species as being a **strong acid**, **weak acid**, , **neutral**, when dissolved in water. (You may need to refer to Table 1 and 4.) For those substances that affect the acidity of the solution, write a **proton transfer** equation to shows this.

a. HCl
b. Cl^-
c. HNO_3
d. NO_3^-
e. Ca^{2+}
f. NH_4^+
g. NH_3
h. Na^+
i. H_3PO_4
j. $H_2PO_4^-$
k. HPO_4^{2-}
l. PO_4^{3-}
m. Mg^{2+}
n. H_2SO_4
o. HSO_4^-
p. CH_3COO^-
q. CH_3COOH
r. H_2CO_3
s. HCO_3^-
t. CO_3^{2-}

18. The following compounds (a) to (l) are all soluble salts that readily dissolve in water. Determine the ions present in a solution of these salts and state which of these, if any, will cause one of the following changes.

- Cause the salt solution to become **acidic**, ie have a pH < 7.
- Cause the salt solution to become **basic**, ie have a pH > 7.
- Have **no effect** on the solution pH.

a. Na_2CO_3
b. $NaCl$
c. NH_4Cl
d. $MgCl_2$
e. $Mg(HSO_4)_2$
f. $CaBr_2$
g. $NaCH_3COO$
h. K_2S
i. KNO_3
j. $KHCO_3$
k. K_2HPO_4
l. $Mg(NO_3)_2$


A burette containing the acid solution.

A tap allows the controlled addition of acid to base.

The flask contains a base and final reaction mixture.

Figure 4 Titrating a base with the acid solution placed in a burette. The **equivalence** point in this titration happens when sufficient acid has been added to just neutralise the base without an excess of acid or base remaining.

19. Brendon carried out several acid-base titrations involving the neutralisation of different acids and bases. In the titrations he added an acid solution from a burette to a base solution in a conical flask. (See Fig 4.) He carefully added acid until **complete neutralisation** had occurred, ie both acid and base were **fully consumed** with neither acid nor base in excess. This point in a titration is known as the **equivalence** point.

Using a pH meter Brendon was able to follow the progress of the titration. In this way he was able to determine the pH at the equivalence point of each titration, which he had hypothesised would be 7
for the pH values he observed for the equivalence point of each titration.

a. An ethanoic acid, CH_3COOH solution was neutralised with a sodium hydroxide, $NaOH$ solution. At the equivalence point the reaction mixture pH was approximately 9.
b. An ammonia, NH_3 solution was neutralised with a nitric acid, HNO_3 solution. At the equivalence point the final mixture had a pH of around 6.

20. **Weak acids** like sulfurous acid, H_2SO_3 are only partially ionised when dissolved in water. For this reason a 1.00 L solution of 1.00 mol L^{-1} H_2SO_3 will only contain **0.12 mole of $H^+(aq)$** instead of containing around 2.0 mol of $H^+(aq)$ if it were a strong acid like sulfuric acid, $H_2SO_4(aq)$. Despite this, it still requires 2.00 mol of NaOH (ie 2 mol of OH^-) to react completely with 1.00 L of 1.00 mol L^{-1} $H_2SO_3(aq)$.

    Using your knowledge of **Le Chatelier's principle** and equilibrium, **explain** why 2.00 mol of NaOH, ie **2 mol of OH^-**, is needed to completely neutralise 1.00 L of 1.00 mol L^{-1} $H_2SO_3(aq)$ even though the sulfurous acid solution originally contains only 0.12 mol of $H^+(aq)$.

21. Despite the soluble nature of some metallic oxides like **Na_2O**, it is not possible to produce an aqueous solution containing the $O^{2-}(aq)$ ion.

    a. **Explain** this observation. You should include a **dissociation** equation for the dissolving of Na_2O in water and an **hydrolysis equation** for the reaction of the oxide ion with water to support your answer.

    b. What does an Na_2O solution actually become?

22. The **strong acid** sulfuric acid, H_2SO_4 has the greatest annual worldwide production of any manufactured compound. This **diprotic** acid is used in fertiliser manufacture, ore processing and chemical synthesis of other compounds. The common car battery (lead-acid battery), for example, contains a **concentrated** solution ($\approx$ 4.5 mol L^{-1}) of sulfuric acid.

    Carbonic acid, H_2CO_3 by comparison is the **weak acid** that is formed when carbon dioxide dissolves in water. Carbonated or fizzy drinks like soft drink and various brewed beverages such as beer and sparkling wines contain a **dilute solution** of this weak acid.

    a. Use the compound sulfuric acid to explain the meaning of the term '**diprotic acid**'.

    b. Write equations for the single ionisation, ie formation of a single hydrogen ion per acid molecule, of both sulfuric acid and carbonic acid. With reference to these equations explain the difference between a **strong acid** and **weak acid**.

    c. Explain the meaning of the terms **dilute** and **concentrated** as used in the above passage.

    d. One effect of carbonic acid in aerated beverages is to give the beverage a distinctive sharp, sour tang due to its acidity. Although an acid like sulfuric acid would probably give beverages a similar sour tang it would definitely be unsuitable to use sulfuric acid of a similar concentration in beverages. **Explain** why sulfuric acid should not be used this way.

23. The **diprotic** acid H_2CO_3 can undergo **successive ionisations**, ultimately producing two moles of hydrogen ions per mole of carbonic acid. In practice however, as carbonic acid is a weak acid, the hydrogen ion concentration in a 1 mol L^{-1} solution of H_2CO_3 is only around 7 x 10^{-4} mol L^{-1}, much less than the 2 mol L^{-1} that would be expected if this acid underwent complete ionisation.

    a. Write **two separate equations** showing the first and second ionisation (releasing of a hydrogen ion) of the acid H_2CO_3.

    b. One of these two reactions is responsible for producing all of the hydrogen ions present in a solution of carbonic acid. Which is it? Explain.

    c. Consider the series of three related species shown here:

    H_2CO_3 **HCO_3^-** **CO_3^{2-}**

    How does the chemical composition of each member of the series differ from the chemical composition of the preceding member of the series?

    d. What **trend** is evident in the strength of the acid-base properties of the three related species H_2CO_3, HCO_3^- and CO_3^{2-}?

    e. Is this trend in acid-base properties (from the preceding question) true for other diprotic acids? Use H_2SO_4 as an example to illustrate your answer.

24. It is quite normal for rain to have a pH of around 5 to 6 due to natural levels of atmospheric carbon dioxide. This happens as CO_2 interacts with rain water producing the **weak acid** H_2CO_3. This acid then partially ionises, lowering the pH of rainfall.

One consequence of industrial air pollution is the effect known as **acid rain**, where rainfall may have a pH as low as 2. Acid rain was first recorded in England in the mid 1800s. Generally acid rain is any form of precipitation, like rain or snow, having a pH lower than 5. It happens as a result of **sulfur oxides** and **nitrogen oxides** that may be present in the atmosphere due to industrial activity or due to the natural effects of volcanoes or lightning. These gases interact with water and air to produce **strong acids** capable of lowering pH to well below 5.

a. Suggest why rainfall of pH 5 to 6 is not classified as '**acid rain**'?
b. What acid may occur in rainfall as a consequence of the industrial pollutant $SO_3(g)$?
c. Even if the atmospheric concentration of $SO_3(g)$ is lower than that of $CO_2(g)$ it can still have a greater effect on rainfall **pH** than $CO_2(g)$ ever can. **Explain**.

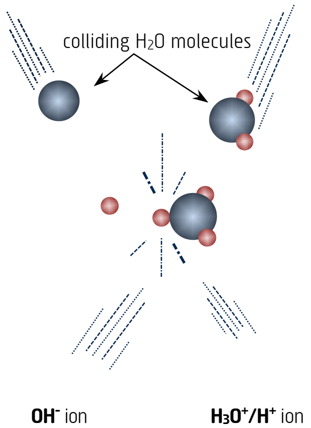


Figure 5 In any sample of pure water (at 25 °C) approximately one in 550 million water molecules (a very small fraction!!) are present as hydrogen ions, represented as H^+ or H_3O^+ and hydroxide ions, OH^-. The illustration above shows how these ions can form.

Remember, the aqueous **hydrogen ion**, also known as a **proton** or **hydronium ion** can be represented as **$H^+(aq)$** or **$H_3O^+(aq)$**. The latter form shows that each hydrogen ion is strongly attached to one water molecule, ie **$H^+ + H_2O = H_3O^+$.**

Table 6 Data showing the inverse relationship between the concentrations of $H^+(aq)$ and $OH^-(aq)$ in any aqueous solution.

pH	[H⁺]	[OH⁻
0	1 mol L^{-1}	1 x 10^{-14} mol L^{-1}
3	1 x 10^{-3}mol L^{-1}	1 x 10^{-11} mol L^{-1}
6	1 x 10^{-6} mol L^{-1}	1 x 10^{-8} mol L^{-1}
7	1 x 10^{-7} mol L^{-1}	1 x 10^{-7} mol L^{-1}
8	1 x 10^{-8} mol L^{-1}	1 x 10^{-6} mol L^{-1}
11	1 x 10^{-11} mol L^{-1}	1 x 10^{-3} mol L^{-1}
14	1 x 10^{-14} mol L^{-1}	1 mol L^{-1}

4.7 K_w and the autoionisation of water

Water has a covalent molecular structure consisting of molecules of formula H_2O. Despite this structure, some H_2O molecules (an extremely small number) change into **$H^+(aq)$** and **$OH^-(aq)$** ions. These ions are produced in equal numbers by a reversible reaction known as **autoionisation**, or simply self-ionisation. (See Fig 5.)

$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$ **or** $2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

This ionisation equilibrium strongly favours the formation of molecular water, H_2O such that in pure water, at equilibrium, both $H^+(aq)$ and $OH^-(aq)$ ions have the same extremely low concentration of 1.0 x 10^{-7} mol L^{-1} at 25 °C (ie a tenth of a millionth of a mole per litre).

In water or any solution where $H^+(aq)$ and $OH^-(aq)$ have the same concentration the solution is said to be neutral, ie its properties are neither acidic nor basic. If some acid or base is added, ie an extra source of $H^+(aq)$ or $OH^-(aq)$ then as with any equilibrium process the system will re-establish a new equilibrium. This happens in such a way that partially minimises the imposed change (as predicted by Le Chatelier). This means adding acid to water not only raises the $H^+(aq)$ concentration but it also lowers the $OH^-(aq)$ concentration and vice versa if a base is added to water. (See Table 6.)

The relationship linking the concentration of $H^+(aq)$ and $OH^-(aq)$ in all aqueous solutions is best understood with reference to the **equilibrium expression** for the self-ionisation of water, known as **K_w**.

$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$ ΔH = 55.8 kJ ....①

$_w$ = $[H^+]\,[OH^-$ - also written as **K_w = $c(H^+)$ x $c(OH^-$ -**

where: **K_w** = the equilibrium constant for the autoionisation of water, ie 1.0 x 10^{-14} at 25 °C
$[H^+]$ = **$c(H^+)$** = the concentration of hydrogen ions
$[OH^-$ **$c(OH^-$**

Some important points to understand about the **K_w** expression:

- It confirms the $[H^+]$ and $[OH^-]$ are **inversely related**, ie an increase in the $[H^+]$ causes a corresponding decrease in the $[OH^-]$ and vice versa. Thus raising the $[H^+]$ by a factor of 3 times will cause a reduction in the $[OH^-]$ by a factor of 3 times.
- Its **extremely small value** (1×10^{-14}) is a reminder of the strong tendency for water to remain in the unionised, molecular form, ie as H_2O molecules, rather than the ionised form $H^+(aq)$ and $OH^-(aq)$.
- Although K_w has a constant value for most conditions, it does change value with **temperature**. As the autoionisation of water is endothermic (see ①

  means the concentration of both $H^+(aq)$ and $OH^-(aq)$ rise with increasing temperature. For this reason K_w will be higher at higher temperatures. (See Table 7.)

At a given temperature the **constant** value of **K_w** means it can be used to find the $H^+(aq)$ or $OH^-(aq)$ concentration for any solution where either the $H^+(aq)$ or $OH^-(aq)$ concentration is known. (See Example 3.)

Example 3 What is the $H^+(aq)$ and $OH^-(aq)$ concentration in 0.15 mol L^{-1} hydrochloric acid, $HCl(aq)$?	
$c(H^+) = c(HCl) = 0.15 \text{ mol } L^{-1}$	HCl is a strong acid and so it is fully ionised in water, ie $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$.
K) x $c(OH^-)$ c(OH $\frac{K_w}{c(H^+)}$ $= \frac{1.0 \times 10^{-14}}{0.15}$ = 6.7 x 10 mol L	K_w shows the relationship between the concentration of hydroxide ions and hydrogen ions for any aqueous solution. Rearranging K_w allows the concentration of $OH^-(aq)$ to be found.

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Table 7 K_w for the ionisation of water at different temperatures.

Temperature (°C)	$K_w = [H^+][OH^-]$
0	0.144×10^{-14}
10	0.292×10^{-14}
20	0.681×10^{-14}
25	1.008×10^{-14}
30	1.47×10^{-14}
40	2.92×10^{-14}
50	5.5×10^{-14}
100	55×10^{-14}

Notice how K_w increases with increasing temperature.
Is this consistent with predictions made from Le Chatelier's principle for an endothermic reaction?

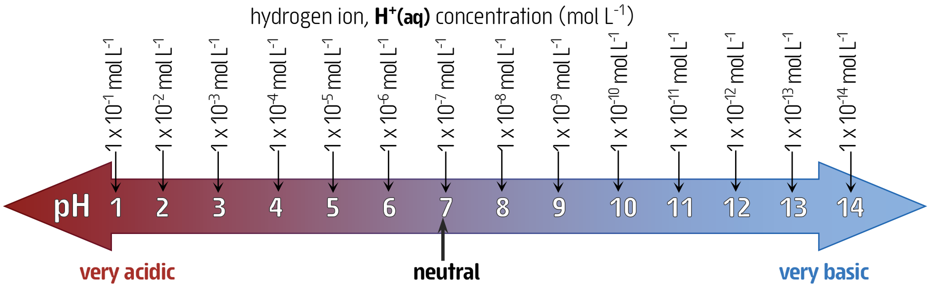
Attempt Set 5 # 1, 2, 3 and 4.

4.8 Acidity and pH

A solution's acidity depends upon its $H^+(aq)$ concentration. Due to limited solubilities of acids and bases, the $H^+(aq)$ concentration in most solutions can range from approximately 10 mol L^- $^{-15}$ mol L^- hydrogen ion concentration is to use the **pH** scale. (See Fig 6, 7 and 8.) pH is a **logarithmic** function related to $H^+(aq)$ concentration as shown here:

$pH = -\log[H^+]$ where $[H^+]$ is the concentration of $H^+(aq)$ in mol L^-

Figure 7 pH is a measure of a solution's hydrogen ion concentration, reflecting its acid-base characteristics. High hydrogen ion concentration, ie an acidic solution, corresponds to a low pH. Basic solutions have a high pH. Pure water is neutral and has a pH of 7 (at 25 °C).

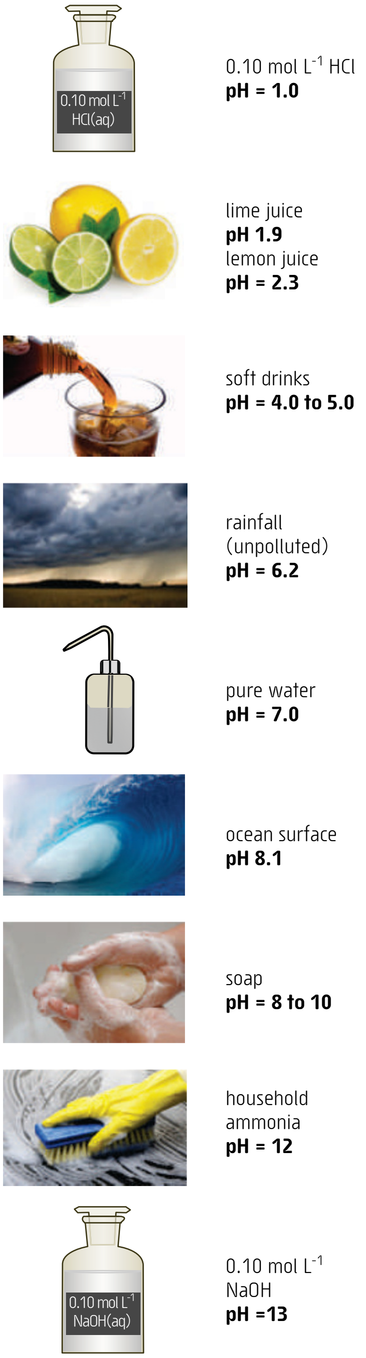


As seen in Fig 7, acidic solutions have a low pH while basic solutions have a high pH. It should also be noted that every **1 unit** difference in pH represents a **10 times** difference in $H^+(aq)$ concentration. Similarly a **2 unit** difference in pH corresponds to a **100 times** difference in $H^+(aq)$ concentration. This reflects the logarithmic nature of the pH scale.

Figure 8 In the laboratory it is convenient to use universal indicator paper (left) or a digital pH meter (right) to determine pH. **Universal indicator paper** consists of a paper strip impregnated with a mixture of indicators (plant dyes). Its colour changes with pH.

For solutions of a **strong acid** or **strong base** with a known concentration, the **pH** equation and the **K_w** relationship can be used to calculate its pH. Similarly if the pH of a solution is known then both the $H^+(aq)$ and $OH^-(aq)$ concentrations can be found. (See Examples 4-6.)

Figure 6 pH of some common substances.



0.10 mol L^{-1} HCl
pH = 1.0

lime juice
pH 1.9
lemon juice
pH = 2.3

soft drinks
pH = 4.0 to 5.0

rainfall
(unpolluted)
pH = 6.2

pure water
pH = 7.0

ocean surface
pH 8.1

soap
pH = 8 to 10

household
ammonia
pH = 12

0.10 mol L^{-1}
NaOH
pH =13

Example 4 Determine the pH of a 0.155 mol L$^-$ $_3$(aq) solution.	
$c(H^+)$ = $c(HNO_3)$ = **0.155 mol L^{-1}**	HNO_3 is a strong acid ∴ it is **completely** ionised in aqueous solution producing H^+(aq) and NO_3^-(aq).
pH = -) = - - - = **0.810**	Scientific calculator keystrokes are: *(-) log 0.155 EXE* will give the answer.

Example 5 Determine the pH of a 0.0155 mol L$^-$ $_2$(aq) solution.	
c(OH = 2 x c[$Ca(OH)_2$] = 2 x 0.0155 = 0.0310 mol L	$Ca(OH)_2$ dissolves to give 2 moles of OH^-(aq) ions from every 1 mole of $Ca(OH)_2$.
$c(H \quad \frac{K_w}{c(OH^-} = \frac{1 \times 10^-}{0.0310} = 3.23 \times 10 \quad mol\ L$	Rearrange the K_w equation to find the $c(H^+)$.
pH = -) = - - = - - 12.5	Scientific calculator keystrokes are: *(-) log 3.23 EXP (-) 13 EXE*

Example 6 Determine the H^+(aq) and OH^- a pH of 6.2.	
pH = -) 6.2 = -) -) inverse log -) thus 6.31 x 10 mol L = c(H	Use the pH relationship to find the $c(H^+)$. Scientific calculator keystrokes are: *SHIFT log (-) 6.2 EXE* will give the answer.
$c(OH \quad \frac{K_w}{c(H^+)} = \frac{1 \times 10^-}{6.31 \times 10^-} = 1.58 \times 10 \quad mol\ L$	Rearrange the K_w expression to determine the $c(OH^-$

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Complete Set 5.

Set 5 pH in water and aqueous solutions

Hint!
In a pure (neutral) sample of water the concentration of H^+(aq) and OH^-(aq) must always be equal, ie $[H^+] = [OH^-]$. Thus for a neutral solution only, the K_w expression can be written as $K_w = [H^+]^2$ or $K_w = [OH^-]^2$.

1. The **equilibrium constant** (**K_w**) for the autoionisation or self-ionisation of water has a value of 1.0×10^{-14} at 25 °C. As temperature rises so does the value of K_w so that at a temperature of 50 °C, for example, $K_w = 5.5 \times 10^{-14}$. (See border note.)
   a. Determine the H^+(aq) concentration in pure neutral water at 25 °C and 50 °C.
   b. Suggest why a pure water sample at 50 °C is considered neutral even though the $c(H^+) = 2.3 \times 10^{-7}$ mol L^{-1}.
   c. Considering your answer to Part (a), comment on the statement, 'In a neutral sample of pure water the hydrogen ion concentration is always 1.0×10^{-7} mol L^{-1}.'

2. The following equation shows the equilibrium process for the autoionisation or self-ionisation of water is **endothermic**. The forward and reverse reactions are labelled ① ②

$$H_2O(l) \underset{②}{\overset{①}{\rightleftharpoons}} H^+(aq) + OH^-(aq) \qquad \Delta H = 55.8\ kJ$$

   With this in mind, use your knowledge of the effect of temperature on the rate of endothermic and exothermic equilibrium reactions to account for the observation that the K_w for the self-ionisation of water increases with increasing temperature.

3. Pure water is said to undergo **self-ionisation** or **autoionisation** to produce H^+(aq) and OH^-(aq). Despite this, pure water shows negligible electrical conductivity? Explain.

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4. What is the **concentration** of both **$H^+(aq)$** and **$OH^-(aq)$** in each of the following solutions of strong acids and bases?
   a. 0.159 mol L^{-1} $HNO_3(aq)$
   b. 0.0150 mol L^{-1} $H_2SO_4(aq)$ (Assume complete ionisation occurs.)
   c. 1.33 mol L^{-1} KOH(aq)
   d. 4.72×10^{-4} mol L^{-1} $Ca(OH)_2(aq)$

5. What is the **pH** of the following solutions?
   a. Stomach fluids (gastric juices) with a $H^+(aq)$ concentration of 0.085 mol L^{-1}.
   b. Aquarium water with a $H^+(aq)$ concentration of 8.2×10^{-6} mol L^{-1}.
   c. Drain cleaning fluid containing 3.37 mol L^{-1} of $OH^-(aq)$.
   d. Swimming pool water with a hydroxide ion concentration of 7.70×10^{-5} mol L^{-1}.

6. Determine the **pH** for the following laboratory reagents.
   a. 4.62×10^{-2} mol L^{-1} HCl(aq)
   b. 9.47×10^{-3} mol L^{-1} $H_2SO_4(aq)$ (Assume complete ionisation occurs.)
   c. 5.8×10^{-4} mol L^{-1} $Al(OH)_3(aq)$

7. What is the **concentration** of **$H^+(aq)$** for each of the following solutions? (See shortcut at right.)
   a. Lemon cordial concentrate with pH 2.2.
   b. Gastric juice with pH 0.82.
   c. Sea water of pH 8.1. (See Fig 9.)

Shortcut! $c(H^+) = 10^{-\mathbf{pH}}$
as $pH = -\log c(H^+)$
then $c(H^+) = 10^{-\mathbf{pH}}$

Eg, if **pH = 2.3**
then $c(H^+) = 10^{\mathbf{-2.3}}$
so $c(H^+) = 5.0 \times 10^{-3}$ mol L^{-1}

Consider for whole number pH.

pH	**$[H^+]$**
2	$1 \times 10^{\mathbf{-2}}$ mol L^{-1}
4	$1 \times 10^{\mathbf{-4}}$ mol L^{-1}
9	$1 \times 10^{\mathbf{-9}}$ mol L^{-1}
12	$1 \times 10^{\mathbf{-12}}$ mol L^{-1}

8. A 0.10 mol L^{-1} solution of CH_3COOH has a pH of 2.9 while a solution of hydrochloric acid of the same concentration has a pH of 1.0.
   a. Determine the **$H^+(aq)$ concentration** for each acid.
   b. Both acids have the same concentration and are monoprotic yet their solutions have very different $H^+(aq)$ concentrations. **Account** for this difference.

9. Is it possible to have solutions of **pH 0**, **-1** or **-2**? Make **appropriate calculations** to support your answer.

Figure 9 The **Earth's ocean** surface **pH** is approximately 8.1. While ocean pH has remained fairly steady over time it is believed to have fallen about 0.1 since the beginning of the Industrial Revolution.

The slight increase in ocean acidity is a direct result of the steadily increasing atmospheric CO_2 levels. Currently this stands at 400.26 ppm by volume (February 2015, NOAH and Scripps) and is expected to continue rising over the next few decades at a rate of around 1% per year.

Approximately 30% of the increased annual output of CO_2 resulting from human activity is estimated to be absorbed by the Earth's oceans.

10. Determine the **pH** of each of the solutions A to D and enter your result into the columns below. What **generalisation** can you make regarding the hydrogen ion concentration in solutions with a pH difference of 1, 2, and 3 and so on? Does this generalisation hold true for solutions E to H?

Solution	$H^+(aq)$ mol L^{-1}	pH	Solution	$H^+(aq)$ mol L^{-1}	pH
A	0.1	?	E	0.32	?
B	0.01	?	F	0.032	?
C	0.001	?	G	0.0032	?
D	0.0001	?	H	0.00032	?

11. A 4.65 g sample of pure NaOH(s) is added to 626 mL of 0.335 mol L^{-1} HCl(aq). Assuming the final volume of mixture is unchanged, determine the **pH** of the **mixture** when the **reaction** is complete.

4.9 Buffers

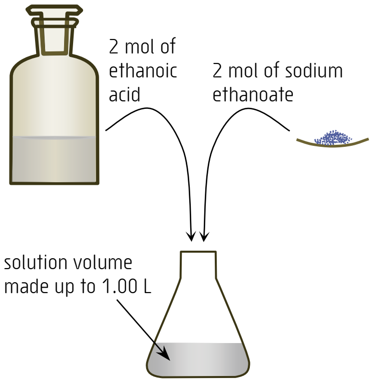
Buffers are solutions that have the ability to resist pH change when either acids or bases are added to them. Generally a buffer solution is one that contains a **weak acid-base conjugate pair**. This means a buffer solution could contain a weak acid and its conjugate weak base or it may contain a weak base and its conjugate weak acid. Buffer solutions work because the weak acid and weak base can co-exist in solution without neutralising one another, yet can still react to neutralise any strong acid or strong base added to the buffer.

A simple example of a buffer solution can be prepared by mixing 2 mol of ethanoic acid, CH_3COOH and 2 mol sodium ethanoate, $NaCH_3COO$, and making the solution volume up to 1.00 L (see Fig 10). This buffer solution contains a high concentration of both a **weak acid**, **CH_3COOH** and its **conjugate weak base**, **CH_3COO^-** (from $NaCH_3COO$). The acid-base equilibrium reaction occurring in this buffer system is shown below. The forward and reverse reactions of the chemical equilibrium are labelled ① ② ① ② O^+(aq) remains fairly constant even if a strong acid or strong base is added to the buffer.

$$CH_3COOH(aq) \quad + \quad H_2O(l) \quad \underset{②}{\overset{①}{\rightleftharpoons}} \quad CH_3COO^-(aq) \quad + \quad H_3O^+(aq)$$

The behaviour of this buffer system can be predicted using Le Chatelier's principle (LCP). For example, adding some base to the buffer solution imposes an increased OH^-(aq) ion concentration on the system. The extra OH^-(aq) from the added base will neutralise some of the H_3O^+(aq) present in the buffer solution causing its concentration to initially fall. However, the falling H_3O^+(aq) concentration then causes the equilibrium reaction (above) to shift to the right (LCP) by reaction ① O^+(aq) and preventing its concentration from falling significantly. By behaving this way the buffer solution is able to maintain a fairly constant pH even though a base has been added to it.

In a similar way, adding acid to the buffer solution initially causes the H_3O^+(aq) concentration to rise. This imposed change causes the buffer equilibrium system to shift to the left (LCP) by reaction ② O^+(aq) is consumed. This action prevents the H_3O^+(aq) concentration from rising significantly, helping the buffer maintain a fairly constant pH, even though a strong acid has been added to it.



ethanoic acid /sodium ethanoate buffer

Figure 10 A **buffer solution** can be made by adding 2.00 mol of ethanoic acid, CH_3COOH and 2.00 mol of sodium ethanoate, $NaCH_3COO$ to enough water to produce 1.00 L of solution. The resulting solution will have a pH of 4.74.

If 0.100 mol of the strong acid hydrochloric acid, HCl is then added to this buffer it will have only a minor effect on its pH, lowering it by a mere 0.04 to a pH of 4.70. By contrast this same amount of hydrochloric acid added to 1.00 L of distilled water will have an enormous effect on its pH, lowering it from pH 7.00 to pH 1.00. This represents a million times increase in the hydrogen ion concentration for the pure water sample compared to a 0.1 times increase for the buffer solution.

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Attempt Set 6 # 1, 2 and 3.

4.10 Buffer capacity

The ability of a buffer solution to neutralise excess acid or base without an appreciable change to its pH, is known as its **buffer capacity**. It is a measure of the amount of acid or base the buffer can neutralise before the pH begins to change appreciably.

As was seen above, the action of a buffer depends on the buffer solution containing both a weak acid and its conjugate weak base. The weak acid-base conjugate pair will consume almost all of any added H_3O^+(aq) or OH^-(aq). For a buffer solution to be most effective, ie to have a high buffer capacity, it should have a **high concentration** of both the **weak acid** and **weak base**. This ensures neither the weak acid or its conjugate weak base will be significantly depleted or reduced in concentration on the addition of either OH^-(aq) or H_3O^+(aq). Buffers are also found to be most effective when the weak acid and weak base have **similar concentrations**.

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Attempt Set 6 # 4 and 5.

Figure 11 **Alkalinity** is a term used to describe 'acid only' buffer capacity in swimming pools and spas. Specifically it is the acid neutralizing capacity of the water and represents its ability to neutralize any added strong acid.

If the alkalinity of a pool or spa is too low then its pH will be difficult to adjust as the pool water pH will be very sensitive to small amounts of added acid used to manage its pH (typically HCl or $NaHSO_4$).

Pool pH and alkalinity can be checked using inexpensive test strips available at swimming pool and spa supply stores. If alkalinity is too low it is increased by adding sodium bicarbonate ($NaHCO_3$), a weak base. A concentration of 80 to 120 ppm provides a suitable level of alkalinity.

4.11 A biological case study: Buffering in blood

The single most abundant compound found in the human body is **water**, which comprises around 55% to 60% by mass of the average young adult body. Water occurs within cells and in fluids like blood, gastric juices, sweat and interstitial fluid (tissue fluid). The pH of these bodily fluids is a critical factor in controlling and maintaining healthy metabolic processes. Optimum pH for bodily fluids varies considerably. Gastric fluids, for example, have a pH range of 1 to 3.5 while blood pH is maintained at about 7.40 ±0.05. If blood pH falls outside this range it can affect the operation of cell membranes, prevent enzymes from functioning correctly or alter protein structure. Blood pH higher than 7.8 or lower than 6.8 can be fatal.

Blood maintains this narrow pH range of 7.4±0.05 with the aid of the **carbonic acid** and **hydrogencarbonate ion** buffer system. In this buffer system, carbonic acid, H_2CO_3 is the

Figure 12 **Blood** is an important part of the circulatory system. One of its major functions is the transport of oxygen and carbon dioxide around the body. The two components of blood involved in this process are **plasma** (a fluid comprising water, proteins, metal ions and phosphates) and **red blood cells** (erythrocytes). Red blood cells contain haemoglobin (see p28) which is responsible for almost all of the oxygen transported in the blood.

An important **enzyme** (a biological catalyst) called **carbonic anhydrase** is also found in the red blood cells. This enzyme catalyses the formation of carbonic acid from carbon dioxide:

$CO_2(aq) + H_2O(l) \rightleftharpoons CO_3(aq)$

This enzyme ensures the $CO_2(aq)/H_2CO_3(aq)$ equilibrium adjusts quickly to any changes in either the concentration of $CO_2(aq)$ or $H_2CO_3(aq)$.

weak acid and the hydrogencarbonate ion, HCO_3^- is the weak conjugate base. The normal concentration of these ions in blood is 0.0254 mol L^{-1} for HCO_3^- and 0.0012 mol L^{-1} for H_2CO_3. This gives blood a buffered **pH** of **7.4**. If excess $H^+(aq)$ should be present in blood this is eliminated as the equilibrium ①

$_3O^+(aq)$ falls too low then the equilibrium ① $O^+(aq)$.

$H_2CO_3(aq, blood) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$ .... ①

capacity, are the **lungs** and **kidneys**. These organs help to maintain blood concentrations of $H_2CO_3(aq)$ and $HCO_3^-(aq)$ so that they do not alter too much as they are consumed or produced in forward and reverse equilibrium reaction ①

$CO_2(g, lung\ cavity) \rightleftharpoons CO_2(aq, blood\ in\ lung\ capillaries)$ .... ②

$_2(aq, blood) + H_2O(l) \rightleftharpoons H_2CO_3(aq, blood)$ .... ③

rate because of the greater energy demand. This increased rate of consumption of sugars, **$C_6H_{12}O_6$** by increased cellular respiration in muscle tissue (see reaction ④

$_2$ concentration in localised body fluids like blood.

$C_6H_{12}O_6(aq) + 6O_2(aq) \rightarrow 6CO_2(aq, blood) + 6H_2O(l) + energy$ .... ④

③

$_2(aq, blood)$ concentration. As a result the $H_2CO_3(aq, blood)$ concentration rises. Subsequently, equilibrium ①

$_2CO_3(aq, blood)$ concentration and leading to a slightly higher $H^+(aq)$ concentration and lower blood pH. If unchecked, this lower pH would lead to serious physiological consequences.

Importantly however, receptors in the brain that are sensitive to the raised $H^+(aq)$ concentration, signal a reflex to **breathe** more **deeply** and more **quickly**. This results in a greater rate of loss of $CO_2(g)$ from the lung cavity by **exhalation**, ie $CO_2(g, lung\ cavity)$ concentration falls. As a result, equilibrium ②

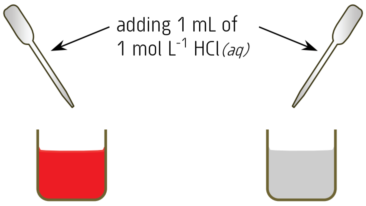
$_2(g, lung\ cavity)$ concentration and also causing a fall in the concentration of dissolved blood CO_2 in the lung capillaries, ie $CO_2(aq, blood\ in\ lung\ capillaries)$ falls. Again by Le Chatelier's principle, we can see equilibrium ③

$_2(aq, blood)$ and causing a fall in the $H_2CO_3(aq, blood)$ concentration. Finally, equilibrium ① $CO_3(aq, blood)$ and in the process lowers the $H^+(aq)$ concentration and returns blood pH towards its normal range.

It must be noted the increased breathing rate occurring during strenuous exercise is also important as it leads to a faster rate of O_2 absorption into the blood stream. This helps to maintain a suitable blood oxygen concentration despite its faster rate of consumption due to the faster rate of respiration. However, it is the reduced blood pH and the need to expel CO_2 that triggers the faster and deeper rate of breathing during strenuous exercise.

Kidneys also help to maintain a steady blood pH by excreting excess $H^+(aq)$ in urine. For this reason urine typically has a pH of around 5.5 to 7.5. Another contributor to blood buffering (although less significant than the carbonate system) is the **dihydrogenphosphate**, $H_2PO_4^-$ and **hydrogenphosphate**, HPO_4^{2-} buffer. The concentration of the weak acid, $H_2PO_4^-$ and weak base, HPO_4^{2-} are such that they also help to maintain blood pH at 7.4.

Figure 13 The effectiveness of the **buffer system in blood** can be shown experimentally. The addition of 1 mL of 1 mol L^{-1} HCl to 100 mL of blood will cause its pH to change from 7.5 to 7.4, a drop of 0.1 pH units. By comparison the same amount of hydrochloric acid added to 100 mL of distilled water will cause its pH to change from 7.0 to 2.0. A change of 5 pH units, equal to a 100,000 times increase in the hydrogen ion concentration. The latter pH change would be seriously fatal if this occurred in blood.



100 mL of blood changes **pH** from **7.5** to **7.4** when 1 mL of 1 mol L^{-1} HCl is added.

100 mL of water changes **pH** from **7.0** to **2.0** when 1 mL of 1 mol L^{-1} HCl is added.

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Complete Set 6.

Set 6 Buffers

$CH_3COOH(aq)$
concentration
fall
right
left
weak acid
$CH_3COO^-(aq)$
consuming
acid
conjugate
$H_3O^+(aq)$
neutralise
replacing
reduction

1. Use the list of terms given to complete the following passage about buffers.

Buffers are solutions that resist changes in hydrogen ion or hydroxide ion (a) ___________. They are able to do this as they consist of a solution of a (b) ___________ and its (c) ___________ weak base. Conversely a buffer may contain a weak base and its conjugate weak (d) ___________.

An example of a buffer is a solution containing the weak acid (e) ___________ and its conjugate weak base (f) ___________. The equilibrium reaction occurring in this buffer system is shown here:

$$CH_3COOH(aq) \quad + \quad H_2O(l) \quad \rightleftharpoons \quad CH_3COO^-(aq) \quad + \quad H_3O^+(aq)$$

Adding some strong acid to this buffer solution will initially raise its (g) ___________ concentration and cause its pH to (h) ___________. However, the addition of $H_3O^+(aq)$ causes the buffer equilibrium system to readjust by shifting to the (i) ___________. This has the effect of (j) ___________ most of the added $H_3O^+(aq)$ and thus prevents the pH from changing significantly.

Similarly, adding a strong base to the buffer will initially cause a (k) ___________ in the $H_3O^+(aq)$ concentration as the added $OH^-(aq)$ and $H_3O^+(aq)$ (l) ___________ each other. However, as the $H_3O^+(aq)$ concentration begins to fall this causes the buffer equilibrium system to readjust by shifting to the (m) ___________. This has the effect of (m) ___________ most of the depleted $H_3O^+(aq)$ thus preventing the pH from changing significantly.

2. The following questions refer to the **buffer** solutions **A**, **B** and **C** listed here.

Buffer	**Description**
A	1.0 L of solution containing 1.0 mol L^{-1} CH_3COOH and 1.0 mol L^{-1} CH_3COONa
B	1.0 L of solution containing 0.10 mol L^{-1} NH_3 and 0.10 mol L^{-1} NH_4Cl
C	1.0 L of solution containing 0.10 mol L^{-1} NaH_2PO_4 and 0.10 mol L^{-1} Na_2HPO_4

a. **Identify** the weak acid and its conjugate weak base in buffers A, B and C.

b. Write an **equation** for the equilibrium reaction involving the weak acid and its conjugate weak base for buffers A, B and C.

c. **Describe** in terms of **Le Chatelier's principle** how buffer B behaves when a small amount of the strong acid hydrochloric acid, $HCl(aq)$ is added to it. Thus **justify** why its pH is relatively unaffected by the added acid.

d. A small pellet of solid sodium hydroxide, $NaOH(s)$ is added to buffer C. **Explain** why the pH of the buffer is relatively unchanged.

Le Chatelier's principle can be used to predict how an equilibrium system readjusts when changes are imposed on it. It states, "If a system is at equilibrium and a change in conditions is imposed on the system then the system will re-establish a new equilibrium in such a way as to **partially counteract** the **imposed change**." (See 2.6)

3. A most important property of buffer solutions is their ability to resist changes in pH when small amounts of strong acid or base are added to the buffer. This happens as equilibrium reactions in the buffer solution respond to any added $H^+(aq)$ or $OH^-(aq)$. Use **Le Chatelier's** principle to **predict** how a buffer solution behaves when a strong acid or base is added to it. Hence **justify** the statement 'buffers resist pH change' **Illustrate** your answer with the ethanoic acid/ethanoate (CH_3COOH/CH_3COO^-) buffer system.

4. Use the list of terms given to **complete** the following passage about **buffer capacity**.

The ability of a buffer to neutralise or 'mop up' any strong acid or strong base added to it is known as its (a) __________. This ability to prevent or minimise (b) __________ depends upon the concentration of weak acid and (c) __________ present in the buffer solution.

If some strong base is added to a buffer it causes the equilibrium system to adjust by consuming some of the (d) __________ present in the system. In this way the buffer can resist its (e) __________ from changing. A buffer can continue doing this until the weak acid in the buffer solution has been significantly (f) __________. At this point the buffer is no longer able to resist its pH from rising strongly if more strong base is added.

In a similar way a buffer can resist its pH falling; due to added (g) __________; until the weak base in the buffer is almost depleted. Thus buffer capacity increases with the (h) __________ of weak acid and weak base present in the buffer solution.

weak base
pH change
depleted
strong acid
buffer capacity
concentration
weak acid
pH

5. Use the buffers **A** and **B** to show your understanding of **buffer capacity**.

Buffer	**Description**
A	1.0 L of solution containing 1.0 mol L^{-1} CH_3COOH and 1.0 mol L^{-1} CH_3COONa
B	1.0 L of solution containing 0.10 mol L^{-1} CH_3COOH and 0.10 mol L^{-1} CH_3COONa

6. In some industrialised regions air quality may become compromised by pollutant gases like **SO_2** and **NO_2**. These gases dissolve in rain producing strong acids that lower **rainfall pH**. (See Fig 14.) When rainfall like this, makes its way to rivers and lakes, it can upset the lakes delicate pH balance with negative consequences for marine organisms.

In some freshwater lakes, the presence of **carbonic acid**, H_2CO_3 and the **hydrogencarbonate ion**, HCO_3^- can produce a **buffer system** protecting the lakes from pH change. Depending upon the relative concentration of the two species these buffered lakes may be between pH 5.7 to 6.0. For this buffer to work there must be a significant concentration of both H_2CO_3 and HCO_3^-. While atmospheric $CO_2(g)$ provides a source of H_2CO_3 and its ionisation produces some HCO_3^- its concentration is far too low to produce a significant buffering effect. Higher concentrations of HCO_3^-, sufficient to produce a buffering effect, may occur in lakes where the surrounding soil contains limestone like minerals.

a. Show by use of an **equation** how atmospheric carbon dioxide and rainwater can combine to provide a source of carbonic acid in freshwater lakes.

b. **Explain** the role of HCO_3^- in buffering a lake against the effects of acid rain. Why must there be a significant amount of HCO_3^- in the lake for its buffering effect to work?

c. A mineral common in many water catchment areas is limestone. The major component of limestone is the very low solubility compound $CaCO_3(s)$ [solubility 1.3×10^{-2} g L^{-1}]. Although $CaCO_3$ has a very low solubility it contributes significantly to the natural buffering effect in aquatic environments. **Show** how the dissolving of $CaCO_3(s)$ produces CO_3^{2-} ions and **explain** with the aid of an equation how these ions contribute to the water's buffering effect.

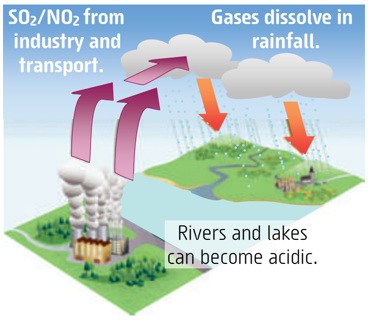

Figure 14 Acid rain can affect the pH of soil, rivers and lakes. It is quite normal for rain to have a slightly acidic pH of around 5 to 6 due to the presence of atmospheric carbon dioxide. This happens as CO_2 interacts with rain water producing the weak acid H_2CO_3.

Acid rain however, is the result of gaseous pollutants like sulfur oxides and nitrogen oxides. These gases readily dissolve in rain water to form acids like nitric acid and sulfuric acid. As a result acid rain can have a pH as low as 2.

The marine life in some lakes and rivers is protected from the effects of acid rain by natural buffering. Soil minerals that contribute to **buffering** in natural bodies of water include calcite (ie limestone, $CaCO_3$) and dolomite ($CaMg(CO_3)_2$). While these minerals are practically insoluble, sufficient amounts do dissolve giving the body of water some protection from acid rain.

7. An important buffer system occurring in **blood** is the H_2CO_3/HCO_3^- buffer system. This system helps to keep blood pH at around 7.40±0.05. In order to maintain this desirable pH the concentrations of H_2CO_3 and HCO_3^- must be kept fairly close to 0.025 mol L^{-1} for HCO_3^- and 0.0012 mol L^{-1} for H_2CO_3. However, carbon dioxide produced by cellular respiration (reaction ①

②

$C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) +$ energy .... ①

$_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$ .... ②

Importantly, the **lungs** provide one way for the body to regulate blood $H_2CO_3(aq)$ concentration. As blood pH falls due to an increased $H_2CO_3(aq)$ concentration so pH sensitive receptors in the brain signal the body to breathe at a faster rate. Faster breathing results in an increased rate of excretion of carbon dioxide in exhaled air and subsequently reduces the blood concentration of $H_2CO_3(aq)$ back towards the desirable 0.0012 mol L^{-1}. This can be visualised by the following simplified equilibrium reaction.

CO_2(aq, blood capillaries) $\rightleftharpoons$ CO_2(g, lung cavities) .... ③

Figure 15 An important **enzyme** (a biological catalyst) called **carbonic anhydrase** occurs in red blood cells. This enzyme catalyses the formation of carbonic acid from carbon dioxide:

$\mathbf{CO_2(aq) + H_2O(l) \rightleftharpoons {}_2CO_3(aq)}$

This ensures the $CO_2(aq)/H_2CO_3(aq)$ equilibrium is able to rapidly re-establish itself as the concentration of either $CO_2(aq)$ or $H_2CO_3(aq)$ alters.

$CO_2(aq)$ concentration in muscle tissue and surrounding blood as a result of the increased cellular respiration occurring during vigorous exercise? **Explain** with the aid of suitable **equilibrium equations** how this change in $CO_2(aq)$ concentration causes a change in blood $H_2CO_3(aq)$ concentration and pH. Support your answer with reference to **Le Chatelier's principle**.

b. The increased breathing rate that accompanies vigorous exercise increases the rate of loss of blood CO_2 by exhalation. This important effect of a faster breathing rate helps to raise blood pH back to a normal level. Using **appropriate equations** and with reference to **Le Chatelier's principle explain** how this process works.

c. Respiratory **alkalosis** is a condition where blood pH rises excessively. It can be caused by rapid or heavy breathing, known as **hyperventilation**. This may be the result of a range of factors including severe anxiety or hysteria. One remedy for this situation is to breathe into a paper bag. **Explain** with the use of appropriate equations and with reference to **Le Chatelier's principle** how breathing into a paper bag can restore normal blood pH for a person suffering from alkalosis due to hyperventilation.

CHAPTER 5 | ACID-BASE VOLUMETRIC ANALYSIS

5.1 Acid-base titrations: An overview

Acid-base titrations are an analytical procedure involving a reaction between an **acid solution** and a **base solution**. The concentration of one solution must be accurately known. This is called the **standard solution**. The other solution's concentration isn't known. The purpose of the titration is to determine the concentration of the acid or base in the solution of **unknown concentration**.

In the titration process a carefully measured volume of one solution, called an **aliquot**, is added to a **conical flask**. (See Fig 1.) A variable volume of the other solution, called the **titre**, is then carefully added from a **burette** into the conical flask until the reaction between the acid and base is complete. This theoretical point in the titration, ie when neither acid nor base remain is known as the **equivalence point**. In practice the equivalence point of an acid-base titration is not visibly obvious and so requires the use of an **acid-base indicator** to show that equivalence has occurred. The **end point** of a titration is the point where the indicator changes colour signalling that equivalence has occurred. In practice, the end point is a **very close approximation** of the equivalence point.

The concentration of the unknown solution can then be found from the known concentration of the standard solution and the aliquot and titre volumes.(See 5.4.)

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Attempt Set 7 # 1.

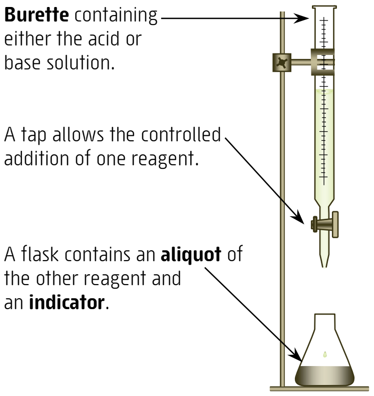


Figure 1 An **acid-base titration** is performed by adding one solution from a **burette** (the titre) to a carefully measured volume of the other solution (the aliquot) which is placed into a **conical flask**.

The **equivalence point** happens when sufficient acid or base has been added to just neutralise each other, ie neither acid nor base remain in the flask.

An **indicator** colour change signals the end point of the titration. The end point should coincide as closely as possible with the equivalence point. In practice these are never exactly the same.

5.2 Primary standards and primary standard solutions

A **primary standard solution** is one of accurately known concentration that can be used in a titration to find the concentration of other reagents. It is prepared by carefully weighing a sample of **primary standard**, dissolving this in distilled water and then making the solution up to a precise volume (eg 250.0 mL) in a **volumetric flask**. (See Fig 2.)

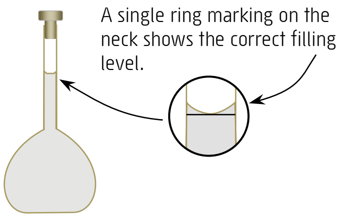
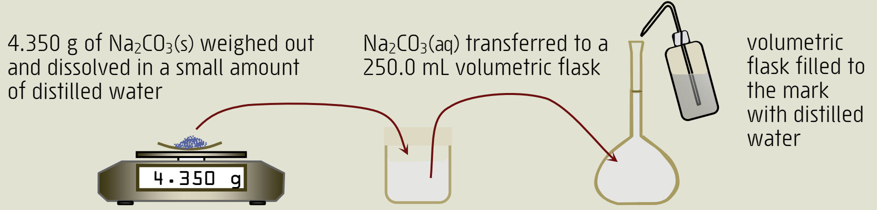


Figure 2 A **volumetric flask** measures a single precise volume of liquid. It can be used for preparing primary standard solutions and for dilutions. After cleaning, its final rinse prior to use is with distilled water.

Example 1 A primary standard solution of sodium carbonate was prepared by dissolving 4.350 g of Na_2CO_3 in a small amount of water. The solution volume was then made up to 250.0 mL using a volumetric flask. Determine the concentration of this solution in mol L^{-1}.



$n(Na_2CO_3) = \frac{m}{M} = \frac{4.350}{105.99} = 0.04104$ mol	Find the moles of primary standard from its given mass.
$c(Na_2CO_3) = \frac{n}{V} = \frac{0.04104}{0.2500} = 0.1642$ mol L	Use the solution volume, 0.2500 L and moles of Na_2CO_3 to find its concentration in mol L^{-1}.

Common acids like hydrochloric acid or sulfuric acid and bases like sodium hydroxide or potassium hydroxide are not suitable as primary standards as they are not available in a suitably pure form. NaOH(s) and KOH(s) for example are affected by exposure to air as they absorb variable amounts of water vapour (Fig 3) while also reacting with atmospheric CO_2(g) forming Na_2CO_3 and K_2CO_3 respectively. This alters their purity making them unsuitable as primary standards. Typically, a **primary standard must**:

- be able to be obtained in a **very pure** form consistent with its chemical formula.
- be sufficiently **stable** so that on exposure to air it does not readily change its water content or react with other gases (like CO_2) in the air.
- have a relatively **high molar mass**.

These features allow the moles of a primary standard to be precisely calculated from its accurately measured mass and molar mass. Two primary standards having these features are **anhydrous sodium carbonate**, Na_2CO_3(s) and **oxalic acid**, $H_2C_2O_4.2H_2O$(s).

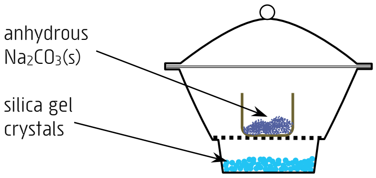


Figure 3 The primary standard, Na_2CO_3(s) is made anhydrous by heating it in an oven at 260-270 °C. To prevent the anhydrous Na_2CO_3(s) from reabsorbing water vapour from the air, it is kept in a **desiccator**, like the one shown above. **Silica gel** crystals inside the desiccator keep the air dry by absorbing water vapour.

Sometimes small sachets of desiccant materials like silica gel are found packaged along with electronic goods. Used this way the silica gel helps protect the electronic equipment from moisture damage by keeping the air inside the packaging dry.

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Although reagents like hydrochloric acid or sodium hydroxide cannot be prepared as primary standard solutions their concentration in solution can still be found by titration. A solution whose concentration is found this way is known as a **secondary standard** solution. A secondary standard solution can then be used as the solution of known concentration in other titrations. However, as the technique for finding the concentration of a secondary standard involves extra measurements and procedures, its concentration will be subject to greater uncertainty (error) than the concentration of a primary standard solution.

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Attempt Set 7 # 2 and 3.

5.3 Performing an acid-base titration

In an **acid-base titration** a carefully measured volume, called an **aliquot**, usually 20.00 mL of either the acid or base solution, is measured using a **pipette**. (See Fig 4.) This solution is transferred to a clean conical flask that has been pre-rinsed with distilled water. A few drops of a suitable **pH indicator** (see 5.7 and 5.8) is also added to the conical flask.

The other solution is placed into a clean burette that has been pre-rinsed with some of the same solution with which it is to be filled. Reagent is then released in a controlled way from the burette into the aliquot present in the conical flask. (See Fig 5.) An indicator colour change signals the **end point** of the titration and no further reagent is added. The volume of solution added from the burette, known as the **titre**, can be found by subtracting the **initial** burette reading from the **final** burette reading.

Care should be taken to read the burette scale with the **meniscus** at eye level. However, as the titre is the difference between the initial and final readings then the burette scale readings can be taken from the top or the bottom of the meniscus. Use whichever is more convenient but use the same technique for both readings.

For **consistent results**, just prior to the end point, rinse down the inside of the conical flask with distilled water from a wash bottle. Then add the final amount of reagent, dropwise, from the burette until the end point is signalled. The titration procedure is repeated several times to obtain titre volumes that are consistent to within ± **0.20 mL** (ie a range of 0.40 mL from the highest to lowest values). This allows for a reasonable random error (half the smallest scale division) of ± 0.05 mL in each of your two burette readings and ± 0.06 mL for your pipette volume. (These error values can vary, see Table 1.) Results that vary much more than this may be due to unacceptable **random errors** such as from incorrect rinsing procedures, using dirty glassware that does not drain correctly or poor titration techniques.

To avoid parallax error view horizontally at eye level and align the bottom of the **meniscus** with the marking.

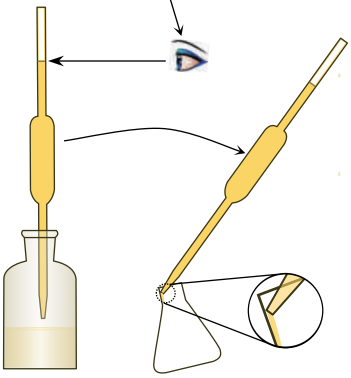

Figure 4 A **pipette** is used to deliver a precise and fixed volume of solution called an **aliquot**, eg 20.00 mL.

Before use a pipette should be thoroughly cleaned. The final rinse is always with the reagent to be measured. This ensures the solution being measured is not diluted by the presence of distilled water that may otherwise remain in the pipette.

When draining the contents of the pipette ensure its tip and the solution escaping both make good contact with the inside wall of the conical flask. Allow 20 second drainage time once the contents have emptied. The small amount of liquid that stays inside the pipette tip must be left in the pipette.

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5.4 The titration calculation

Data collected from an acid-base titration includes the **initial** and **final burette readings** (to 2DP eg 18.20 mL) for one of the reagents and the **pipette volume** (aliquot) of the other reagent (eg 20.00 mL). As well as this, the **concentration** of the primary or secondary standard is also accurately known. Using this data the concentration of the other solution can be found. (See Example 2.)

The burette contains 9.039×10^{-2} mol L^{-1} sodium carbonate solution.

The flask contains a 20.00 mL aliquot of hydrochloric acid solution plus a few drops of a suitable indicator.

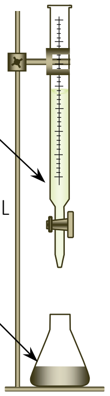

Figure 5 In this **titration**, the base $Na_2CO_3(aq)$, is placed into the burette and the acid, $HCl(aq)$, of unknown concentration is placed into the conical flask. The titration is performed by adding $Na_2CO_3(aq)$ from the burette into the 20.00 mL aliquot of $HCl(aq)$ in the conical flask.

Example 2 20.00 mL aliquots of a hydrochloric acid solution are titrated with 9.039×10^{-2} mol L^{-1} sodium carbonate solution. (See Fig 5.) Several titrations were performed and the volumes of sodium carbonate solution used were 19.45 mL, 18.90 mL, 18.77 mL and 18.85 mL. What is the concentration of the hydrochloric acid solution?

$V(\text{average}) = \dfrac{18.90 + 18.77 + 18.85}{3} = 18.84 \text{ mL}$ $n(Na_2CO_3) = c \times V$ $= 9.039 \times 10^{-2} \times 18.84 \times 10^{-3}$ $= 1.703 \times 10^{-3} \text{ mol}$ $2HCl(aq) + Na_2CO_3(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$	When finding the average titration volume, (titre) **discard any inconsistent data**, eg 19.45 mL. Typically values should be within a range of 0.4 mL (or less) from highest to lowest. Often the first titration result is discarded, as it may be done quickly to obtain a 'rough' estimate of the titre.
$n(HCl) = 2 \times n(Na_2CO_3)$ $= 2 \times 1.703 \times 10^{-3}$ $= 3.406 \times 10^{-3} \text{ mol}$	The equation stoichiometry shows the moles of HCl used are twice those of Na_2CO_3 used.
$c(HCl) = \dfrac{n}{V} = \dfrac{3.406 \times 10^{-3}}{20.00 \times 10^{-3}} = 1.703 \times 10^{-1} \text{ mol L}^{-1}$	Since 20.00 mL (0.02000 L) of solution contains 3.406×10^{-3} moles of HCl.

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Attempt Set 7 # 4, 5 and 6.

5.5 Errors in titrations

Volumetric analysis is a precise and accurate technique for analysing solution concentration. However, it is important to realise that measurements obtained during volumetric analysis **always** contain some degree of uncertainty or **error**.

Accuracy and **precision** are two aspects of the error in titration measurements. (See Example 3.) The closer a measured value is to the true or actual value, the more **accurate** it is. Thus, in Example 3, the titres from Student 3 are accurate while those of Students 1 and 2 are inaccurate. **Precision** can be seen in a **set** of measurements that agree very closely, ie the measurements are spread over a **narrow range** of values. The titres from Student 1 and 3 are precise (small range) but those of Student 2 are imprecise, ie there is a wide range of values. It is possible for a set of measurements to be precise (small range) but inaccurate, eg as seen in the titres from Student 1.

Example 3 Three students each performed several titrations using the same solutions, all of known concentration. They titrate a 20.00 mL aliquot of 1.00 mol L^{-1} $CH_3COOH(aq)$ with 1.00 mol L^{-1} $NaOH(aq)$. The correct titre for this titration is **20.00 mL** of NaOH(aq). Their results are shown below. **Comment** on the **precision** and **accuracy** of their results if the correct titre is 20.00 mL.

Student	NaOH titre (mL)	Average
1	19.10, 19.05, 19.20	**19.12 mL**
2	19.05, 20.35, 18.60	**19.33 mL**
3	20.05, 20.02, 20.05	**20.04 mL**

Answer: **Student 1**: These results are **precise**, ie agree closely (small range) but **inaccurate**, ie not close to the correct value of 20.00 mL.
Student 2: These results are **inaccurate** and **imprecise**, ie they are not close to the accepted value and the results vary a lot (large range).
Student 3: These results are **precise**, ie agree closely and **accurate**, ie close to the correct value of 20.00 mL.

Table 1 Manufacturer specified random error of some volumetric analysis equipment.

Apparatus	Random error as ±
Pipette (20 mL)	± 0.03 mL (class A) ± 0.06 mL (class B)
Burette (50 mL)	± 0.05 mL (class A) ±0.1 mL (class B)
Volumetric flask (250 mL)	± 0.15 mL (class A) ± 0.3 mL (class B)

These ± error values do not include any extra error that may arise due to limitations in the ability of the operator to use them correctly.

The degree of precision and accuracy in titration measurements depends upon the presence of two types of error, **random error** and **systematic error**. A systematic error may cause results to be **consistently lower** or **consistently higher** than the actual value. In Example 3, the results for Student 1 contain a systematic error. This could happen, for example, if the student chose the wrong indicator, eg using methyl orange instead of phenolphthalein in this titration would cause consistently low titres. (See 5.7 and 5.8.)

Random errors, however, cause inconsistent results, ie some high and some low results. Random errors could be due to inconsistent rinsing techniques, careless attention to the colour change at the end point or some other poor technique. Small random errors also occur due to limitations in the instruments used and the ability of the operator to use them correctly. (See Table 1.)

In a well designed and conducted investigation it may be possible to eliminate systematic error by using **correct technique**, (see Table 2) however, **random error** can be reduced but **never eliminated**. Even the accurate and precise results of Student 3 contain some random error, ie some values are a little high and some are a little low.

Table 2 Some procedures that minimise error

Procedure	Correct technique
Cleaning glassware	Initially clean all glassware with detergent ensuring water forms a film rather than droplets on the glass surface.
Rinsing glassware	The final rinse for a pipette, burette or storage bottle is always with the reagent they are to be filled with. For a volumetric flask and conical flask the final rinse is with distilled water.
Indicator	Use only a few drops. Choose one with a distinct colour change close to the equivalence point pH. (See 5.7 and 5.8.)
Reading scales	Avoid parallax error, read all scale markings horizontally at eye level. (See Fig 4.)
Discharging a pipette	Allow a suitable drainage time (20 seconds) and leave the small amount of liquid that remains in the pipette tip. (See Fig 4.)
End point	When close to equivalence use a wash bottle to rinse down the insides of the conical flask and then add reagent dropwise, while swirling the flask contents until a suitable indicator colour is achieved.

The effect of **random error** is minimised by taking several titre values and **averaging** the result. This works, as in a large set of results there will be some randomly high results and some equally low results. Averaging tends to cancel out these minor errors leaving a more reliable answer. Occasionally a set of titres contains a single result that is significantly different to the others or to the average. This may be the result of the first or rough estimate or due to some unacceptable large random operator error. A result like this is known as an **anomaly** or **outlier**. The **outlier** should be eliminated from the averaging process.

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Attempt Set 7 # 7.

5.6 Titrations involving a dilution

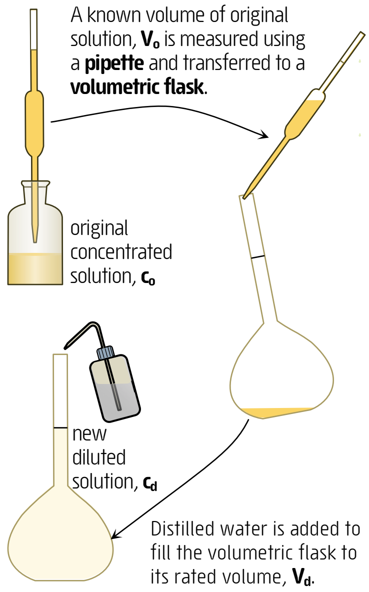
Sometimes the solution to be analysed is known to be too concentrated for the available primary standard solution. Titrating a solution like this may result in a titre several times larger than the burette volume, clearly an unsuitable situation. To avoid this problem the solution of high concentration must be **diluted** so that it can be properly titrated.

This involves using a **pipette** to transfer a suitable amount of the **original** concentrated solution (eg 10.00 mL, 20.00 mL or similar) into a suitably sized **volumetric flask** and filling it up to the mark with distilled water. (See Fig 6.) The **diluted** solution is then analysed by titration and its concentration is used to determine the original concentration of the undiluted solution. The following dilution equation can be used for this purpose.

$c_o V_o = c_d V_d$

where: c_o is the original (undiluted) solution concentration in (mol L^{-1})
V_o is the original (undiluted) solution volume in litres (L)
c_d is the new (diluted) solution concentration in (mol L^{-1})
V_d is the new (diluted) solution volume in litres (L)

Figure 6 Producing an accurately **diluted** solution from a concentrated solution.

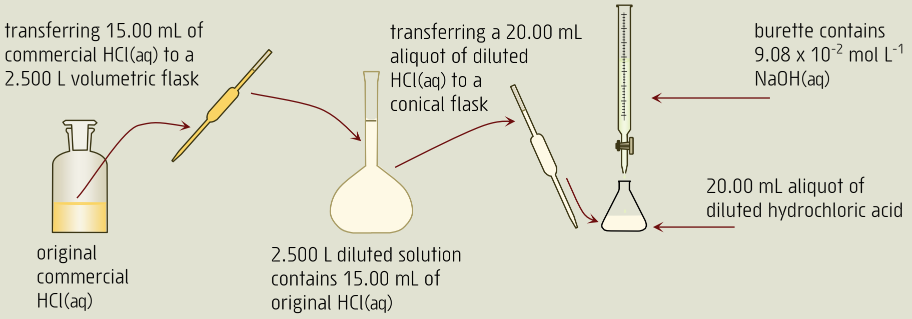


Example 4 A student analysed the ethanoic acid concentration of a commercial brand of vinegar. To do this a 25.0 mL sample of the vinegar was diluted to 500.0 mL in a volumetric flask. 20 mL aliquots of the diluted vinegar were analysed by titration and found to have an ethanoic acid concentration of 0.0429 mol L^{-1}. Determine the concentration of ethanoic acid in the original undiluted vinegar?

$c_o V_o = c_d V_d$ ie $c_o = \frac{c_d V_d}{V_o}$	Rearrange the dilution equation to find c_o, the concentration of ethanoic acid in the original undiluted vinegar.
$c_o = \frac{0.0429 \times 0.5000}{0.02500} = \mathbf{0.858\ mol\ L^{-1}}$	The diluted ethanoic acid solution has a volume of (V_d) 0.500 L and a concentration (c_d) of 0.0429 mol L^{-1}. The original undiluted volume of vinegar solution (V_o) was 0.02500 L.

Example 5 Commercial hydrochloric acid, also known as spirits of salts (Fig 7), has a maximum concentration of around 12 mol L^{-1}. A laboratory technician needs to accurately confirm the concentration of a batch of this commercial hydrochloric acid. In order to do so a 15.00 mL sample of it is transferred to a 2.500 L volumetric flask and made up to the mark with distilled water.

20.00 mL samples of diluted HCl(aq) required on average, 16.65 mL of 9.08×10^{-2} mol L^{-1} NaOH(aq) for equivalence. Determine the concentration of HCl(aq) in the commercial solution.



$n(NaOH) = c \times V$ $= 9.08 \times 10^{-2} \times 16.65 \times 10^{-3}$ $= 1.51 \times 10^{-3}$ mol	Use the concentration and volume of NaOH to find the moles of it used in the titration.
$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$ thus $n(HCl) = n(NaOH)$ $= 1.51 \times 10^{-3}$ mol	Coefficients in the balanced equation show the moles of HCl used are the same as the moles of NaOH used.
$c(\text{HCl diluted}) = \frac{n}{V} = \frac{1.51 \times 10^{-3}}{20.00 \times 10^{-3}} = 7.56 \times 10^{-2}$ mol L^{-1}	As 1.51×10^{-3} moles of HCl were present in the 20.00 mL aliquot.
now $c_o V_o = c_d V_d$ thus $c_o = \frac{c_d V_d}{V_o}$ $c_o = \frac{c_d V_d}{V_o} = \frac{7.56 \times 10^{-2} \times 2.50}{15.00 \times 10^{-3}} = \mathbf{12.6\ mol\ L^{-1}\ HCl(aq)}$	As 15.00 mL (**V_o**) of the concentrated acid solution was diluted to 2.500 L (**V_d**) of solution with a concentration of 7.56×10^{-2} mol L^{-1} (**c_d**).

Figure 7 Commercially, **hydrochloric acid** is sometimes known as **spirits of salts** or **muriatic acid**. Its uses include:

- **rust removal** from steel products prior to coating or galvanising with zinc
- **pH control** in various industrial chemical processes as well as swimming pools
- a **raw material** for the manufacture of plastics like polyvinylchloride and chloride salts like $FeCl_3$ from iron(III) oxide
- **removing cement** and mortar from brickwork.

Hydrochloric acid is also present in the **stomach**. Here it assists in the digestion of food. It also prevents stomach infections as most microorganisms can not tolerate the low pH it causes.

Photograph courtesy of Recochem Inc.

Example 5: Alternative. The following alternative method for solving the question in Example 5 (previous page) eliminates the need to find the concentration of HCl in the diluted solution.

$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$ n(HCl in 20.00 mL aliquot) = n(NaOH used) $= 1.51 \times 10^{-3}$ mol	As before, determine the moles of NaOH used in the titration (1.51×10^{-3} mol). This gives the moles of HCl used.
n(HCl in 2.500 L of dilute solution) $= \frac{2500}{20.00} \times 1.51 \times 10^{-3}$ = 0.189 mol	There are 1.51×10^{-3} moles of HCl in 20.00 mL of diluted solution so in the full 2500 mL of diluted solution the moles of HCl are greater by a factor of 2500/20.
n(HCl in original 15.00 mL) = n(HCl in 2.500 L of dilute solution) = 0.189 mol	As 15.0 mL of commercial HCl solution was diluted to 2.500 L.
c(HCl in original 15.00 mL solution) $= \frac{n}{V} = \frac{0.189}{15.00 \times 10^{-3}}$ = **12.6 mol L^{-1} HCl(aq)**	As 0.189 mol of HCl was present in the original 15.00 mL of commercial hydrochloric acid solution.

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Attempt Set 7 # 8.

5.7 End point and equivalence in acid-base titrations

The **equivalence point** of a titration is the theoretical point in the titration when neither acid nor base remain. It occurs when sufficient reagent has been added from the burette so that neutralisation is **stoichiometrically complete**, ie neither acid nor base is in excess.

In practice the equivalence point of an acid-base titration is not visibly obvious and so requires the use of an **acid-base indicator** to give a visible indication of when equivalence has occurred. (See Fig 8 and 9.) The **end point** of a titration occurs when the added indicator changes colour signalling that equivalence has occurred and for the titration to be stopped. In practice, the end point is a **very close approximation** of the equivalence point.

A **titration curve** shows how the pH of the reaction mixture in the conical flask changes rapidly at equivalence. It is a graph of solution volume added from the burette versus pH in the reaction mixture. (See Fig 8.) The equivalence point of the titration is the point of **inflection** in the titration curve. Here a single drop of solution will change the reaction mixture pH by several units as its pH passes through equivalence. Any indicator showing a strong colour change in this steep part of the titration curve will give a suitable estimate of the equivalence point for the titration.

$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

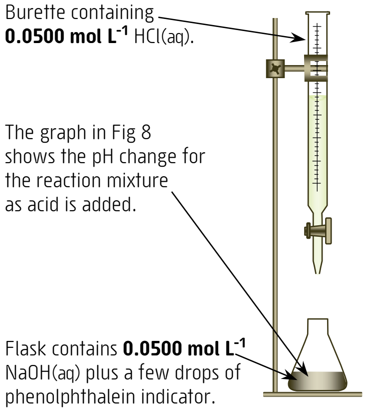
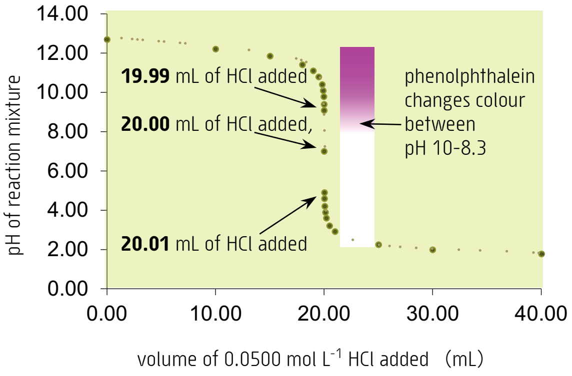


Figure 8 The **titration curve** at right is for the **titration** (above) of **20.00 mL** of **0.0500 mol L^{-1} NaOH**(aq) (a strong base) with **0.0500 mol L^{-1} HCl**(aq) (a strong acid). The titration curve shows how pH changes in the reaction mixture as HCl(aq) is added to NaOH(aq). For this titration, **equivalence** occurs at **pH = 7** when exactly 20.00 mL of acid has been added.

Notice how the reaction mixture pH changes very little at first. The addition of the first 19.99 mL of acid only lowers the reaction mixture pH from 12.70 to 9.10. Then as the reaction nears equivalence, a mere 0.02 mL, **≈½ a drop** of HCl(aq), lowers the pH from above 9 through equivalence (at pH=7) to below 5. Over this range the indicator phenolphthalein changes colour strongly from **pink** to **colourless** and thus is suitable for estimating the equivalence point of this titration. Any indicator showing a strong colour change over the pH 9 to 4 range, eg bromothymol blue, which is yellow at pH<6 and blue at pH>7.6 (Fig 9), would be suitable for estimating the equivalence point of this titration.



Although at equivalence **complete neutralisation** has occurred, it does not necessarily follow that the reaction mixture is neutral, ie equivalence is not necessarily at pH=7. Instead, the pH at equivalence depends upon the acid-base properties of the **products** formed from the titration reaction. In particular, if the salt formed in the acid-base reaction is itself acidic or basic then the equivalence point will not be at pH=7. (See Example 6.)

The indicator chosen for an acid-base titration should change colour in a pH range that closely matches the anticipated equivalence point pH. (See Fig 8, Fig 9 and Example 6.) For most titrations performed in a school laboratory situation, it is sufficient to use **phenolphthalein** for neutral or slightly basic equivalence points. Slightly acidic equivalence points can be found using **methyl orange**. However, if the actual pH at equivalence is known then a more suitable indicator may be chosen. (See Fig 9.) Alternatively a pH meter may be used to more precisely monitor pH changes during a titration.

Example 6 Consider the products of the following acid-base titrations and decide if the equivalence point would be acidic, basic or neutral. Choose from phenolphthalein or methyl orange as a suitable indicator for estimating the equivalence point of each titration. State the end point colour change. (See shortcut at right.)

Acid and base used in the titration.		Equivalence pH	Suitable indicator	Colour change (the acid is in the flask)
HCl and (strong acid)	**NH_3** (weak base)	**acidic**, due to the formation of acidic NH_4^+ ions	methyl orange	red to yellow
HCl and (strong acid)	**NaOH** (strong base)	**neutral**, the reaction products, H_2O, Na^+ and Cl^- are all neutral	phenolphthalein	colourless to pink
CH_3COOH and (weak acid)	**NH_3** (weak base)	**neutral**, as the effect of the weakly acidic NH_4^+ and weakly basic CH_3COO^- cancel out	phenolphthalein	colourless to pink
CH_3COOH and (weak acid)	**NaOH** (strong base)	**basic**, due to the formation of basic CH_3COO^- ions	phenolphthalein	colourless to pink

Shortcut: Equivalence point pH can be predicted from the strength of the acid and base used in the titration. Remember, the salt of a weak base is usually acidic and the salt of a weak acid is usually a weak base.

acid	base	equivalence pH
strong	strong	neutral
weak	weak.................	neutral
strong	weak.................	acidic
weak	strong	basic

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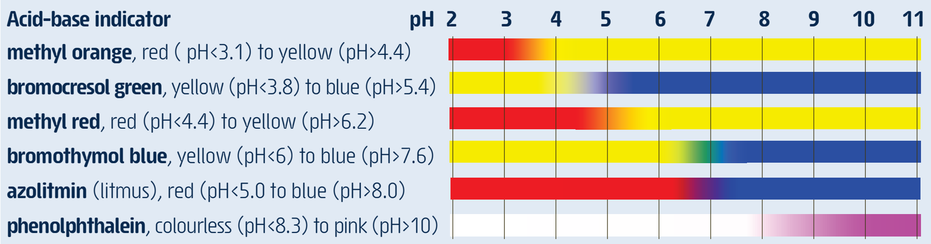
5.8 Acid-base indicators

Indicators used in acid-base titrations usually change between two distinct colour forms over a narrow pH range. (See Fig 9.) For example, phenolphthalein changes from colourless, if pH is less than 8.3, to pink when pH exceeds 10. This colour change may be achieved by the addition of one or two drops of reagent as the mixture in the conical flask passes through equivalence.



Acid-base indicator pH 2 3 4 5 6 7 8 9 10 11

methyl orange, red (pH<3.1) to yellow (pH>4.4)

bromocresol green, yellow (pH<3.8) to blue (pH>5.4)

methyl red, red (pH<4.4) to yellow (pH>6.2)

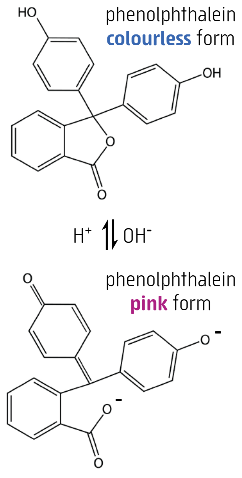
bromothymol blue, yellow (pH<6) to blue (pH>7.6)

azolitmin (litmus), red (pH<5.0 to blue (pH>8.0)

phenolphthalein, colourless (pH<8.3) to pink (pH>10)

Figure 9 Acid-base indicators are pH sensitive dyes that change colour with pH. Many are extracted from plants. Red cabbage for example produces a dye that changes colour from red to purple to green and then yellow as the solution pH changes from being strongly acidic to strongly basic.

Figure 10 The two colour forms of phenolphthalein are pH dependant.



Indicators are themselves weak acids or bases whose acid form and base form have **different colours**. These two different forms co-exist in an acid-base equilibrium that is strongly pH dependent. (See Fig 10.) This can be seen in equation ①

of the indicator is represented by **H*Ind*** and the **base form** (its conjugate base) as ***Ind*** ⁻. Actual indicator molecular formulas are quite complex (Fig 10) so it is more convenient to use the simplified H*Ind* form.

$\text{H}Ind\text{(aq)} \quad + \quad H_2O(l) \quad \rightleftharpoons \quad H_3O^+(aq) \quad + \quad Ind^-(aq)$.............. ①

base form (conjugate base of H*Ind*)

When pH is low, ie a high $H^+(aq)$ concentration, equilibrium ①

H*Ind*.

A low $H^+(aq)$ concentration, ie high pH, shifts equilibrium ①

Ind ⁻.

This effect of pH on equilibrium ①

causes a strong shift in the indicator acid-base equilibrium ①

that is the end point of the titration.

Due to the acid-base properties of these indicators it is important to only use only a few drops of indicator solution. Using a consistently large quantity of indicator can alter the volume required for equivalence and may introduce a **systematic measurement error**.

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Set 7 Volumetric analysis: Acid-base titrations

pipette
equivalence point
standard solution
burette
concentration
approximation
excess
volume
dropwise
indicator
end point
conical flask

1. Use the list of terms to complete the following passage about **acid-base titrations**.

   The purpose of an acid-base titration is to accurately determine the (a) ___________ of either an acid or base in a solution of unknown concentration. To do this, the solution of unknown concentration is reacted with another solution of accurately known concentration called a (b) ___________. During the titration the (c) ___________ of both the acid and base solutions must be accurately measured.

   A fixed volume of one solution (an aliquot) is measured using a (d) ___________ and added to a (e) ___________. The other reagent is placed into a (f) ___________ enabling it to be added (g) ___________ into the conical flask until the reaction is complete, ie when neither reagent is in (h) ___________. This point in the titration is known as the (i) ___________ and can be detected by using an (j) ___________ that shows a distinct colour change at or close to equivalence. It is the indicator colour change that signals the (k) ___________ of the titration. The end point of the titration is a very close (l) ___________ of the equivalence point.

The formula for **hydrated oxalic acid** may be written as HOOCCOOH.$2H_2O$ or more simply as $H_2C_2O_4.2H_2O$. When the hydrated crystals are weighed their water of crystallisation will contribute their mass.

Once in solution though, only the oxalic acid, $H_2C_2O_4$ is the active reagent. From its formula, it is evident that the moles of $H_2C_2O_4$ in a sample of it are the same as the moles of $H_2C_2O_4.2H_2O$ weighed.

2. Anhydrous sodium carbonate, $Na_2CO_3(s)$ and oxalic acid-2-water, $H_2C_2O_4.2H_2O(s)$ are two commonly used **primary standards** for acid-base titrations.

   a. Determine the **mass** of primary standard that should be used to produce the following primary standard solutions.

      i. 250.0 mL of 0.150 mol L^{-1} sodium carbonate primary standard solution

      ii. 500.0 mL of 0.250 mol L^{-1} oxalic acid primary standard solution

   b. You are required to prepare the 250.0 mL of 0.150 mol L^{-1} sodium carbonate primary standard solution described above. Name the **equipment** you would use and **describe** in **detail** your **technique** for making the solution from a sample of $Na_2CO_3(s)$.

Figure 11 Chardonnay grapes being prepared for crushing. Before fermentation the grape mixture of juice, skins and seeds, called **must**, should have a pH of around 3.5 or less. If pH is too high, **tartaric acid** (a white crystalline **diprotic** acid $C_4H_6O_6$) is added to increase its acidity. If pH is too low then **potassium bicarbonate** ($KHCO_3$) can be added to make it more alkaline.

3. The **fermentation** of grape juice to produce wine requires careful pH monitoring and control. (See Fig 11.) A titration method is used by many wineries to determine the total acid content or **titratable acidity** (**TA**) of grape juice prior to fermenting. It is best to titrate the weak acids present in grape juice using a strong base like sodium hydroxide. As sodium hydroxide is not a primary standard, a solution of it must first be prepared and then titrated with a **secondary standard** solution of hydrochloric acid. This standardises the NaOH(aq) giving its exact concentration. The hydrochloric acid itself must have also been standardised by titration with a **primary standard** solution of **sodium carbonate**.

   a. **Explain** the statement 'Sodium hydroxide is not a primary standard.'

   b. **Explain** why the hydrochloric acid solution used in the procedure is a **secondary standard** solution, ie can a hydrochloric acid be a primary standard?

   c. **Determine** the concentration of a sodium carbonate primary standard solution produced by dissolving 3.25 g in distilled water and making this up to 250.0 mL.

   d. Before preparing the sodium carbonate primary standard the $Na_2CO_3(s)$ is heated in an oven at 260-270 °C for about half an hour. After heating it is placed into a **desiccator** while it cools back to room temperature. What is the purpose of **heating** the $Na_2CO_3(s)$ then placing it into a **desiccator** to cool?

   e. **Name** the piece of **glassware** used to prepare the 250.0 mL of sodium carbonate solution and **describe** the **rinsing** procedure for this apparatus?

4. A sodium hydroxide solution was standardised with phosphoric acid. 20.00 mL aliquots of NaOH solution required an average titre of 29.55 mL of 2.95 x 10^{-2} mol L^{-1} H_3PO_4. Assume the phosphoric acid acts as a **triprotic** acid and determine the NaOH concentration.

5. The sharp sour taste of household vinegar is due to the presence of ethanoic acid, CH_3COOH. The ethanoic acid content of commercial vinegar can be found by titration with a standardised sodium hydroxide solution. In such a procedure a student placed 25.00 mL of vinegar into a conical flask and titrated this using standardised NaOH(aq). On average, 23.40 mL of 0.928 mol L^{-1} NaOH(aq) was needed to reach the end point.
   a. **Name** the piece of **equipment** used to measure and transfer the 25.00 mL aliquot of vinegar into the conical flask. Describe the **rinsing** procedure for this apparatus.
   b. Determine the concentration of ethanoic acid, CH_3COOH in this vinegar.

6. **Oxalic acid**, $H_2C_2O_4$ is a moderately strong **diprotic** acid, considerably stronger than phosphoric acid. It is a natural product found in many food plants. Rhubarb leaves for example, can have rather high concentrations of it, as much as 1.4 % by mass. Its concentration in solution can be found by titration with a strong base like sodium hydroxide. In one such titration a 25.00 mL sample of an oxalic acid solution reacted completely with 26.25 mL of 0.1195 mol L^{-1} NaOH solution.
   a. Write an **equation** for the reaction of sodium hydroxide with oxalic acid.
   b. Determine the **concentration** of oxalic acid in this solution.

7. An **experienced** and **competent** laboratory technician prepared a 0.0804 mol L^{-1} Na_2CO_3(aq) primary standard solution. Using a digital balance she carefully weighed 2.13 g of anhydrous Na_2CO_3(s) into a 100 mL beaker. The solid was dissolved in a little distilled water then transferred to a 250.0 mL volumetric flask and filled to the mark.
   a. She estimates the error in her calculated concentration of the Na_2CO_3(aq) primary standard solution to be ± 0.0002 mol L^{-1}. What are some of the **unavoidable** sources of **random error** contributing to her error estimate?
   b. Her junior assistant then stores the primary standard solution for later use. Using distilled water she rinses a reagent bottle to which she then immediately adds the primary standard solution. What **rinsing error** has the junior assistant introduced and what rinsing procedure should have been used?
   c. Later on, the Na_2CO_3(aq) primary standard solution was added to a burette and used to standardise 20.00 mL samples of an approximately 0.1 mol L^{-1} HCl(aq) solution. How will the error in (b) affect the accuracy and precision of the **titre results**? Explain.
   d. Using her titration data the technician determined the secondary standard solution of HCl(aq) had a concentration of 0.109 mol L^{-1}. Considering the error in (b), is the true HCl(aq) concentration higher or lower than her calculated result? **Explain**.

8. Craig and Steve used a titration procedure to find the concentration of hydrochloric acid, HCl(aq) in a commercial bottle of **spirits of salts**. Steve pipetted a 25.00 mL sample of the spirits of salts and diluted this to 1.000 L in a volumetric flask. Samples of this diluted solution were then titrated with standardised 0.1907 mol L^{-1} Na_2CO_3(aq) solution. Craig finds that on average, 16.50 mL of the Na_2CO_3(aq) solution is needed to achieve an end point with the 20.00 mL samples of the diluted HCl solution.
   a. Write an **equation** for this reaction.
   b. Why is a **pipette** used instead of a measuring cylinder or burette for measuring the 20.00 mL samples of diluted HCl solution?
   c. What is the concentration of HCl(aq) in the diluted spirits of salts?
   d. Determine the **concentration** of HCl(aq) in the commercial spirits of salts.

Too many steps, having trouble **visualising** what's going on?

Try sketching a simple **flow diagram**. (See Example 5 and Fig 14.) Your flow diagram should focus on the **reagents** and show how these are diluted or combined with other reagents during the course of the analysis. It may help to include your **data** in the flow diagram.

Remember a flow diagram is your way of **keeping track** of the various **reagents** in the course of the analysis. It is **not** about drawing the apparatus. Above all, keep it simple so that it can be constructed quickly.

9. Commercial hydrochloric acid, known as **spirits of salts**, is purchased as an approximately 10 mol L^{-1} solution. A procedure to determine the exact hydrochloric acid concentration in some spirits of salts [HCl(aq)] involved the following steps.

Primary standard preparation: A carefully weighed 1.288 g sample of anhydrous Na_2CO_3(s) was dissolved in water and made up to 250.0 mL.
Dilution of the original approximately 10 mol L^{-1} HCl solution: A 25.00 mL sample of the acid was made up to 2.00 L in a volumetric flask.

Titration of the diluted acid: 20.00 mL samples of the diluted acid solution required on average, 20.62 mL of the primary standard for equivalence.

a. Write an **equation** for the titration reaction.

b. What is a suitable **indicator** for this titration? Explain your choice.

c. **Determine** the concentration of the diluted acid.

d. What is the **concentration** of the original approximately 10 mol L^{-1} acid?

10. A student has 200 mL of standardised 0.04955 mol L^{-1} H_2SO_4(aq) which is to be used to find the concentration of an approximately 0.5 mol L^{-1} NaOH solution. Equipment at her disposal includes; a 50.00 mL burette, a 20.00 mL pipette, 100.0 mL and 250.0 mL volumetric flasks, phenolphthalein and methyl orange indicators as well as the usual laboratory glassware like beakers, conical flasks and measuring cylinders.

Describe a **procedure** she could use to accurately find the concentration of NaOH(aq) in the approximately 0.5 mol L^{-1} solution. You should be **specific** in your description of the procedure paying attention to **apparatus** used, **quantities** of **reagents** and **methods** that will improve **accuracy** and **minimise errors** in your final answer. No calculation is required only a **description** of the experimental procedure used and the **data** collected.

Figure 12 The basic technology of the **lead-acid battery** was first demonstrated to the French Academy of Sciences in 1860 by Gaston Planté. Each cell of a lead-acid battery has a lead-dioxide electrode and a spongy metallic lead electrode immersed in an electrolyte of 4.5 mol L^{-1} sulfuric acid solution.
Photograph courtesy of Century Yuasa Batteries Pty Ltd.

11. A batch of sulfuric acid electrolyte for use in **lead-acid batteries** (Fig 12) is analysed for its sulfuric acid content. To do this 50.00 mL of the acid was taken and diluted to 250.0 mL in a volumetric flask. 25.00 mL samples of the diluted electrolyte were titrated with 1.029 mol L^{-1} KOH(aq) solution. The initial and final burette readings are shown:

Final volume (mL)	41.00	39.65	41.90	41.30
Initial volume (mL)	1.05	0.40	2.60	1.95
Titre (ie volume used) (mL)				

$$2KOH(aq) + H_2SO_4(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$$

a. How can the **equivalence point** of this titration be determined?

b. Determine the **average titre** and **account** for the individual variations.

c. What was the **concentration** of H_2SO_4(aq) in the **original battery acid**?

d. What is the **concentration** of H_2SO_4(aq) in **ppm** if the original battery acid solution has a density of 1.21 g mL^{-1} (ie 1.00 mL of solution has a mass of 1.21 g).

Figure 13 Sodium hydrogencarbonate is also known as **bicarbonate of soda** or **baking soda**. It is a white crystalline powder that is commonly used in baking products, as a pH buffer, a medicinal electrolyte replenisher, a systemic alkalizer and in topical cleansing solutions.

Baking soda can also be used as a deodoriser. An open box of it left in the refrigerator or freezer will eliminate odours.

12. One unusual use of **sodium hydrogencarbonate**, also known as bicarbonate of soda or baking soda (Fig 13), is as a refrigerator deodoriser. Left in the refrigerator, in an open packet, it will absorb water and odours from the air inside. A student decided to investigate the water absorbing effect of some $NaHCO_3$ that had been left in the refrigerator in an open pack for a week. To do this she weighed an 8.76 g sample of this $NaHCO_3$ and dissolved it in water making up 250.0 mL of solution. This solution was then titrated with standardised 0.985 mol L^{-1} HCl(aq). 20.00 mL samples of the $NaHCO_3$ solution required, on average, 7.15 mL of standardised HCl(aq) for equivalence.

$$NaHCO_3(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l) + CO_2(g)$$

a. What **indicator** is suitable for showing the equivalence point of this titration?

b. Determine the **concentration** of $NaHCO_3$(aq) in the 250.0 mL solution.

c. What **mass** of $NaHCO_3$ was actually present in the 8.76 g refrigerator sample?

d. What was the percentage by mass of water in the $NaHCO_3$(s) sample after being left in the refrigerator for a week? Assume water is the only impurity present.

13. **Limewater** is a saturated solution of $Ca(OH)_2(aq)$. In the laboratory it is often used to identify $CO_2(g)$. A limewater solution is made by leaving solid $Ca(OH)_2$ in contact with water until no further $Ca(OH)_2$ dissolves. (See Fig 14.)

    A 20.00 mL sample of limewater was titrated with standardised 3.190×10^{-2} mol L^{-1} $HCl(aq)$ and on average, 20.31 mL of acid was needed to achieve equivalence. Determine the mass of $Ca(OH)_2$ present in the 20.00 mL sample of limewater and hence calculate the **solubility** of $Ca(OH)_2$ in **g L^{-1}**.

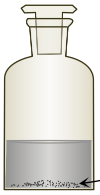


Figure 14 A solution of **limewater** is kept saturated with $Ca(OH)_2$ by leaving it in contact with solid $Ca(OH)_2$.

14. A supermarket brand of **vinegar** is to be analysed for its ethanoic acid content by a titration technique. This requires the preparation of a $Na_2CO_3(aq)$ primary standard. The primary standard is made by dissolving 1.416 g of anhydrous $Na_2CO_3(s)$ in some distilled water and making the solution up to exactly 500.0 mL using a volumetric flask.

    A 50.00 mL sample of the vinegar is then diluted to exactly 1.000 L in another volumetric flask. Four 25.00 mL samples of this solution are placed into separate conical flasks and titrated with the $Na_2CO_3(aq)$ primary standard. The volume of Na_2CO_3 solution used in each titration was 24.85 mL, 23.50 mL, 23.75 mL, 23.85 mL and 23.60 mL.

    $$Na_2CO_3(aq) + 2CH_3COOH(aq) \rightarrow 2NaCH_3COO(aq) + H_2O(l) + CO_2(g)$$

    a. Suggest a suitable **indicator** to show the equivalence point of this titration. Explain your choice.

    b. What is the **CH_3COOH concentration** in the supermarket brand of vinegar?

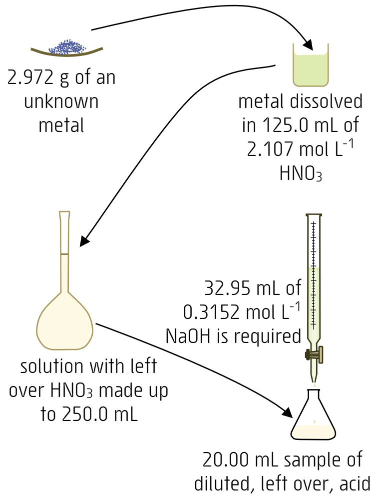
    c. Determine **percentage by mass** of ethanoic acid in the undiluted vinegar if this vinegar has a density of 1.060 g mL^{-1}, ie 1.00 L of vinegar has a mass of 1060 g.

15. A 2.972 g sample of an **unknown metallic element** was dissolved in 125.0 mL of 2.107 mol L^{-1} $HNO_3(aq)$. The reaction produced a salt with formula **$M(NO_3)_4$**.

    $$3M(s) + 16HNO_3(aq) \rightarrow 3M(NO_3)_4(aq) + 4NO(g) + 8H_2O(l)$$

    The remaining solution containing excess $HNO_3(aq)$ was diluted to 250.0 mL. A 20 mL sample of the **diluted** solution containing excess $HNO_3(aq)$ was titrated to equivalence using 32.95 mL of 0.3152 mol L^{-1} $NaOH(aq)$. (See Fig 15.) What is the **molar mass** of the metal? Use your answer to **identify** the metal element.

Figure 15 A **sketch** is useful in seeing the relationship between the various solutions and substances involved in a multi-step analysis, as in Question 15.



16. **Vitamin C** tablets contain the active ingredient **ascorbic acid** ($C_6H_8O_6$, see Fig 16). This weak **monoprotic** acid can release one mole of hydrogen ions per mole of acid molecules. A single vitamin C tablet of mass 3.55 g is crushed and dissolved in 500.0 mL of 4.640×10^{-1} mol L^{-1} NaOH solution. A 20.00 mL sample of the solution containing the excess NaOH was then titrated to equivalence with 38.48 mL of 0.1120 mol L^{-1} $H_2SO_4(aq)$. What **mass** of vitamin C is present in the 3.55 g tablet?

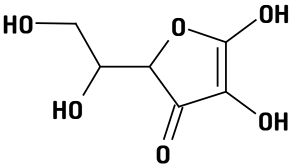


Figure 16 Vitamin C ($C_6H_8O_6$), also known as **ascorbic acid**, contains 8 hydrogen atoms per molecule but only one of these is acidic. This monoprotic acid is related to glucose. It is found naturally in citrus fruits and many vegetables. Ascorbic acid is an essential nutrient in human diets and necessary for maintaining connective tissue and bone.

17. An 11.80 g sample of a strong **monoprotic acid** of unknown formula was dissolved in water and made up to a volume of 100.0 mL. Samples of this acid solution were titrated with 6.070×10^{-1} mol L^{-1} $Ba(OH)_2$ solution. On average, 16.97 mL of base was needed to achieve equivalence with 20.00 mL of the acid solution. (Hint: Using a general formula of HB for the monoprotic acid allows an equation to be written for its reaction with $Ba(OH)_2$.)

    a. What was the **molar mass** of the acid?

    b. How would the molar mass of the acid be different if it had been a **diprotic acid** and all the measurements were unchanged?

18. **Methyl red** is a suitable indicator for estimating the **equivalence point** for the titration of $HCl(aq)$ with $NaOH(aq)$. What is the expected end point **colour change** for this titration if the acid is added from the burette? Using the simplified formula for an indicator, H*Ind* and your knowledge of equilibria **account** for the colour change observed.

CHAPTER 6 | OXIDATION AND REDUCTION

Figure 1 The explosive combustion reactions occurring in the Space Shuttle engines and the slow process of corrosion both involve redox reactions. In each case oxygen is the oxidising agent.
Above photograph courtesy of NASA.

6.1 Redox reactions

The biological processes of photosynthesis and respiration, and the industrial processes of metal extraction involve redox reactions. Similarly, the combustion of fossil fuels, corrosion of iron and the operation of portable power supplies, like cells and batteries also involve redox reactions. (See Fig 1.)

In a **redox reaction** some elements are said to be oxidised while others become reduced. An atom or ion has been **oxidised** when it loses one or more of its electrons. Conversely **reduction** occurs when an atom or ion gains one or more electrons.

Oxidation numbers are a way of keeping track of the extent to which an atom has gained or lost electrons. The more positive an atom's oxidation number, the greater its degree of oxidation (electron loss). An atom's oxidation number can be described as, 'the charge the atom would have if the bonds to it were purely ionic'. (See Table 1 and Example 1.)

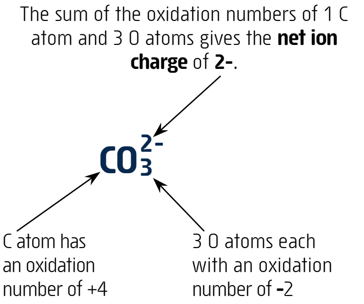
Table 1 Assigning oxidation numbers (See Fig 2.)

Rule	Examples with oxidation numbers below in brackets						
① Atoms in the free state have an oxidation number of zero.	Al (0)	H (0)	O (0)	S (0)	Cl (0)	Fe (0)	
② Monatomic ions have an oxidation number equal to their charge.	H (+1)	Al (+3)	Fe (+2)	AlCl (+3) (-		Na O -	
③ Hydrogen atoms bonded to other elements have an oxidation number of +1 Metal hydrides* are an exception where the oxidation number of hydrogen is -	H (+1)	H (+1)	H (+1)	H $_4$ (+1)	H $_3$ (+1)	NaH* (-	
④ Oxygen atoms bonded to other elements, have an oxidation number of -2. Peroxides* are an exception where the oxidation number of oxygen is -1.	H_2O (-	H_3PO -	O -	$_4^{2-}$ -	NO_3^- -	Na_2O * -	H *

Attempt Set 8 # 1.

In any chemical formula, 'the **sum of the oxidation numbers** of all the atoms in the formula **equals the net charge** shown on the formula'. Using this idea allows an oxidation number to be assigned to any atom that is part of a compound or polyatomic ion. (See Fig 2 and Example 1.)

Figure 2 **Oxidation number** is a property of a single atom. This is true even if the atom is part of a cluster of atoms that collectively form a polyatomic ion or molecule.



Example 1 Calculate the oxidation number (o.n.) for the stated element in each formula.

a. Find the oxidation number of **P** in PO_4^{3-}.

net charge of the ion = 1 x o.n.(P) + 4 x o.n.(O)
-3 = 1 x o.n.(P) + 4 x (-2)
-3 = 1 x o.n.(P) + (-8)
-3 + 8 = o.n.(P)
+5 = o.n.(P)

b. Find the oxidation number of **Cr** in $Cr_2O_7^{2-}$.

net charge of the ion = 2 x o.n.(Cr) + 7 x o.n.(O)
-2 = 2 x o.n.(Cr) + 7 x (-
-2 = 2 x o.n.(Cr) + (-
+12 = 2 x o.n.(Cr)
+6 o.n.(Cr)

c. Find the oxidation number of **C** in $H_2C_2O_4$.

net charge = 2 x o.n.(C) + 2 x o.n.(H) + 4 x o.n.(O)
0 = 2 x o.n.(C) + 2 x (+1) + 4 x (-
0 = 2 x o.n.(C) + 2 + (-
+6 = 2 x o.n.(C)
+3 = o.n.(C)

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Attempt Set 8 # 2.

6.2 Identifying redox reactions

A **redox reaction** involves a **transfer of electrons** between some **species** in the reaction. For a chemical change to be a redox reaction both oxidation (loss of electrons) and reduction (gain of electrons) must occur. The **oxidised species** can be identified by an increase in its oxidation number while the **reduced species** shows a reduction in its oxidation number.

In a chemical context the term '**species**' refers to a particle such as an **atom**, **ion** or **molecule**.
independently in a chemical reaction, ie appear on its own in the reaction. As an example, a solution of **Na_2SO_4** in **water** would contain the species **Na^+(aq)**, **SO_4^{2-}(aq)** and **H_2O(l)**.

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The species that is reduced is known as the **oxidising agent** or **oxidant** while the species that is oxidised is called the **reducing agent** or **reductant**. Some species in the reaction may show no change in their oxidation number as they have neither gained nor lost electrons. By observing oxidation number changes the oxidised and reduced species can be identified.

Example 2 Are the following redox reactions? If so, which element is oxidised and which is reduced? Name the oxidising and reducing agents.

Equation showing oxidation numbers (o.n.) of all atoms.	Oxidised atom	Reduced atom	Oxidising agent	Reducing agent	Type of reaction
$Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + H_2(g)$ 0 +1 - +2 - +1 0	Ca, as **o.n.** increases, 0 to +2	H, as **o.n.** reduces, +1 to 0	H_2O	Ca	**Redox**, as both oxidation (of Ca) and reduction (of H) occur.
$Ca^{2+}(aq) + 2OH^-(aq) \rightarrow Ca(OH)_2(s)$ +2 - - +1	none	none	none	none	No change in **o.n.** hence this is **not redox**.
$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$ +7 - -	Fe^{2+}, as **o.n.** increases, +2 to +3	Mn, as **o.n.** reduces, +7 to +2	MnO_4^-	Fe^{2+}	**Redox**, as both oxidation and reduction occur.
$2CrO_4^{2-}(aq) + 2H^+(aq) \rightarrow Cr_2O_7^{2-}(aq) + H_2O(l)$ +6 - +6 - +1 -	none	none	none	none	No change in **o.n.** hence this is **not redox**.

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Attempt Set 8 # 3 and 4.

6.3 Common redox reactions

An analysis of oxidation number changes shows many chemical reactions operate on the same electron transfer principle, ie are redox reactions. Some common examples include:

Metal-metal ion displacement: These redox reactions involve electron transfer from one **metal element** to the **metal ions** of a **less reactive** metal. The more reactive metal becomes oxidised as it loses electrons to form positive aqueous metal ions. Simultaneously, positive aqueous metal ions of the less reactive metal become reduced as they gain electrons to form a solid metallic precipitate. The following equation shows how Cu, the more reactive metal, is oxidised by $Ag^+(aq)$, ions of the less reactive metal Ag. (See Fig 3.)

Cu/Ag^+ displacement reaction: $Cu(s) + 2Ag^+(aq) \rightarrow 2Ag(s) + Cu^{2+}(aq)$
Oxidation number changes 0 +1 0 +2

Figure 3 A copper coil placed into a silver nitrate solution quickly develops a thick silvery deposit of **metallic silver** as the colourless solution turns **pale blue**.

In this metal-metal ion displacement reaction, metallic copper (the more reactive metal) dissolves forming $Cu^{2+}(aq)$ while $Ag^+(aq)$ ions (ions of the less reactive metal) are reduced to metallic silver, Ag(s).

Halogen-halide ion displacement: In these redox reactions, electrons are transfered to a **halogen**, ie a group 17 element, from the **halide ions** of a **less reactive halogen**. The more reactive halogen (ie one from higher up in group 17) becomes reduced as it gains electrons to form negative aqueous halide ions. The aqueous negative halide ions of the less reactive halogen become oxidised as they lose electrons and form the elemental halogen. Figure 4 shows the Cl_2/Br^- halogen-halide ion displacement reaction.

Cl_2/Br^- displacement reaction: $2Br^-(aq) + Cl_2(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$
Oxidation number changes -1 0 -1 0

In the laboratory it is most convenient to use halogen reagents, ie $Cl_2(g)$, $Br_2(l)$ and $I_2(s)$ in aqueous solution form, ie $Cl_2(aq)$, $Br_2(aq)$ and $I_2(aq)$. These are known as chlorine water, bromine water and iodine water respectively.

Combustion: These redox reactions involve the oxidation of a **fuel** [eg hydrogen gas (H_2) methane (CH_4), petrol, coal or wood] and the reduction of **oxygen gas**. (See Fig 1 and p132.)

Ethane, C_2H_6 combustion: $2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(g)$
Oxidation number changes -3 +1 0 +4 -2 +1 -2

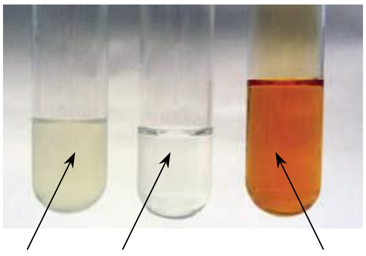
Corrosion: In this case, a metal such as iron, aluminium or zinc is oxidised in the presence of agents like water and air (O_2). While water is important in the corrosion process it is **oxygen gas** that is the oxidising agent. Dissolved salts will also speed up corrosion. (See Fig 1.)

Corrosion of iron: $2Fe(s) + O_2(g) + 2H_2O(l) \rightarrow 2Fe(OH)_2(s)$
Oxidation number changes 0 0 +1 -2 +2 -2 +1

More reactive metals like Na, Ca, Mg and Fe show a greater tendency to corrode than those of lower reactivity (eg Cu, Ag, Pt and Au). Despite this, some quite reactive metals like Al, Cr and Zn show little or no effects of corrosion. This is due to the natural formation of a thin protective oxide coating that forms upon exposure to air (eg Al_2O_3 on Al and Cr_2O_3 on Cr). This layer excludes oxygen and water from the underlying metal thus inhibiting its corrosion.

Figure 4 Halogen-halide ion displacement reactions occur when a halogen (eg Cl_2, Br_2 or I_2) is added to a solution containing halide ions (eg Cl^-, Br^- or I^-) of a **less reactive** halogen.

For example, if chlorine water, $Cl_2(aq)$ is added to a KBr solution [ie contains $Br^-(aq)$] then the pale **yellow** chlorine, $Cl_2(aq)$ is reduced to **colourless** chloride ions, $Cl^-(aq)$. Simultaneously **colourless** bromide ions, $Br^-(aq)$ are oxidised to **orange** coloured bromine, $Br_2(aq)$.



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Complete Set 8.

Set 8 Oxidation numbers and redox reactions

1. **State** the oxidation number of each element in the following species.

a. Na
b. S
c. O_2
d. H_2
e. Cl_2
f. Al
g. Fe^{2+}
h. O^{2-}
i. Ni^{2+}
j. H^+
k. K_2S
l. NaCl
m. $SnCl_4$
n. Fe_2O_3
o. OH^-
p. H_2O_2
q. KH
r. $Al(OH)_4^-$

2. **Calculate** the oxidation number of the underlined element in each of the following species.

a. $\underline{C}O$
b. $\underline{C}O_2$
c. $\underline{C}H_4$
d. $\underline{N}H_3$
e. $H_3\underline{P}O_4$
f. $Na_2\underline{S}O_3$
g. $H_2\underline{C}_2O_4$
h. $\underline{N}_2O_4$
i. $Ca(\underline{Cl}O)_2$
j. $Al(\underline{N}O_3)_3$
k. $\underline{N}H_4^+$
l. $\underline{Mn}O_4^-$
m. $\underline{C}O_3^{2-}$
n. $\underline{S}O_4^{2-}$
o. $\underline{Cr}_2O_7^{2-}$
p. $\underline{C}_2O_4^{2-}$
q. $H\underline{S}_2O_3^-$
r. $[Zn(\underline{N}H_3)_4]^{2+}$

3. Use the list of terms to **complete** the following passage about **redox reactions**.

In the normal or standard state, atoms of all elements will have as many electrons in their electron cloud as they have (a) ___________ in their nucleus. In this standard state atoms are neutral and their oxidation number is (b) ___________. If a neutral atom loses one or more of its electrons it becomes (c) ___________ charged and is said to have been (d) ___________. As a result of this, its oxidation number (e) ___________. Conversely, neutral atoms that have gained electrons will form negative ions and their oxidation number (f) ___________. These atoms are said to have been reduced.

Chemical reactions where both oxidation and reduction take place are known as (g) ___________ reactions. This type of reaction is distinguished from other reactions as one element in the reaction shows an increase in its oxidation number, the (h) ___________ element, while some other element has a decrease in its oxidation number and thus has been (i) ___________. In a redox reaction the species that is oxidised is known as the reductant or (j) ___________ while the species that is reduced is known as the (k) ___________ or oxidising agent.

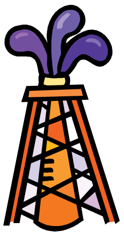
positively
redox
oxidised
zero
reducing agent
reduces (ie decreases)
protons
oxidant
reduced
increases
oxidised

4. Some of the following balanced equations are **redox reactions**. Examine the oxidation numbers of the elements in the reaction to determine if they are redox reactions. For those that are **state** the following:

i. the **element** which is **reduced**
ii. the **element** which is **oxidised**
iii. the **species** (see border note p64) acting as the **oxidising agent** (**oxidant**)
iv. the **species** acting as the **reducing agent** (**reductant**).

a. $Cl_2(g) + 2Na(s) \rightarrow 2NaCl(s)$
b. $Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$
c. $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$
d. $CaBr_2(s) \rightarrow Ca^{2+}(aq) + 2Br^-(aq)$
e. $OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$
f. $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$
g. $2Cu^+(aq) \rightarrow Cu(s) + Cu^{2+}(aq)$ (**See border note at left.**)
h. $2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$
i. $Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + H_2(g)$
j. $2NaOH(aq) + CO_2(g) \rightarrow Na_2CO_3(aq) + H_2O(l)$
k. $H_2SO_3(aq) \rightarrow H_2O(l) + SO_2(g)$
l. $Cu(s) + 4H^+(aq) + 2NO_3^-(aq) \rightarrow 2NO_2(g) + 2H_2O(l) + Cu^{2+}(aq)$
m. $3HCHO(l) + 8H^+(aq) + Cr_2O_7^{2-}(aq) \rightarrow 3HCOOH(aq) + 2Cr^{3+}(aq) + 4H_2O(l)$
n. $H_2O(l) + Cr_2O_7^{2-}(aq) \rightarrow 2CrO_4^{2-}(aq) + 2H^+(aq)$
o. $H_2O(l) + 2NO_2(g) \rightarrow 2H^+(aq) + NO_3^-(aq) + NO_2^-(aq)$

Remember! **OIL RIG**



Oxidation
Is
Loss of electrons

Reduction
Is
Gain of electrons

If the oxidation number increases then **oxidation** has taken place. Species that are oxidised are themselves **reducing agents (reductants)**.

If the oxidation number reduces (ie decreases) then **reduction** has taken place. Species that are reduced are themselves **oxidising agents (oxidants)**.

Some redox reactions, eg Q4 g, h and o involve the same species simultaneously undergoing both oxidation and reduction to form two different products. Redox reactions like this are known as **disproportionation** reactions.

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5. The following chemical reactions occur in a variety of familiar situations. Are any of these redox reactions? Use your knowledge of redox processes to **justify** your answer.
   a. **Respiration**, which involves the overall reaction shown here.
      $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$
   b. The complete **combustion** of natural gas in a household gas heater.
      $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$
   c. The **incomplete combustion** of bees wax, essentially $C_{46}H_{92}O_2$, in a candle flame.
      $C_{46}H_{92}O_2(s) + 22O_2(g) \rightarrow 46C(s) + 46H_2O(g)$
   d. The **corrosion of iron** in a ship's hull. (See Fig 1.)
      $4Fe(s) + 3O_2(g) + 6H_2O(l) \rightarrow 4Fe(OH)_3(s)$

6.4 Half-equations

Redox reactions involve two simultaneous changes, oxidation and reduction. It is possible to write individual half-equations to represent each of these processes. An **oxidation half-equation** shows the species which is oxidised (lost electrons). It has electrons on the product side of the half-equation. The **reduction half-equation** shows the species which is reduced (gained electrons). It has electrons on the reactant side of the half-equation. Together the two half-equations describe the overall redox reaction.

Example 3	**a.** Write the **oxidation half-equation** for I^- changing to I_2.	**b.** Write the **reduction half-equation** for Fe^{3+} forming Fe.
Show the oxidised or reduced species and its product.	$\mathbf{I^- \rightarrow I_2}$	$\mathbf{Fe^{3+} \rightarrow Fe}$
Balance the element.	$\mathbf{2}I^- \rightarrow I_2$	$Fe^{3+} \rightarrow Fe$
Balance charge by adding electrons to the more positive side.	$2I^- \rightarrow I_2 + \mathbf{2e^-}$	$Fe^{3+} + \mathbf{3e^-} \rightarrow Fe$
Show the phase of each species.	$2I^-\mathbf{(aq)} \rightarrow I_2\mathbf{(s)} + 2e^-$	$Fe^{3+}\mathbf{(aq)} + 3e^- \rightarrow Fe\mathbf{(s)}$

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Attempt Set 9 # 1.

6.5 Half-equations with polyatomic ions in acidic solutions

Oxidising agents like nitrate, NO_3^-, permanganate, MnO_4^-, dichromate, $Cr_2O_7^{2-}$ and hypochlorite, ClO^- for example will only function effectively if hydrogen ions, **H^+(aq)** are available in the reaction mixture, ie the solution is **acidic**. The H^+(aq) itself is neither oxidised nor reduced but is involved in the half-reaction. Sulfuric acid is often used to acidify these reactions as it is a strong acid that can provide a high H^+(aq) concentration without the acid itself being oxidised.

Example 4 Write a balanced half-equation for each half-reaction. Assume **acidic** conditions apply.	**Reaction 1** Reduction of MnO_4^- in an **acidic** solution forming Mn^{2+}.	**Reaction 2** Oxidation of Cl_2 in an **acidic** solution forming HClO.
Show the reactant and product.	$\mathbf{MnO_4^- \rightarrow Mn^{2+}}$	$\mathbf{Cl_2 \rightarrow HClO}$
Balance the oxidised or reduced element (the element showing a change of oxidation number).	Mn is reduced (o.n. changes, +7 to +2). Balance Mn first. Mn is already balanced.	Cl is oxidised (o.n. changes, 0 to +1). Balance Cl first. $Cl_2 \rightarrow \mathbf{2}HClO$
Balance **oxygen** by adding **H_2O**.	$MnO_4^- \rightarrow Mn^{2+} + \mathbf{4H_2O}$	$Cl_2 + \mathbf{2H_2O} \rightarrow 2HClO$
Balance **hydrogen** by adding **H^+** ions.	$MnO_4^- + \mathbf{8H^+} \rightarrow Mn^{2+} + 4H_2O$	$Cl_2 + 2H_2O \rightarrow 2HClO + \mathbf{2H^+}$
Balance **charge** by adding **electrons**. Phases may also be shown.	$MnO_4^-(aq) + 8H^+(aq) + \mathbf{5e^-} \rightarrow Mn^{2+}(aq) + 4H_2O(l)$	$Cl_2(g) + 2H_2O(l) \rightarrow 2HClO(aq) + 2H^+(aq) + \mathbf{2e^-}$

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Attempt Set 9 # 2.

6.6 Balancing redox equations using half-equations

Some common laboratory redox reactions include **metal-metal ion** displacement reactions, **halogen-halide ion** displacement reactions and **combustion reactions**. A **balanced redox equation** can be written for reactions like these and others by adding together the oxidation and reduction half-equations occurring in the reaction.

This is done in such a way that the number of electrons produced in the oxidation half-equation equals the number of electrons consumed in the reduction half-equation. Consequently when the two half-equations are added together electrons do not appear in the overall redox equation. (See Examples 5 and 6.)

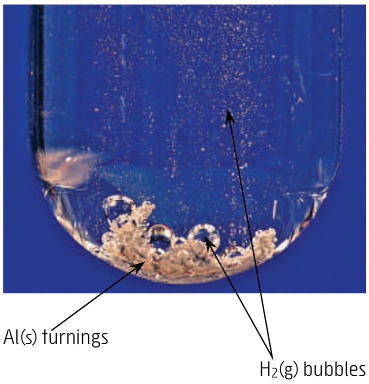

Figure 5 All acid-metal reactions, such as occurs between aluminium turnings and dilute hydrochloric acid (above), are redox reactions.

In this example **Al** turnings (the metal) are dissolved, being oxidised to **Al^{3+}(aq)**. At the same time **H^+**(aq) ions from the acid solution are reduced to colourless bubbles of hydrogen gas, **H_2(g)**. The gas can be seen forming on the aluminium surface.

Example 5 Write the **redox equation** for the oxidation of Al metal turnings by H^+(aq). The reaction produces H_2(g) and Al^{3+}(aq). (See Fig 5.)

Write the oxidation and reduction half-equations in the usual way.	① .... $Al \rightarrow Al^{3+} + \mathbf{3e^-}$ ② .... $\mathbf{2e^-} + 2H^+ \rightarrow H_2$
Multiply the coefficients of each half-equation so that **electrons** are **equalised** in both equations.	multiply ① $\mathbf{2}Al^{3+} + \mathbf{6}e^-$ multiply ② $e^- + \mathbf{6}H^+ \rightarrow \mathbf{3}H_2$
Add the two half-equations and cancel the electrons.	$2Al + 6H^+ \rightarrow 3H_2 + 2Al^{3+}$ Note: **6**e^- has been cancelled from each side of the equation.
Show the phases.	$2Al\mathbf{(s)} + 6H^+\mathbf{(aq)} \rightarrow 3H_2\mathbf{(g)} + 2Al^{3+}\mathbf{(aq)}$

Example 6 Write the redox equation for the oxidation of $H_2C_2O_4$(aq) by **acidified** $KMnO_4$(aq). The reaction produces Mn^{2+}(aq) and CO_2(g).

Write the oxidation and reduction half-equations in the usual way.	①.......... $\mathbf{5e^-} + MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$ ② $H_2C_2O_4 \rightarrow 2CO_2 + 2H^+ + \mathbf{2e^-}$
Multiply the coefficients of each half-equation so that **electrons** are **equalised** in both equations.	multiply ① $^- + 2MnO_4^- + \mathbf{16H^+} \rightarrow 2Mn^{2+} + \mathbf{8}H_2O$ multiply ② $H_2C_2O_4 \rightarrow \mathbf{10}CO_2 + \mathbf{10}H^+ + \mathbf{10e^-}$
Add the two half-equations.	$2MnO_4^- + 5H_2C_2O_4 + \mathbf{16H^+} \rightarrow 2Mn^{2+} + 10CO_2 + \mathbf{10H^+} + 8H_2O$
Simplify the coefficients of any species occurring on both sides.	$2MnO_4^- + 5H_2C_2O_4 + \mathbf{6H^+} \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$ The equation has been simplified by cancelling **$10H^+$** from each side.
Show the phases.	$2MnO_4^-\mathbf{(aq)} + 5H_2C_2O_4\mathbf{(aq)} + 6H^+\mathbf{(aq)} \rightarrow 2Mn^{2+}\mathbf{(aq)} + 10CO_2\mathbf{(g)} + 8H_2O\mathbf{(l)}$

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Complete Set 9.

Set 9 Balancing half-equations and redox reactions

1. Write balanced **half-equations** for each of the chemical changes described here.
   a. oxidation of Fe(s) producing Fe^{3+}(aq)
   b. oxidation of Sn^{2+}(aq) producing Sn^{4+}(aq)
   c. reduction of Cl_2(g) producing Cl^-(aq)
   d. reduction of H^+(aq) producing H_2(g)
   e. oxidation of Hg(l) producing Hg_2^{2+}(aq)

2. The following half-equations may involve **H^+(aq)**. Write balanced **half-equations** for each of these reactions.
   a. reduction of MnO_4^-(aq) in acid solution giving Mn^{2+}(aq)
   b. reduction of H_2SeO_3(aq) in acid solution giving Se(s)
   c. reduction of PbO_2(s) in acid solution forming Pb^{2+}(aq)
   d. oxidation of sulfur, S(s) in acid solution forming sulfurous acid, H_2SO_3(aq)
   e. reduction of nitrate ions in acid solution producing nitrogen monoxide gas
   f. reduction of nitrate ions in acid solution forming dinitrogen tetroxide gas
   g. oxidation of water in an acid solution producing oxygen gas

3. A student investigation involves several simple redox reactions as listed below.
   i. **Classify** these as metal-metal ion or halogen-halide ion displacement reactions or as acid-metal reactions.
   ii. Note an expected ***observation** for each of the reactions.
   a. $Zn(s) + Cu^{2+}(aq) \rightarrow Cu(s) + Zn^{2+}(aq)$
   b. $2Br^-(aq) + Cl_2(aq) \rightarrow Br_2(aq) + 2Cl^-(aq)$
   c. $2Al(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2(g)$
   d. $2Cr^{3+}(aq) + 3Mg(s) \rightarrow 2Cr(s) + 3Mg^{2+}(aq)$

* The colour and appearance of selected substances can be found in the Appendix section.

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4. Several **unbalanced** redox equations are listed below. For each example **write**:

   i. the **oxidation** half-equation
   ii. the **reduction** half-equation
   iii. the **overall redox** equation.

   a. $Cl_2(g) + Br^-(aq) \rightarrow Br_2(aq) + Cl^-(aq)$
   b. $Cu^{2+}(aq) + Al(s) \rightarrow Al^{3+}(aq) + Cu(s)$
   c. $Sn^{4+}(aq) + Cr(s) \rightarrow Cr^{3+}(aq) + Sn(s)$
   d. $H^+(aq) + Cr_2O_7^{2-}(aq) + Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + Cr^{3+}(aq) + H_2O(l)$
   e. $CH_3OH(aq) + MnO_4^-(aq) + H^+(aq) \rightarrow HCOOH(aq) + Mn^{2+}(aq) + H_2O(l)$
   f. $Tl^+(aq) + H^+(aq) + MnO_4^-(aq) \rightarrow Mn^{2+}(aq) + H_2O(l) + Tl^{3+}(aq)$
   g. $H^+(aq) + Cr_2O_7^{2-}(aq) + Cr^{2+}(aq) \rightarrow Cr^{3+}(aq) + H_2O(l)$
   h. $H^+(aq) + NO_3^-(aq) + Ni(s) \rightarrow Ni^{2+}(aq) + NO(g) + H_2O(l)$
   i. $VO^{2+}(aq) + H_2O(l) + Cl_2(aq) \rightarrow Cl^-(aq) + H^+(aq) + VO_2^+(aq)$

5. Each of the questions that follow give some information about the reactants and products of a **redox** reaction. Write a **redox equation** for each of these reactions and describe any **observations** you would expect as the reactions proceed.

   a. Granules of **Zn** are added to **$HCl(aq)$** [ie $H^+(aq)$ and $Cl^-(aq)$] liberating **$H_2(g)$** and forming **$ZnCl_2(aq)$** [ie $Zn^{2+}(aq)$ and $Cl^-(aq)$].
   b. Chlorine water, **$Cl_2(aq)$** was added to an aluminium iodide, **AlI_3** solution [ie $Al^{3+}(aq)$ and $I^-(aq)$] causing the formation of **$I_2(aq)$** and **$AlCl_3(aq)$** [ie $Al^{3+}(aq)$ and $Cl^-(aq)$].
   c. Acidified **$K_2Cr_2O_7(aq)$** [$H^+(aq)$, $K^+(aq)$ and $Cr_2O_7^{2-}(aq)$] is added to **$Na_2S(aq)$** [$Na^+(aq)$ and $S^{2-}(aq)$] forming **sulfur** and **chromium(III) ions**, $Cr^{3+}(aq)$.
   d. **Chlorine** gas is bubbled through a concentrated **tin(II) chloride** solution [$Sn^{2+}(aq)$ and $Cl^-(aq)$] forming **sodium chloride** [$Na^+(aq)$ and $Cl^-(aq)$] and **tin(IV) chloride** [$Sn^{4+}(aq)$ and $Cl^-(aq)$].
   e. Some **steel wool**, $Fe(s)$ is added to a dilute **sulfuric acid** solution to produce **hydrogen gas** and **iron(II) sulfate**.
   f. **Bromine water** was added to a **sodium iodide** solution, causing the formation of aqueous **iodine** and **sodium bromide**.
   g. Concentrated **nitric acid** is added to **copper** metal, resulting in the formation of **nitrogen dioxide** gas and **copper(II) nitrate**.
   h. A **hydrogen peroxide** solution decomposes by disproportionation, to form **oxygen** gas and **water**. H_2O_2 is both oxidised and reduced in this reaction.

6. Amelia and Jason carried out several experiments using a variety of oxidising and reducing agents. Elena recorded their observations and details about the substances used. Can you deduce the chemical change occurring in each of their experiments? Write a **balanced redox equation** to show the redox reaction occurring in each of the experiments.

   a. A small piece of **barium** metal, $Ba(s)$ was added to a **hydrochloric acid** solution, $HCl(aq)$. The metal dissolved giving a colourless solution and a colourless gas.
   b. Some **steel wool**, $Fe(s)$ is added to a copper **sulfate solution**, $CuSO_4(aq)$. The steel wool slowly dissolves while forming a salmon pink coating. The solution changes colour from blue to pale green.
   c. **Chlorine gas** was bubbled into a solution of **sodium iodide**. The solution went from colourless to brown in colour.
   d. An acidified **potassium permanganate** solution was added slowly to an **iron(II) sulfate** solution. The solution slowly changed colour from **pale green** to **pale brown**.
   e. Excess **oxalic acid** solution, $H_2C_2O_4(aq)$ was added to an **acidified potassium permanganate** solution. A **colourless gas** was observed to form, while the solution eventually changed in colour from **purple** to **colourless** (very pale pink).

CHAPTER 7 | ELECTROCHEMISTRY

7.1 Galvanic cells

Galvanic cells, also known as **electrochemical cells** or voltaic cells, are commonly referred to as cells or batteries. Their invention is attributed to **Alessandro Volta** who in 1800 published his discovery of the voltaic pile, a chemical cell that produced a steady electric current. Over the next few years **Humphry Davy** would use Volta's discovery and the process of electrolysis (see p78) to isolate and discover many new elements.

Today these cells are a highly developed technology used to power a great variety of industrial, medical and consumer devices like mobile phones, laptop computers, heart pacemakers, i-pods, cameras (Fig 1) and flashlights. All motor cars rely on batteries to power their ignition system and modern electric vehicles operating entirely with the aid of lithium-ion batteries have now been commercialised. It is hoped that vehicles like this and ones operating on the hydrogen/oxygen fuel cell (p86) may provide a more sustainable and lower carbon emitting alternative to fossil fuel powered vehicles.

Figure 1 The **digital camera** shown here uses a rechargeable **lithium-ion battery** as its power source. These batteries are becoming the cell of choice for many portable electronic devices as they have a good shelf life and an exceptional **energy density**.

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7.2 Operation of a galvanic cell

Galvanic cells use a **redox reaction** to produce a **voltage** (potential difference) that results in an electric current. They work by allowing a redox reaction to occur without direct contact between the oxidising and reducing agent. Under normal circumstances, chemical reactions only take place when the reacting particles come into contact (Collision theory).

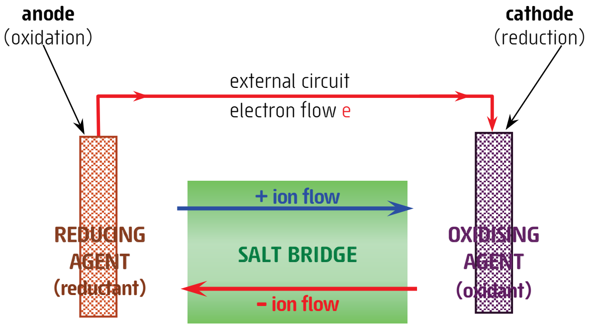
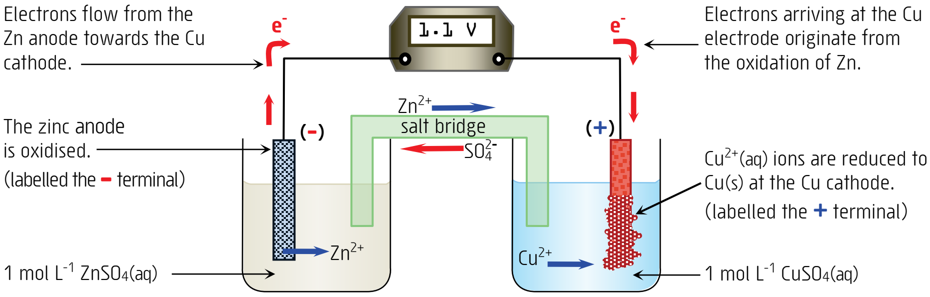


Figure 2 A **galvanic cell**, also known as an electrochemical cell, harnesses the electron transfer of a redox reaction to produce an electric current. It does this by preventing direct contact between the oxidising agent and reducing agent. To get from the reducing agent to the oxidising agent, electrons are forced to flow between **two electrodes**, from the anode to the cathode, via an external circuit. A **salt bridge** allows ions to move between the oxidising and reducing agent. If the external circuit is disconnected the redox reaction in the cell stops.

To achieve a redox reaction while maintaining separation of reagents a galvanic cell uses **two electrodes**. (See Fig 2.) One electrode, the **cathode**, is in contact with the **oxidising agent**; reduction occurs here. The other electrode, the **anode**, is in contact with the **reducing agent**; oxidation occurs here. The redox reaction can occur when a conductor (eg a copper cable) joins the two electrodes as it is the conductor that provides a pathway for electrons to flow from the reducing agent to the oxidising agent. In this way the reaction can take place without the reagents making physical contact. In normal use the conducting path directs this flow of electrons (ie the electric current) through the circuit of an appliance, eg an electric motor, where the energy of the electric current can do useful work.

For a galvanic cell to operate and produce an electric current, there must also be a pathway for both positive and negative ions to move between the anode and cathode. This is achieved using a structure called a **salt bridge**. The salt bridge prevents direct contact between the oxidising agent and reducing agent while allowing ions to pass between them. This movement of ions is essential as it prevents a build up of charge (caused by electrons flowing onto the cathode) from occurring on the electrodes. If this charge build up is not prevented then the cell will cease operating.

A simple example of a galvanic cell is the **Daniell Cell** (Fig 3) invented in 1836 by John Daniell. This simple but effective cell was a big improvement on Alessandro Volta's **voltaic pile**, the first ever galvanic cell.



oxidation half-cell $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

reduction half-cell $2e^- + Cu^{2+}(aq) \rightarrow Cu(s)$

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

Figure 3 The **Daniell cell** uses copper sulfate (**Cu^{2+}**) as the **oxidising agent** and zinc metal (**Zn**) as the **reducing agent**.

The zinc electrode, Zn becomes oxidised releasing zinc ions, $Zn^{2+}(aq)$ and electrons. These electrons flow from the zinc electrode, through the external conducting path, to the copper electrode. Here copper ions, $Cu^{2+}(aq)$ from the electrolyte move to the copper electrode to gain these electrons and become reduced to metallic copper, Cu.

A salt bridge completes the circuit allowing ions to move between the cathode and anode. This prevents a build up of negative charge at the cathode (due to excess SO_4^{2-} ions) and positive charge at the anode (due to excess Zn^{2+} ions).

The Daniel cell (above) can be represented schematically as **$Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s)$**. This **schematic cell diagram** represents the galvanic cell as two **couples**, the oxidised couple, ie $Zn(s)|Zn^{2+}(aq)$ and the reduced couple, ie $Cu^{2+}(aq)|Cu(s)$ with the oxidised couple written first followed by the reduced couple. A pair of vertical lines, representing a salt bridge, separates the two couples.

The essential components of all galvanic cells include the following.

- **Anode**: Oxidation occurs here. This electrode makes contact with the **reducing agent** (reductant) and is labelled the negative (**−**) terminal. (See border note.)
- **Cathode**: Reduction occurs here. This electrode makes contact with the **oxidising agent** (oxidant) and is labelled the positive (**+**) terminal. (See border note.)
- **Electrolyte**: Electrodes are immersed in an electrolyte solution. Ions in the electrolyte conduct charge in the solution and may themselves become oxidised or reduced.
- **Salt bridge**: Contains a non reactive electrolyte solution. It prevents direct contact of the oxidising and reducing agents while permitting ions to flow through it. Anions flow through the salt bridge towards the anode while cations flow to the cathode.
- **Oxidation half-cell**: This is the part of the cell where oxidation occurs. It consists of the anode plus the surrounding electrolyte.
- **Reduction half-cell**: This is the part of the cell where reduction occurs. It consists of the cathode plus the surrounding electrolyte.

Labelling the **anode** (**-**) and **cathode** (**+**) serves to remind us of the direction in which electrons flow as they enter and leave the galvanic cell. For this reason the **cathode** is labelled **+** (positive), as electrons enter the galvanic cell at this electrode. The **anode** is labelled **-** (negative) as electrons leave the galvanic cell from this electrode.

It must be noted that the electrode polarity and direction of electron flow are a result of the spontaneous redox reaction occurring in the cell.

Remember:

Anions = negative ions, eg Cl^-

Cations = positive ions, eg K^+, NH_4^+

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Attempt Set 10 # 1 and 2.

7.3 Measuring the strength of oxidising agents (oxidants)

The voltage produced by a galvanic cell is a measure of the **driving force** of the redox reaction occurring in the cell. It reflects the combined strength of the oxidising and reducing agents involved. The stronger these are the greater the tendency for the reaction to occur and the higher the cell voltage. (See Fig 4.) This property is used to rank the strength of different oxidising agents. The **table of standard reduction potentials** (p230) is such a ranking.

Standard reduction potential data is obtained by measuring the ability of a substance to be reduced by **hydrogen gas**. To measure this, the **standard substance, $H_2(g)$** along with its oxidation product **$H^+(aq)$**, is placed into the left half of a galvanic cell. The right half of the galvanic cell contains the **test substance**, the one having its standard reduction potential measured, along with its reduction product. (See Fig 5.)

When operating at standard conditions (ie 25 °C, 1.0 mol L^{-1} for aqueous species and 100.0 kPa for gases, see Fig 5) the cell produces a voltage known as the **standard cell potential**, **E^o_{cell}**. This cell voltage (E^o_{cell}) is due to the voltage or driving force of both the oxidation and reduction processes occurring in the cell. For ranking purposes though, the voltage of this galvanic cell is assigned wholly to the couple being tested. Thus the potential or voltage associated with the hydrogen half cell is arbitrarily assigned exactly **0 volts**. Cell voltages found this way give the **standard reduction potential**, **E^o_{red}** of the test couple.

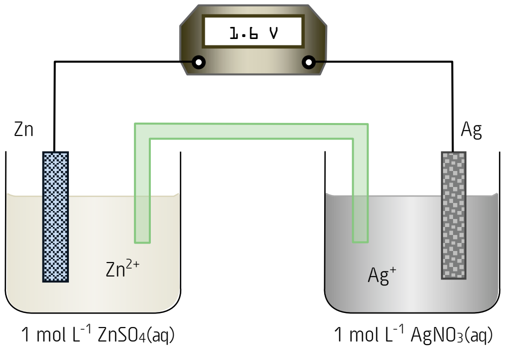
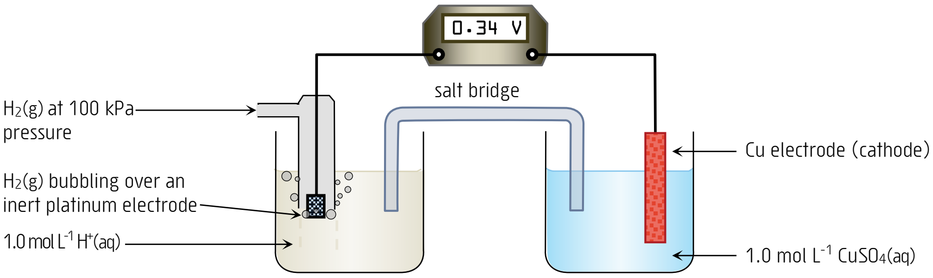


Figure 4 If the **Cu^{2+}**(aq)**|Cu**(s) couple of the Daniell cell shown in Fig 3 is replaced with a **Ag^+**(aq)**|Ag**(s) couple (above) then the cell voltage changes from **1.1 V** to **1.6 V**. The higher voltage shows $Ag^+(aq)$ is a stronger oxidising agent than $Cu^{2+}(aq)$.

By comparison, using a **Pb^{2+}**(aq)**|Pb**(s) couple in place of the **Cu^{2+}**(aq)**|Cu**(s) couple gives a voltage of only **0.6 V**. Thus $Pb^{2+}(aq)$ is a weaker oxidising agent than $Cu^{2+}(aq)$.



standard hydrogen half-cell $H_2(g) \rightarrow 2H^+(aq) + 2e^-$ **E^o = 0 Volts** (by definition)

copper half-cell (test cell) $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ **$E^o_{unknown}$**

overall redox $Cu^{2+}(aq) + H_2(g) \rightarrow 2H^+(aq) + Cu(s)$ **E^o_{cell} = 0.34 V** (measured)

Figure 5 This galvanic cell arrangement measures the ability of Cu^{2+} to oxidise $H_2(g)$. To do this, a **standard hydrogen half-cell** is connected to a test cell containing a copper electrode in 1.0 mol L^{-1} $CuSO_4(aq)$.

For the purposes of assigning standard reduction potentials, the reduction potential of $H^+(aq)$ or oxidation potential of $H_2(g)$ at standard conditions is arbitrarily assigned a value of exactly **0 volts**. Thus the **measured voltage**, 0.34 volts, is assigned as the **standard reduction potential** of $Cu^{2+}(aq)$, ie $E^o_{red}(Cu^{2+})$ = 0.34 volts.

Furthermore, as **temperature**, **ion concentration** and gas **pressure** affect the cell voltage it is necessary to use standard conditions so that consistent voltages are obtained. The **standard conditions** used are:

- aqueous concentrations of **1.0 mol L^{-1}**
- gas pressures of **100.0 kPa**
- a cell temperature of **298K (25 °C)**

The measured standard reduction potential of a substance may be positive or negative in value. The more positive it is the greater is the tendency for the substance to be reduced, ie the greater is its ability to oxidise other substances. Used this way, standard reduction potentials give a ranking of the oxidising strength of different substances. The stronger the oxidising agent the higher (more positive) is its E^o_{red}, conversely the weaker the oxidising agent the lower (more negative) is its E^o_{red}. (See Table 1.)

Table 1 Standard Reduction Potentials (E^o_{red}) compare the strength of oxidising agents.

Oxidising agent	Reduction half-equation	E^o_{red}(volts)	Tendency to occur	Oxidising agent strength	Reducing agent strength
F_2	$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.89	highest	$F_2(g)$ strongest	$F^-(aq)$ weakest
Br_2	$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.08	↑	$Br_2(l)$ ↑	$Br^-(aq)$ ↓
Ag^+	$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80		$Ag^+(aq)$	$Ag(s)$
Fe^{2+}	$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	-0.44		$Fe^{2+}(aq)$	$Fe(s)$
Na^+	$Na^+(aq) + e^- \rightleftharpoons Na(s)$	-2.71	lowest	$Na^+(aq)$ weakest	$Na(s)$ strongest

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Attempt Set 10 # 3.

7.4 Using the standard reduction potentials (SRP) table

The SRP table lists various reduction half-reactions along with their E^o_{red} values. Reactions are arranged from the most favourable (highest E^o_{red}) at the top, to least favourable (lowest E^o_{red}) at the bottom. Thus oxidising agents (oxidants), shown in red in Table 2, are ordered from **strongest** at the **top left** of the table to **weakest** at the **bottom left**.

Oxidation half-reactions are found in the table by reading each half-equation from **right to left** and changing the sign of its E^o. (See Example 1.) In this way the strongest oxidation half-reaction is found at the bottom of the table, reading right to left, and the weakest at the top. Thus the strongest reducing agents (reductants), shown in green in Table 2, are at the bottom right of the table and the weakest are at the top right of the table.

Example 1 Use the table of standard reduction potentials (SRP) to determine the **standard oxidation potential** for the following half-reactions.

	a. the oxidation of $I^-(aq)$ forming $I_2(s)$	**b.** the oxidation of $Fe(s)$ forming $Fe^{2+}(aq)$
Write the relevant oxidation half-equation.	$2I^-(aq) \rightleftharpoons I_2(s) + 2e^-$	$Fe(s) \rightleftharpoons Fe^{2+}(aq) + 2e^-$
Reverse this to make a reduction half-equation and use the SRP table to find **E^o_{red}**.	$I_2(aq) + 2e^- \rightleftharpoons 2I^-(aq)$ **$E^o_{red}(I_2)$ = +0.54 V**	$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$ **$E^o_{red}(Fe^{2+})$ = - 0.44 V**
Reverse the reduction half-equation and change the sign of E^o. This gives **E^o_{ox}**.	$2I^-(aq) \rightleftharpoons I_2(s) + 2e^-$ **$E^o_{ox}(I^-)$ = -0.54 V**	$Fe(s) \rightleftharpoons Fe^{2+}(aq) + 2e^-$ **$E^o_{ox}(Fe)$ = + 0.44 V**

Attempt Set 10 # 4 and 5.

The organisation of the SRP table allows it to be used to predict if a given redox reaction will actually take place, ie is **spontaneous**. (See Fig 6 p73.) A quick method to use is to '**inspect the position**' of the oxidising agent and reducing agent in the SRP table. If the **oxidising agent** is situated **above** the **reducing agent**, ie higher up in the table, then the reaction will occur. The reaction will not occur if the reducing agent is higher up in the table than the oxidising agent. (See border note 'shortcut' p73.)

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Table 2 Selection of standard reduction potentials.

	Reduction half-reaction with oxidising agents in red and reducing agents in green		E° (volts)
strongest oxidising agents	$F_2(g) + 2e^- \rightleftharpoons 2F^-$	weakest reducing agents	+2.89
	$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$		+1.76
	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$		+1.51
	$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-$		+1.36
	$Br_2(l) + 2e^- \rightleftharpoons 2Br^-$		+1.08
	$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$		+0.96
	$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$		+0.80
increasing oxidising agent strength	$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	increasing reducing agent strength	+0.77
	$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-$		+0.40
	$S(s) + 2H^+(aq) + 2e^- \rightleftharpoons H_2S(aq)$		+0.17
	$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$		0 Exactly
	$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$		-0.14
	$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$		-0.28
	$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$		-0.40
	$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$		-0.76
weakest oxidising agents	$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	strongest reducing agents	-2.36
	$Ba^{2+}(aq) + 2e^- \rightleftharpoons Ba(s)$		-2.91

Shortcut: For a **spontaneous** redox reaction, the oxidising agent (**red**) must be positioned above the reducing agent (**green**). For a quick check, place your **left index finger** on the oxidising agent (**red**) and place your **right index finger** on the reducing agent (**green**). If your **left** index finger is **above** your right index finger, then the redox reaction between these two reagents will be **spontaneous**.

Essentially this shortcut works as this arrangement of the oxidising and reducing agents always gives a positive value for $\mathbf{E^o_{cell}}$.

Limitations of SRP data: While SRP data can be used to determine the spontaneity of a reaction it says nothing about **rate**. This means a reaction with a large positive E^o_{cell} may have such a high activation energy that at normal conditions it is extremely slow and may appear as if the reaction is not occurring at all.

Furthermore, SRP data applies to reactions occurring at standard conditions. Thus if the concentration or pressure of an individual species in a half-reaction is significantly different to standard conditions then its E° changes and the half-reaction is now ranked differently compared to other reactions.

An alternative way to see if any given redox reaction will actually take place, ie if it is **spontaneous**, is to find its $\mathbf{E^o_{cell}}$. To do this, refer to the SRP table (Table 2) and find E^o_{ox} for the oxidation half-reaction and add this to E^o_{red} for the reduction half-reaction. This gives E^o_{cell} for the redox reaction as if it were occurring in a galvanic cell.

$\mathbf{E^o_{cell} = E^o_{reduction} + E^o_{oxidation}}$ (See border note.)

A **positive** value of E^o_{cell} means the redox reaction in question will be spontaneous, ie it will occur as written. A **negative** value of E^o_{cell} means the redox reaction will not occur, instead it would occur spontaneously in the reverse direction. (See Example 2.)

Defining E^o_{cell}: By convention, the standard cell potential, $\mathbf{E^o_{cell}}$ of a galvanic cell is given by the standard reduction potential of the cathode, $\mathbf{E^o_{red(cathode)}}$, **minus** the standard reduction potential of the anode, $\mathbf{E^o_{red(anode)}}$.

$\mathbf{E^o_{cell} = E^o_{reduction(cathode)} - E^o_{reduction(anode)}}$

As the numerical value of $\mathbf{- E^o_{reduction(anode)}}$ is equivalent to the value for the oxidation potential for the half-reaction occurring at the anode, ie $\mathbf{E^o_{oxidation(anode)}}$ then $\mathbf{E^o_{cell}}$ can be given as:

$\mathbf{E^o_{cell} = E^o_{reduction(cathode)} + E^o_{oxidation(anode)}}$

Example 2 Determine the E^o_{cell} for the following redox reactions and use this to predict if the reactions are spontaneous as written.

	Problem 1: Can bromine oxidise silver metal as shown? $Br_2(l) + 2Ag(s) \rightarrow 2Br^- + 2Ag^+(aq)$	**Problem 2**: Will $H^+(aq)$ oxidise silver metal as shown? $2H^+(aq) + 2Ag(s) \rightarrow H_2(g) + 2Ag^+(aq)$
Determine E° for both half-reactions.	$Br_2(l) + 2e^- \quad 2Br^-$ $\quad \mathbf{E^o_{red} = +1.08\ V}$ $Ag(s) \rightarrow Ag^+(aq) + e^-$ $\quad \mathbf{E^o_{ox} = -}$	$2H^+(aq) + 2e^- \quad H_2(g)$ $\quad \mathbf{E^o_{red} = 0.00\ V}$ $Ag(s) \rightarrow Ag^+(aq) + e^-$ $\quad \mathbf{E^o_{ox} = -\ 0.80\ V}$
Add the two E° values to find E^o_{cell}.	$\mathbf{E^o_{cell}} = (+1.08) + (-$ **= +0.28 volts**	$\mathbf{E^o_{cell}} = (0.00) + (-$ **= -**
Conclude reaction tendency.	As E^o_{cell} has a positive value (+0.28 volts) the reaction is **spontaneous** (will happen) as written.	As E^o_{cell} has a negative value (- spontaneous (will not happen) as written.

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Attempt Set 10 # 6, 7 and 8.

7.5 Predicting changes in a galvanic cell

Standard reduction potential data can be used to predict the chemical changes that are most likely to occur in a galvanic cell. Of all the species in a galvanic cell, the one most likely to be **reduced** is the one from the **left** of the table (in red in Table 2) and **highest** in the table. This will be the oxidising agent and it has the greatest reduction potential, E^o_{red} of any species in the cell.

The species most likely to be **oxidised** in a galvanic cell is the one closest to the **right** of the arrow (in green in Table 2) and **lowest** in the table. This is the reducing agent and it has the greatest oxidation potential, E^o_{ox} of any species in the cell. Thus the redox reaction occurring in the cell combines strongest oxidising agent with the strongest reducing agent. The maximum voltage available from the cell is the $\mathbf{E^o_{cell}}$ value for this redox reaction.

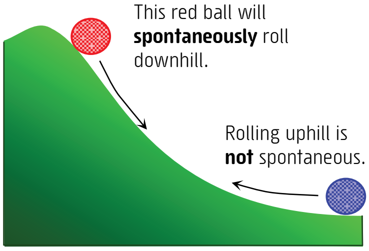


Figure 6 A chemical reaction that occurs as written is said to be **spontaneous**. Redox reactions are spontaneous in one direction but not in the opposite direction.

Take care when using SRP data as it only applies to **standard conditions**. (See Fig 5.) All of the species shown in the half-reaction (reactants and products) must be present in the galvanic cell at, or close to standard conditions for the reaction to be considered. This is especially relevant for **reactions involving $H^+(aq)$** or **$OH^-(aq)$**, even if these are not the species being oxidised or reduced. They must still be present in the galvanic cell, at or close to 1.0 mol L^{-1} if the reaction involving them is to be considered.

Example 3 Consider the galvanic cell shown here. Use SRP data and assume standard conditions apply to determine the following.

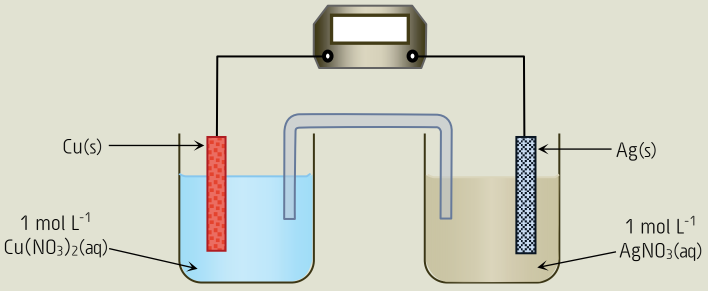
a. The **oxidising agent** and **reducing agent** in the cell.

b. The **anode** and **cathode**.

c. The overall **redox reaction** and the cell voltage, **E^o_{cell}**.

d. Direction of flow for **electrons**, **cations** and **anions**.

e. Initial changes that you would expect to **observe** at the anode and **cathode**.



a.	List all of the species in the cell at or close to standard conditions (ignore water).	Species shown to be present at standard conditions are: **$Ag(s)$, $Ag^+(aq)$, $NO_3^-(aq)$, $Cu(s)$ and $Cu^{2+}(aq)$.**
	Use the SRP table to find the species with the most positive reduction potential (E^o_{red}). This gives the reduced species (oxidising agent). **Alternatively** choose the oxidising agent by simply inspecting the table. (See 'shortcut' p73.)	$Ag^+(aq) + e^- \rightarrow Ag(s)$ $E^o_{red} = +0.80$ Volts ← **most favourable** $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E^o_{red} = +0.34$ Volts Thus **$Ag^+(aq)$ will be reduced**, ie $Ag^+(aq)$ is the oxidising agent. **Note**: The reduction of $NO_3^-(aq)$ requires $H^+(aq)$ to be present at or near 1.0 mol L^{-1} (ie standard conditions). As this is not the case then the reduction of $NO_3^-(aq)$ need not be considered.
	Use the SRP table to find the species with the most positive oxidation potential (E^o_{ox}). This gives the oxidised species (reducing agent). **Alternatively** choose the reducing agent by simply inspecting the table. (See 'shortcut'p73.)	$Ag(s) \rightarrow Ag^+(aq) + e^-$ $E^o_{ox} = -0.80$ Volts $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ $E^o_{ox} = -0.34$ Volts ← Thus **$Cu(s)$ will be oxidised**, ie $Cu(s)$ is the reducing agent. **Note**: No oxidation half-reaction is listed for $Ag^+(aq)$, $Cu^{2+}(aq)$ or $NO_3^-(aq)$.
b.	Oxidation occurs at the anode. Reduction occurs at the cathode.	$Cu(s)$ is oxidised so the anode is the **$Cu(s)$ electrode.** $Ag^+(aq)$ is reduced so the cathode is the **$Ag(s)$ electrode.**
c.	Add the two most favourable half-equations. This gives the overall redox equation. Add their respective E^o values to find the E^o_{cell}. Remember, changing the coefficients of a half-equation does not affect its E^o.	$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s)$ $E^o_{red} = +0.80$ Volts $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$ $E^o_{ox} = -0.34$ Volts $Cu(s) + 2Ag^+(aq) \rightarrow 2Ag(s) + Cu^{2+}(aq)$ **$E^o_{cell} = +0.46$ Volts = cell voltage**
d.	Electrons flow from the anode (through the external circuit) to the cathode. Anions (**-**) flow through the salt bridge towards the anode. Cations (**+**) flow through the salt bridge towards the cathode.	**Electrons** flow out of the cell, from the $Cu(s)$ electrode (anode) into the external circuit and onto the $Ag(s)$ electrode (cathode). **$NO_3^-(aq)$** ions flow internally through the salt bridge from the $Ag^+(aq)\|Ag(s)$ cell (cathode half-cell) to the $Cu(s)\|Cu^{2+}(aq)$ cell (anode half-cell). **$Cu^{2+}(aq)$** ions flow internally through the salt bridge from the $Cu(s)\|Cu^{2+}(aq)$ cell (anode half-cell) to the $Ag^+(aq)\|Ag(s)$ cell (cathode half-cell).
e.	Consider the half-reactions occurring in each half-cell and so determine the visible changes that would occur at each electrode and in the electrolyte.	**Anode half-cell**: The copper electrode will dissolve and lose mass. The electrolyte which is a blue colour will become more intensely blue. **Cathode half-cell**: The silver electrode will gain mass as a shiny silvery deposit forms on the electrode. No apparent change occurs in the electrolyte.

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Complete Set 10.

Set 10 Understanding galvanic cells

1. Use the list of terms to **complete** the following passage about **galvanic cells**.

   Everyday devices, like the dry cell used in torches and lithium-ion batteries found in portable laptop computers, are examples of (a) __________. These devices use a (b) __________ to create an electric potential, ie voltage, giving the galvanic cell its ability to produce an (c) __________.

   Galvanic cells are designed so that the oxidising agent and reducing agent are not in (d) __________. Instead, the oxidising agent is located in the (e) __________ half-cell in contact with an electrode called the (f) __________. The reducing agent is in the oxidation half-cell in contact with another (g) __________ called the (h) __________. This arrangement prevents the (i) __________ reaction from occurring in the cell when the cell isn't being used.

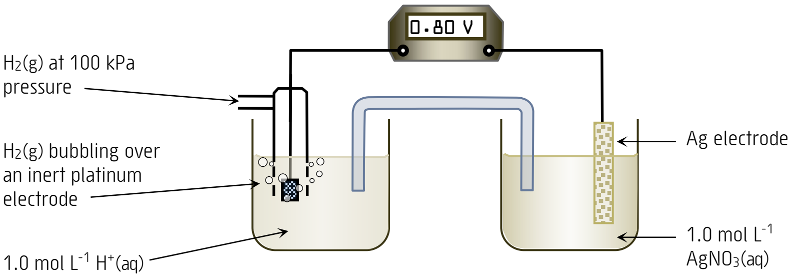
   When in use an external conducting path attaches the anode to the cathode. This allows (j) __________ to occur at the cell's anode, releasing electrons that pass out of the cell through the external conducting path and into the cell's cathode. At the cathode electrons are (k) __________ as the oxidising agent becomes reduced.

   Free ion flow between the oxidation half-cell and the reduction half-cell is provided by the (l) __________. It allows (m) __________ to flow from the anode to the cathode. Anions flow in the opposite direction. Without a salt bridge, both the cathode half-cell and anode half-cell would each form a (n) __________ that would stop the cell from operating.

electrode
redox reaction
redox
reduction
direct contact
cathode
anode
galvanic cells
positive ions
salt bridge
net charge
oxidation
used
electric current

2. **Sketch** the galvanic cell represented by $Mg(s)|Mg^{2+}(aq)||Co^{2+}(aq)|Co(s)$. Label the anode, cathode, salt bridge and show the composition of each electrode and half-cell.

3. The galvanic cell shown here is used to measure the standard reduction potential for silver ions, $Ag^{+}(aq)$. You may assume **$Ag^{+}(aq)$ is reduced** as the cell operates.



   The following questions refer to the operation of this cell.

   a. Write a **half-equation** for the reaction occurring in the $Ag/AgNO_3$ half-cell.
   b. Write a **half-equation** for the reaction occurring in the hydrogen half-cell.
   c. Give the **schematic cell diagram** (see p71) for this cell.
   d. Why is it necessary for hydrogen gas to be present at the electrode surface at a pressure of 100 kPa and for the $H^{+}(aq)$ concentration to be 1.0 mol L^{-1}?
   e. What is the **role** of the platinum electrode in the hydrogen half-cell?
   f. In measuring standard reduction potentials, as shown here, the voltage reading on the voltmeter (0.80 V) is attributed solely to the reduction of silver ions, $Ag^{+}(aq)$. Does the hydrogen half-cell contribute to the overall voltage of this galvanic cell? **Explain**.

4. Use a table of standard reduction potentials to determine **E^{o}** for the following half-reactions as described.

   a. $Cl_2(g) + 2e^{-} \rightarrow 2Cl^{-}(aq)$
   b. $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$
   c. $H_2C_2O_4(aq) \rightarrow 2CO_2(g) + 2H^{+}(aq) + 2e^{-}$
   d. $NO(g) + 2H_2O(l) \rightarrow NO_3^{-}(aq) + 4H^{+}(aq) + 3e^{-}$
   e. The oxidation of $Cu(s)$ forming $Cu^{2+}(aq)$.
   f. The oxidation of $Mn^{2+}(aq)$ in an acid solution to form $MnO_4^{-}(aq)$.

5. Use a table of standard reduction potentials to answer the following.
    a. **Rank** these oxidising agents from strongest to weakest.
        i. $Br_2(l)$ $I_2(s)$ $Cl_2(g)$
        ii. acidified $Cr_2O_7^{2-}(aq)$ acidified $MnO_4^-(aq)$ $Cl_2(g)$
        ii. $H^+(aq)$ $Cu^{2+}(aq)$ $Ag^+(aq)$
    b. **Rank** these reducing agents from strongest to weakest.
        i. $Cu(s)$ $Ca(s)$ $Ni(s)$
        ii. $Br^-(aq)$ $I^-(aq)$ $Cl^-(aq)$

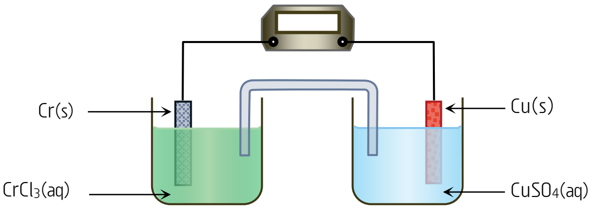
6. Are the following redox reactions going to happen as written, ie are these reactions spontaneous? **Support your answer** with reference to the table of standard reduction potentials. You may do this by determining E^0_{cell} for the reaction as written or you may wish to refer to the relative positions of the oxidising and reducing agents in the table of standard reduction potentials. Assume all species are present at standard conditions.
    a. $Cu^{2+}(aq) + Sn(s) \rightarrow Sn^{2+}(aq) + Cu(s)$
    b. $2Cl^-(aq) + I_2(s) \rightarrow Cl_2(g) + 2I^-(aq)$
    c. $Cl_2(g) + 2I^-(aq) \rightarrow I_2(s) + 2Cl^-(aq)$
    d. $2Al(s) + 6H^+(aq) \rightarrow 3H_2(g) + 2Al^{3+}(aq)$
    e. $2Ag(s) + 2H^+(aq) \rightarrow 2Ag^+(aq) + H_2(g)$
    f. $Cu(s) + 2H^+(aq) \rightarrow Cu^{2+}(aq) + H_2(g)$
    g. $2MnO_4^-(aq) + 10Cl^-(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5Cl_2(g) + 8H_2O(l)$

7. Kirsten has proposed a series of chemical experiments to test the hypothesis '**Metal elements produce hydrogen gas when added to acid solutions**.' She has chosen to use 10.0 mL of 1.0 mol L^{-1} hydrochloric acid with each of the metals **nickel**, **copper**, **tin**, **aluminium**, **zinc** and **silver**. Assume she planned to carry out the experiments at standard conditions.
    a. What **chemical test** can be used to verify the formation of hydrogen gas?
    b. Would you expect her results to support her hypothesis? **Support your answer** with reference to **SRP** data.
    c. If Kirsten had chosen to use a different acid like dilute sulfuric acid, phosphoric acid or even ethanoic acid then apart from different reaction rates her results would have been much the same as with hydrochloric acid. **Nitric acid**, however, would have produced significantly different results. Instead of hydrogen gas, the gas nitrogen monoxide, NO would have been produced with all of the metals, including $Cu(s)$ and $Ag(s)$. **Explain**, with reference to **SRP** data (p230), why this would happen with nitric acid.

8. Matthew has been given the laboratory task of correctly identifying some samples of different metals. He has been given an **unlabelled strip** of each of the metals in pairs as listed below. Matthew has the usual laboratory equipment and reagents at his disposal. He has decided to use a chemical test based on redox reactions to tell the metals apart. His proposed tests are described below. Will these tests work as planned? Answer **yes** or **no**. Refer to standard reduction potential data to **support your answer**. You may assume all species are present at standard conditions.
    a. Pair of metals: **Silver** and **tin**
        Test: Place both metal strips separately into a solution of $CuSO_4(aq)$. [$Cu^{2+}(aq)$ and $SO_4^{2-}(aq)$]
        Result: Tin dissolves forming a salmon-pink deposit while silver shows no change.
    b. Pair of metals: **Cobalt** and **nickel**
        Test: Add some hydrochloric acid solution [$H^+(aq)$ and $Cl^-(aq)$] to both.
        Result: Nickel produces a colourless gas while cobalt shows no reaction.
    c. Pair of metals: **Zinc** and **lead**
        Test: Place a piece of each metal in separate test tubes with some nickel(II) nitrate solution [$Ni^{2+}(aq)$ and $NO_3^-(aq)$].
        Result: Zinc will dissolve and form a coating of a grey metallic substance while lead shows no reaction.

9. Two chemistry students working on an electrochemical cell project have constructed the galvanic cell shown here. From their research they understand the half-reactions occurring in the galvanic cell are the ones shown.

$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$ and $Cr(s) \rightarrow Cr^{3+}(aq) + 3e^{-}$



Using this information, answer the following questions about the operation of their cell.

a. What is the **overall redox reaction** occurring in this cell?

b. What **potential difference** (voltage) can this cell produce at standard conditions?

c. Having constructed the cell as shown, our two students are disappointed to see the maximum voltage obtained is only 0.5 volts. **Suggest** why the voltage is not as predicted in (b).

d. Name the **anode** and **cathode** of this cell.

e. Over time, what **changes** would be seen at each electrode?

f. Describe the movement of **electrons** as the cell operates.

g. Describe the movement of **ions** as the cell operates.

10. An investigation into the operation of galvanic cells involves the following cells. Each cell is set up to operate at standard conditions. Refer to the table of standard reduction potentials to help answer the following questions about these cells.

i. Name the **anode** and **cathode** of each cell.

ii. Write an equation to show the most likely **anode half-reaction**.

iii. Write an equation to show the most likely **cathode half-reaction**.

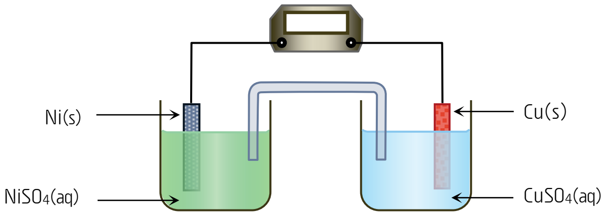
iv. What is the overall **redox reaction** occurring in each cell and what is the expected **cell voltage** under standard conditions?

v. Over time, what **changes** would be seen at each electrode?

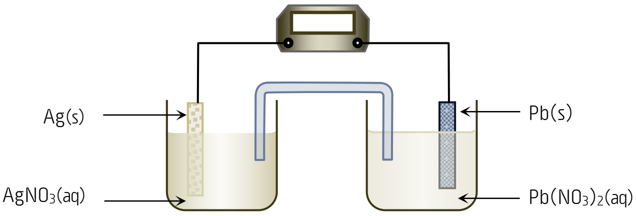
vi. Describe the movement of **electrons** as the cell operates.

vii. Name the **ions** present in the electrolyte of this cell and describe the **direction** they move as the cell operates.

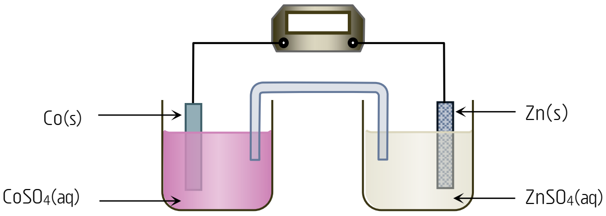
a.



b.



c.



LEOAN and **GERCP**

For a **galvanic cell**:

Loss of **E**lectrons is **O**xidation which occurs at the **A**node and is labelled the **N**egative electrode, ie **LEOAN**.

Gain of **E**lectrons is **R**eduction which occurs at the **C**athode and is labelled the **P**ositive electrode, **GERCP**.

Electrons flow from the negative electrode of a galvanic cell through an external circuit to the positive electrode.

7.6 Electrolysis

The process of electrolysis is carried out in a type of electrochemical cell known as an **electrolytic cell** (or electrolysis cell). These cells consist of a pair of **electrodes** connected to a DC electric power supply. When the electrodes are dipped into a **molten** or **dissolved** electrolyte the energy of the applied DC electric potential causes an otherwise non-spontaneous redox reaction to occur. (See Fig 7.) In this regard the operation of an electrolysis cell is the **reverse** of what occurs in a **galvanic cell** as in the galvanic cell the energy available from a spontaneous redox reaction is used to produce an electric potential.

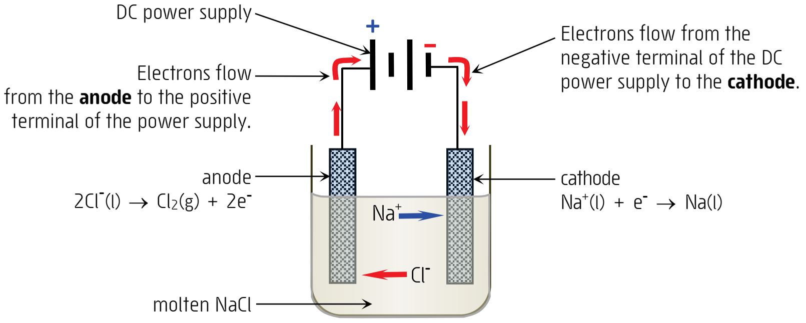


Figure 7 The electrolysis of **molten NaCl** using inert platinum, Pt electrodes results in the formation of Na(l) and $Cl_2(g)$ by the non-spontaneous redox reaction:

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

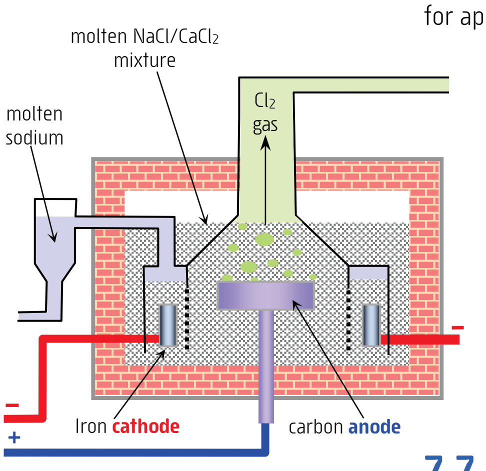
Positive ions, Na^+ in the electrolyte migrate toward the negative electrode where they gain an electron to form Na(l). Simultaneously, negative ions, Cl^- move to the positive electrode, lose an electron and form $Cl_2(g)$.

It is important to realise that in an electrolytic cell it is the applied DC voltage that provides the energy needed to cause the movement of charge and the resulting redox reaction. This is the reverse of what happens in a galvanic cell; here a spontaneous redox reaction happens inside the cell and it provides the energy needed to cause a flow of charge and electrons, ie the electric current.

The components of an electrolytic cell include:

- **DC power supply**: This draws electrons away from one electrode, the anode (**+**) and forces them onto the other electrode, the cathode (**-**) of the electrolytic cell. It is the applied DC voltage that provides the energy needed to cause oxidation to occur at the anode and reduction to occur at the cathode.
- **Anode**: Oxidation occurs here. This is the electrode attached to the positive terminal of the DC power supply. It conducts electrons out of the cell towards the positive terminal of the power supply.
- **Cathode**: Reduction occurs here. This is the electrode attached to the negative terminal of the DC power supply. It conducts electrons from the power supply into the electrolyte.
- **Electrolyte**: Electrodes are immersed in a molten electrolyte (or an aqueous electrolyte, ie one that contains water). **Anions** (**-**) in the electrolyte are attracted to the anode (**+**) while **cations** (**+**) move to the cathode (**-**).

Electrolysis is a very useful chemical technique for the extraction of metals like aluminium and gold, production of substances like chlorine (Fig 8.), sodium and sodium hydroxide and for applications such as silver and chrome plating of metals.



cathode: $Na^+(l) + e^- \rightarrow Na(l)$

anode: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

Figure 8 The **Downs cell** is an electrolytic cell used for the extraction of **sodium** and **chlorine** from NaCl. The cell consists of steel and carbon electrodes immersed in a molten mixture (above 600 °C) of NaCl and $CaCl_2$.

Sodium metal is formed at the cathode of the electrolytic cell. At these temperatures (>600 °C) sodium forms a low density liquid that floats to the surface of the molten salt mixture. Here it is siphoned off, taking care to prevent its contact with air as it would react explosively to form an oxide.

Chlorine gas is formed at the anode and is a valuable by-product of this process. Chlorine gas must also be prevented from contacting the molten sodium as these would react explosively in a spontaneous reaction to reform NaCl.

Electrolytic processes like this, which extract metals from their ores, are known as **electrowinning**. Reactive metals like Li, Na, K, Ca, Mg and Al are typically extracted from their ores by electrowinning.

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Attempt Set 11 # 1.

7.7 Electrolysis of a molten salt

This process uses an **electrolytic cell** consisting of a pair of **inert electrodes** (eg platinum electrodes) dipped into a **molten** salt and connected to a DC electric power supply. (See Example 4.) Applying a DC voltage to the electrodes causes these to become oppositely charged. If the applied voltage is sufficiently high then negative ions (anions) from the molten salt migrate to the positive electrode (anode) where upon contact with the electrode they lose electrons to become oxidised. Simultaneously, positive ions (cations) from the salt migrate to the negative electrode (cathode) where they gain electrons to become reduced.

Example 4 An electrolytic cell contains molten $CuBr_2$ and two inert platinum electrodes, A and B. The cell is connected to a DC power supply as shown. For this cell:

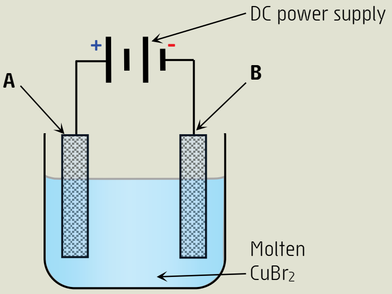
a. Determine the direction of electron flow

b. Name the cathode

c. Determine which ions

d. Write half and **B**.

e. Describe any changes you would expect to observe



Answer	Explanation
a. Electrons flow from A through the conducting wire and power supply to B.	The applied DC voltage determines the flow of electrons, ie electrons will flow out of the power supply negative terminal and into its positive terminal.
b. B is the cathode, reduction occurs here.	Electrons leave the negative terminal of the power supply and flow onto the electrode attached to it. This electrode gains electrons thus reduction occur here.
c. Br^- ions flow to electrode A. Cu^{2+} ions flow to electrode B.	Anions (**-** ions) flow to the anode (**+** electrode). Cations (**+** ions) flow to the cathode (**-** electrode).
d. Electrode A: $2Br^-(l) \rightarrow Br_2(g) + 2e^-$ Electrode B: $Cu^{2+}(l) + 2e^- \rightarrow Cu(s)$	Oxidation occurs at the anode. Reduction occurs at the cathode.
e. Electrode A: A brown gas with a choking odour forms here. Electrode B: The electrode increases in mass as it forms a shiny salmon-pink deposit.	Since Br_2 is formed at A and it is a brown gas (bromine is a gas above 59 °C) with a choking odour. As Cu is formed at B and is a shiny salmon-pink metal.

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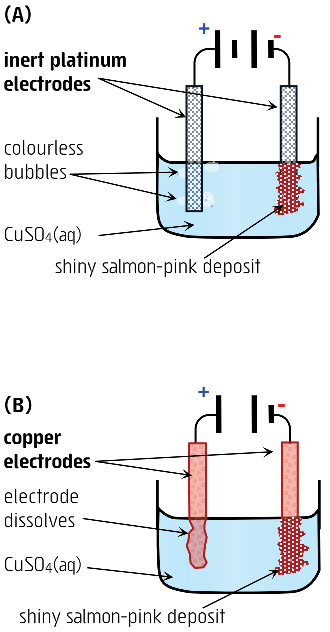
Attempt Set 11 # 2 and 3.

7.8 Electrolysis of an aqueous solution

It is a more complex problem to predict the electrode reactions that occur for electrolytic cells containing an **aqueous salt** (ie contain water) or having electrodes that are potentially reactive. (See Fig 9.) In these cells water is often oxidised or reduced or the anode itself may be oxidised. Changes taking place in these cells can be **inferred** from **observing** the cell as it operates.

- If **water** is **oxidised** then a colourless gas is formed at the anode and the solution pH falls in the vicinity of the anode. The anode reaction is:
  $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
- If **water** is **reduced** then a colourless gas is formed at the cathode and pH rises in the vicinity of the cathode. The cathode reaction is:
  $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$
- If a **metallic electrode** is **oxidised** then the **anode** is seen to dissolve and lose mass.

Figure 9 Electrolysis of a copper(II) sulfate solution using **inert platinum** electrodes **(A)** and **copper electrodes (B)**.



Example 5 A student investigating the electrolysis of an **aqueous** copper(II) sulfate solution performed the experiment with **inert platinum electrodes (A)** then repeated the process using a pair of **copper electrodes (B)**. (See Fig 9.)

With platinum electrodes a colourless gas formed at the anode and a few drops of indicator showed the pH had dropped in its vicinity. The cathode formed a coating of a shiny salmon-pink material.

Using copper electrodes produced the same observation at the cathode; however, no gas was noted at the anode. Instead the copper anode dissolved and was observed to lose mass over time.

a. What can be inferred from the observations for the electrolysis experiment using **platinum** electrodes? Write a half-equation for the reaction occurring at each electrode.

b. What can be inferred from the observations for the electrolysis experiment using **copper** electrodes? Write a half-equation for the reaction occurring at each electrode.

a. Anode The colourless gas and drop in pH indicate $O_2(g)$ and $H^+(aq)$ are formed from the oxidation of water, ie $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$.

Cathode . Thus $Cu^{2+}(aq)$ ions are being reduced, ie $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$.

b. Anode Dissolving and loss of mass of the copper electrode suggest it was being oxidised to soluble $Cu^{2+}(aq)$, ie $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$.

Cathode . Thus $Cu^{2+}(aq)$ ions are being reduced, ie $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$.

In a **galvanic** cell and **electrolytic** cell:

Anions (**-** ions) always move to the **anode**.

Cations (**+** ions) always move to the **cathode**.

Also:

LEOA: **L**oss of **E**lectrons is **O**xidation which always occurs at the **A**node.

and

GERC: **G**ain of **E**lectrons is **R**eduction which always occurs at the **C**athode.

One significant difference:
In an **electrolysis** cell the applied DC voltage determines the flow of electrons and this determines the anode and cathode.

In a **galvanic** cell it is the spontaneous redox reaction occurring inside the cell that determines the flow of electrons and hence which electrode is the anode and cathode.

#**Caution:** Half-equations for the oxidation and reduction of water involve some of the species: $H_2(g)$, $O_2(g)$, $H^+(aq)$ and $OH^-(aq)$. Although it is an oversimplification to assume all of these species are present at standard conditions it is necessary to do so in order to use SRP data.
Neither the SRP data table in this book nor the current WACE data sheet carry reduction potential data for non-standard conditions.

eBook Quiz 7.8 @ lucaspublications.com.au.

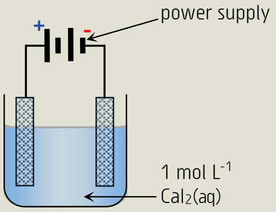
Complete Set 11.

Reactions occurring during the electrolysis of an **aqueous** salt solution (Example 6) can be predicted from standard reduction potential data. As with a galvanic cell, the most probable electrode reactions in an electrolysis cell will be the ones with the most positive E^o. It should be noted that these predictions are limited to situations involving standard conditions of temperature, pressure and concentration.

Example 6 Consider the electrolysis of an aqueous $CaI_2(aq)$ solution using **inert** platinum electrodes.

Determine the most probable **anode** and **cathode** half reactions and the **overall reaction** for this cell.

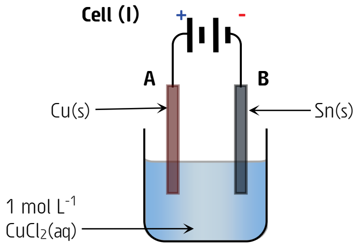
Assume **standard conditions** of temperature, pressure and concentration apply.

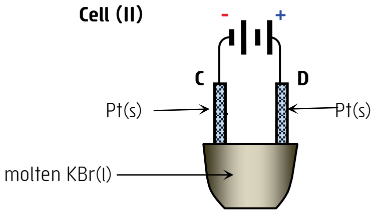


List all of the species present in the cell; include water. One of these is **reduced** and one is **oxidised**.	The species present are $Ca^{2+}(aq)$, $I^-(aq)$ and **$H_2O(l)$**#.
Use SRP data to find the species with the most positive E^o_{red}. This gives the **reduction** half-equation, ie the cathode half-reaction. #**Caution**, see border note.	$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ E^o_{red} = - # ← **most favourable** $Ca^{2+}(aq) + 2e^-$ $Ca(s)$ E^o_{red} = -2.87 Volts Of the two possible reduction half-reactions, the reduction of water is the more favourable as it has the more positive (less negative) E^o_{red}.
Use SRP data to find the species with the most positive E^o_{ox}. This gives the **oxidation** half-reaction, ie the anode half-reaction.	$2I^- \rightarrow I_2(s) + 2e^-$ E^o_{ox} = -0.54 Volts ← **most favourable** $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $_{ox}$ = -1.23 Volts# Of the two possible oxidation half-reactions, the oxidation of I^- more favourable as it has the more positive (less negative) E^o_{ox}.
Add the anode and cathode half-reactions to give the **overall cell reaction**.	Cathode half-reaction: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ Anode half-reaction: $2I^- \rightarrow I_2(s) + 2e^-$ **Overall cell reaction**: $2H_2O(l) + 2I^- \rightarrow I_2(s) + H_2(g) + 2OH^-(aq)$

Set 11 Electrolysis

1. Consider the two electrolytic cells shown here.
   a. Describe the direction of electron flow occurring between the electrodes A, B, C and D and the terminals of the power supply.
   b. What type of half-reaction is occurring at the electrodes A, B, C and D?
   c. Name the ions that migrate towards each of the electrodes A, B, C, and D.
   d. Identify the cathode in each cell.





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2. Two chemistry students investigating the electrolysis process assembled an electrolytic cell. They used inert platinum electrodes and a **molten** tin(II) bromide electrolyte [$SnBr_2(l)$, melting point 216 °C].
   a. Construct a **sketch** for the cell. Label your sketch showing the polarity of the power supply, materials of which the cell is made, anode, cathode, direction of electron flow and the direction of ion flow in the electrolyte.
   b. The students apply a suitably high voltage to the electrodes of the cell until they observe a reaction occurring within the electrolysis cell. Write the **half-equation** for the resulting anode and cathode reaction in their electrolysis cell.
   c. List three **safety precautions** the students should take when operating this cell. **Justify** your choices.

3. Write the anode and cathode **half-reactions** which would occur during the electrolysis of the following **molten salts** (no water) using **inert** electrodes. Also **describe** the changes you would expect to see at each of the electrodes.
   a. $NaBr(l)$ b. $MgCl_2(l)$ c. $Al_2O_3(l)$ d. $CuI_2(l)$

Note: In Question 3, if a metal is produced, you may assume the temperature of the molten salt is such that the metal is in a molten form.

4. As described earlier, the **Downs cell** (Fig 8, page 78) is used for the extraction of sodium metal and chlorine gas from molten sodium chloride, $NaCl(l)$. The electrolytic process uses steel and carbon electrodes immersed in a molten mixture of NaCl and $CaCl_2$. A temperature of above 600 °C is needed to melt the mixture of salts. Under these conditions, sodium is reduced at the steel cathode. As sodium is a low density liquid at these temperatures it floats to the surface where it can be removed by siphoning off.
   a. For economic reasons, $CaCl_2$ is deliberately added to the electrolyte melt. Research the melting point of NaCl and $CaCl_2$ and then **account** for the addition of $CaCl_2$ to the electrolyte mixture.
   b. Describe the movement of sodium and chloride ions in the electrolyte of the Downs cell.
   c. Write the **anode** and **cathode half-reactions** for the Downs cell.
   d. Although it would be much cheaper to electrolyse an aqueous solution of NaCl it is no use in the production of sodium. **Suggest** how the presence of water might interfere with the reduction of sodium ions.

5. Several electrolysis cells were assembled using **inert platinum electrodes** and various **aqueous** solutions. The composition of the electrolyte for each cell is shown below. Assume the cells are operating at **standard conditions** and use standard reduction potentials to predict the most likely **anode** and **cathode** half-reaction for each cell.
   a. Electrolyte contains: $H_2O(l)$, $Zn^{2+}(aq)$ and $Br^{-}(aq)$.
   b. Electrolyte contains: $H_2O(l)$, $Cu^{2+}(aq)$, $Sn^{2+}(aq)$, and $Cl^{-}(aq)$.

6. Two chemistry students assembled an electrolytic cell using inert platinum electrodes. They tested the cell with the different electrolyte solutions a-d.
   a. $CuI_2(aq)$ b. $NiSO_4(aq)$ c. $HBr(aq)$ d. $NaCl(aq)$

   For each of the electrolytes used answer the following. Standard conditions apply.
   i. What is the most favourable **cathode** reaction?
   ii. What is the most favourable **anode** reaction?
   iii. Describe any **observations** you would expect at each of the electrodes

CHAPTER 8 | ELECTROCHEMISTRY IN ACTION

8.1 Electrochemistry in society

Figure 1 Galvanic cells like the dry cell are typically referred to as batteries. Specifically though, a battery is a group of two or more galvanic cells, usually connected in series (terminals connected **+** to **-**), to produce a higher voltage than a single cell would.

The common rectangular 9 V dry cell battery for example, has six dry cells arranged in series inside a single container. Individually each cell produces 1.5 V but connected in series they produce 9 V.

Australians, like other people in modern societies rely heavily on the portable power of **galvanic cells**, more commonly referred to as **batteries**. (See Fig 1.) An Australian Government commissioned report for example, estimates 137,000 to 153,000 tonnes of lead-acid batteries (car batteries) were used and disposed of in Australia in 2012-2013. While batteries like this are used in the ignition systems of all motor vehicles, a great variety of other battery types are used to power a diverse range of electrical devices, from heart pacemakers to iPads, mobile phones, backup power supplies, spacecraft electrical systems and much more.

The concept of using a **chemical reaction** in a battery to **generate electricity** was first demonstrated in 1800 by Alessandro Volta. His battery, the voltaic pile as it became known was mainly the preserve of scientific researchers. Today, galvanic cells (also known as voltaic cells or electrochemical cells) in their many diverse forms are an essential part of our daily lives. The continuing development of more efficient galvanic cells is an active area of scientific research. In particular, current research and development in the area of **lithium-ion battery** technology and hydrogen-oxygen **fuel cell** technology aims to produce a potentially lower emission alternative to the internal combustion engine currently used in most motor vehicles. While these galvanic cells will most probably still rely on the use of fossil fuels to produce their power source, ie electricity or hydrogen gas, their high efficiency will result in reduced greenhouse gas emissions. The possibility also exists for producing hydrogen gas by electrolysis using electricity generated from renewable energy sources like hydro, wind, wave, geothermal or solar energy.

Figure 2 The Tesla 'Gigafactory' commenced construction in June 2014 outside Sparks, Nevada. Lithium-ion battery construction will commence there in 2017. Once in full production the Gigafactory's annual lithium-ion battery output will exceed the 2013 total worldwide production. Renewable energy (solar and wind) will provide all of the plant's energy needs while lithium-ion batteries will be used for energy storage.

Image courtesy Tesla Motors, Inc: Alexis Georgeson.

Although the commercial use of fuel cells in motor vehicles is now a reality (Fig 15 p86) their widespread future use will be limited by the availability of hydrogen and the infrastructure needed to generate and distribute it. One organisation, the 'International Partnership for Hydrogen and Fuel Cells in the Economy'; consisting of eighteen partner countries including Australia, Germany, Japan and the US, is dedicated to fostering global cooperation on infrastructure development, research and common standards relating to a hydrogen economy and fuel cell technology.

Other significant applications of electrochemistry include the use of electrolysis for **electrorefining** metals like copper and **electroplating** to produce durable and decorative metal coatings. This chapter explores how the principles of electrochemistry operate in commercial galvanic cells, electrorefining and electroplating.

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Attempt Set 12 # 1.

8.2 Types of galvanic cells*

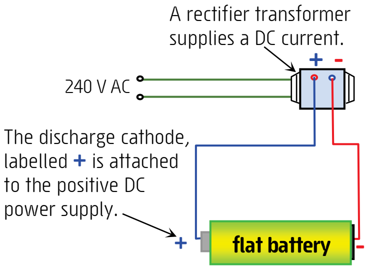
Non-rechargeable galvanic cells like the **dry cell** (p83) are known as **primary cells**. These contain a fixed amount of oxidant and reductant which once consumed cannot be replaced or regenerated. These single use cells are discarded once 'flat'.

Secondary cells like the **lead-acid cell** (typically called a car battery, p84-5) are **rechargeable**. When galvanic cells like this go flat they can be recharged by applying a DC voltage that forces current through the cell in an opposite direction to that which occurs spontaneously during its discharge. (See Fig 3.) Recharging is essentially a process of electrolysis where electrical energy is used to force the spontaneous discharge reactions to be **reversed** and in the process regenerate the oxidant and reductant originally present in the charged cell. Although secondary cells are rechargeable there is a limit to the number of recharge cycles they will undergo before their electrodes become physically degraded and no are longer able to be recharged.

A third type of galvanic cell is the **fuel cell**. In these cells the oxidant and reductant are continuously fed into the cell. The reductant is typically a fuel (ie a combustible substance) such as hydrogen, methane or methanol for example. The oxidant is usually oxygen gas. Fuel cells have a very long life and can theoretically operate without limit as long as the oxidant (oxygen) and reductant (fuel) are supplied into the cell.

* -8.5 are typical examples of the various cell types. These are not intended to be prescriptive of the WACE Chemistry course. **Consult the Chemistry WACE manual** for more specific guidance.

Figure 3 Recharging a secondary cell.



A rectifier transformer supplies a DC current.

The discharge cathode, labelled **+** is attached to the positive DC power supply.

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Attempt Set 12 # 2.

8.3 Primary cells

The dry cell: Originally patented in 1866 by Georges Leclanché, the dry cell is the simplest and most inexpensive of the non-rechargeable cells in use today. It produces a maximum voltage of 1.5 V. Its design, however, is such that the voltage produced by the cell slowly decreases over the life of the cell. A further disadvantage of this cell is its very low energy to mass ratio (energy density). However, these batteries are inexpensive and ideal for use in flashlights, portable radios and calculators where low currents are required and a decreasing voltage is not an issue.

Primary cells like the dry cell, are not able to be recharged, so flat batteries are discarded. The materials used in a dry cell (Zn, MnO_2, NH_4Cl and C) pose **negligible environmental impact**. Thus spent dry cells are considered non-hazardous waste and can be disposed of in the normal household waste stream, though this is becoming increasingly discouraged. (See Fig 4.) At present there is no economic process for recycling spent dry cells.

Figure 4 While **dry cell batteries** are considered **non-hazardous** waste, they do contain large quantities of zinc, which upon disposal can leach into the soil and groundwater. The toxicity of zinc in the environment is a complex issue as the element **zinc** is actually an important dietary component while also being potentially toxic.

It is normal for wheat, for example, to contain up to 60 ppm zinc. In fact diets lacking in zinc can result in a variety of illnesses. However, **excessive intake** of zinc is **harmful** and potentially fatal. In particular even low concentrations of zinc ions, $Zn^{2+}(aq)$ are known to be **toxic** to plants and some animals.

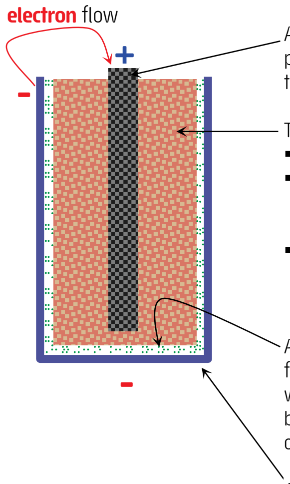


Figure 5 The dry cell uses zinc as the reducing agent and manganese(IV) oxide, MnO_2 as the oxidising agent. A graphite rod, C and powdered graphite, C conduct electrons to the surface of individual MnO_2 particles within the cathode paste. Ammonium chloride is also incorporated into the cathode paste and serves as a salt bridge as well as providing protons (NH_4^+ is a weak acid) needed in the reduction of MnO_2.

However, the use of ammonium ions is problematic, as over time their acidic nature causes the zinc anode to dissolve forming Zn^{2+} ions. For this reason dry cells have a low shelf life of around a year.

A **carbon** rod, C is the conducting path for electrons moving into the cathode paste.

The **cathode paste** contains:

- MnO_2, the oxidising agent.
- NH_4Cl, the electrolyte. NH_4^+ ions provide protons needed for MnO_2 reduction.
- graphite powder, C conducts electrons through the cathode paste.

A **porous fibre** membrane allows ion flow between the cathode and anode while preventing direct contact between the reductant, Zn and oxidant, MnO_2.

A **zinc anode** is the reducing agent.

The overall cell reactions for a dry cell are:

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

half-reaction: $2MnO_2(s) + 2NH_4^+(aq) + 2e^- \quad\quad Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$

Overall redox reaction: $2MnO_2(s) + 2NH_4^+(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$

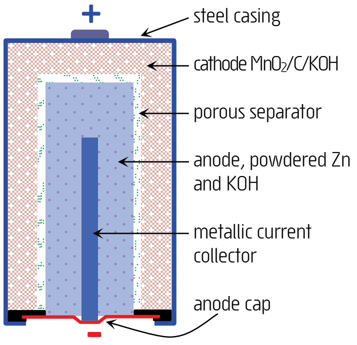
The alkaline cell: As in the dry cell, zinc is used as the reducing agent and manganese dioxide, MnO_2 as the oxidising agent. Instead of an ammonium chloride electrolyte, it uses potassium hydroxide, KOH in the electrolyte paste. (See Fig 6.) This considerably improves its shelf life by eliminating the effect of acidic ammonium ions that ultimately dissolve the zinc anode of a dry cell. The zinc anode is in the form of powdered zinc, instead of Zn foil as in the dry cell. These design features allow the alkaline cell to achieve faster reaction rates thus giving it the ability to sustain a high current flow without the fall in voltage that happens in a dry cell. Typically an alkaline cell contains a greater mass of reductant, Zn and oxidant, MnO_2 than a dry cell of similar size. This gives the cell a higher energy density and a longer operating life. The discharge cell reactions for an alkaline Zn/MnO_2 cell are:

Anode half-reaction: $Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^-$

half-reaction: $2MnO_2(s) + H_2O(l) + 2e^- \quad\quad Mn_2O_3(s) + 2OH^-(aq)$

Overall redox reaction: $Zn(s) + 2MnO_2(s) \rightarrow ZnO(s) + Mn_2O_3(s)$

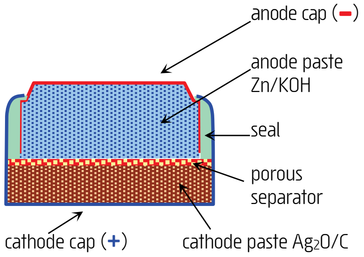
Figure 6 A simplified view showing the arrangement of chemical components in an **alkaline Zn/MnO_2 cell**.



Alkaline cells are ideal for use in devices that require a higher current flow, eg toys, portable radios, CD players, electronic games and torches. As with the dry cell, spent alkaline cells pose minimal environmental impact. They are considered non-hazardous waste. While at present these cells are disposed of in the normal household waste stream, in the future it is hoped they can be recycled. At present there is no economic process for recycling the materials in these cells.

Attempt Set 12 # 3.

Figure 7 **Ag_2O/Zn button cell**.



Silver oxide button cells: These are small primary cells with a very steady, constant voltage of 1.86 V. Their small size and reliable voltage output make them suitable for use in cameras, watches, hearing aids and pacemakers. Button cells have a good shelf life and a greater energy density than the alkaline cell. The reactions occurring in a button cell are:

Anode half-reaction: $Zn(s) + 2OH^-(aq) \rightarrow ZnO(s) + H_2O(l) + 2e^-$

half-reaction: $Ag_2O(s) + H_2O(l) + 2e^- \quad 2Ag(s) + 2OH^-(aq)$

Overall redox reaction: $Zn(s) + Ag_2O(s) \rightarrow ZnO(s) + 2Ag(s)$

Most silver button cells contain small amounts of **mercury** and as such should be considered **hazardous waste**. These cells should not be disposed of in the normal household waste stream. Instead they can be recycled by returning them to retailers or jeweller's and watchmaker's stores.

Manufacturers and regulators are currently working to eliminate mercury use in these cells.

The lithium cell: The high oxidation potential and low density of lithium, Li make it an ideal reducing agent for use in galvanic cells. One version of the **primary lithium cell** uses a lithium anode and manganese dioxide, MnO_2 as the oxidising agent. The high reactivity of lithium with air and water means the cell must not contain water and needs to be of a robust airtight construction. For this reason lithium cells are potentially dangerous and can lead to accidental fires during use or especially if disposed of incorrectly.

Individual Li/MnO_2 cells have an operating voltage of 3.0 V. The anode and cathode reactions for this cell are:

Anode half-reaction: $Li(s) \rightarrow Li^+(l) + e^-$

half-reaction: $MnO_2(s) + Li^+(l) + e^- \quad LiMnO_2(s)$

Overall redox reaction: $Li(s) + MnO_2(s) \rightarrow LiMnO_2(s)$

Energy density in a galvanic cell may be defined as the energy available per unit mass of the cell (eg **kJ kg^{-1}**) or as the energy available per unit volume of the cell (eg **kJ L^{-1}**). Thus, for a given application, the higher the energy density of a cell, the smaller its mass and or volume will be. For this reason, energy density is a very important aspect of a galvanic cell. This is especially true for cells in **portable** devices.

Although these cells are typically more expensive, they have a **very high energy density**, (see border note) long shelf life and a long operational life making them ideal for many applications. Lithium cells do not contain toxic metals, but they do pose a **fire hazard** if disposed of incorrectly. As lithium is a highly reactive metal they must be fully discharged, to consume all of the metallic lithium, before disposal. Disposable lithium cells are different to and should not be confused with the rechargeable **lithium-ion cell**. (See 8.4 p85.)

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Attempt Set 12 # 4 and 5.

8.4 Secondary cells

The lead-acid cell: This **rechargeable** cell produces a voltage of 2 V and is typically used in the form of a battery consisting of several cells connected in a series. The **car battery**, for example, contains six of these cells connected in series to produce approximately 12 V. (See Fig 8.) The lead accumulator (lead-acid cell) used in most vehicles can undergo many **discharge-recharge cycles** over a period of several years before the internal components eventually lose their structure and the cell no longer functions. The ability to be recharged and to deliver **very large currents** makes this battery ideal for running the electric starter motor of cars and trucks, a purpose for which it has been used for over a century. These batteries also find application in electric vehicles like wheel chairs, fork lifts and golf carts as well as in emergency power systems and solar power storage systems.

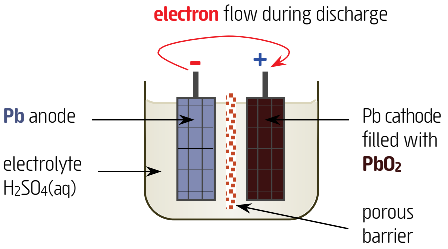
Figure 8 A typical **car battery** contains six lead-acid cells (Fig 9) connected in series in a single container producing 12 V.

Batteries like this are low cost and have the advantage of being able to deliver high currents for prolonged periods. They are ideal for applications like car ignition and lighting systems.

A major limitation of these batteries is their **low energy density** (≈ 150 kJ kg^{-1}) and the **environmental** and **safety hazards** they pose. The sulfuric acid electrolyte is a corrosive and hazardous substance whilst lead and its compounds are acutely and chronically toxic. Although generally insoluble, lead compounds can be absorbed through ingestion and inhalation. Lead is also highly toxic to fish, other animals and plants.

Spent lead-acid batteries are classified as **hazardous waste** by the Australian Government under the Hazardous Waste Act 1989.

Figure 9 A simplified view of a single **lead-acid cell**. A porous separator ensures the oxidising agent and reducing agent do not make contact.



A single lead-acid cell (Fig 9) has two lead grid electrodes, immersed in an electrolyte of ≈ 4.5 mol L^{-1} $H_2SO_4(aq)$. The **anode** grid contains spongy **lead**, Pb while the **cathode** grid is packed with powdered **lead dioxide**, PbO_2. During discharge, spongy Pb at the anode is oxidised to Pb^{2+} which immediately precipitates onto the electrode as insoluble $PbSO_4(s)$. Simultaneously, at the cathode, PbO_2 is reduced to Pb^{2+} which also precipitates onto the electrode as insoluble $PbSO_4(s)$. The **powdered** nature of the Pb and PbO_2 on the anode and cathode give these reagents a high **surface area** (increases reaction rate) contributing to one of the cell's important features, its ability to produce high currents.

Anode half-reaction: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

half-reaction: $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \quad PbSO_4(s) + 2H_2O(l)$

Overall redox reaction: $Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

A lead-acid cell can be recharged by applying a direct current of slightly greater than 2 V to each cell. The recharging current is made to flow in a direction opposite to the discharge current. This has the effect of **reversing** the anode and cathode half-reactions that occur during discharge, thus regenerating Pb at the anode and PbO_2 at the cathode.

A major drawback of the lead-acid cell is the high density of lead (11.3 kg L^{-1}) which results in the cells having a **very low energy density** of around 150 kJ kg^{-1}. This is especially an issue where the cells are used in transport situations. These batteries must be handled with care as lead and its compounds are acutely and chronically **toxic** whilst sulfuric acid is **corrosive**. Used lead-acid batteries are classed as **hazardous waste** and as such they must be disposed of appropriately. This usually involves **recycling**. An Australian Government estimate found about 70,000 to 80,000 tonnes of waste lead-acid batteries were produced in Australia in 2005; 65,000 tonnes of which were reprocessed at Australian smelters.

Attempt Set 12 # 6, 7 and 8.

The lithium-ion cell: As with the non-rechargeable lithium cell, the **lithium-ion cell** utilises lithium to produce a rechargeable cell with an **exceptional energy density**, good shelf life and the capability of many recharge cycles. Despite their higher cost, these cells are now extensively used in laptops, iPads, cameras, mobile phones and portable power tools. Ongoing research and improvement in lithium-ion cell technology is supporting the current growth in the electric vehicle industry (Fig 23 p91) and has also led to the introduction of large scale lithium-ion storage units for household and commercial use. (See Fig 10.)

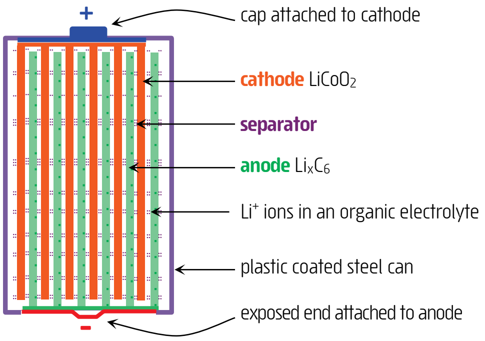
Figure 10 Powerwall is a lithium-ion home battery that charges using electricity generated from solar panels or when utility rates are low and then returns power to your home in the evening.

Image: Tesla Motors, Inc: Alexis Georgeson.

These cells do not contain a metallic lithium anode, as in the non-rechargeable lithium cell. Instead the **anode** is made of porous graphite with lithium ions interspersed between the graphite layers, called intercalation, designated as **Li_xC_6**. The **cathode** is a porous lithium metal oxide such as **$LiCoO_2$**. (See Fig 11.) The electrodes are in sheet form with a porous separator sheet in between and rolled into a convenient shape. The electrode assembly is immersed in a **non-aqueous** organic electrolyte containing mobile Li^+ ions.

Figure 11 A simplified view of a cylindrical **Li-ion cell**. The anode, cathode and separator are in sheet form and rolled into a cylinder housed in a pressurised steel can.

Rechargeable Li-ion battery packs like those in a laptop must have an inbuilt microprocessor that manages its charging. Overcharging is dangerous and can lead to a process called venting and thermal runaway. This can also happen if spent cells are pierced or crushed.



During discharge lithium ions migrate out of the **Li_xC_6** anode and into the **$LiCoO_2$** cathode while electrons flow from the anode, via an external conducting path (through an appliance) to the cathode. This maintains a charge balance in both the anode and cathode.

Anode half-reaction: $Li_xC_6 \rightarrow xLi^+ + C_6 + xe^-$

half-reaction: $Li_{1-x}CoO_2 + xLi^+ + xe^- \quad LiCoO_2$

Overall redox reaction: $Li_xC_6 + Li_{1-x}CoO_2 \rightarrow C_6 + LiCoO_2$

During recharge these processes are reversed by applying a sufficient voltage to the cell so that electrons are forced to flow from the $LiCoO_2$ electrode to the Li_xC_6 electrode. This regenerates Li_xC_6 at the anode and $LiCoO_2$ at the cathode.

Figure 12 Li-ion cells, like these two, are becoming increasingly popular as a rechargeable power source for portable electrical devices. They can be produced in a variety of shapes and sizes, have a long shelf life and an exceptional energy density. Li-ion cells typically have an energy density of 350-950 kJ kg^{-1}. The upper level energy density is steadily increasing as researchers continue to improve cell design.

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Attempt Set 12 # 9.

Figure 13 A **hydrogen refuelling pump**.

Hydrogen gas is a desirable fuel as its combustion produces considerably more energy per gram of fuel than does the combustion of natural gas (≈ 120 kJ g^{-1} for H_2 compared to 50 kJ g^{-1} for CH_4). Furthermore the only waste product of its combustion is water. However, as **natural sources** of hydrogen gas do not occur on Earth it must be produced industrially and this is an energy intensive process.

The major method of hydrogen production is the steam methane reforming process.

$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g) \quad \Delta H = 206\ kJ$

Heat energy needed to drive this endothermic reaction is gained from the combustion of further methane.

The resulting CO/H_2 gas mixture from this reaction is treated with steam at 400 °C to further increase the yield of hydrogen gas.

$H_2O(g) + CO(g) \rightarrow CO_2(g) + H_2(g)$

Producing hydrogen gas this way is **not sustainable** as it uses natural gas, a non-renewable resource. Also this method generates a large amount of CO_2, a **greenhouse gas**.

Electrolysis of water is another method used to produce $H_2(g)$.

$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$

It is most favourable where cheap sources of electrical energy are available. Electrolysis has the advantage of producing pure $O_2(g)$ as a valuable by-product.

Producing hydrogen gas this way can be a **sustainable** process if the electrical energy used is produced from **renewable sources** like hydro, wind, wave, geothermal or solar energy. Doing this avoids both the use of non-renewable hydrocarbon fuels and the production of the greenhouse gas CO_2.

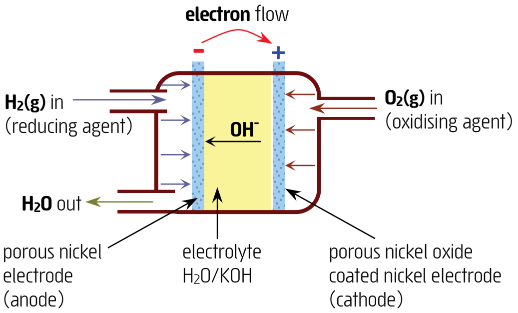
Attempt Set 12 # 10 and 11.

8.5 Fuel cells

Alkaline hydrogen-oxygen fuel cell: This is one of the earliest fuel cell designs. The Apollo space missions during the late 1960s and early 1970s used these cells to generate electricity and provide drinking water for the astronauts. NASA also used this technology on board its space shuttles.

Fuel cells like this differ from primary cells and secondary cells in that they do not store the oxidising or reducing agent. Instead, these reactants are constantly fed into the cell to generate electricity. Chemical by-products of the cell reactions are expelled from the cell as it operates. The cell shown below uses gaseous **hydrogen** as the reductant and gaseous **oxygen** as the oxidant. These circulate under pressure over porous nickel electrodes that incorporate particles of a catalyst (eg platinum). A hot concentrated solution of KOH is used as the electrolyte. Some of the water formed at the anode can be seen leaving the cell as steam mixed with the circulating hydrogen gas.

Figure 14 A simplified view of an **alkaline H_2/O_2 fuel cell**. The reducing agent, H_2, diffuses into the porous Ni electrode and is oxidised forming H^+ ions and free electrons. These electrons are conducted by the Ni electrode out of the cell to the cathode. Oxygen absorbed into the cathode then gains electrons forming OH^- ions. The resulting H^+ ions and OH^- ions migrate through the electrolyte to combine and form water, the only chemical product. This cell operates at ≈150-200 °C with an efficiency of around 70%.



Half-reactions for this cell are:

Anode half-reaction: $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$

half-reaction: $O_2(g) + 2H_2O(l) + 4e^- \quad 4OH^-(aq)$

Overall redox reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

The overall reaction occurring in the hydrogen-oxygen fuel cell is identical to burning hydrogen in air (or oxygen). Conducting the reaction in the fuel cell, however, is a much more efficient way of converting the available enthalpy change directly into electrical energy. Modern electrical power plants burning fossil fuels for example are typically constrained to energy conversion efficiencies of 35-40% (excluding cogeneration plants). Motor vehicles using fossil fuels to operate an internal combustion engine can achieve energy conversion efficiencies of around 25-30%. By comparison the hydrogen-oxygen fuel cell described here has an energy conversion efficiency of around 70%.

Proton exchange membrane fuel cell (PEMFC): The PEMFC was first developed in the US during the early 1960s. Its original intended uses were for military and space applications, though it was never widely commercialised. Research and development of this fuel cell technology continues today in the hope that it can find wide application and commercialisation as the fuel cell of choice for future hydrogen powered cars and buses. (See Fig 15.)

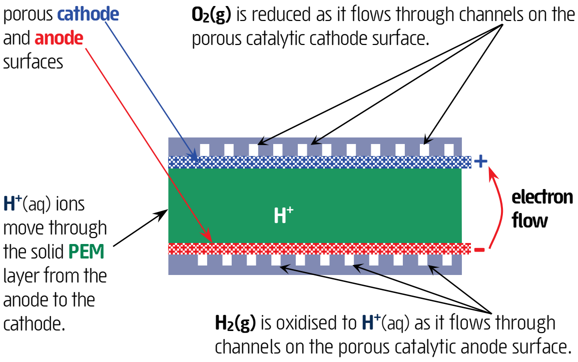
The **PEMFC** uses 99.999% pure $H_2(g)$ and $O_2(g)$, from the air to produce a DC electric current, water and heat. A special PEMFC feature is the thin, **solid** polymer **proton exchange membrane** (**PEM**) used as the electrolyte and electrode separator. This avoids the use of a corrosive liquid electrolyte, as in the alkaline fuel cell. The PEM allows protons (H^+ ions) to move through it, from the anode to the cathode, while preventing $H_2(g)$ or $O_2(g)$ from moving across the thin, solid electrolyte membrane.

Figure 15 This Toyota Fuel Cell Vehicle (FCV) is scheduled for selected release into the Japanese car market in early 2015 prior to its release in the US and Europe. It utilises solid polymer electrolyte membrane fuel cells (similar to the PEMFC) and a nickel metal hydride storage battery to power its electric motor. Hydrogen is stored at 70 MPa in several storage cylinders giving the vehicle a range of around 700 km.

Image courtesy Toyota Motor Corporation, http://www.toyota-global.com/innovation/environmental_technology/fuelcell_vehicle/

The solid nature of the electrolyte in a PEMFC allows a compact, flexible fuel cell design as the electrolyte layer (PEM) can be as thin as 0.050 mm with the entire cell (PEMFC) being around 1 mm thick. Both the anode and cathode consist of **nanoparticles** of **platinum** impregnated onto **porous carbon**. The platinum acts as a **catalyst**, speeding up the anode and cathode reactions, while the carbon conducts electrons from the electrode surface. Although each cell produces only 1.1 V, arranging the cells into stacks in series produces higher voltages.

Figure 16 During the operation of a **PEMFC**, pure hydrogen gas is oxidised as it flows through channels on the anode surface. The resulting H^+ ions migrate into the solid electrolyte membrane (**PEM**) and move towards the cathode. Electrons released at the anode move through an external circuit to the cathode. Oxygen gas passing through channels on the cathode surface gain these electrons and combine with the migrating H^+ ions to form water.



Half-reactions for this cell are:

Anode half-reaction: $H_2(g) \rightarrow 2H^+(aq) + 2e^-$

half-reaction: $O_2(g) + 4H^+(aq) + 4e^- \quad 2H_2O(l)$

Overall redox reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

Attempt Set 12 # 12.

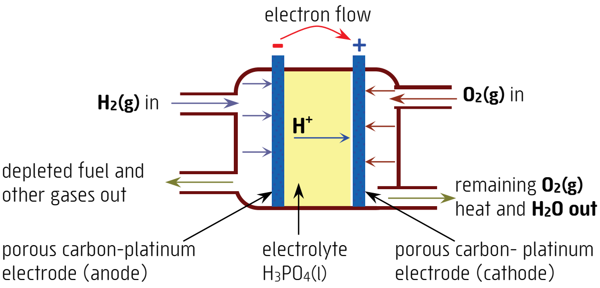
Phosphoric acid fuel cell (PAFC): The **PAFC** uses hydrogen gas from petroleum reforming and is able to tolerate the low levels of CO impurities that are often present. Oxygen gas from the air is the oxidising agent. The cells produce a DC potential (voltage), water and heat. These cells operate using a phosphoric acid electrolyte contained in a ceramic matrix of silicon carbide. They operate at temperatures of 150-220 °C. This high temperature increases $H_3PO_4(l)$ conductivity while minimising catalyst **poisoning** (rendering inactive due to CO absorption) from gas impurities like CO that are present in the hydrogen fuel stream. Both electrodes consist of **porous carbon** and **platinum catalyst** particles.

The **phosphoric acid fuel cell** (PAFC) is one of the more widely developed commercial fuel cell technologies. These cells have an electrical output **efficiency** of around 40% but overall efficiency can rise to 85% with **cogeneration**, ie where the waste heat is also utilised.

While PAFCs are a costly way to produce electricity they are quiet, maintain good air quality and can run on hydrogen produced from traditional hydrocarbon fuels. The high operational temperature of these cells (150-220 °C) makes the platinum electrode catalyst reasonably tolerant of contaminants like carbon monoxide. In low temperature fuel cells, the electrode catalyst, platinum, is easily '**poisoned**' (made inactive) by even minute traces of impurity gases like CO.

PAFC is currently the dominant fuel cell system used for **static power generation** in applications like emergency power for banks, hotels, hospitals and police stations. Recent developments in commercial Li-ion cells however, may see these soon become the cell of choice for this type of application.

Figure 17 A simplified view of a **phosphoric acid fuel cell**. The reducing agent H_2 diffuses into the porous C/Pt electrode and is oxidised forming H^+ ions and free electrons. These electrons are conducted by the C/Pt electrode out of the cell to the cathode. H^+ ions migrate through the electrolyte to the cathode. Here they combine with oxygen absorbed into the cathode. In the process, oxygen gains electrons arriving from the anode and becomes reduced to form water, the only chemical product.



Half-reactions for this cell are:

Anode half-reaction $H_2(g) \rightarrow 2H^+(aq) + 2e^-$

half-reaction $O_2(g) + 4H^+(aq) + 4e^- \quad 2H_2O(l)$

Overall redox reaction $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

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Attempt Set 12 # 13, 14 and 15.

8.6 Electrolysis in industry

The original discovery of electrolysis is attributed to the English chemist **William Nicholson** (1753-1815). Using the newly published discovery of the Voltaic pile (1800) Nicholson along with his friend Anthony Carlisle had demonstrated the electrolysis of water into hydrogen and oxygen. Soon after, in 1807-8, Humphry Davy used electrolysis to isolate several previously unknown elements (K, Na. Ba, Ca, Sr and Mg) from their compounds.

Today electrolysis continues to be an important technique for the **extraction** of reactive metals like sodium, magnesium and aluminium and for the **purification** of metals like gold and copper. Electrolysis is also important for the **production** of substances like chlorine and sodium hydroxide, and for applications such as silver and chrome **plating of metals**.

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8.7 Electrorefining of copper

Figure 18 Pure copper cathodes being removed from an electrolyte bath of copper(II) sulfate dissolved in dilute sulfuric acid.

During the electrorefining process impure copper anodes dissolve while pure copper metal is deposited on the copper cathodes.

Copper's high resistance to corrosion and excellent electrical conductivity make it an exceptionally useful metal. However, the presence of even small amounts of other metal impurities can significantly diminish these attributes. In order to benefit from its unique properties copper must be obtained in a very pure form, >99.95% Cu. The extraction of copper from its ores however, typically results in an impure form called **blister copper** (≈98% Cu). Impurities typically include valuable metals like Ag, Au, Pt, Fe, Zn and Ni which frequently occur along with copper in its ores.

The ultimate purification of blister copper to >99.95% Cu is achieved by **electrorefining** (electrolysis). To do this, blister copper is formed into anodes and immersed in an electrolyte solution of copper(II) sulfate dissolved in dilute sulfuric acid. Applying a carefully controlled DC voltage to the impure copper anodes results in the oxidation (dissolving) of copper along with the more reactive metal impurities like Ni, Fe and Zn. These metals dissolve to produce $Cu^{2+}(aq)$, $Ni^{2+}(aq)$, $Fe^{2+}(aq)$ and $Zn^{2+}(aq)$ respectively.

Keeping the applied voltage suitably low prevents the the oxidation of less reactive anode metal impurities such as Ag, Au and Pt. Instead, these less reactive metals simply fall to the bottom of the electolysis cell as a solid 'anode slime' (also called sludge). Recovery of this anode slime provides a valuable source of these precious metals and contributes significantly to the economics of electrorefining blister copper.

Pure copper (>99.95%) is then recovered from the electrolyte solution by the reduction of $Cu^{2+}(aq)$ ions onto a thin cathode sheet made of pure copper. (See Fig 18.) The applied cell voltage is carefully controlled so that only $Cu^{2+}(aq)$ ions are able to be reduced. Other cations in the solution, eg, $H^{+}(aq)$, $Fe^{2+}(aq)$, $Zn^{2+}(aq)$ and $Ni^{2+}(aq)$ are unaffected and remain in solution. (See Fig 19.) The concentration of these ions gradually builds up in the electrolyte and so they are periodically removed by suitable chemical treatment.

Figure 19 Electrorefining of blister copper.

The **blister copper** anode partially dissolves.

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$ $E^{o}_{ox} = -0.34$ V

$Ni(s) \rightarrow Ni^{2+}(aq) + 2e^{-}$ $E^{o}_{ox} = +0.24$ V

$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-}$ $E^{o}_{ox} = +0.44$ V

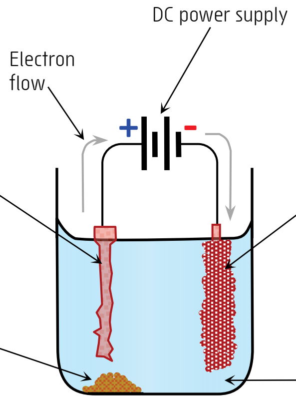
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$ $E^{o}_{ox} = +0.76$ V

The **anode slime** consists of less reactive metals that do not dissolve due to their much lower oxidation potentials. (**NR**=No reaction.)

$Ag(s) \xrightarrow{NR} Ag^{+}(aq) + e^{-}$ $E^{o}_{ox} = -0.80$ V

$Pt(s) \xrightarrow{NR} Pt^{2+}(aq) + 2e^{-}$ $E^{o}_{ox} = -1.20$ V

$Au(s) \xrightarrow{NR} Au^{+}(aq) + e^{-}$ $E^{o}_{ox} = -1.69$ V



$Cu^{2+}(aq)$ ions become reduced at the **pure copper cathode**.

$Cu^{2+}(aq) + 2e^{-}$ $Cu(s)$ $E^{o}_{red} = +0.34$ V

The much lower reduction potential of the other metal ions in solution prevents them from being reduced. (**NR**=No reaction.)

$Ni^{2+}(aq) + 2e^{-} \overset{NR}{\quad} Ni(s)$ $E^{o}_{red} = -0.24$ V

$Fe^{2+}(aq) + 2e^{-} \overset{NR}{\quad} Fe(s)$ $E^{o}_{red} = -0.44$ V

$Zn^{2+}(aq) + 2e^{-} \overset{NR}{\quad} Zn(s)$ $E^{o}_{red} = -0.76$ V

The electrolyte solution is initially a mixture of $CuSO_4(aq)$ and $H_2SO_4(aq)$.

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Attempt Set 12 # 16.

Copper recovered from these cathodes is >99.95% pure and is particularly suitable for applications where high electrical conductivity (ie low resistance) is required.

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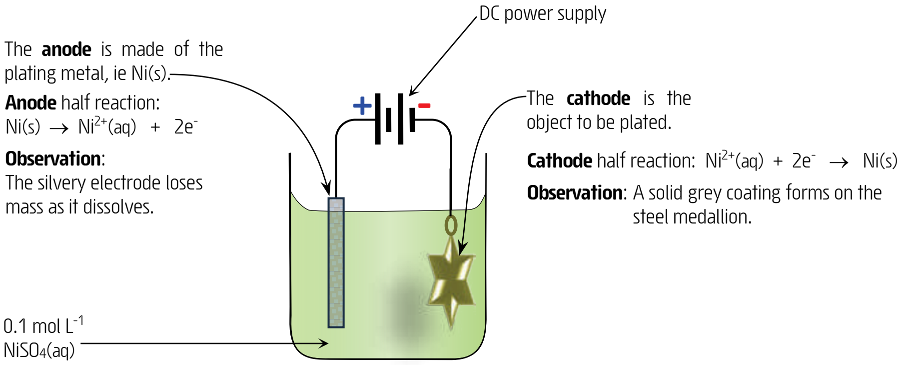
8.8 Electroplating

This involves using electrolysis to place a thin coating of one metal onto another metal. Electroplating may be used to improve the appearance of a metal or its resistance to corrosion. Silver plated cutlery or gold plated jewellery for example may have the appearance and durability of real silver or gold articles but they can be produced at a fraction of the cost. Tin cans used for food storage are made of tin plated steel that is sometimes also laquered on the inside. Tin coating the can helps to prevent its corrosion.

Electroplating (Fig 20) is achieved by making the metal object to be plated the **cathode** of an electrolytic cell. The **anode** is made of the plating metal while the electrolyte is a salt solution of the same metal. Applying a small DC voltage to the electrodes causes metal ions from the electrolyte to become reduced onto the cathode. As the cell operates, oxdidation of the anode replaces the reduced metal ions thus helping to ensure a steady concentration of these is maintained within the electrolyte. Figure 20 shows the arrangement for electroplating nickel onto a steel medallion.

Figure 20 Electroplating nickel onto a steel medallion.



The **anode** is made of the plating metal, ie Ni(s).

Anode half reaction:
$Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$

Observation:
The silvery electrode loses mass as it dissolves.

$0.1\ mol\ L^{-1}$
$NiSO_4(aq)$

The **cathode** is the object to be plated.

Cathode half reaction: $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$

Observation: A solid grey coating forms on the steel medallion.

Figure 21 This Harley-Davidson motorcycle uses chrome-plating for corrosion protection and decorative effects.

Nickel plated steel has a dull, though corrosion resistant finish. Often nickel plating is used as a precursor to **chromium plating**. Chromium adheres well to nickel plated steel but not directly onto steel products. The chromium finish is capable of being highly polished and gives good protection against corrosion as well as being a decorative finish. Chrome plating (Fig 21) is used to good effect on some types of metallic car body trim, tools, tableware and on taps and various hardware fittings.

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Complete Set 12.

Set 12 Electrochemistry in action

1. **Who** comprises the 'International Partnership for Hydrogen and Fuel Cells in the Economy' and what are their **goals**?

Note to students: Many of the following questions relate to the operation and application of commercial galvanic cells. While the current ATAR Chemistry syllabus (2015) does outline a requirement for students to understand and interpret the chemistry and application of **primary** cells, **secondary** cells and **fuel** cells it does not specify which cells should be studied.

Thus while it may be useful to know the operation of one example of each type of galvanic cell there is clearly no expectation that you should **recall** the operation of all of the galvanic cells covered in this chapter.

Consult the current **Chemistry WACE manual** for more specific guidance.

2. Everyday commercial galvanic cells can be classified as primary cells, secondary cells and fuel cells. Give an **example** of each and briefly **describe** how they differ. (**See note to students at left**.)

3. While the **alkaline cell** is considered to be superior to the **dry cell** they do share many common features. The overall discharge reactions for these two cells are shown here.

Dry cell: $2MnO_2(s) + 2NH_4^+(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Mn_2O_3(s) + 2NH_3(aq) + H_2O(l)$

Alkaline cell: $Zn(s) + 2MnO_2(s) \rightarrow ZnO(s) + Mn_2O_3(s)$

Answer the following questions about the operation of these cells.

a. Both of these cells are referred to as **primary** cells. What does this mean?

b. What is the **oxidising agent** and **reducing agent** for each of these cells?

c. One problem with the dry cell is the inclusion of **NH_4Cl** in the electrolyte paste.

   i. What is the **role** of ammonium chloride in the dry cell?

   ii. Why does its presence reduce the shelf life of these cells? Support your answer with the aid of an **equation**.

d. One feature of the alkaline cell is a porous **powdered** zinc anode. How is this different to the anode of the dry cell?

e. The alkaline cell is suitable for applications like the power supply for a camera flash unit where a high current is required. Devices with high current demands essentially require a **fast rate** of supply of electrons. Write the anode half-reaction for both the dry cell and the alkaline cell. Refer to these equations and explain how the **design** of the **anode** in the alkaline cell allows a greater current to be produced, ie allows a **faster rate** of production of electrons, than the dry cell.

f. Another feature of the dry cell that limits its ability to produce high currents is the formation of ammonia gas within the cell as it discharges. **Explain** why ammonia gas will form as the cell operates. Use an **equation** to support your answer.

4. What **disposal problems** are associated with silver button cells and lithium cells? Do alkaline cells and dry cells have similar associated disposal issues?

The **energy density** of a galvanic cell may be defined as the energy available per unit mass of the cell (eg $kJ\ kg^{-1}$) or as the energy available per unit volume of the cell (eg $kJ\ L^{-1}$).

The total **amount of electrical energy** available from a cell depends upon the **voltage** it can produce, the size of **current** and length of **time** for which it can continue to operate.

5. Primary lithium cells have a much **higher energy density**, up to 3 times more than alkaline cells. (See border note.) The following questions refer to these two cell types.

a. Both cell types use **MnO_2**(s) as the oxidising agent. What is the **reducing agent** in each of these cells?

b. Write the oxidation half-equation for lithium and zinc and give the **oxidation potential** for each half-reaction. How would the different oxidation potentials of these two elements contribute to the **voltage** of the two different cells and hence the **energy available** from the two cell types? (See border note.)

c. 2 moles of lithium metal in a primary lithium cell can produce the same electric current for the same length of time as 1 mole of zinc in an alkaline cell. How does this factor contribute to the **energy density** (in terms of available electrical energy per gram of metal) of the two cell types? **Explain**.

d. Explain why lithium cells cannot contain water as the electrolyte solvent.

6. Why are lead-acid batteries classified as **hazardous waste**?

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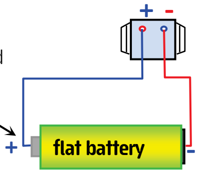
7. An important feature of the lead-acid **secondary** cell is its ability to deliver a high current flow for long periods. This has made the lead-acid **battery** an ideal choice for motor vehicle ignition systems and as a power source for electric vehicles like electric wheel chairs, forklifts and golf carts. Unfortunately their very low energy density has limited their widespread use as a power source for electric powered vehicles.
   a. What **design feature** of the anode and cathode allows the lead-acid battery to produce **high currents**, ie fast reaction rates?
   b. The oxidation of **one mole** of **lead** in a lead-acid battery can produce as much current (flow of electrons) as the oxidation of **one mole** of **zinc** in an alkaline cell. How does this one factor alone affect the mass and hence energy density of the lead-acid battery compared to an alkaline cell? **Explain**.
   c. The lead-acid cell is a **secondary** cell. Why is this an important feature in its use for motor vehicles and electric vehicles?
   d. Describe the difference between a lead-acid **cell** and a lead-acid **battery**?

8. Lead-acid batteries are able to be **recharged** (Fig 22) by attaching the electrodes to a DC power supply. The anode (**-**) of the cell is connected to the negative terminal of the power supply while the positive terminal is attached to the cell's cathode (**+**). This causes the discharge reactions at each of the electrodes to occur in the **reverse direction**. An **undesirable** side reaction that occurs during recharge is the **electrolysis** of water. The following questions refer to the recharge of a lead-acid cell.
   a. Write the recharge half-equations for the anode and cathode when a lead-acid cell is being **recharged**. Note: The anode and cathode refer to the electrodes as labelled during discharge of the lead-acid cell.
   b. How does the composition of the anode and cathode change during recharge and thus **explain** why the cell is now considered recharged.
   c. Recharging the lead-acid battery of an electric wheel chair increases the **enthalpy** (stored energy) of the cell. Where does this energy come from?
   d. Describe what happens to the **electrolyte pH** as a lead-acid cell is recharged? Hint, consider the overall recharge reaction.
   e. Why is it important to regularly check the **water level** inside a lead-acid battery?
   f. Why might it be **dangerous** to recharge lead-acid batteries of a dozen electric golf carts in a **confined unventilated** room?

Figure 22 Recharging a secondary cell.

A rectifier transformer supplies a DC current.

The discharge cathode (labelled **+**) is attached to the positive DC power supply.



9. **Lithium-ion cells** have now replaced **lead-acid battery** technology as the cell of choice in many types of electric vehicles. What features does the lithium-ion cell have that make it suited to this use and what significant **advantage** does the lithium-ion cell have over lead-acid cells in this type of application? **Explain**.

Figure 23 Tesla Model S. This All-Wheel Drive Dual Motor electric vehicle uses lithium-ion battery technology. It is capable of accelerating from zero to 100 kph in as little as 3.4 seconds and has a range of up to 502 kilometres. Image courtesy Tesla Motors, Inc: Alexis Georgeson.

10. The **alkaline hydrogen-oxygen** cell is referred to as a **fuel cell**. How does a fuel cell differ from other types of galvanic cells?

11. NASA first used **fuel cells** for its manned Gemini space programme in the early 1960s. These fuel cells used oxygen and hydrogen in a galvanic cell to produce an electric current. The anode and cathode reactions for an alkaline fuel cell are shown here:

Anode half-reaction: $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$

half-reaction: $O_2(g) + 2H_2O(l) + 4e^- \quad 4OH^-(aq)$

   a. Write the **overall** redox equation for the alkaline fuel cell. With reference to this equation **explain** one advantage of using fuel cells as an energy source on manned space missions like Gemini and Apollo.
   b. Identify the **oxidising** and **reducing agent** used in the fuel cell. Support your answer with reference to **oxidation numbers**.
   c. How does the redox reaction occurring in this fuel cell **compare** to the redox reaction occurring during the **combustion** of hydrogen gas?

12. The **PEMFC** is a promising though not yet widely commercialised fuel cell technology considered superior to alkaline fuel cells. A similar type of cell is now in commercial use in the Toyota FCV. (See Fig 15 p86.)
    a. How do the **anode** and **cathode** reactions of the PEMFC **compare** to those in an alkaline fuel cell?
    b. The **polymer electrolyte membrane** (PEM) of a PEMFC cell is considered to be a major improvement on the electrolyte from an alkaline fuel cell.
        i. What is the **role** of the PEM in a fuel cell?
        ii. How is the PEM considered to be an **improvement** on the alkaline fuel cell electrolyte?
    c. What is the role of the **nanoparticles** of **platinum** present on the surfaces of both the anode and cathode and what is the **advantage** of having nanosized particles?

13. The **phosphoric acid fuel cell** (PAFC) is one of the more commercialised of the fuel cell technologies. It uses liquid phosphoric acid as the electrolyte and operates at temperatures from 150-220 °C.
    a. How is the high operating temperature an **advantage** for the operation of a PAFC?
    b. While the PAFC is only around 40% efficient as an electrical energy generator its efficiency can rise to 85% with **cogeneration**.
        i. **Explain** the meaning of the 40% efficiency of a PAFC.
        ii. What is **cogeneration** and how does it allow the PAFC to achieve 85% efficiency?
        iii. Suggest a reason why the PAFC has mainly found application as a power source for **stationary** facilities?
    c. Briefly **compare** the operation and design features of the PAFC and PEMFC systems.

14. Fuel cell technology using hydrogen as an **energy carrier** has been suggested as the ultimate power system for electric vehicles. Such fuel cells are quiet, potentially producing very little air pollution while operating with a higher energy efficiency than traditional petrol or diesel vehicles.
    a. Why is hydrogen referred to as an energy **carrier** rather than an energy **source**?
    b. Hydrogen/oxygen fuel cells are described as **potentially** producing very little air pollution. Describe how the use of hydrogen gas as a fuel does result in the greenhouse gas pollutant **CO_2**.
    c. Hydrogen can be a **sustainable** fuel, ie producing little or no pollution and without depleting non-renewable resources. **Explain** how this might be achieved.

The **DMFC** offers significant advantages over other portable fuel cells that rely on hydrogen as an energy carrier. In most cases both methanol and hydrogen are produced from natural gas or other fossil fuels. Hydrogen use, however, presents storage and purity problems. Methanol is **easily stored** and transported as it is a liquid and does not have purity issues. Methanol also has a much **higher energy density** compared to pressurised hydrogen gas.

15. The **direct methanol fuel cell** (DMFC) uses liquid methanol and oxygen from the atmosphere to produce electrical energy. This technology is yet to be commercialised; however, electronic devices like laptops and mobile phones powered by a DMFC may be only a few years away. While this cell technology is still evolving, it has some promising advantages over hydrogen-oxygen fuel cells. (See border note.) DMFCs use an aqueous solution of methanol, CH_3OH a plentiful and cheap fuel along with air to produce carbon dioxide and water as the only products.
    a. Use the given information to write the **overall redox** equation for the discharge of a DMFC.
    b. What is the **oxidising agent** and **reducing agent** in a DMFC? Support your answer with reference to oxidation numbers.
    c. Compared to H_2/O_2 fuel cells, what **fuel storage** problems are solved with the DMFC? Explain.
    d. Is methanol an energy source or energy carrier? **Describe** the difference and justify your answer.

16. **Copper** is typically obtained from the roasting of sulfide ores. The end product of this roasting process is impure copper metal containing around 98% copper along with impurities like zinc, iron, silver and gold. In order to obtain more than 99.9% pure copper a process of **electrorefining** is used.

    The impure copper metal is cast into thick electrodes and placed into a copper(II) sulfate solution. Another thin electrode of very pure copper is placed into the same solution. A direct current power supply is connected to the two electrodes. Over time the current causes the impure copper electrode to dissolve. (See Fig 24.) More reactive metals from the impure electrode, such as **copper**, **zinc** and **iron** dissolve to form ions in solution. Metals less reactive than copper are not oxidised. Eventually, as the impure copper electrode dissolves, these less reactive metals fall to the bottom of the cell forming a deposit known as the anode slime.

    Pure copper is obtained as the copper ions from solution become reduced at the other electrode. The ions of the more reactive metals remain in solution and are not reduced.

    a. With reference to the information given, **sketch** a simple electrolysis cell that shows the process being described for the electrorefining of copper. **Label** the materials in the cell, the anode and cathode and show the polarity of the power supply. You should indicate which electrode is made of impure copper and which is the pure copper electrode. Also indicate all ions present in the solution and show where the impurities like silver and gold will be found.

    b. Use the information given to **write three half-equations** for the reactions occurring at the anode of the cell.

    c. **Write the half-equation** for the reaction occurring at the cathode.

Figure 24 The pure and impure copper electrodes of a **commercial electrorefining** plant are shown here. The electrodes are suspended in a copper(II) sulfate electrolyte. A potential difference applied to the electrodes causes impure copper to dissolve while pure copper is deposited at the cathode. Below you can see stacks of **99.99% pure copper cathodes** ready for export.

17. **Electroplating** of silver is used to protect and beautify metallic objects like teapots, cutlery and jewellery. (See border note.) The technique involves electrolysis where reduction at the cathode produces a thin film of metallic silver on the object to be plated. A simple cell for electroplating silver uses a dilute silver nitrate solution as the electrolyte with a silver metal anode. Oxidation of the silver anode replaces silver ions which are reduced at the cathode.

    a. With reference to the information given, **sketch** a simple electrolysis cell that could be used in the laboratory to electroplate silver onto a copper medallion. Label the materials in the cell, the anode and cathode, show the polarity of the power supply, indicate the direction of electron flow between the electrodes and power supply and show the direction of motion of the silver ions.

    b. Using the given information, determine the half-reactions occurring at the anode and cathode of your silver plating cell. For each electrode, write the equation for the **half-reaction** occurring and **describe the changes** you would expect to observe.

In the laboratory **silver plating** can be achieved using a silver nitrate solution. Some references suggest adding excess saturated NaI to the $AgNO_3(aq)$ until the mixture turns clear forming soluble AgI_2^- ions.

Commercial silver plating is achieved using the soluble complex ion $Ag(CN)_2^-$. This helps to produce a high quality silver plate. There are, however, serious safety and waste disposal problems associated with the use of cyanide ions, CN^-. Exposure to low concentrations of cyanide can be lethal. There is an alternative and safe procedure using ammonium ethanoate instead of cyanide ions.

18. The **Hall-Heroult process** (see Fig 25) for the **electrowinning** of aluminium, Al from alumina, Al_2O_3 uses an electrolytic cell like the one shown here. Examine this cell and answer the following questions.

    a. In order to obtain aluminium from the reduction of alumina, Al_2O_3, the alumina must be in a molten form. **Explain** why solid alumina can not be electrolysed.

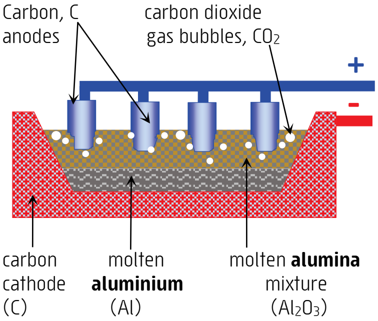
    b. Write the **cathode half-reaction** for the Hall-Heroult cell.

    c. The anode half-reaction in the Hall-Heroult process is shown here.

    $$C(s) + 2O^{2-}(l) \rightarrow CO_2(g) + 4e^-$$

    With reference to this equation justify the statement, **'The carbon anodes become oxidised over time and must be periodically replaced'**.

Figure 25 Apparatus used in the **Hall-Heroult** process for the **electrowinning** (electrolytic extraction) of aluminium, Al from alumina, Al_2O_3.



CHAPTER 9 | CHEMICAL CHANGE: STOICHIOMETRY

9.1 Review: Quantities in chemical reactions

The **coefficients** in a balanced chemical equation give the **relative number** (see border note) of molecules, formula units or moles of each substance in the reaction.

Stoichiometry is a specialised science term. It is comes from the Greek, '*stoikheion*' which means element and 'metry' to measure. In Chemistry, stoichiometry is the study of the relationship between quantities of reactants and products in a chemical reaction.

The balanced chemical equation is the foundation of chemical stoichiometry. It shows the **relative** number of **moles** of each substance involved in a reaction. It does not, however, give the **actual** amounts involved; this depends upon the quantities of reagents actually available in the reaction. The actual molar amounts involved in the reaction are always in the same **proportion** as the coefficients from the equation.

Example 1 What information is given by the coefficients in the balanced equation for the combustion of ethane, C_2H_6?

$$\mathbf{2}C_2H_6(g) + \mathbf{7}O_2(g) \rightarrow \mathbf{4}CO_2(g) + \mathbf{6}H_2O(g)$$

Substances involved in the reaction	**$C_2H_6(g)$**	**$O_2(g)$**	**$CO_2(g)$**	**$H_2O(g)$**
Relative number of **molecules**	2 molecules	7 molecules	4 molecules	6 molecules
Relative number of **moles**	2 moles	7 moles	4 moles	6 moles

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9.2 Review: Mole to mole calculations

The molar amount of any two substances used or produced in a reaction is in the same ratio as their **stoichiometric ratio** in the balanced equation. Consider the **general chemical equation** shown below. The **stoichiometric relationships** between substance **A** and any other substance in the reaction is shown below:

$\mathbf{a}A + \mathbf{b}B \rightarrow C + \mathbf{d}D$

Where: **a, b, c** and **d** are the **coefficients** of substances A, B, C and D and **n**(A), **n**(B), **n**(D) are the **moles** of substances A, B, C and D

Thus, for substance **A**: $\mathbf{n(A)} = \dfrac{\mathbf{a}}{\mathbf{b}}\ \mathbf{x\ n(B)}$ *and* $\mathbf{n(A)} = \dfrac{\mathbf{a}}{\mathbf{c}}\ \mathbf{x\ n(C)}$ *and* $\mathbf{n(A)} = \dfrac{\mathbf{a}}{\mathbf{d}}\ \mathbf{x\ n(D)}$

The stoichiometric relationship is often written as:

$$\mathbf{n(unknown)} = \frac{\text{coefficient of } \mathbf{unknown}}{\text{coefficient of } \mathbf{known}}\ \mathbf{x\ n(known)}$$

This form of the stoichiometric relationship allows the molar amount of an unknown to be found from the known or given amount of any other reagent in the reaction.

Example 2 Determine the molar amount of oxygen, O_2 used and carbon dioxide, CO_2 produced when 0.795 mole of ethane, C_2H_6 is burnt in air.

$$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(g)$$

$\mathbf{n(O_2)} = \dfrac{7}{2}$ x $n(C_2H_6)$ = $\dfrac{7}{2}$ x 0.795 = **2.78 mol**

The coefficient of O_2 is **seven**, while that of C_2H_6 is **two**, thus the molar amount of O_2 in the reaction is **3.5** times (7/2) the molar amount of C_2H_6.

$\mathbf{n(CO_2)} = \dfrac{4}{2}$ x $n(C_2H_6)$ = $\dfrac{4}{2}$ x 0.795 = **1.59 mol**

The coefficient of CO_2 is **four**, while that of C_2H_6 is **two**, thus the molar amount of CO_2 is **twice** (4/2) the molar amount of C_2H_6.

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Attempt Set 13 # 1.

9.3 Review: Calculations involving mass and moles

If the mass of any one substance involved in a reaction is known it can be converted to an equivalent amount in moles (**n = m/M**). This can then be used to find the molar amounts of all the other substances involved in the reaction. The relationship **m = nM** is then used to find the mass of a substance once the molar amount of it is found.

Example 3 Determine the moles of hydrochloric acid, HCl used and hydrogen, H_2 produced when 6.08 g of aluminium, Al reacts with excess hydrochloric acid. (See Fig 1.)

$$2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$$

$\mathbf{n(Al)} = \dfrac{m}{M} = \dfrac{6.08}{26.98}$ = **0.225 mol**

Find the moles of Al from the given mass.

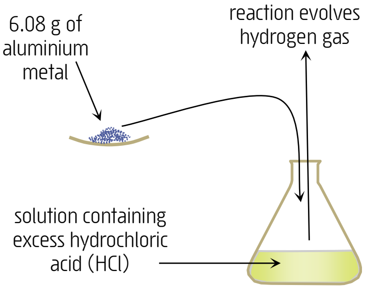
$\mathbf{n(HCl)} = \dfrac{6}{2}$ x n(Al) = $\dfrac{6}{2}$ x 0.225 = **0.676 mol**

The coefficient of HCl is **six**, while that of Al is **two**, thus the molar amount of HCl in the reaction is **three times** (6/2) that of Al.

$\mathbf{n(H_2)} = \dfrac{3}{2}$ x n(Al) = $\dfrac{3}{2}$ x 0.225 = **0.338 mol**

The coefficient of H_2 is **three**, while that of Al is **two**, thus the molar amount of H_2 is **one and a half times** (3/2) the molar amount of Al.

Figure 1 Aluminium and excess hydrochloric acid react to form hydrogen gas.



Example 4 What mass of aluminium chloride, $AlCl_3$ is formed if 1.22×10^{-2} g of hydrochloric acid, HCl reacts with excess aluminium, Al?

$$2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$$

n(HCl) $= \frac{m}{M} = \frac{1.22 \times 10^{-2}}{36.46} = \mathbf{3.35 \times 10^{-4}\ mol}$	Find the moles of HCl from its mass.
n($AlCl_3$) $= \frac{2}{6} \times n(HCl) = \frac{2}{6} \times 3.35 \times 10^{-4} = \mathbf{1.12 \times 10^{-4}\ mol}$	The coefficient of $AlCl_3$ is two, while that of HCl is six, ∴ the molar amount of $AlCl_3$ is one third (2/6) that of HCl.
m($AlCl_3$) $= n \times M = 1.12 \times 10^{-4} \times 133.33 = \mathbf{1.49 \times 10^{-2}\ g}$	Convert the moles of $AlCl_3$ to mass.

Numerical answers are rounded to the proper number of **significant figures** using the rules outlined in Appendix 1. For **your convenience**, where **partial working** has been evaluated it is shown with the correct number of significant figures. However, the complete number is carried forward into later parts of a calculation. It is advised that you also **carry full numerical answers** until the completion of a calculation. Your **final answer** should be rounded to the proper number of significant figures.

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Attempt Set 13 # 2.

9.4 Measuring gases in chemical change

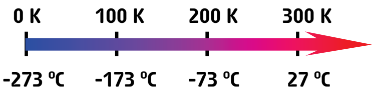
The amount of gas used or produced during a chemical change is most easily found by measuring its **volume**. The unit of volume used most frequently by chemists is the **litre**, **L**. Other related units of volume are:

1 L = **1 dm^3** = **1000 cm^3** = **1000 mL** also **1000 L = 1 m^3**

When quoting a gas volume it is essential to note the gas **temperature** and **pressure** as these will affect its volume. The SI unit for measuring pressure is the **pascal**, **Pa** and for temperature is the **kelvin**, **K**, though it is often recorded in **Celsius**, °C. Average atmospheric pressure at sea level for example is 101,325 Pa, ie 101.325 kPa. This is equivalent to **one standard atmosphere** (**atm**) of pressure. (Not to be confused with STP.)

normal atmospheric pressure = **1.000 atm** = **101.325 kPa** = **1.01325×10^5 Pa**

Figure 2 Temperature is used to describe how **hot** or **cold** an object is. By definition, it is a measure of the **average kinetic energy** of the particles of a substance. Absolute zero, **0 K** (or -273.15 °C) is the lowest temperature that can be achieved. It is the temperature at which **particles** of matter are **motionless**, ie have zero kinetic energy.



The Kelvin scale of temperature is related to the more commonly used Celsius scale as shown here:

$$T_{(kelvin)} = T_{(Celsius)} + 273.15$$

One method for finding the molar amount of a gas is to measure its volume at **standard temperature and pressure**, **STP**. This refers to a pressure of **100.0 kPa** and a temperature of **273.15 K** (0 °C). One mole of gas measured at these conditions will always occupy a volume of **22.71 L**, irrespective of what the gas is. Thus the STP volume (V_{STP}) of a gas can be used to find the moles of gas as shown below.

$$n_{(gas)} = \frac{V_{(STP)}}{22.71}$$

where: $n_{(gas)}$ = the moles of gas (mol)
$V_{(STP)}$ = the volume of gas in litres (L) at STP

Example 5 Excess hydrochloric acid was added to some zinc granules producing 4.39 L of hydrogen gas measured at STP (ie 100.0 kPa and 273 K). How many moles of hydrogen were formed?

n(H_2) $= \frac{V_{(STP)}}{22.71} = \frac{4.39}{22.71} = \mathbf{0.193\ mol}$	Since the gas volume is measured at STP then one mole of it will have a volume of 22.71 L.

Alternatively, the **moles** of gas can be found from its volume using the **ideal gas equation**. This more general relationship gives the molar amount of gas where its volume is measured at any temperature or pressure.

$$n_{(gas)} = \frac{PV}{RT}$$

where: **P** = the pressure of gas in kPa
V = the volume of gas in litres (L)
n = the moles of gas (mol)
R = the universal gas constant 8.3145 J K^{-1} mol^{-1}
T = the temperature of gas in kelvin (K, see Fig 2.)

The **ideal gas equation** is frequently expressed as:

PV = nRT

When using this relationship, it is essential to use the correct value of **R**, the **universal gas constant**. When temperature, pressure and volume are expressed in kelvins (K), kilopascals (kPa) and litres (L) respectively, then R has the value **8.3145 J K^{-1} mol^{-1}**.

If using 8.3145 J K^{-1} mol^{-1} for the universal gas constant, R then **temperature**, **pressure** and **volume** must be in the correct units of **kelvins** (**K**), **kilopascals** (**kPa**) and **litres** (**L**) respectively. If the gas pressure is measured or given in other units like **atmospheres** (**atm**) or **millimetres of mercury**, (**mmHg**) then convert these as shown here.

$$P_{(kPa)} = P_{(atm)} \times 101.3 \quad \text{or} \quad P_{(kPa)} = \frac{P_{(mm\ Hg)} \times 101.3}{760}$$

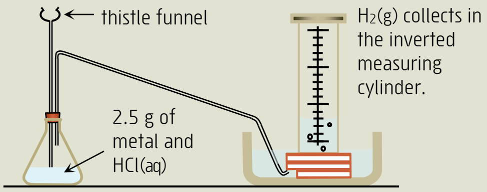
If temperature has been measured or given in Celsius units (°C), it can be converted to the Kelvin scale (Fig 2) of temperature using the relationship shown here.

$\mathbf{T_{(K)} = 273.15 + T_{(^oC)}}$ where $\mathbf{T_{(K)}}$ = Temperature in kelvin units, K
$\mathbf{T_{(^oC)}}$ = Temperature in Celsius units, °C

Example 6 In an investigation into the chemical properties of an unknown metal, Peter adds 2.5 g of the metal to excess hydrochloric acid as shown. How many moles of hydrogen gas are formed if 25.0 mL of it are collected:

a. At STP?

b. At 102.1 kPa and 23.00 °C?



a. $\mathbf{n(H_2\ at\ STP)} = \frac{V(L)}{22.71} = \frac{25.0 \times 10^{-3}}{22.71} = \mathbf{1.10 \times 10^{-3}\ mol}$	This gas volume is measured at STP. Also volume must be in litres (L), ie 25.0 mL = 25.0 x 10^{-3} L.
b. $\mathbf{T(K)} = T(^oC) + 273.15 = 23.00 + 273.15 = \mathbf{296.15\ K}$	Gas temperature must be in kelvin (K).
$\mathbf{n(H_2)} = \frac{P\,V}{R\,T} = \frac{102.1 \times 25.0 \times 10^{-3}}{8.3145 \times 296.15} = 1\quad \mathbf{mol}$	When using the ideal gas equation use R = 8.3145, kPa for pressure, L for volume and K units for temperature.

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Attempt Set 13 # 3.

9.5 Stoichiometry with gas volumes

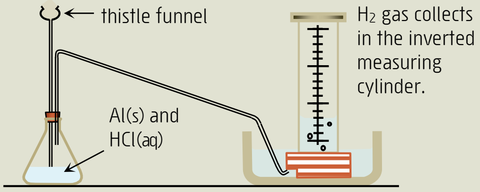
Using the STP molar volume relationship (**$n=V_{(STP)}\div22.71$**) or the more general **ideal gas equation** (**PV=nRT**) it is possible to determine the moles of gas from a **given volume**. This molar amount of gas is then related in the usual way to the molar amount of other reagents involved in the reaction.

***** When **collecting gases over water**, as show in Example 6 and 7, the collected gas will be at atmospheric pressure (room pressure) when the water level inside the gas jar and pneumatic trough are the same. However, this assumes the effect of water vapour pressure to be **negligible**.

Throughout this book the effect of water vapour pressure in calculations of this type will be **considered negligible** and hence can be ignored.

Example* 7 Excess hydrochloric acid, HCl reacts with a small amount of aluminium foil, Al forming 3.98 L of hydrogen gas, H_2 measured at 18.00 °C and 103.5 kPa. What mass of aluminium was used in the reaction?

$2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$



$\mathbf{n(gas)} = \frac{P\,V}{R\,T} = \frac{103.5 \times 3.98}{8.3145 \times 291.15} = \mathbf{0.170\ mol}$	Temperature must be in kelvin units. Ensure pressure and volume are in the units of kPa and L respectively.
$\mathbf{n(Al)} = \frac{2}{3} \times n(H_2) = \frac{2}{3} \times 0.170 = \mathbf{0.114\ mol}$	The coefficient of H_2 is three, while that of Al is two, thus the molar amount of Al is two thirds (2/3) that of H_2.
$\mathbf{m(Al)} = n \times M = 0.114 \times 26.98 = 3$	Convert the moles of Al to an equivalent mass.

If the volume of a gas involved in a chemical reaction is **unknown** then its volume can be calculated using the given or known amount of any other reagent.

Remember: Exact numbers such as the **coefficients** from a balanced equation may appear to have only one significant figure; however, they actually have unlimited significant figures. Hence they place no restriction on the number of significant figures appearing in the final answer. See the **Appendix 1** for rules on using significant figures.

Example 8 Excess aluminium, Al foil is added to a solution containing 5.22 g of hydrochloric acid, HCl. What volume of hydrogen gas is formed if the gas is measured at 155 kPa and 32.00 °C?

$2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$

$\mathbf{n(HCl)} = \frac{m}{M} = \frac{5.22}{36.46} = \mathbf{0.143\ mol}$	Find the moles of HCl from the given mass.
$\mathbf{n(H_2)} = \frac{3}{6} \times n(HCl) = \frac{3}{6} \times 0.143 = \mathbf{7.16 \times 10^{-2}\ mol}$	The molar amount of H_2 involved in the reaction is half (3/6) the molar amount of HCl.
$\mathbf{V(H_2)} = \frac{n\,R\,T}{P} = \frac{7.16 \times 10^{-2} \times 8.3145 \times 305.15}{155} = \mathbf{1.17\ L}$	Rearrange the ideal gas equation so that the gas volume can be found.

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Attempt Set 13 # 4 and 5.

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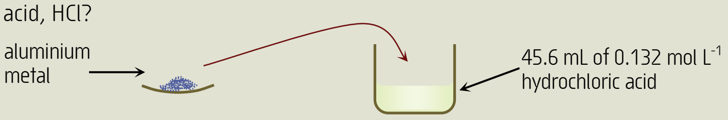
9.6 Stoichiometry with solutions

Chemical procedures in the laboratory often involve reactions where one or more of the reagents are in solution. The molar amount of these reagents is calculated from the **solution volume** and **concentration** by applying the relationship, **$n = cV$**. (See border note.) The moles of these reagents can then be stoichiometrically related to other substances in the reaction.

Remember, when using **$n = cV$**:

c is concentration (mol L^{-1})
n is moles of solute (mol)
V is the solution volume (L)

Example 9 What mass
hydrochloric acid, HCl?

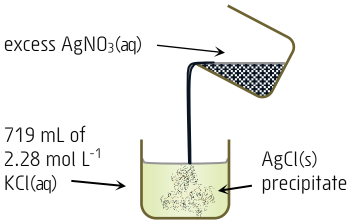


$2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$	Write an equation for the chemical change.
$n(HCl) = c \times V = 0.1320 \times 45.65 \times 10^{-3} = 6.026 \times 10^{-3}$ mol	Use the concentration equation to find the n(HCl). Volume must be in L, ie 45.6 mL = 45.6×10^{-3} L.
$n(Al) = \frac{2}{6} \times n(HCl) = \frac{2}{6} \times 6.026 \times 10^{-3} = 2.009 \times 10^{-3}$ mol	The coefficient of Al is 2, while that of HCl is 6, thus the molar amount of Al in the reaction is one third (2/6) that of HCl.
m(Al) $= n \times M = 2.009 \times 10^{-3} \times 26.98 =$ **5.419×10^{-2} g Al**	Convert moles of Al to mass.

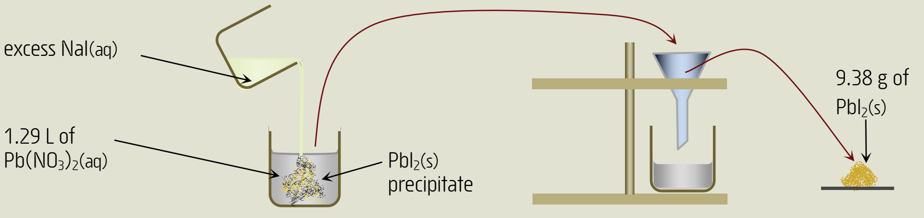
Example 10 Determine the mass of silver chloride
nitrate solution is added to 295 mL of 2.3 mol L^{-1} potassium chloride solution. (See Fig 3.)

$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$	Write an equation for the change described.
$n(KCl) = c \times V = 2.3 \times 0.295 = 0.68$ mol	Volume must be in L, ie 719 mL = 0.719 L.
$n(Cl^-) = n(KCl) = 0.68$ mol	The Cl subscript in KCl is 1, thus one mole of KCl contains 1 mole of Cl^-.
$n(AgCl) = n(Cl^-) = 0.68$ mol	Both AgCl and Cl^- have a coefficient of 1 in the equation for the precipitation of AgCl.
m(AgCl) $= n \times M = 0.68 \times 143.35 =$ **97 g AgCl**	Convert the moles of AgCl to an equivalent mass.

Figure 3 Precipitation of AgCl, Example 10.



Example 11 To find the concentration of a lead(II) nitrate solution, $Pb(NO_3)_2(aq)$, excess sodium iodide solution, NaI(aq) was added to 1.29 L of it. The resulting precipitate of $PbI_2(s)$ was filtered, washed and dried and found to have a mass of 9.38 g. Determine the concentration



$Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$	Write an equation for the change described.
$n(PbI_2) = \frac{m}{M} = \frac{9.38}{461.0} = 2.03 \times 10^{-2}$ mol	Convert the mass of PbI_2 to an equivalent molar amount.
$n(Pb^{2+}) = n(PbI_2) = 2.03 \times 10^{-2}$ mol	Both PbI_2 and Pb^{2+} have a coefficient of 1 in the equation.
$n[Pb(NO_3)_2] = n(Pb^{2+}) = 2.03 \times 10^{-2}$ mol	The lead ion subscript in $Pb(NO_3)_2$ is 1.
$c[Pb(NO_3)_2]$ $= \frac{n}{V} = \frac{2.03 \times 10^{-2}}{1.29} =$ **1.58×10^{-2} mol L^{-1}**	

Example 12 Determine the volume of 0.12 mol L^{-1} sulfuric acid solution $SO_4(aq)$ that would be needed to neutralise 162 mL of 2.90 mol L^{-1} sodium hydroxide solution, NaOH(aq).

$2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$	Write an equation for the change described.
$n(NaOH) = c\,V = 2.90 \times 162 \times 10^{-3} = 0.470$ mol	Determine the n(NaOH) to be neutralised.
$n(H_2SO_4) = \frac{1}{2} \times n(NaOH) = \frac{1}{2} \times 0.470 = 0.235$ mol	The equation shows the molar amount of H_2SO_4 used in the reaction is half (1/2) that of NaOH.
$V(H_2SO_4)$ $= \frac{n}{c} = \frac{0.235}{0.12} =$ **2.0 L $H_2SO_4(aq)$**	The rearranged concentration equation is used to find the required volume of $H_2SO_4(aq)$.

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Attempt Set 13 # 6.

9.7 Stoichiometry with percentage purity

Figure 4 Open cut gold mining.
The percentage purity of ores and minerals is a significant factor in determining the feasibility of a mining project. Gold ores mined in Australia may be economically viable to mine even though the percentage of gold in the ore is as low as 1×10^{-4}% gold (ie 1 ppm). Iron deposits by contrast need to be around 60% iron for the deposit to be economical. Many other factors are also considered in the feasibility study of any new mining project.

Many laboratory reagents are less than 100% pure. While this is acceptable for most applications, some procedures like titrations, require reagents called primary standards which must be of very high purity (close to 100%). Minerals and ores typically have low purity while pharmaceuticals must be produced as close to 100% pure as practical due to possible unwanted side effects of impurities.

The **percentage purity** of an element or compound gives the percentage by mass of the element or compound in an impure sample.

$$\%\ \text{purity} = \frac{m_{(\text{pure substance})} \times 100}{m_{(\text{impure sample})}}$$

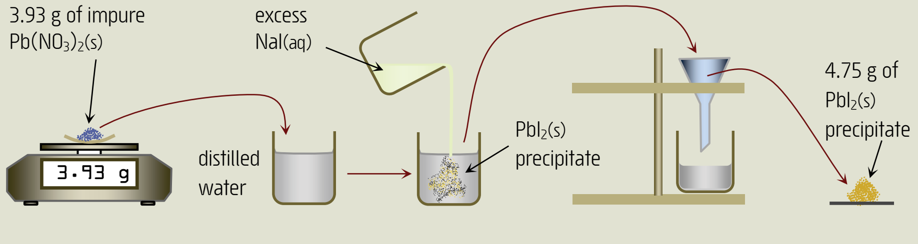
Note: Ensure the same units of mass are used for both mass measurements.

Analytical procedures are used in the laboratory to find the percentage purity of an impure sample. To do this, a measured mass of the impure substance is analysed by stoichiometric means to determine the actual mass of pure substance it contains. (Examples 13 and 14.)

Example 13 A 7.29 g sample of ore from a Broken Hill mine was analysed by chemical means and found to contain 1.43 g of zinc sulfide. What is the percentage purity of zinc sulfide in the rock sample from the Broken Hill mine site?

$\%\text{ZnS} = \dfrac{m(\text{ZnS}) \times 100}{m[\text{sample}]} = \dfrac{1.43 \times 100}{7.29} = \mathbf{19.6\%}$	Since the rock sample has a mass of 7.29 g and contained 1.43 g of zinc sulfide.

Example 14 The purity of a lead(II) nitrate, $Pb(NO_3)_2$ sample is determined by dissolving a 3.93 g sample of the mixture in approximately 150 mL of water then adding excess sodium iodide solution, NaI(aq). The resulting precipitate of $PbI_2(s)$ was filtered, washed and dried and found to have a mass of 4.75 g. What is the percentage purity



$Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$	Write an equation for the change described.
$n(PbI_2) = \dfrac{m}{M} = \dfrac{4.75}{461.0} = 1.03 \times 10^{-2}$ mol	Convert the mass of PbI_2 to an equivalent molar amount.
$n(Pb^{2+}) = n(PbI_2) = 1.03 \times 10^{-2}$ mol	Both PbI_2 and Pb^{2+} have a coefficient of 1 in the equation.
$n[Pb(NO_3)_2] = n(Pb^{2+}) = 1.03 \times 10^{-2}$ mol	The lead ion subscript in $Pb(NO_3)_2$ is 1.
$m[Pb(NO_3)_2] = n \times M = 1.03 \times 10^{-2} \times 331.22 = 3.41$ g	Converting moles of $Pb(NO_3)_2$ to an equivalent mass.
$\%[Pb(NO_3)_2] = \dfrac{m[Pb(NO_3)_2] \times 100}{m[Pb(NO_3)_2\ \text{mixture}]} = \dfrac{3.41 \times 100}{3.93} = \mathbf{86.8\%}$	As the 3.93 g of mixture is found to contain 3.41 g of $Pb(NO_3)_2$.

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Attempt Set 13 # 7 and 8.

9.8 Percentage yield of a chemical reaction

The **theoretical yield** (maximum yield) of a chemical reaction gives the amount of product that would be formed when the limiting reagent is fully consumed. It is calculated in the normal way using the stoichiometric relationship shown in the balanced chemical equation. In most instances the **actual yield** of a given product will be less than the theoretical yield. This may happen for any one of several reasons. The reaction may not go to completion; this is especially relevant to equilibrium reactions; unwanted or side reactions may give different products or it simply may not be possible to completely separate all of the product from the final reaction mixture.

The comparison of actual yield to the theoretical gives the **percentage yield** of a reaction.

$$\textbf{\% yield} = \frac{\textbf{actual yield x 100}}{\textbf{theoretical yield}}$$

Note: Use the same units of mass (or moles) for both actual and theoretical yield.

Chemical engineers who manage industrial chemical processes often try to achieve a maximum percentage yield at minimum cost.

Example 15 The industrial manufacture of sulfuric acid by the **Contact process** uses sulfur, water and air to produce sulfuric acid. The overall equation for this process is shown below. A chemist notes the consumption of 4.50 tonne of sulfur results in the formation of 12.9 tonne of sulfuric acid. Determine the theoretical yield of sulfuric acid for this amount of sulfur and hence calculate the percentage yield for the overall process.

$$2S(l) \ + \ 2H_2O(l) \ + \ 3O_2(g) \ \rightarrow \ 2H_2SO_4(l)$$

$n(S) = \frac{m}{M} = \frac{4.50 \times 10^6}{32.07} = 1.40 \times 10^5$ mol	Find the moles of sulfur from the given mass. Remember 1 tonne = 1×10^6 g.
$n(H_2SO_4) = \frac{2}{2} \times n(S) = \frac{2}{2} \times 1.40 \times 10^5 = 1.40 \times 10^5$ mol	Use the stoichiometric ratio to find the **theoretical yield** of H_2SO_4 in moles.
$m(H_2SO_4) = n \times M = 1.40 \times 10^5 \times 98.086 = 1.38 \times 10^7$ g	Convert the **theoretical yield** of H_2SO_4 to mass (ie grams).
%yield $= \frac{\text{actual yield x 100}}{\text{theoretical yield}} = \frac{1.29 \times 10^7 \times 100}{1.38 \times 10^7} =$ **93.7%**	As the actual yield is 1.29×10^7 g and the theoretical yield is 1.38×10^7g.

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Complete Set 13.

Set 13 Stoichiometry: Quantities in chemical change

1. The overall equation for the **electrolytic extraction** of aluminium, Al from alumina, Al_2O_3 in the Hall-Heroult process is shown here:

   $$2Al_2O_3(l) \ + \ 3C(s) \ \rightarrow \ 4Al(l) \ + \ 3CO_2(g)$$

   a. How many moles of carbon are used in the treatment of 36 moles of alumina?

   b. Determine the moles of carbon dioxide that would be produced in the formation of 5.9 moles of aluminium.

   c. The use of metals like aluminium in the construction industry are said to carry associated **'upstream greenhouse gas emissions'**. What might this refer to?

2. One method of producing the renewable fuel **ethanol** is by the **fermentation** of **glucose**. The chemical equation for the conversion of glucose to ethanol by yeast is:

   $$C_6H_{12}O_6(aq) \ \rightarrow \ 2C_2H_5OH(aq) \ + \ 2CO_2(g)$$

   a. How many moles of ethanol can be made from the fermentation of 155 g of glucose, $C_6H_{12}O_6$?

   b. What mass of $CO_2(g)$ is produced from the fermentation of 16 moles of glucose?

   c. The fermentation of glucose from sugar cane or any other plant product, produces $CO_2(g)$. Despite this, the production of ethanol by this method does not contribute to increased levels of atmospheric $CO_2(g)$. Account for this observation.

3. A student investigation of the **fermentation** process involves collecting and measuring the amount of $CO_2(g)$ produced by the reaction. Over a 48 minute period the student collected 195 mL of the gas in an inverted measuring cylinder. Determine the moles of gas this represents if the gas volume was measured at the following conditions.

   a. At STP.

   b. At a pressure and temperature of 103.2 kPa and 27.00 °C respectively.

Figure 5 Since 2002 the Australian Government has encouraged the industrial production of ethanol in Australia through the '**Ethanol Production Grants** (EPG) program'. Ethanol producers receive a grant of around 38.1 cents per litre of ethanol produced, if the ethanol is to be used in transportation.

Ethanol produced from **biomass**, such as molasses waste from the sugar refining industry, has the advantage of being a **renewable energy source** while also potentially reducing greenhouse emissions as a partial petrol replacement.

The manufacture of biofuels such as ethanol can pose environmental and social issues. Large scale production would require vast amounts of agricultural land, fertilisers and water resources. These issues are minimised if agricultural waste products like molasses can be used instead of cropping specifically for biofuel production.

4. An easy way to produce pure **oxygen** gas for use in the laboratory is to decompose hydrogen peroxide. The reaction is best carried out using some $MnO_2(s)$ catalyst.

   $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

   What mass of hydrogen peroxide should be used to produce 6.5 L of oxygen gas measured at STP?

5. The fuel known as **petrol** is a mixture of various hydrocarbon compounds. The following equation shows the combustion of **octane**, a component of petrol.

   $2C_8H_{18}(l) + 25O_2(g) \rightarrow 18H_2O(g) + 16CO_2(g)$

   a. What volume of carbon dioxide can be expected from the combustion of 34.9 kg of octane (equivalent to a 50 L tank of petrol)? You may assume the gas is released to the atmosphere at 102 kPa and 35.00 °C.
   b. Determine the volume of oxygen the engine would need to use to complete this reaction. Assume the same conditions of temperature and pressure as in Part (a).
   c. What volume of air would the engine have to take in to complete this reaction? Assume the same conditions of temperature and pressure as in Part (a). Remember the percentage purity of oxygen in air is 21 % by volume.

6. A sulfuric acid solution is used as the electrolyte in motor vehicle **lead-acid batteries**. (See p84-5.) An accidental spill of 20.5 L of 4.80 mol L^{-1} battery acid at a manufacturing plant needs to be neutralised by adding sodium hydrogencarbonate powder, $NaHCO_3$ (commonly known as **sodium bicarbonate**).

   a. Write an equation for the reaction between a sulfuric acid solution and solid sodium bicarbonate powder.
   b. What minimum mass of sodium bicarbonate should be used to neutralise the spill?
   c. Instead of using sodium hydrogencarbonate, the spill could have been neutralised with a saturated 4.30 mol L^{-1} solution of sodium carbonate, $Na_2CO_3(aq)$. What minimum volume of this sodium carbonate solution would be needed?

7. Many ionic substances have a tendency to absorb water vapour from the air. Substances like this are said to be hygroscopic. Common table salt, NaCl used in cooking and on food is one such example. In humid conditions it can become moist and difficult to apply from the salt shaker. For this reason table salt bought from the supermarket often contains a small amount of **anti-caking agent**, like calcium silicate, $CaSiO_3$ added to prevent clumping in **humid** conditions.

   a. Explain in terms of intermolecular forces, why some ionic compounds like NaCl should be hygroscopic?
   b. A sample of household **table salt** that was freshly removed from its plastic packaging was analysed to determine its purity. The analysis showed a 25.6 g sample of the salt contained 24.9 g of NaCl. Determine the **percentage purity** of salt, NaCl in the sample and suggest the nature of the impurity.
   c. A student obtains a 3.25 g sample of table salt from an open box in their kitchen pantry. They analyse the sample by dissolving it in 150 mL of water and then adding excess silver nitrate solution, $AgNO_3(aq)$. The resulting silver chloride, AgCl precipitate is filtered, washed and dried and found to have a mass of 7.68 g. Determine the mass of NaCl in the table salt sample and use this to calculate the **percentage purity** of the their table salt.

8. What amount of gold is present in an ore body estimated at 2.5×10^6 tonnes that contains an average of 2.3×10^{-4} % gold?

9. As explored earlier (Question 2) the renewable fuel **ethanol** can be made by the fermentation of glucose (Fig 6) as shown by following overall equation.

$$C_6H_{12}O_6(aq) \rightarrow 2C_2H_5OH(aq) + 2CO_2(g)$$

A student investigating the **yield** of this reaction used yeast to ferment 209 g of glucose until no further reaction was evident. By stoichiometric means the student calculated this should produce 107 g of ethanol. Using distillation, the student was able to separate 49.3 g of ethanol from the final reaction mixture.

a. What percentage yield did the student achieve?

b. Suggest two possible reasons for not achieving a 100% yield in this experiment.

Figure 6 Fermenting sugar from sugar cane produces ethanol. Notice the foaming surface. This is due to the formation of $CO_2(g)$.

10. A student plans an investigation into the relationship between the **moles of copper used** and **moles of silver produced** for the metal-metal ion displacement reaction of copper metal with silver nitrate solution. (See Fig 7.) The student's literature search gives the following equation for this reaction.

$$Cu(s) + 2AgNO_3(aq) \rightarrow 2Ag(s) + Cu(NO_3)_2(aq)$$

a. From her research suggest a reasonable hypothesis for her investigation of the stoichiometry between **silver** and **copper** in this reaction.

b. What changes would the student observe during the progress of this reaction?

c. In one investigation, a coil of copper wire was weighed then placed into a silver nitrate solution. (See Fig 7.) After three days the copper coil was removed, washed with distilled water then dried and reweighed. The solid silver reside that formed was collected by filtration and after washing and drying was also weighed. Use the data below to determine the **mole ratio** of **silver to copper** for this reaction ie **n(Ag) : n(Cu)**.

mass of **copper coil before** reaction with silver nitrate solution..	15.53 g
mass of **copper coil after** reaction with silver nitrate solution	14.69 g
mass of **filter paper** used for collecting silver residue	1.08 g
mass of **filter paper** and **silver** residue	3.78 g

d. Does the result from Part (c) support the hypothesis you outlined in Part (a)? Explain.

e. From the mass of copper consumed, determine the **theoretical yield** of silver using the equation given above.

f. What was the **percentage yield** of silver in the experiment described here?

g. Suggest why the percentage yield was less than 100%.

Figure 7 A copper coil placed into a silver nitrate solution quickly develops a thick deposit of **metallic silver**. As it does so, the metallic copper dissolves forming $Cu^{2+}(aq)$ and gives the solution a pale blue colour.

11. **Antacid tablets** can contain a variety of different substances that neutralise stomach acid (hydrochloric acid) to give relief from indigestion. One particular tablet contains magnesium carbonate, $MgCO_3$ as the neutralising agent along with an inert binding agent. The tablet claimed to contain 95% by mass of the active ingredient magnesium carbonate. To test this claim Glenda added five tablets to a conical flask containing excess hydrochloric acid solution. (See Fig 8.) She recorded the following data.

total mass of 5 antacid tablets	26.85 g
mass of flask + HCl(aq) solution	157.98 g
mass of flask + HCl(aq) solution + 5 antacid tablets after reaction	172.60

a. Determine the mass of $CO_2(g)$ released in the reaction. Assume the weight loss of the flask and its contents is entirely due to the evolution of $CO_2(g)$. (See Fig 8.)

b. Write an equation for the reaction between magnesium carbonate and hydrochloric acid and determine the mass of magnesium carbonate actually present in the five antacid tablets.

c. Using the experimental data, determine the **% purity** of $MgCO_3$ in the antacid tablets.

d. Suggest a reason why Glenda chose to use five antacid tablets rather than one.

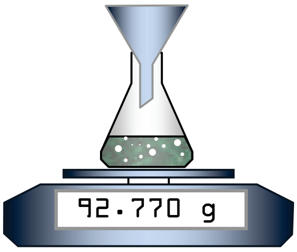

Figure 8 Carbon dioxide has a very low solubility in warm acid solutions like the reaction mixture involved in this experiment, so as the CO_2 gas is formed it escapes from the reaction mixture. The loss of mass in the reaction mixture can be assumed to be equal to the mass of CO_2 produced. A filter funnel may be placed into the neck of the conical flask to prevent loss of solution as the reaction mixture fizzes rapidly. In practice, loss of water vapour may be an issue to consider.

12. The active ingredient giving household **vinegar** its distinct taste and odour is the **weak monoprotic acid** ethanoic acid (acetic acid, CH_3COOH). One way to easily determine the concentration of ethanoic acid in vinegar is to add a single large calcite crystal to some of the solution. Calcite crystals consist of pure insoluble calcium carbonate, $CaCO_3(s)$. The crystal will partially dissolve and hence lose mass in the acid solution. The equation for this reaction is:

$$2CH_3COOH(aq) + CaCO_3(s) \rightarrow Ca(CH_3COO)_2(aq) + CO_2(g) + H_2O(l)$$

A large 27.7 g crystal of calcite was left overnight in 120.0 mL of vinegar solution. The following day, when the reaction was complete, the calcite crystal was removed, carefully washed, dried and reweighed. The remaining piece of calcite had a mass of 20.2 g.

a. Why doesn't a calcite crystal lose mass when left overnight in water alone but the presence of an acid does cause it to lose mass?

b. Explain the meaning of '**weak monoprotic acid**'. Include an equation to support your explanation.

c. Determine the mass of calcite reacting with ethanoic acid and hence determine the mass of ethanoic acid in the vinegar solution.

d. Most vinegars are around 5% by mass ethanoic acid though some can be as high as 18%. Given the vinegar tested has a density of 1010 g L^{-1} (ie 1.01 g mL^{-1}) determine the percentage of ethanoic acid in the vinegar tested.

e. Using your result from 12(d) calculate the molar concentration (mol L^{-1}) of ethanoic acid in vinegar.

f. While ethanoic acid is the most distinctive acid found in vinegar it is not the only one present. Varying amounts of tartaric acid, malic acid, citric and other organic acids will also be present. With this in mind, would the true percentage of ethanoic acid in the test sample be higher or lower than calculated here? Explain.

13. Inside a **blast furnace** used for the extraction of iron from iron ore, many different reactions take place. The particular reaction that produces iron is shown here.

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(l) + 3CO_2(g)$$

Determine the mass of iron that is produced for every 1.00 tonne of ore if the ore contains 97% Fe_2O_3 by mass and the extraction process achieves a 98% yield of iron.

14. Erin needed some **barium phosphate**, $Ba_3(PO_4)_2$ for a fertiliser investigation she was planning; however, the school laboratory didn't stock any. Knowing that insoluble ionic compounds can be produced in the laboratory by a simple precipitation reaction she decided to make some. Erin decided to utilise the reaction between **phosphoric acid** and **barium chloride** solution to make the required barium phosphate.

a. Write a balanced molecular equation for this precipitation reaction.

b. What volume of 4.50 mol L^{-1} phosphoric acid should Erin use if she requires a minimum of 25 g of barium phosphate? Assume she uses excess barium chloride solution.

c. Erin estimated her yield for the production of barium phosphate would be around 85%. Why might Erin expect less than a 100% yield?

d. Assuming she was correct about the 85% yield, determine the volume of 4.50 mol L^{-1} phosphoric acid she should use to obtain the required 25 g of barium phosphate.

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15. **Copper** is an extremely useful metal due to its excellent combination of properties of high electrical and heat conductivity and its low chemical reactivity with air and water. Australia is the world's fourth largest producer of this important metal. Most of this copper comes from deposits containing the mineral **chalcopyrite**, **$CuFeS_2$**. Copper is extracted from chalcopyrite by strongly heating the finely powdered mineral in air, in a process called roasting. The two important chemical changes that happen in the roasting process are shown here.

$$2CuFeS_2(s) + 4O_2(g) \rightarrow Cu_2S(s) + 2FeO(s) + 3SO_2(g)$$

$$Cu_2S(s) + O_2(g) \rightarrow 2Cu(l) + SO_2(g)$$

a. Write the **overall equation** for the formation of copper from chalcopyrite.

b. A particular ore body contains 11.9% chalcopyrite by mass. In order to extract the copper contained in the ore it must first be mined, crushed and the mineral component, chalcopyrite, concentrated. What mass of pure copper can be obtained from 1.00 tonne of the final concentrate if it contains **96.4% chalcopyrite** by mass?

c. A by-product of this process is a harmful pollutant. What is the pollutant and why is it harmful to buildings as well as people's health?

16. As examined in Question 15, the extraction of copper from chalcopyrite results in the formation of the **environmental pollutant**, **sulfur dioxide**, SO_2. If this gas is released to the atmosphere it can cause respiratory problems for nearby populations as well as contributing to acid rain. While the best option is to avoid producing such harmful substances another solution is to use the sulfur dioxide to produce sulfuric acid. This enhances the **sustainability** (see border note) of the copper extraction process by providing a valuable by product from an otherwise serious pollutant. The overall reactions involved in this conversion are shown here.

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$$

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$$

a. Write the overall equation for the formation of sulfuric acid from sulfur dioxide.

b. Determine the **volume** of sulfur dioxide, SO_2 that would result from the treatment of 1.00 tonne of pure chalcopyrite, $CuFeS_2$. Assume the gas is released at atmospheric conditions of 27.0 °C and 101 kPa with a yield of exactly 100%.

c. What **mass** of **sulfuric acid** could be produced from 1.00 tonne of pure chalcopyrite, $CuFeS_2$?

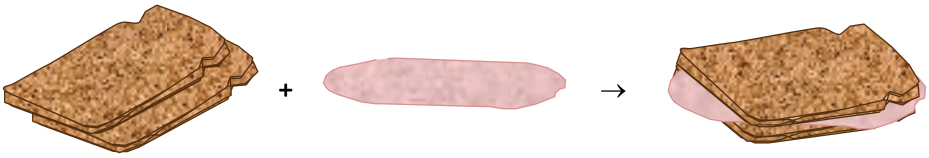
d. If the percentage yield of sulfuric acid in this process is only 93.0% determine the **actual mass** of sulfuric acid resulting from the treatment of 1.00 tonne of chalcopyrite.

The most widely accepted definition of **sustainability** originates from 'The World Commission on Environment'. Established in 1983 by the United Nations, its purpose was to address 'the accelerating deterioration of the human environment and natural resources and the consequences of that deterioration for economic and social development.' A report from the commission in 1987 titled, 'Our Common Future', (The Brundtland Report) defined **sustainable development**, describing it as 'development which meets the needs of the present without compromising the ability of future generations to meet their own needs'.

Green chemistry aims to promote sustainable development by minimising the use and generation of hazardous substances. The chemical industry can also make a contribution to a sustainable future by minimising resource depletion through recycling and the use of renewable resources.

9.9 Limiting reagents: How much is enough?

In most situations where a chemical reaction is carried out, one of the two reagents will be present in **excess**. This means some of it will be left over when the reaction has stopped. The other reagent is **fully consumed** and is known as the **limiting reagent**. If the amount of each reagent is known, it is possible to find which of these is the limiting reagent. It is important to know which is the limiting reagent as it fixes the amount of all other substances used or produced in the reaction. The concept of a limiting reagent can be seen in many everyday situations. (See Fig 9.)



2 slices of bread + **1 slice of salami** → **1 salami sandwich**

Figure 9 A party problem? You are having friends over for a party and need to make as many salami sandwiches as possible. You have 24 slices of bread and 16 slices of salami.

Each sandwich needs two slices of bread and one slice of salami. There are enough ingredients for 12 salami sandwiches with 4 left over slices of salami.

The **limiting ingredient** here was the **bread**. It determined how many sandwiches were able to be made and how much salami was used. The salami was the **excess ingredient**.

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9.10 Finding the limiting reagent

One method for finding the limiting reagent is to compare the **actual mole ratio** of the two reagents (ie from the moles added to the reaction) to their **stoichiometric mole ratio** (ie from the moles shown by the equation coefficients). (See Example 16.) Another method for finding the limiting reagent is by **trial and error**. (See Example 17.)

Example 16 Determine the **limiting reagent** when 9.87 moles of aluminium is added to 24.5 moles of hydrochloric acid.

$$2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$$

actual ratio $= \dfrac{n(HCl)}{n(Al)} = \dfrac{24.5}{9.87} = \mathbf{2.48}$	Find the actual mole ratio of the two reagents using the amounts given. Either reagent can be the numerator.
stoichiometric ratio $= \dfrac{n(HCl)}{n(Al)} = \dfrac{6}{2} = \mathbf{3}$	Find the stoichiometric mole ratio using the equation coefficients. Keep the same numerator.
actual ratio < stoichiometric ratio ∴ **HCl is the limiting reagent.**	If the actual ratio (AR) is greater than the stoichiometric ratio (SR) then the **denominator** (see border note) is the limiting reagent. Alternatively if the AR is less than the SR then the **numerator** is the limiting reagent.

numerator

$$\frac{\mathbf{24.5}}{\mathbf{9.87}}$$

denominator

Example 17 Determine the **limiting reagent** when 9.87 moles of aluminium is added to 24.5 moles of hydrochloric acid.

$$2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$$

Let Al $\mathbf{n(HCl)} = \dfrac{6}{2} \times n(Al) = \dfrac{6}{2} \times 9.87 = \mathbf{29.6\ mol}$	Either reagent Al or HCl, is assumed to be the limiting reagent. Use the assumed limiting reagent to calculate the required amount of the other reagent.
Hence there is insufficient HCl for the complete reaction of Al. Thus **HCl is the limiting reagent.**	As 29.6 mol of HCl is needed for the complete reaction of 9.87 mol of Al and only 24.5 mol of HCl is present.

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Attempt Set 14 # 1 and 2.

9.11 Stoichiometry with a limiting reagent

In order to calculate the amounts of different substances involved in a chemical reaction it is necessary to know the limiting reagent. Often, only the amount of one reactant is given so this is assumed to be the limiting reagent and the other reagent must be present in excess. If the amount of two reactants in a chemical reaction is given, then the **limiting reagent** must first be identified. This can be achieved either by comparing the **actual ratio** to the **stoichiometric ratio** or by a **trial and error** method. (See Examples 16 and 17.) The limiting reagent is then used to calculate the amount of any other substance involved in the reaction. (See Examples 18 and 19.)

Example 18 A student adds a 10.50 g piece of zinc metal to a solution containing 10.50 g of hydrochloric acid. (See Fig 10.) Find the mass of zinc chloride formed and determine the amount of excess reagent left unused.

$$Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

$n(HCl) = \frac{m}{M} = \frac{10.50}{36.46} = 0.2880$ mol	Find the moles of HCl from the given mass.
$n(Zn) = \frac{m}{M} = \frac{10.50}{65.38} = 0.1606$ mol	Find the moles of Zn from the given mass.
actual ratio $= \frac{n(HCl)}{n(Zn)} = \frac{0.2880}{0.1606} = 1.793$ stoichiometric ratio $= \frac{n(HCl)}{n(Zn)} = \frac{2}{1} = 2$	Find the actual and stoichiometric mole ratio of the two reagents. Either reagent can be the numerator but use the same numerator for both.
Insufficient HCl for complete reaction of Zn ∴ **HCl is the limiting reagent**.	Since the actual ratio (AR) is less than the SR then the **numerator** is the limiting reagent.
$n(ZnCl_2) = \frac{1}{2}$ x $n(HCl) = \frac{1}{2}$ x $0.2880 = 0.1440$ mol **m($ZnCl_2$)** = n x M = 0.1440 x 136.28 = **19.62 g**	Use the limiting reagent to determine the moles and hence mass of $ZnCl_2$ formed.
n(Zn used) $= \frac{1}{2}$ x $n(HCl) = \frac{1}{2}$ x $0.2880 = 0.1440$ mol m(Zn used) = n x M = 0.1440 x 65.38 = 9.414 g	Use the limiting reagent to determine the moles and hence mass of Zn used.
m(Zn remaining) = m(Zn original) - m(Zn used) = 10.50 - 9.414 = **1.09 g** (2DP, ie now only 3SF)	Originally 10.50 g of Zn was added and only 9.414 g is consumed by the HCl.

Figure 10 The **zinc strip** shown here is reacting with some **HCl(aq)**. Notice the bubbles of colourless hydrogen gas forming on the zinc surface. In this experiment **zinc** was the **excess** reagent as some of it was left over when the reaction ceased. Thus **HCl(aq)** was fully consumed and is the **limiting reagent**.

Example 19 A student adds 55.0 mL of 1.26 mol L^{-1} lead(II) nitrate solution to 25.0 mL of 2.60 mol L^{-1} magnesium iodide solution. A precipitation reaction occurs forming the yellow solid PbI_2. (Fig 11.)

$$Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$$

a. Determine the moles of PbI_2 formed.

b. What is the concentration of $Pb^{2+}(aq)$ and $I^-(aq)$ in the final reaction mixture?

a. $n(Pb^{2+}) = n(Pb(NO_3)_2) = c\,V = 1.26$ x 55.0x10^{-3} = 0.0693 mol	Each mole of $Pb(NO_3)_2$ contains 1 mole of Pb^{2+} hence determine the $n(Pb^{2+})$ added.
$n(I^-)$ = 2 x $n(MgI_2)$ = 2 x c V of MgI_2 = 2 x 2.60 x 25.0x10^{-3} = 0.130 mol	As the subscript for **I** in Mg**I**$_2$ is 2. Also volume must be in L, ie 25.0 mL = 25.0 x 10^{-3} L.
Let Pb^{2+} be the limiting reagent.	For the trial and error method, either reagent, Pb^{2+} or I^- is assumed to be the limiting reagent.
$n(I^-) = \frac{2}{1}$ x $n(Pb^{2+}) = \frac{2}{1}$ x $0.0693 = 0.139$mol	Use the assumed limiting reagent (Pb^{2+}) to find the required amount of I^-.
As there is insufficient I^- for the complete reaction of Pb^{2+} then I^- is the limiting reagent.	There is only 0.130 mol of I^- and 0.139 mol is needed to fully consume 0.0693 mol of Pb^{2+}.
n(PbI_2) $= \frac{1}{2}$ x $n(I^-) = \frac{1}{2}$ x 0.130 = **0.0650 mol**	Use the limiting reagent to find the amount of PbI_2 formed.
b. $n(Pb^{2+}$ used) $= \frac{1}{2}$ x $n(I^-) = \frac{1}{2}$ x 0.130 = 0.0650 mol	Use the limiting reagent to find the amount of Pb^{2+} used.
$n(Pb^{2+}$ remaining in solution) = $n(Pb^{2+}$ originally present) - $n(Pb^{2+}$ reacting with I^-) = 0.0693 - 0.0650 = 0.0043 mol (4DP, ie 2SF)	Some Pb^{2+} remains in solution as it is the excess reagent.
c(Pb^{2+}) $= \frac{n}{V} = \frac{0.0043}{80 \text{ x } 10^{-3}}$ = **0.054 mol L^{-1}** (2SF)	The total solution volume is: 55.0 mL + 25 mL = 80.0 mL
$n(I^-$ remaining in solution) = 0 mol ∴**c(I^-) = 0 mol L^{-1}**	I^- is the limiting reagent so it is fully consumed and none of it remains in solution.

Figure 11 As **$Pb(NO_3)_2$** is slowly added to some **MgI_2(aq)** solution, it forms a bright **yellow precipitate** of **PbI_2(s)**. Initially lead(II) nitrate is the **limiting** reagent. As more of it is added, so more yellow PbI_2(s) forms. Eventually, if too much **$Pb(NO_3)_2$** solution is added, it then becomes the **excess** reagent. When this happens no further PbI_2(s) will be formed even if more **$Pb(NO_3)_2$** solution is added.

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Complete Set 14.

Set 14 Limiting reagent calculations

1. In an investigation into the precipitation of $Fe_2(CO_3)_3$(s) a student uses a solution of $FeCl_3$(aq) and reacts this with varying amounts of K_2CO_3(aq). In each case she uses 1.30 mol of $FeCl_3$(aq) and repeats the procedure with 1.80 mol, 2.00 mol and 2.20 mol of K_2CO_3(aq). For each experiment determine the **limiting reagent** and use this to calculate the **moles** of **$Fe_2(CO_3)_3$(s)** that should form. The molecular equation is:

   $2FeCl_3(aq) \ + \ 3K_2CO_3(aq) \ \rightarrow \ Fe_2(CO_3)_3(s) \ + \ 6KCl(aq)$

2. The preparation of **hydrogen gas** in the laboratory is achieved by the reaction between hydrochloric acid and zinc metal.

   $Zn(s) \ + \ 2HCl(aq) \ \rightarrow \ ZnCl_2(aq) \ + \ H_2(g)$

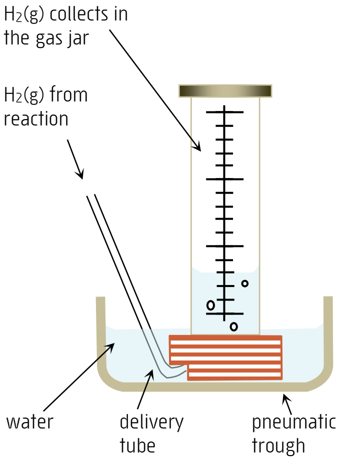
   A student tested the **hypothesis**, 'The volume of hydrogen gas formed (in the above reaction) increases in direct proportion to the mass of zinc consumed.' He performed several experiments reacting zinc with hydrochloric acid. In each case 50.0 mL of 2.5 mol L^{-1} hydrochloric acid was used. The reaction was allowed to go to completion by leaving the Zn and HCl mixture to react overnight. The volume of hydrogen formed was recorded the following day. (See Fig 12.) The mass of zinc used in each of his experiments is shown here.

   Experiment 1: Mass of zinc added to the hydrochloric acid solution .... 3.12 g
   Experiment 2: Mass of zinc added to the hydrochloric acid solution .... 3.85 g
   Experiment 3: Mass of zinc added to the hydrochloric acid solution 4.21g
   Experiment 4: Mass of zinc added to the hydrochloric acid solution .... 4.57 g

   The student was puzzled to find the same volume of hydrogen was produced in Experiment 3 and 4 even though more zinc was present in Experiment 4. Explain why this happened. Support your answer with suitable calculations.

Figure 12 Gases with very low solubility in water, like hydrogen, can be collected by the **downward displacement of water**. The volume of gas collected is found by collecting it in an inverted measuring cylinder.

The temperature of a gas collected this way will be similar to room temperature and its pressure will be room pressure when the water level inside the gas jar matches the water level inside the pneumatic trough.



3. Alka-Seltzer tablets are sometimes taken for the relief of indigestion. When dissolved in water the active ingredients react vigorously producing a strong **fizzing action**. The reaction is shown here.

   $H_3C_6H_5O_7(s) \ + \ 3NaHCO_3(s) \ \rightarrow \ Na_3C_6H_5O_7(aq) \ + \ 3CO_2(g) \ + \ 3H_2O(l)$

   A particular tablet contains 2.15 g of **citric acid**, $H_3C_6H_5O_7$ and 2.65 g of **sodium bicarbonate**, $NaHCO_3$.

   a. Determine the limiting reagent for this Alka-Seltzer tablet.
   b. What volume of carbon dioxide gas would be produced in a person's stomach after accidentally swallowing a single Alka-Seltzer tablet? You may assume the gas is present in the stomach at STP.
   c. Conditions are such that the actual pressure and temperature of the gas produced in the stomach is 106 kPa and 37 °C (normal body temperature). What is the actual volume of carbon dioxide gas at these conditions?
   d. The average adult stomach has a volume of 50 mL when empty and around 1 L when comfortably full. What **physical effect** will the carbon dioxide gas most probably have on the person who swallowed the tablet?

4. Determine the **limiting reagent** and the moles of **left over** excess reagent when 5.55 g of pure marble chips, $CaCO_3$ are added to 21.0 mL of 3.95 mol L^{-1} nitric acid, HNO_3.

   $CaCO_3(s) \ + \ 2HNO_3(aq) \ \rightarrow \ Ca(NO_3)_2(aq) \ + \ CO_2(g) \ + \ H_2O(l)$

5. A student prepared some aluminium carbonate in the laboratory by combining 55.0 mL of 1.55 mol L^{-1} aluminium nitrate with 135 mL of 1.00 mol l^{-1} sodium carbonate.

   $3Na_2CO_3(aq) \ + \ 2Al(NO_3)_3(aq) \ \rightarrow \ 6NaNO_3(aq) \ + \ Al_2(CO_3)_3(s)$

   a. What mass of aluminium carbonate can the student expect from this reaction?
   b. Determine the concentration of Al^{3+}(aq) and CO_3^{2-}(aq) in the remaining solution.

6. **Sulfuric acid** production worldwide is amongst the highest by mass of any synthesised chemical substance. It can be manufactured by the **Contact process** where elemental sulfur is burnt in air, converted to sulfur trioxide and eventually forms sulfuric acid by combining with water. The simplified overall equation for this process is shown here.

   $2S(l) \quad + \quad 2H_2O(l) \quad + \quad 3O_2(g) \quad \rightarrow \quad 2H_2SO_4(l)$

   a. Air is used as the source of oxygen for this process. In a one hour period a particular plant takes in 1.24 x 10^7 L of air measured at 365 °C and 235 kPa. Find the moles of oxygen involved in the process each hour. Assume air to be 20.9% O_2 by volume.

   b. During this one hour period 1.69 tonnes of liquid sulfur is sprayed into the reacting furnace. Determine the limiting reagent in the process.

   c. Assume a plentiful supply of water is available for the reaction and determine the theoretical yield of sulfuric acid in moles per hour.

Figure 13 Worldwide, **sulfuric acid** is one of the most important manufactured chemicals. A major use of sulfuric acid in Australia is for the production of **phosphate fertilisers** used in wheat farming.

Sulfuric acid is also used in the manufacture of explosives, other acids, dyes, glue, synthetic fibres and for the purification of petroleum, the pickling of metal and the electrorefining of copper.

7. Several raw materials used in the blast furnace for the extraction of iron from iron ore include limestone, air, coke and of course the iron ore itself. A variety of reactions happen inside the furnace but the two simplified reactions shown here are responsible for the extraction of iron from iron ore.

   $2C(s) \quad + \quad O_2(g) \quad \rightarrow \quad 2CO(g)$

   $Fe_2O_3(s) \quad + \quad 3CO(g) \quad \rightarrow \quad 2Fe(l) \quad + \quad 3CO_2(g)$

   A particular load of raw materials added to the furnace includes 63.5 tonne of finely powdered coke and 245 tonne of crushed and powdered iron ore. The coke has a carbon content of 98% and the iron ore is 97% pure Fe_2O_3.

   a. Using the information given and only the reactions shown here, determine the limiting reagent for this load of raw materials added to the blast furnace.

   b. What maximum mass of iron can be expected from this combination of reagents?

   c. What mass of excess reagent was present in the furnace?

   d. The actual mass of iron produced by this batch of raw materials turned out to be less than calculated in Part (b). Suggest a reason for this.

8. Laura was investigating the concentration of **carbon dioxide gas** in the Earth's atmosphere. As part of her investigation she designed a chemical process that would let her measure atmospheric CO_2 concentration. She decided to use a fish tank air pump to bubble air through a solution of sodium hydroxide. (See Fig 14.) This, she had learnt, would absorb atmospheric $CO_2(g)$ by converting it to a sodium carbonate solution.

   $CO_2(g) \quad + \quad 2NaOH(aq) \quad \rightarrow \quad Na_2CO_3(aq) \quad + \quad H_2O(l)$

   She could then determine the amount of absorbed carbon dioxide by precipitating the carbonate ions from solution as insoluble calcium carbonate.

   In her experiment Laura bubbled air through 0.75 L of 1.25 mol L^{-1} NaOH(aq). Air was bubbled through the solution for 72 hours at a rate of 2.25 L min^{-1}. For Laura's experiment to work the sodium hydroxide must be an excess reagent. Her literature research told her to **expect** an atmospheric CO_2 level of around **0.038 % CO_2** by **volume** in the Earth's atmosphere.

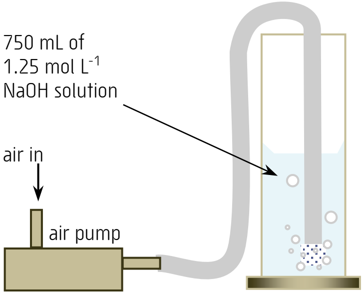
   a. **Determine** the **volume** of **air** and hence the **volume of carbon dioxide gas** that Laura could expect to bubble through the sodium hydroxide solution in the 72 hour period of the experiment.

   b. How many moles of carbon dioxide should Laura anticipate will need to be absorbed by the NaOH(aq) solution? You may assume the air bubbled through the solution is 0.038% by volume $CO_2(g)$ and is at a temperature of 26 °C and pressure of 102 kPa.

   c. Was the sodium hydroxide the excess reagent as Laura had expected? Show your working.

   d. **Explain** why it was important for the sodium hydroxide to be the excess reagent for Laura's experiment to produce meaningful results.

Figure 14 Laura's apparatus for absorbing atmospheric CO_2 gas is shown here.



CHAPTER10 | ORGANIC CHEMISTRY: ALKANES AND ALKENES

Figure 1 The lighter contains both liquid and gaseous **butane**, C_4H_{10} (BP -0.5 °C) while the candle is composed of a mixture of higher melting point **hydrocarbons** (eg $C_{25}H_{52}$) known as **paraffin wax**.

10.1 Review: Hydrocarbons

Hydrocarbons are molecular compounds containing the elements **hydrogen** and **carbon** only; they are the simplest of the **organic compounds**. Fossil fuels like petroleum (crude oil), natural gas and coal are the world's major source of hydrocarbons. Natural gas for example consists primarily of methane mixed with ethane and smaller amounts of propane and butane. Petroleum is a liquid mixture with varying composition and contains literally thousands of different hydrocarbon compounds.

Hydrocarbons are classified into various families based on their structural similarities. Some families include **alkanes**, **alkenes**, **cycloalkanes**, **cycloalkenes** and **aromatics**. We will review some of these compounds in the following sections.

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10.2 Alkanes: Structure and nomenclature

Alkanes consist of molecules with the general formula C_nH_{2n+2}. Their molecules contain **single bonds only** and for this reason are called **saturated** hydrocarbons. Alkane names have the suffix **-ane**. Some alkanes include methane, (CH_4), ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), pentane (C_5H_{12}), hexane (C_6H_{14}), heptane (C_7H_{16}) and octane (C_8H_{18}).

The first part of an alkane name indicates the number of carbon atoms in the molecular chain.

meth....1 carbon atom
eth ......2 carbon atoms
prop ....3 carbon atoms
but ......4 carbon atoms
pent ....5 carbon atoms
hex......6 carbon atoms
hept ....7 carbon atoms
oct.......8 carbon atoms
non .....9 carbon atoms
dec ......10 carbon atoms

Table 1 Structure and nomenclature of selected alkanes.

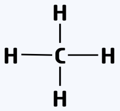
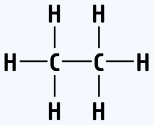
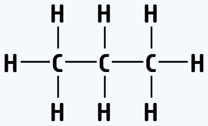
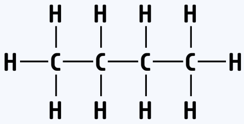
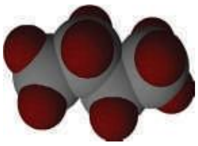
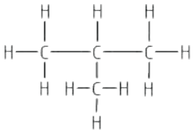
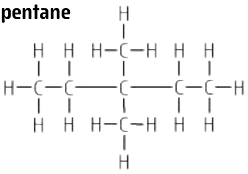
Name	Structural formula	Condensed formula	Molecular shape
methane CH_4		CH_4	
ethane C_2H_6		CH_3CH_3	
propane C_3H_8		$CH_3CH_2CH_3$	
butane C_4H_{10}		$CH_3CH_2CH_2CH_3$	

Figure 2 The ability of hydrocarbon molecules to form branched structures, like the ones shown below, contributes to the great variety and number of possible alkane compounds.

methylpropane



3,3-dimethylpentane



The alkanes shown in Table 1 are all **straight chain** alkanes. Their terminal carbon atoms (ie end ones) are bonded to three hydrogen atoms ($-CH_3$) while the inner carbon atoms bond to two hydrogen atoms ($-CH_2-$). Sometimes alkanes form **branched** structures (see Fig 2) where an inner carbon atom is bonded to three or four carbon atoms and has fewer bonded hydrogen atoms. Variations like this contribute to the great variety and number of different alkane compounds, all of the same general formula C_nH_{2n+2}.

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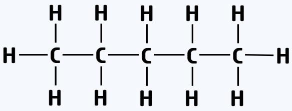
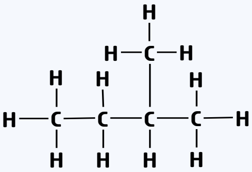
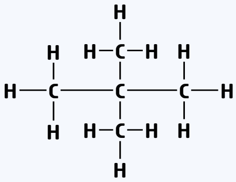
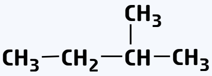
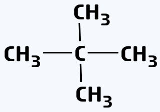
Attempt Set 15 # 1.

10.3 Alkanes: Structural isomerism

Alkanes sometimes form compounds with the same **molecular** formula but a different **structural** formula. This happens when molecules contain the same number and type of atoms but the sequence in which the atoms are bonded is different. Such compounds are known as **structural isomers**. For the three simplest alkanes, CH_4, C_2H_6 and C_3H_8, there exists only one possible structure (Table 1) so these compounds do not have structural isomers. C_4H_{10} however, has two possible structures, C_5H_{10} has three (Table 2) and C_6H_{14} has five structural isomers. Structural isomerism like this contributes to the great variety of possible organic compounds. $C_{40}H_{82}$ for example has over 6 x 10^{13} possible isomers.

Table 2 Structural and condensed formulas for the three **structural isomers** of C_5H_{12}

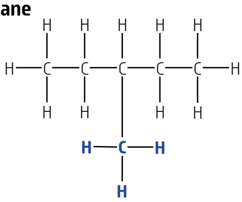
pentane	methylbutane	dimethylpropane
		
$CH_3-CH_2-CH_2-CH_2-CH_3$	 $CH_3-CH_2-\overset{CH_3}{\overset{\vert}{C}H}-CH_3$	 $CH_3-\underset{CH_3}{\underset{\vert}{\overset{CH_3}{\overset{\vert}{C}}}}-CH_3$
$CH_3CH_2CH_2CH_2CH_3$	$CH_3CH_2CHCH_3CH_3$	$CH_3C(CH_3)_2CH_3$

Structural isomers may have similar chemical and physical properties but they are not identical. Pentane for example, boils at 36.1 °C while its structural isomers methylbutane and dimethylpropane boil at 27.9 °C and 9.5 °C respectively. (See Table 2.)

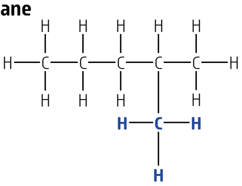
The structural isomers shown above are specifically known as **chain isomers**. Isomers like this vary in the length of their main carbon chain. Table 2 shows the chain isomers of C_5H_{12} can have a main chain length of five, four or three carbon atoms. **Position isomers** are structural isomers with the same chain length that differ in the position of an attached group. Figure 3 shows two position isomers of C_6H_{14}. Each of these isomers has a main chain of five carbon atoms but they differ in the position of the attached methyl group.

Figure 3 The two structural isomers shown here are **position isomers** of C_6H_{14}.

3-methylpentane



2-methylpentane



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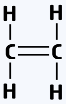
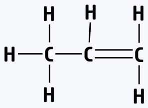
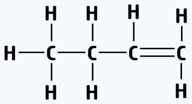
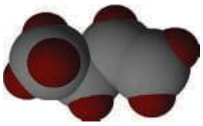
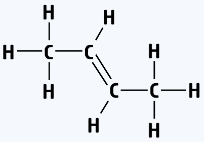
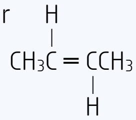
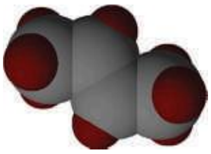
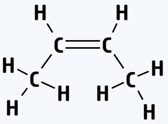
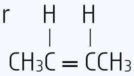
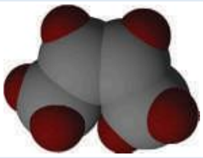
Attempt Set 15 # 2.

10.4 Alkenes: Structure and nomenclature

Alkenes are **unsaturated** hydrocarbons with molecules that contain a carbon to carbon **double bond**. The presence of a double bond means their molecules have two less hydrogen atoms than a corresponding alkane. This is why they are said to be unsaturated. They have the general formula C_nH_{2n}. Alkene names have the suffix **-ene**.

Table 3 Structure and nomenclature of some alkenes.

Name	Structural formula	Condensed structural formula	Molecular shape
ethene C_2H_4		CH_2CH_2 or $CH_2=CH_2$	
propene C_3H_6		CH_3CHCH_2 or $CH_3CH=CH_2$	
but-1-ene C_4H_8		$CH_3CH_2CHCH_2$ or $CH_3CH_2CH=CH_2$	
***trans*-but-2-ene** C_4H_8 (See 10.5)		$CH_3CHCHCH_3$ or  $CH_3\overset{H}{\overset{\vert}{C}}=\underset{H}{\underset{\vert}{C}}CH_3$	
***cis*-but-2-ene** C_4H_8 (See 10.5)		$CH_3CHCHCH_3$ or  $CH_3\overset{H}{\overset{\vert}{C}}=\overset{H}{\overset{\vert}{C}}CH_3$	

As seen with the three versions of C_4H_8 in Table 3, isomerism in alkenes can arise due to the **position** of the double bond as well as due to the **orientation** of the atoms attached to the carbon atoms of the double bond. This latter form of isomerism is called ***cis-trans* isomerism**. (See 10.5.)

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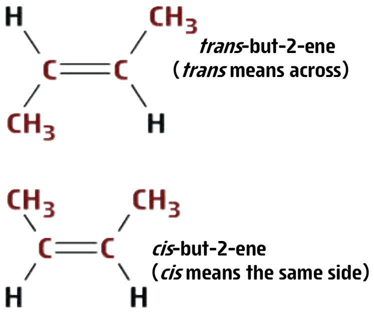
Attempt Set 15 # 3.

10.5 Alkenes: *Cis-trans* isomerism

Some alkene compounds have ***cis-trans* isomers**, formerly called geometric isomers. These isomers have the same molecular formula and structural formula, ie the same sequence of bonding between their atoms, but a different spatial arrangement of their atoms. In an alkene, this different geometry results from the inability of the double bonded carbon atoms to rotate along the axis of their double bond. This has the effect of locking the position of their attached groups on one particular side of the double bond and results in two different arrangements. These different forms are known as ***cis*** and ***trans*** isomers. (See Fig 4.)

Cis-trans isomerism can occur in an alkene if **both** carbon atoms involved in the double bond have **two different groups** attached. If **either** of these carbon atoms has **two identical groups** attached to it, then *cis-trans* isomerism will not occur. Thus 1,1-dichloroprop-1-ene does not have *cis-trans* isomerism but 1,2-dichloroprop-1-ene does. (See Fig 5.)

Figure 4 These two molecules have the **same sequence** of bonding yet the molecules have a **different geometry**. These substances are the ***cis*** and ***trans*** isomers of but-2-ene.



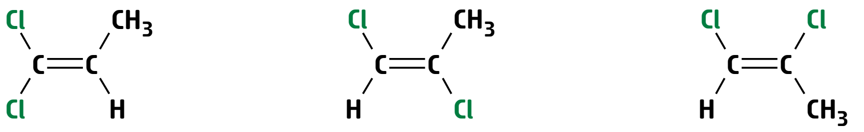

1,1-dichloroprop-1-ene
***trans*-1,2-dichloroprop-1-ene**
***cis*-1,2-dichloroprop-1-ene**

Figure 5 The presence of identical attached groups on one of the double bonded carbon atoms of 1,1-dichloroprop-1-ene prevents it from having *cis-trans* isomerism. Both of the double bonded carbon atoms of 1,2-dichloroprop-1-ene have two different attached groups. This configuration allows the formation of *cis-trans* isomers.

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Attempt Set 15 # 4 and 5.

10.6 IUPAC nomenclature for alkanes and alkenes

The International Union of Pure and Applied Chemistry (IUPAC) has the task of devising and maintaining an up-to-date worldwide system for naming compounds. The IUPAC name for an organic compound such as an alkane or alkene is based on the compound's **parent** or **stem** structure. (See Fig 6 and Table 4.) **Substituent groups** that may be attached to, or form part of the parent chain are identified by adding suffixes and/or prefixes to the name of the parent compound. For example, the presence of a **double bond** is identified using the suffix **-ene**. If only **single bonds** are present then the suffix **-ane** is used. If an **alkyl** group (ie a hydrocarbon side chain on the parent chain) is present, it is identified using prefixes such as **methyl-**, **ethyl-**, **propyl-** and so on. (See Table 5.) If a **halogen** atom ie F, Cl, Br or I occurs on the parent chain then its presence is indicated by the prefixes **fluoro-**, **chloro-**, **bromo-** and **iodo-**.

Figure 6 **IUPAC** names are based on a compound's **parent** or **stem** structure. **Prefixes** and **suffixes** along with **numbers** are used to show the identity and location of substituent groups.

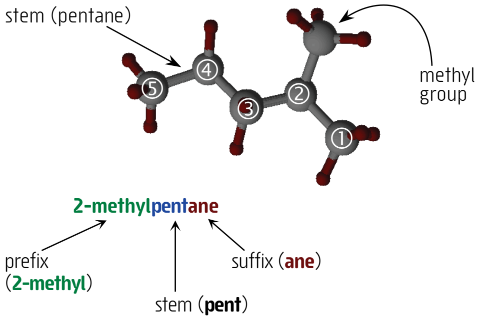


Table 4 Parent alkanes and their **stem** name.

Parent alkane	Stem name	Carbon number
methane	**meth**	**1** carbon atom
ethane	**eth**	**2** carbon atoms
propane	**prop**	**3** carbon atoms
butane	**but**	**4** carbon atoms
pentane	**pent**	**5** carbon atoms
hexane	**hex**	**6** carbon atoms
heptane	**hept**	**7** carbon atoms
octane	**oct**	**8** carbon atoms

Table 5 Some alkyl substituent groups.

Name	Condensed formula
methyl	CH_3-
ethyl	CH_3CH_2-
propyl	$CH_3CH_2CH_2-$
butyl	$CH_3CH_2CH_2CH_2-$

Use the following IUPAC rules when naming **simple** alkanes and alkenes.

① Find the **longest continuous chain** of carbon atoms to which **all** substituent groups are attached. This is the parent chain and determines the **stem** name. If a **carbon to carbon double bond** (-C = C-) is present then the parent chain must be chosen to include it; even if this does not give the longest chain.

② **Number the carbon atoms** of the parent chain sequentially from either end so that the substituent group has the lowest possible number. If several groups are present then number from the end giving the lowest number to the first encountered substituent. (See Fig 7.) Alkyl groups and halogen groups are treated equally for this purpose.

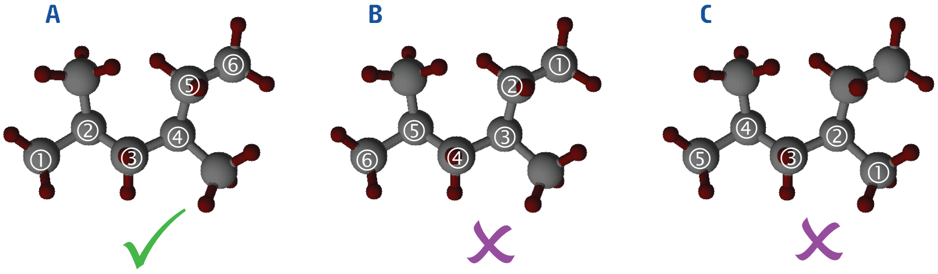
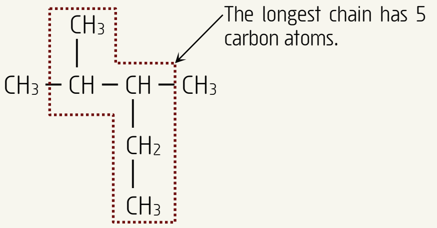
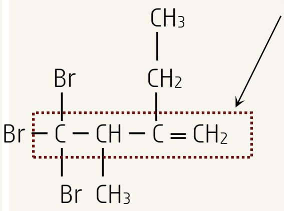
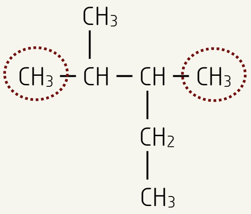
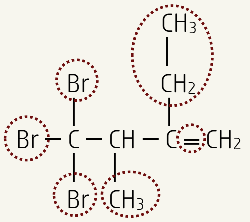
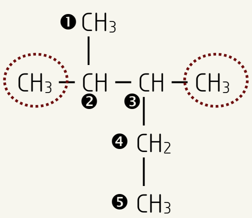
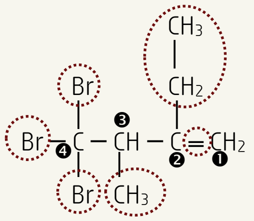


Figure 7 The correct parent chain (six carbon atoms) is shown in **A** and **B**. Alternative **A** also has the correct numbering sequence as it gives the lowest possible number to the first encountered substituent.

③ If a double bond is present it has **numbering priority** so the parent chain is numbered from the end giving it the lowest number irrespective of the position of alkyl or halogen substituents. (See Example 1 Problem 2.)

④ In the final name a double bond is identified by adding the suffix **–ene** to the stem name. Other substituents are named as prefixes and **ordered alphabetically**. All substituents are numbered according to the carbon atom to which they are attached. Prefixes **di**, **tri** and **tetra** are used if multiples of a group are present. These do not affect the alphabetic order. Numbers are separated from letters with a **hyphen** (-) while a **comma** is used to separate numbers. There are no spaces in the final name.

Example 1 Use the IUPAC rules to name the organic compounds shown in Problem 1 and 2.

Procedure	**Problem 1 (a hydrocarbon)**	**Problem 2 (a haloalkene)**
Identify the **longest continuous chain** of carbon atoms (see boxed area) which has all of the substituent groups attached. The number of carbon atoms in this chain determines the stem name.	 The longest chain has 5 carbon atoms. The stem name is pentane	 The longest chain having all the substituent groups attached has 4 carbon atoms. The longer chain of 5 carbon atoms is not used as the double bond is not part of this chain. The stem name is butene
Identify all **substituent groups** attached to the main chain. (These have been circled.)	 Two methyl groups are present.	 One double bond, an ethyl group, three bromo groups and a methyl group are present.
Number each carbon sequentially from the end of the stem that gives the attached group the lowest possible number. If two or more groups are present, number from the end that gives either group the lowest number.		 The double bond has numbering priority.
Write the name of the substance. All prefixes are in alphabetical order.	**2,3-dimethylpentane**	**4,4,4-tribromo-2-ethyl-3-methylbut-1-ene**

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Attempt Set 15 # 6 to 11.

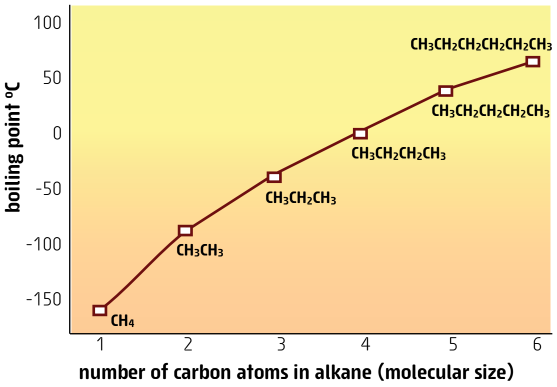
10.7 Hydrocarbons: Physical properties

The physical properties of **melting point**, **boiling point** and **solubility** of molecular compounds such as the hydrocarbons is greatly influenced by the nature and strength of their intermolecular forces. (See border note*.) Boiling points for example, increase with increasing strength of intermolecular forces. In hydrocarbons the only type of intermolecular force of attraction are **dispersion forces**. These forces are weak for molecules with few electrons and show increasing strength for molecules with a greater number of electrons (or more generally with increasing molecular size). The stronger these intermolecular forces are, the higher the boiling point will be. This effect is clearly seen in the alkane family of compounds where boiling points increase with increasing molar mass#. (See Fig 8 next page.)

*For a complete review of intermolecular forces see '**Essential Chemistry Unit 1 + 2**' p123-130.

#As **molar mass** increases along with the number of molecular electrons it is often stated that dispersion forces increase with **molar mass** or **molecular size**.

Figure 8 The boiling points of the various alkanes increase with increasing molecular size/mass. This trend is due to increasing dispersion forces which are stronger in molecules of greater molecular size or more specifically with the number of molecular electrons.

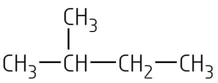


Dispersion forces are also **stronger** in molecules whose shape allows **maximum surface contact** between molecules, ie linear in preference to branched or spherical shapes. Thus hydrocarbons with linear molecules will have stronger dispersion forces and hence higher boiling points than spherical or branched molecules of similar mass. This is particularly evident in structural isomers where there is a constant number of electrons per molecule but the molecular shape varies. (See Fig 9.)

pentane, boiling point 36.1 °C

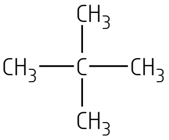
$CH_3-CH_2-CH_2-CH_2-CH_3$

methylbutane, boiling point 27.9 °C



$CH_3-\underset{}{\overset{\overset{\Large CH_3}{|}}{CH}}-CH_2-CH_3$

dimethylpropane, boiling point 9.5 °C



$CH_3-\overset{\overset{\Large CH_3}{|}}{\underset{\underset{\Large CH_3}{|}}{C}}-CH_3$

Figure 9 The three **chain isomers** above, all have the same molecular formula, **C_5H_{12}**, ie same molecular size and number of electrons per molecule. Their differing boiling points are due to their differing shape which in turn affects the strength of their dispersion forces.

The **solubility** of molecular substances also depends upon the nature of **intermolecular forces** acting within these substances. Generally it is seen that substances whose molecules attract by similar types of intermolecular forces will be soluble in one another. For this reason hydrocarbons, which are all non-polar and interact only by dispersion forces, will be soluble in other non-polar substances that also interact mainly by dispersion forces. This explains why hydrocarbons are miscible with one another. This also means hydrocarbons will not be soluble in polar substances whose molecules attract mainly by dipole-dipole forces or in substances that attract mainly by hydrogen bonding. This is why a non-polar substance like octane (C_8H_{18}, a major ingredient in petrol) is quite soluble in dodecane ($C_{12}H_{26}$, a major ingredient in kerosene) but essentially insoluble in water, a polar liquid whose molecules attract mainly by hydrogen bonding.

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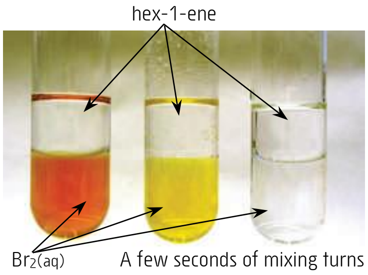
Attempt Set 15 # 12 to 16.

10.8 Alkenes: Addition reactions

Alkenes are known as **unsaturated** hydrocarbons as their bonding capacity is not fully utilised, ie their molecules have the capacity to bond to more atoms. For this reason they readily undergo **addition** reactions where the double bond ($C=C$) is replaced by bonds to other atoms like H, F, Cl, Br or I. Alkanes and benzene do **not** undergo addition reactions.

Hydrogenation is the addition of hydrogen by reacting an alkene with $H_2(g)$ in the presence of a suitable catalyst (eg finely divided nickel, platinum or palladium metal). The addition of a halogen atom (F, Cl, Br or I) to an alkene can be achieved using reagents like Cl_2, Br_2, HCl, HBr or HI. This process is called **halogenation** or **hydrohalogenation** (using HCl, HBr or HI). These reactions do not require a catalyst. In the laboratory it is most convenient to use $Br_2(g)$ and $Cl_2(g)$ in aqueous solution form, ie $Br_2(aq)$ and $Cl_2(aq)$. These are known as bromine water and chlorine water respectively. (See Table 6 and Fig 10.)

Figure 10 Bromine water is essentially a solution of Br_2 in water. It has an orange colour due to the presence of bromine. **Hex-1-ene** is a colourless liquid hydrocarbon (BP=63.5 °C) that does not dissolve in water. When bromine water is added to hex-1-ene they naturally form two separate layers as seen below. If the layers are mixed, the orange colour of bromine quickly disappears. This is due to a rapid **addition reaction** involving bromine and hex-1-ene.



A few seconds of mixing turns the $Br_2(aq)$ layer colourless.

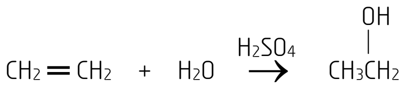
Table 6 Addition reactions of alkenes.

Example	Observation
$CH_2=CHCH_2CH_2CH_2CH_3 + Br_2 \rightarrow CH_2BrCHBrCH_2CH_2CH_2CH_3$ hex-1-ene 1,2-dibromohexane	In both cases two immiscible layers form. With mixing, the bromine water **quickly** changes colour from orange to colourless. (See Fig 10.)
$CH_3CH=CHCH_2CH_2CH_3 + Br_2 \rightarrow CH_3CHBrCHBrCH_2CH_2CH_3$ hex-2-ene 2,3-dibromohexane	
$CH_2=CH_2 + HCl \rightarrow CH_2ClCH_3$ ethene chloroethane	In both cases two colourless gases react to form a colourless liquid.
$CH_3CH=CH_2 + HCl \rightarrow CH_3CHClCH_3$***** propene 2-chloropropane	

***** Interestingly, only **2-chloropropane** is formed, ie 1-chloropropane does not form. It is found that when HCl, HBr or HI gases react by addition, 'the added **hydrogen** atom attaches to the carbon of the double bond already having the **most** attached **hydrogen** atoms'. This observation is known as Markovnikov's rule.

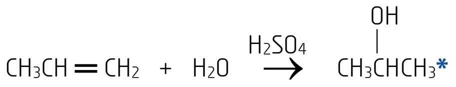
The addition of bromine can be used to verify the presence of a double bond in an unknown hydrocarbon. **Rapid** decolourisation of the added bromine water (Fig 10) confirms the presence of a suspected double bond. It is important to note that **saturated** hydrocarbons (ie no double bonds) will **slowly** discolour bromine water due to a different reaction called **substitution**. This reaction involves the replacement of hydrogen atoms in the hydrocarbon with bromine atoms and produces HBr as a secondary product. However, as substitution is a distinctly slow reaction it is easily distinguished from the rapid discolouration produced by the addition of bromine to an alkene.

Hydration is another addition reaction of alkenes. It involves the acid-catalysed addition of water, H_2O to the double bond of an alkene. Concentrated sulfuric acid is most commonly used as the catalyst for this reaction. The reaction results in the loss of the double bond and the addition of an OH group and a hydrogen atom to produce a compound known as an alcohol. (See p118-9.) This addition reaction forms the basis of one method for the industrial production of the alcohol ethanol. (See p163.)



$$CH_2{=}CH_2 + H_2O \xrightarrow{H_2SO_4} CH_3\overset{\overset{OH}{|}}{CH_2}$$

ethene ethanol



$$CH_3CH{=}CH_2 + H_2O \xrightarrow{H_2SO_4} CH_3\overset{\overset{OH}{|}}{C}HCH_3{*}$$

propene propan-2-ol

*****As with halogen addition (Table 6) the extra H atom usually attaches to the carbon of the double bond already having the most attached H atoms.

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Complete Set 15.

Set 15 Organic chemistry: Alkanes and alkenes

1. Complete the following passage regarding **hydrocarbons** and **alkanes**. A word list has not been provided for this exercise.

   Hydrocarbons consist of molecules containing the elements (a) ____________ and (b) ____________ only. The simplest hydrocarbons are the alkanes. These have a general formula of (c) ____________. Alkanes are said to be saturated as they contain (d) ____________ covalent bonds only. The terminal carbon atoms of an alkane molecule are always attached to (e) ____________ hydrogen atoms while other carbon atoms may be attached to (f) ____________, (g) ____________ or (h) ____________ hydrogen atoms.

2. Draw structural formula for all of the **alkanes** containing **six carbon atoms**. Ensure your structures show all of the atoms and bonds in each molecule. Make reference to the structures you have drawn to help answer the following questions.
   a. What are structural isomers?
   b. Describe and compare position isomers and chain isomers.

3. The general formula of an alkene is C_nH_{2n} while that of an alkane is C_nH_{2n+2}. Account for the slight difference in these general formulas and hence explain what is meant by the statement 'alkenes are **unsaturated**'.

4. Some alkenes are capable of a type of isomerism called ***cis-trans*** isomerism. Use the alkene of molecular formula C_4H_8 to describe this type of isomerism.

5. One of the alkenes of molecular formula C_4H_8 is not able to form ***cis-trans*** isomers. Draw the structural formula of this alkene and use this to help explain why it does not show *cis-trans* isomerism.

Halogenated hydrocarbons are a most useful family of organic compounds. They are formed when one or more of the hydrogen atoms of a hydrocarbon are replaced with a **halogen atom**, ie **F**, **Cl**, **Br** or **I**.

6. Draw **full structural formula** for the following hydrocarbons and **halogenated** compounds. **Show all bonds**.
    - a. methylbutane
    - b. 2,4-dimethylpentane
    - c. 1-chloro-3-ethylpentane
    - d. 2-iodoprop-1-ene
    - e. 3,5-dimethylhept-1-ene
    - f. 5,5-dibromo-4-methylpent-1-ene
    - g. *cis*-1,2-dibromoethene
    - h. *trans*-pent-2-ene

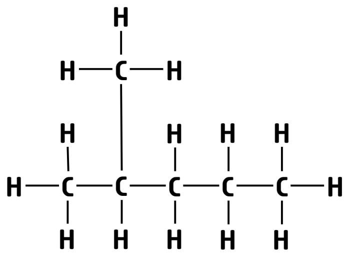
Numbering the suffix!

2-pentene or pent-2-ene

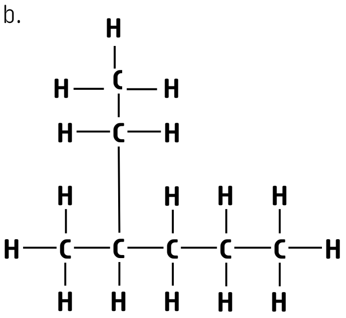
Both names are acceptable though **pent-2-ene** is the preferred nomenclature used throughout this book.

7. Give the **IUPAC name** for the substances shown below. Various forms of structural and semi-structural formula have been used to represent these.

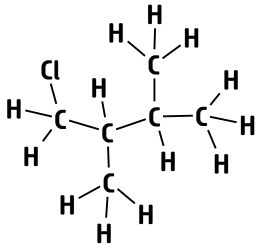
a.



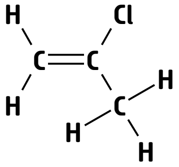
b.



c.



d.



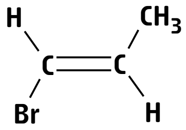
e.

$CH_3CH_2CHCHCH_3$

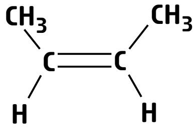
f.

$CH_2BrCH_2CHCHCH_3$

g.



h.



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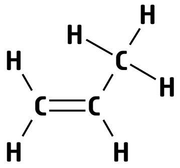
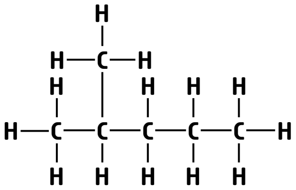


8. The following substances are represented with a variety of structural and semi-structural formula (see Fig 11). Some of these pairs of compounds actually represent different substances while some are the same substance simply drawn differently. Some are structural or *cis-trans* isomers. Classify these pairs of molecules as representing **different substances**, the **same substance**, **structural isomers** or ***cis-trans* isomers**. Further classify any structural isomers as **chain** isomers or **position** isomers.

a.



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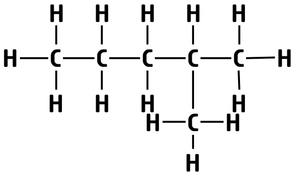

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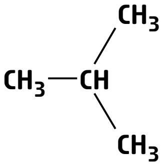

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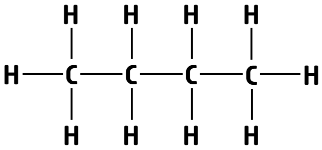

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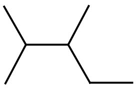

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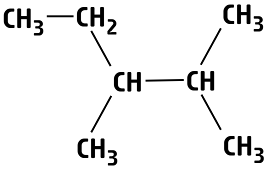

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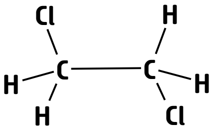

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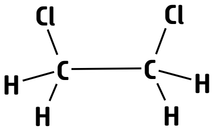

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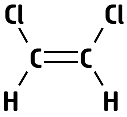

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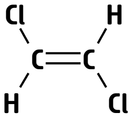

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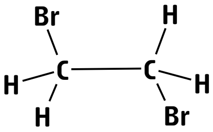

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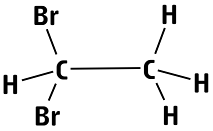

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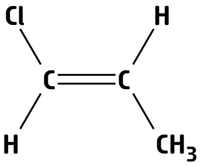

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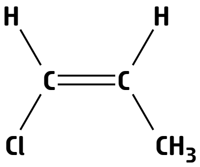

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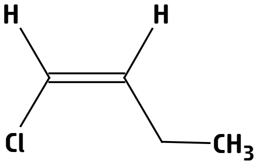

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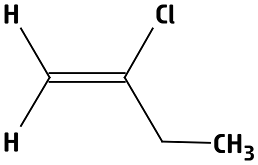

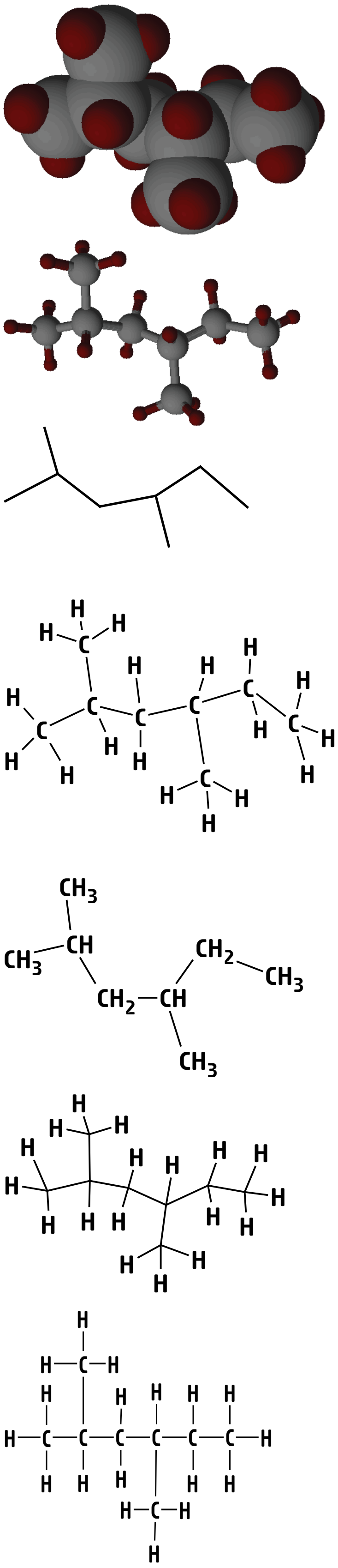

Figure 11 These 3D images, structural formula and semi-structural formula all represent **2,4-dimethylhexane**.

9. Give the IUPAC names for **all** the **isomers** of each of the following compounds. (No need to include any cyclic structures as part of the answer.)

   a. C_5H_{12} b. C_3H_5F c. C_4H_8

10. A student named several organic compounds as indicated below. Unfortunately, although each name specifies a correct structure, the name given does not correctly follow the IUPAC system of nomenclature. Use the given name to determine the structure and hence give the **correct IUPAC name** for each compound.

    a. 3-methylbutane
    b. 2-methylpent-4-ene
    c. 1-methylpropane
    d. 2-ethylpropane
    e. 1,2-dibromoethene
    f. but-2-ene

11. Some of the following structures have *cis-trans* isomerism (formerly called geometric isomerism). Where this is possible, **draw** the two *cis-trans* isomers and **name** each.

    a. $CH_3CH{=}CHCH_2CH_3$
    b. $CHCl{=}CHCl$
    c. $CH_2{=}CBr_2$
    d. $CH_2{=}CHBr$
    e. $CH_3CH{=}CHBr$
    f. CH_2ClCH_2Cl

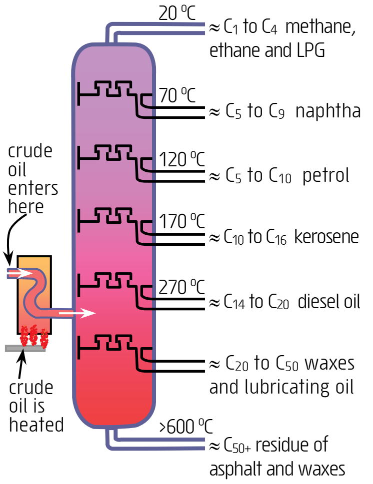

Figure 12 Crude oil is separated into various fractions using a fractionating tower like this one. Each **fraction** is a **mixture** of hydrocarbons with its own **boiling point range**. The temperatures and C numbers indicated here for the different fractions are an approximate guide only.

12. **Petroleum** (crude oil) is the world's major source of hydrocarbons. Petroleum refineries use the physical process of **fractional distillation** (Fig 12) to separate the vast mixture of hydrocarbons present in crude oil into 'fractions' that have similar boiling points and molecular mass. These fractions are obtained by vaporising crude oil at temperatures as high as 400 °C, then condensing its vapours at progressively lower temperature ranges. This partial separation relies on the boiling points of hydrocarbons increasing with increasing number of carbon atoms per molecule. Explain why the boiling points of hydrocarbon compounds increases like this.

13. Another important source of hydrocarbons is **natural gas**. This gaseous mixture consists primarily of methane mixed with ethane and small amounts of propane and butane. Use your knowledge of intermolecular forces to account for the gaseous nature of these hydrocarbons.

14. The alkane of molecular formula C_6H_{14} has five structural isomers. (See Question 2.) Consider the following three of these isomers:

    hexane **2,2-dimethylbutane** **3-methylpentane**

    Rank these isomers in order of **increasing boiling point**. Give a short **explanation** for your ranking order.

15. Accidental **oil spills** from ocean-going oil tankers or offshore oil production facilities is one of the environmental hazards associated with our use of petroleum products. Oil spills like this float on the water surface and pose an immediate danger to marine birdlife and surface dwelling marine organisms. Use your knowledge of **intermolecular forces** to explain why petroleum products like crude oil do not mix with ocean water.

16. **Tetrachloroethene** is a commonly used dry-cleaning solvent. It is ideal for removing stains from clothing that can not be washed in water. Although it has many structural similarities to **ethene** its boiling point is much higher, 121 °C compared to -104 °C for ethene.

    a. **Explain** why tetrachloroethene has a much higher boiling point than ethene.
    b. What type of stain would tetrachlorethene be good at dissolving? **Explain**.

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17. Write a balanced equation for each of the **addition** reactions described here.

a. $CH_2 = CH_2(g) \quad + \quad Br_2(aq) \quad \longrightarrow$ ____

b. $CH_2 = CHCH_3(g) \quad + \quad Cl_2(aq) \quad \longrightarrow$ ____

c. $CH_3CH = CHCH_3(g) \quad + \quad H_2(g) \quad \xrightarrow{Pt}$ ____

d. $CH_2 = CH_2(g) \quad + \quad H_2O(g) \quad \xrightarrow{H_2SO_4}$ ____

Hint!
Having trouble visualising the reaction products? Try drawing the full structural formula for the organic reactant and its product.

18. A few drops of **bromine water** are added to each of the following pairs of reagents. Can the resulting observations be used to **distinguish** each of the two compounds? **Explain** your answer.

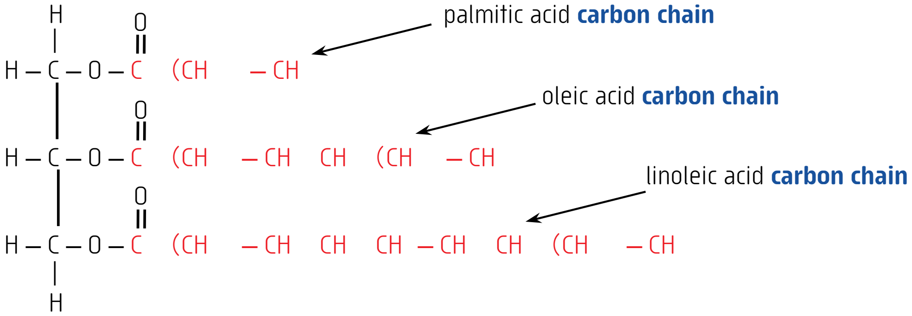
a. propane gas and propene gas

b. hexene and benzene

c. pentane and butane

d. 2-methylhexane and 2-methylhex-1-ene

19. Cooking products known as **shortenings** and **table margarine** are produced by the partial **hydrogenation** (addition of hydrogen) of vegetable oils. This involves reacting the vegetable oil with hydrogen gas in the presence of fine particles of platinum metal. The effect is to partially hydrogenate the liquid oil and in the process form a solid fat that is suitable for baking and spreading. The structural diagram below shows an example of a vegetable oil, ie a **triglyceride**, that might be obtained from soybean.



a. How does the **edible vegetable oil** shown here differ from **non-edible petroleum oils** (ie hydrocarbons)?

b. How are the fatty acid **carbon chains** (highlighted in **red**) altered by hydrogenation?

c. What is the role of the fine particles of **platinum** metal in the hydrogenation process?

d. The conditions used in the hydrogenation process can cause an unwanted side reaction. As a result, rather than undergoing addition, some fatty acid carbon chains are altered from the **bent** or **V** shaped ***cis*** form to the **straight** ***trans*** form. Use the **oleic acid carbon chain** (highlighted in red) to explain what this means.

Figure 13 Vegetable oils like olive oil and canola oil can be converted into a spreadable product called margarine simply by adding in hydrogen. Adjusting the amount of added hydrogen, ie controlling the degree of hydrogenation, controls the hardness of the resulting margarine. Typically there are two main types of margarine, hard margarine, which is sold in blocks like butter, and soft margarine, which is sold in tubs.

CHAPTER11 | ORGANIC CHEMISTRY: FUNCTIONAL GROUPS

11.1 Organic compounds

Historically **organic compounds** were defined as those present in living organisms. It was believed only living things had the 'vital force' thought necessary to make these compounds. However, a single experiment in 1828 by Friedrich Wöhler challenged the validity of this idea. Using the two inorganic compounds, ammonium chloride (NH_4Cl) and silver cyanate ($AgNCO$), Wöhler was able to synthesise the organic compound urea (NH_2CONH_2), found in mammalian urine. This experiment, followed by others, led to the downfall of the vital force theory and a new view of organic compounds.

Today organic compounds are defined as those that contain **carbon** bonded to other non-metal elements like **H**, **N**, **O**, **P**, **S**, **F**, **Cl**, **Br** and **I** (excluding CO_2, CO and carbonates). **Hydrocarbons** are the simplest organic compounds. They contain the elements **hydrogen** and **carbon** only. The presence of atoms like **N**, **O**, **P**, **S**, **F**, **Cl**, **Br** and **I** in hydrocarbon molecules has a significant effect on their physical and chemical properties. These elements and their various groupings are known as **functional groups**. (See Fig 1.) Families of organic compounds are classified and named according to the functional group they contain. Some organic families include **alkanes**, **alkenes**, **alcohols**, **aldehydes**, **ketones**, **carboxylic acids**, **esters**, **amines**, **amides** and **amino acids**.

Organic compounds are found and used in a great variety of applications such as **pharmaceuticals**, **plastics** and **fibres**, **solvents**, **cosmetics**, **fuels**, **foods**, and importantly they form the basis of **living systems**.

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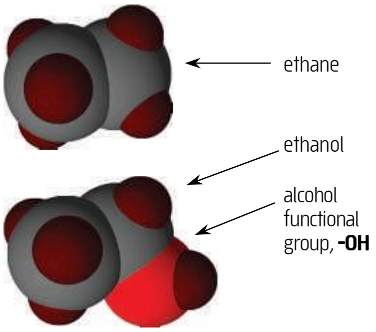
Figure 1 The presence of **functional groups** gives the different organic compounds their unique characteristics and properties.



The hydrocarbon **ethane**, C_2H_6 (above) is a colourless odourless gas that boils at -88.6 °C and is insoluble in water.

Ethanol, C_2H_6O by comparison is a liquid that boils at 78.3 °C, has a characteristic sweet odour and is extremely soluble in water. Its very different properties are due to the alcohol functional group, **-OH**.

11.2 Alcohols: Nomenclature

Alcohols (Fig 2) contain the **—OH** (hydroxyl) functional group in place of one of the hydrogen atoms of an alkane. They are named by dropping the final **e** of the parent alkane name and adding the suffix **-ol**. A number is used (if needed) to denote the position of the functional group. The number may be written with the suffix or in front of the name. (See Table 1.)

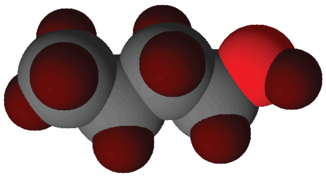


Figure 2 The **structural formula** (Table 1) of a compound gives an understanding of the **sequence** of bonding of the various atoms in its molecules. This **three dimensional view** of butan-1-ol gives a clearer idea of the angular orientation of its various atoms. It should be noted that as the various atoms are free to **rotate** along the axis of any single bond, their true shape is constantly altering even though the sequence of bonding and individual bond angles remain fixed. (See below.)

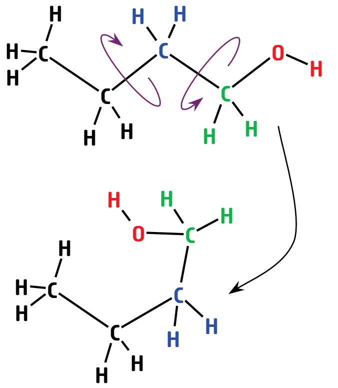
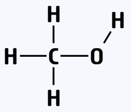
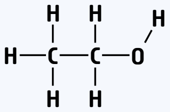
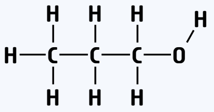
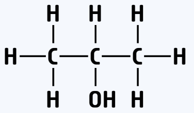
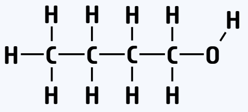
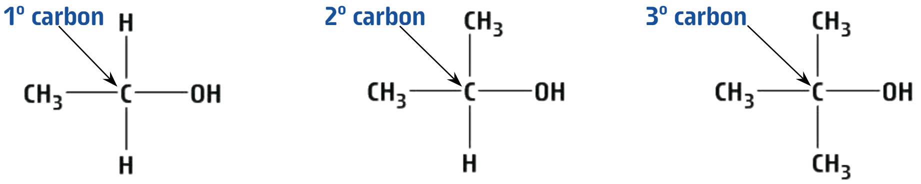


Table 1 Structure and nomenclature of selected alcohols.

Name	Structural formula	Condensed structural formula
methanol		**CH_3OH**
ethanol (See Fig 1.)		**CH_3CH_2OH**
propan-1-ol (or 1-propanol)		**$CH_3CH_2CH_2OH$**
propan-2-ol (or 2-propanol)		**$CH_3CHOHCH_3$**
butan-1-ol (or 1-butanol) (See Fig 2.)		**$CH_3CH_2CH_2CH_2OH$**

The position of the hydroxyl functional group (—OH) in an alcohol molecule can influence its physical and chemical properties.

For this reason alcohols are classified as **primary** (1°), **secondary** (2°) or **tertiary** (3°) depending upon the number of carbon atoms directly attached to the carbon bearing the —OH group. (See Fig 3.)



1° alcohol
(ethanol)

2° alcohol
(propan-2-ol)

3° alcohol
(methylpropan-2-ol)

Figure 3 Classification of **primary**, **secondary** and **tertiary** alcohols is based upon the nature of the carbon atom to which the —OH functional group is attached. A **3°** carbon is one bonded directly to **three** other carbon atoms. A **2°** carbon is bonded to **two** other carbon atoms. A **1°** carbon is bonded to a **single** carbon atom.

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Attempt Set 16 # 1 and 2.

11.3 Alcohols: Physical properties

The range and strength of intermolecular forces (see border note*) present in alcohols have important consequences for their physical properties of melting point, boiling point and solubility in other solvents. Small alcohol molecules are very **polar** with **hydrogen bonding** (Fig 4) being the most significant intermolecular force. **Dispersion** forces, however, become increasingly significant for alcohols of larger molecular size.

The presence of hydrogen bonding explains the much higher **boiling points** of alcohols compared to their parent alkanes. (See Figure 5.) Also, as dispersion forces increase in strength with an increasing number of molecular electrons (or molecular size), then boiling points of alcohols also increase with molecular size.

***For a review of intermolecular forces see ‘**Essential Chemistry Unit 1 + 2**’ p123-130.

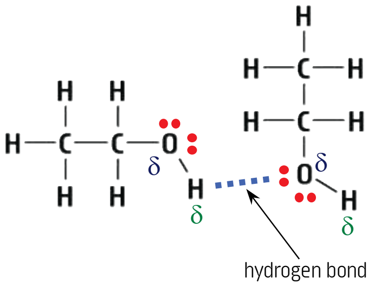
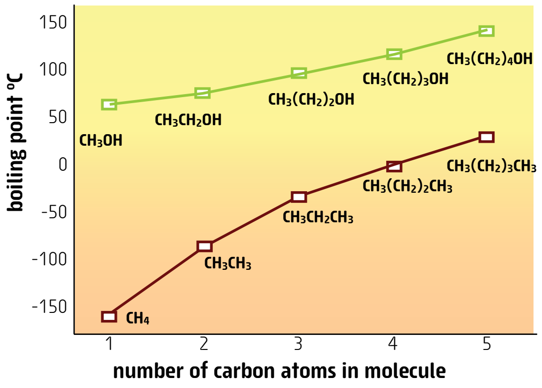


Figure 4 Two ethanol molecules interacting by **hydrogen bonding**. The hydrogen bond forms between a highly polar hydrogen atom (δ from one of the neighbouring highly polar oxygen atoms (δ

Hydrogen bonding like this can also occur between the molecules of different substances. This helps to explain the **miscibility** (ie solubility in all proportions) of ethanol and water.

Figure 5 The **boiling point** of any given alcohol is much higher than its parent hydrocarbon. Alcohol boiling points are higher due to their **hydrogen bonding** capacity.

Furthermore, the alcohols and their parent hydrocarbons both show an increase in boiling point with increasing molecular size. This is due to dispersion forces which increase in strength as molecular size increases, or more specifically as the number of molecular electrons increases.



The **solubility** of molecular compounds depends upon the ability of the different molecules in a mixture to attract one another as strongly as the molecules of the pure substances attract one another. As alcohol molecules of **low molecular size** attract one another mainly by hydrogen bonding or dipole-dipole forces they will be soluble in other molecular compounds also capable of hydrogen bonding or dipole-dipole forces. For this reason, alcohols of low molecular size, like methanol, ethanol and propanol are completely **miscible** in water, ie soluble in all proportions.

However, as the alcohol molecular size increases, so dispersion forces become increasingly significant. As a result longer chain alcohols attract most strongly by dispersion forces. These alcohols are more soluble in non-polar solvents, ie ones that attract by dispersion forces and less soluble in polar solvents or solvents that attract by hydrogen bonding. This is why alcohol solubility in water is seen to decrease with increasing molecular size. (See Table 2.)

Table 2 Solubility of alcohols in water.

	Molar mass g mol^{-1}	Solubility g/100 g H_2O
methanol	32.0	miscible
ethanol	46.1	miscible
propan-1-ol	60.1	miscible
butan-1-ol	74.1	8.1
pentan-1-ol	88.1	2.6
hexan-1-ol	102.2	0.59
heptan-1-ol	116.2	0.093

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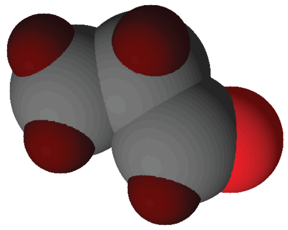
Attempt Set 16 # 3, 4 and 5.

11.4 Aldehydes: Nomenclature and physical properties

Aldehydes (Fig 6) contain the **—CHO** (carbonyl) functional group on the primary carbon (terminal end) of the carbon chain. They are named by dropping the final **e** of the parent alkane name and adding the suffix **-al**. As the aldehyde group (**—CHO**) must always occur at the end of a carbon chain there is no need to number its position. (See Table 3.)
Aldehyde molecules are **polar** but unable to interact with one another by hydrogen bonding. They lack the highly polar hydrogen atom attached to an O, N or F atom.

Figure 6 A three dimensional view of a **propanal** molecule, CH_3CH_2**CHO**.



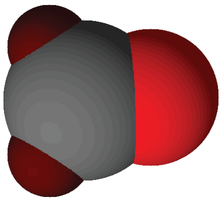


Figure 7 Methanal, the simplest of the aldehydes, also known as **formaldehyde**, is a **highly toxic** pungent gas at room temperature. In solution with water it is known as **formalin** (≈ 37% by mass methanal) which is used for preserving biological specimens.

Methanal has wide application in the manufacture of hard plastic resins and adhesives used in a wide range of products such as carpet, kitchen tops, particle board, foam insulation and even clothing, to make it crease resistant (permanent press). Products like these are also potential environmental sources of methanal emission and exposure.

Table 4 Boiling points of selected aldehydes and ketones.

Aldehyde	Boiling point °C	Ketone	Boiling point °C
methanal	-19.2		
ethanal	20.1		
propanal	47.9	propanone	56.1
butanal	74.8	butanone	79.6
pentanal	102.5	pentan-2-one	102.3
		pentan-3-one	101.8

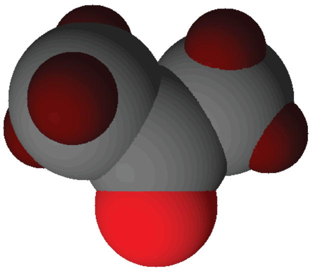
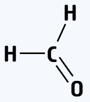
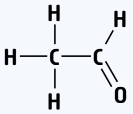
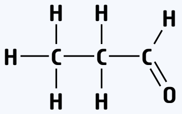
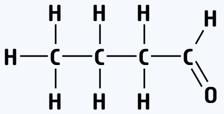


Figure 8 Propanone (acetone), the simplest of the ketones is a clear colourless liquid with a distinctive fruity odour. It is miscible with water and generally has excellent solvent properties.

Propanone is the solvent used in some **nail polish removers**. It is also used extensively as a precursor in the manufacture of polymers like poly(methyl methacrylate), ie perspex and polycarbonates.

As a consequence, aldehydes have higher **boiling points** than their parent alkanes but lower boiling points than alcohols of similar molecular size. (See Table 4.)

Table 3 Structure and nomenclature of selected aldehydes.

Name	Structural formula	Condensed structural formula
methanal (See Fig 7.)		**$HCHO$**
ethanal		**CH_3CHO**
propanal (See Fig 6.)		**CH_3CH_2CHO**
butanal		**$CH_3CH_2CH_2CHO$**

As aldehyde molecules attract by **dipole-dipole forces** (due to their polarity) they will be **soluble** in other molecular compounds also capable of dipole-dipole interaction. Although aldehyde molecules can not hydrogen bond to other aldehyde molecules they can be involved in hydrogen bonding with compounds like water. This involves a lone pair of electrons from the O atom of the aldehyde carbonyl group forming a hydrogen bond to either of the H atoms of a water molecule. For this reason aldehydes of low molecular size like methanal, ethanal and propanal are quite soluble in water. However, as the aldehyde molecular size increases, the strength of dispersion forces becomes more significant. As a result the solubility of longer chain aldehydes in water and other polar solvents decreases, eg pentanal is only slightly soluble in water. Thus longer chain aldehydes are increasingly soluble in non-polar solvents, ie ones that interact most strongly by dispersion forces.

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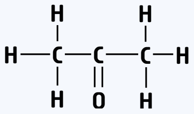
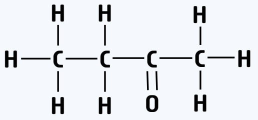
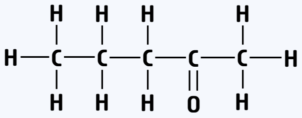
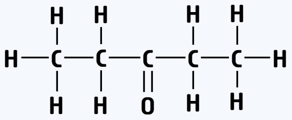
11.5 Ketones: Nomenclature and physical properties

Ketones (Fig 8) contain the **—C = O** (carbonyl) functional group positioned on a secondary carbon (one bonded to two other carbon atoms) of a carbon chain. They are named by dropping the final **e** of the parent alkane name and adding the suffix **-one**. A number is used (if needed) to show the position of the —C = O group. The number may be written with the suffix or in front of the name. (See Table 5.)

Table 5 Structure and nomenclature of selected ketones.

Name	Structural formula	Condensed structural formula
propanone (See Fig 8.)		**CH_3COCH_3**
butanone		**$CH_3CH_2COCH_3$**
pentan-2-one (2-pentanone)		**$CH_3CH_2CH_2COCH_3$**
pentan-3-one (3-pentanone)		**$CH_3CH_2COCH_2CH_3$**

As ketone molecules are **polar**, they will attract by **dipole-dipole** forces. **Dispersion forces** become stronger for ketones with a longer carbon chain, hence the boiling point of ketones increases with chain length. (See Table 4 p120.) Ketones have similar **boiling points** to aldehydes of similar molar mass. As with aldehydes, ketones with short carbon chains are soluble in polar substances. Similarly as their **chain length** increases they become increasingly soluble in non-polar solvents. Propanone for example, is infinitely soluble in water (miscible) while hexan-3-one is only slightly soluble in water.

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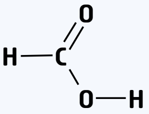
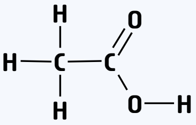
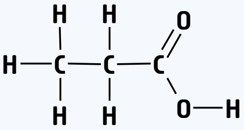
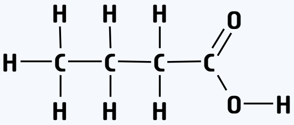
Attempt Set 16 # 6 and 7.

11.6 Carboxylic acids: Nomenclature and physical properties

Carboxylic acids (Fig 9) contain the carboxyl, **—COOH** (carboxyl = carbonyl+ hydroxyl) functional group positioned at the end of a carbon chain. They are named by dropping the final **e** of the parent alkane name and adding the suffix **-oic acid**. As the carboxyl group (**—COOH**) must always occur at the end of a carbon chain there is no need to number its position. (See Table 6.)

Table 6 Structure and nomenclature of selected carboxylic acids.

Name	Structural formula	Condensed structural formula
methanoic acid (formic acid)		**HCOOH**
ethanoic acid (acetic acid)		**CH_3COOH**
propanoic acid		**CH_3CH_2COOH**
butanoic acid (See Fig 9.)		**$CH_3CH_2CH_2COOH$**

Hydrogen bonding is the most significant intermolecular force for carboxylic acids of low molecular size (molar mass). For this reason their **boiling points** are much higher than for hydrocarbons of similar molecular size. **Dispersion forces** become increasingly significant in carboxylic acids with long carbon chains, hence the boiling point of carboxylic acids increases with chain length. Furthermore, the **boiling points** of carboxylic acids are slightly higher than for corresponding alcohols, eg ethanol 78.3 °C, ethanoic acid 117.9 °C.

Carboxylic acids are most **soluble** in polar solvents, especially those which can also hydrogen bond, eg water and alcohols. As dispersion forces become stronger for longer chain carboxylic acids they begin to exhibit increasing solubility in non-polar solvents and are less soluble in polar ones. Methanoic, ethanoic, propanoic and butanoic acids, for example are **miscible** in water while the solubility of hexanoic acid in water is only 1.0 g/100 g H_2O. Carboxylic acids with longer carbon chains are virtually insoluble in water.

Long chain carboxylic acids, known as fatty acids, have a soft greasy feel and are insoluble in water. They occur naturally in many living systems. In plants, the carbon chain of a **fatty acid** is typically **unsaturated** with the double bonds always in a ***cis*** configuration. (See Fig 10.) **Animal fatty acids** by comparison are almost always **saturated**. In either case the carbon chains of naturally occurring fatty acids contain an even number of carbon atoms (most commonly 16 or 18) in an unbranched configuration.

Fatty acids are chemically related to, but not the same as fats and oils. (See 11.10.) In plants and animals, fatty acids are converted to triglycerides, which are commonly known as fats and oils. These compounds are an important store of energy for many living things.

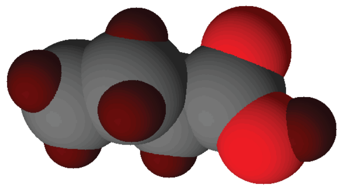


Figure 9 Butanoic acid is a liquid at room temperature and very soluble in water. Its presence in **parmesan cheese** contributes to its distinctive odour and taste. Interestingly it is the same substance present in sweat and rancid butter also contributing to their distinctive odour.

The **hydrogen bonding** ability of carboxylic acids helps to explain their high melting and boiling points and their high solubility in solvents like water.

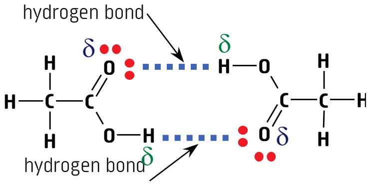
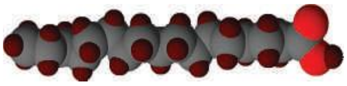
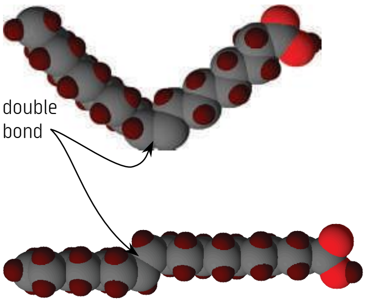


Figure 10 **Stearic acid** and **oleic acid** are two **fatty acids** found in living systems. The unsaturated oleic acid (from plants) forms a ***cis*** isomer with a **bent** shape. Stearic acid by comparison (from animals) is saturated and **linear** in shape. Very small amounts of vaccenic acid, a ***trans*** fatty acid, occurs in cow, sheep and goat products. ***Trans*** isomers like this have a straight configuration.

stearic acid $CH_3(CH_2)_{16}COOH$ (saturated)



oleic acid $CH_3(CH_2)_7CH = CH(CH_2)_7COOH$



vaccenic acid $CH_3(CH_2)_5CH = CH(CH_2)_9COOH$

Short chain carboxylic acids like methanoic acid and ethanoic acid have a characteristic **pungent vinegary odour**. The slightly longer chain carboxylic acids have a distinctly **cheesy odour**. Propanoic acid for example is partly responsible for the distinctive odour and taste of Swiss cheese while butanoic acid contributes to the distinctive odour of parmesan cheese, rancid butter and sweat!

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Attempt Set 16 # 8 and 9.

11.7 Amines: Nomenclature and physical properties

Amines (Fig 11) contain the **—NH_2** (amine or amino) functional group. They are named by dropping the final **e** of the parent alkane name and adding the suffix **-amine**. A number is used (if needed) to denote the position of the functional group. (See Table 7.)

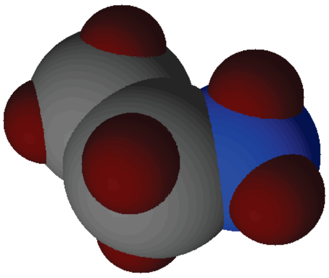
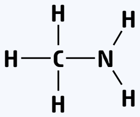
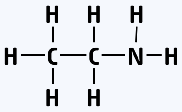
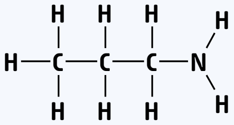
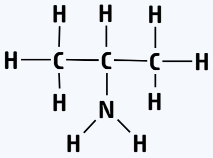


Figure 11 Low molar mass amines like **ethanamine** are soluble in water and notable for their '**fishy**' odour. The odour of decaying fish is largely due to the formation of various amines produced from the decomposition of its proteins.

Table 7 Structure and nomenclature of selected amines.

Name	Structural formula	Condensed structural formula
methanamine		CH_3NH_2
ethanamine (See Fig 11.)		$CH_3CH_2NH_2$
propan-1-amine (1-propanamine)		$CH_3CH_2CH_2NH_2$
propan-2-amine (2-propanamine)		$CH_3CHNH_2CH_3$

Amines are **polar** and capable of **hydrogen bonding**. Consequently their **boiling points** are higher than for hydrocarbons of similar molecular size, but lower than corresponding alcohols. This shows hydrogen bonding in amines is not as strong as in alcohols. For example, methanamine, ethanamine and propan-1-amine have boiling points of -6.3 °C, 16.6 °C and 48.5 °C respectively while by comparison methanol, ethanol and propan-1-ol have boiling points of 64.7 °C, 78.3 °C and 97.2 °C respectively. The weaker hydrogen bonding in amines is a consequence of the lower electronegativity of nitrogen (3.0) compared to oxygen (3.5). This results in a weaker dipole and consequently a weaker hydrogen bond.

Amines are **soluble** in polar solvents, especially those solvents which can also hydrogen bond. As dispersion forces become increasingly significant in longer chain amines so they become increasingly soluble in non-polar solvents, ie ones that attract by dispersion forces, and less soluble in polar solvents or solvents that attract by hydrogen bonding.

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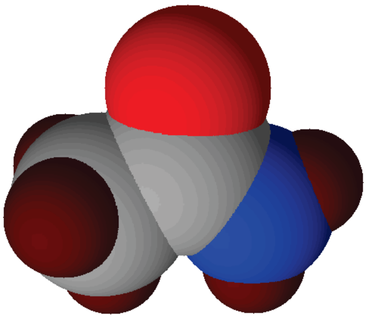
Attempt Set 16 # 10.

11.8 Amides: Nomenclature and physical properties

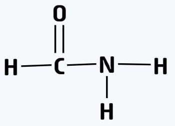
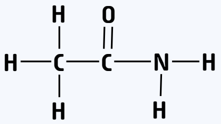
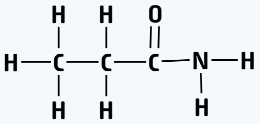
Amides (Fig 12) contain the **—$CONH_2$** functional group. These compounds are derivatives of carboxylic acids where the OH of the carboxyl group (—CO**OH**) is replaced with an amine (**—NH_2**) group. They are named by dropping the suffix **-oic acid** from the parent carboxylic acid name and adding **-amide**. This is equivalent to dropping the final **e** of the parent alkane name and adding the suffix -amide. (See Table 8.)

Figure 12 Ethanamide is an odourless white crystalline solid that melts at 81 °C and boils at 221 °C. The melting and boiling points of low molar mass amides, like ethanamide, are **unusually high** for organic compounds.



Amides are **polar** and capable of **hydrogen bonding**. The **strength** of individual hydrogen bonds and the **extent** of hydrogen bonding in amides is much greater than for similar amines or carboxylic acids. This occurs for two reasons. Firstly, there is a greater number of suitable lone pairs and hydrogen atoms available for hydrogen bonding in an amide molecule than in similar amine or carboxylic acid molecules. Each amide molecule has two hydrogen atoms and three lone pairs that are suitable for hydrogen bonding. (See Fig 13.)

Table 8 Structure and nomenclature of selected amides.

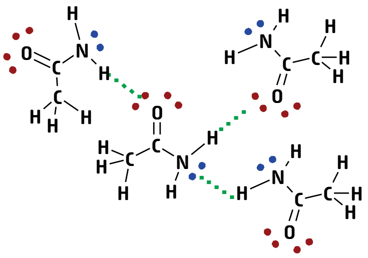
Name	Structural formula	Condensed structural formula
methanamide		$HCONH_2$
ethanamide (See Fig 12 and 13.)		CH_3CONH_2
propanamide		$CH_3CH_2CONH_2$

Also the close proximity of the highly electronegative oxygen atom causes hydrogen atoms from the NH_2 group to develop a larger dipole (δ

compared to amines or carboxylic acids. Consequently, the **boiling point** of an amide is higher than for an amine, alcohol or carboxylic acid of similar molecular size. For example, methanamide, ethanamide and propanamide have boiling points of 210 °C, 221 °C and 213 °C respectively. By comparison methanoic acid, ethanoic acid and propanoic acid have boiling points of 100.8 °C, 117.9 °C and 140.8 °C respectively.

The strong capacity for amides to hydrogen bond makes them particularly **soluble** in other solvents that also interact strongly by hydrogen bonding, eg solvents like water and ethanol.

Figure 13 Hydrogen bonding (green dotted lines) in **ethanamide**.



The **electronegativity** of **oxygen** and **nitrogen** are **3.5** and **3.0** respectively. The close proximity of oxygen to the NH_2 group causes electrons to be drawn away from the hydrogen atom more strongly than if nitrogen alone were present. As a result, the N-H bond dipoles and the polarity of the amides is much greater than similar compounds. For example the polarity (in Debye units) for ethan**amine**, ethan**oic acid** and ethan**amide** are 1.2, 1.7 and 3.7 respectively.

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Attempt Set 16 # 11.

11.9 Esters: Nomenclature and physical properties

Esters contain the **—COO—** (carboxylate or ester) functional group linking **two** alkane chains. They are named by dropping the final **e** of the parent alkane name (the one derived from the parent carboxylic acid, see Fig 14) and adding the suffix **-oate**. The alkyl group attached to the single O atom is named as a prefix (with a space) to the parent structure. (See Table 9.)

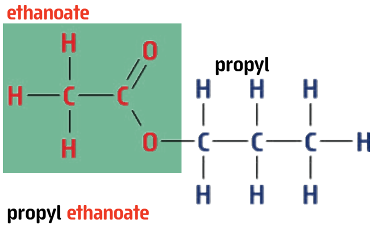
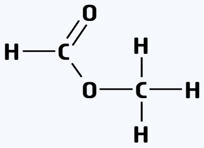
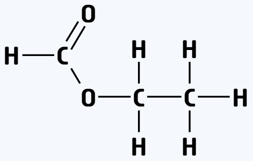
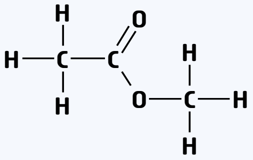
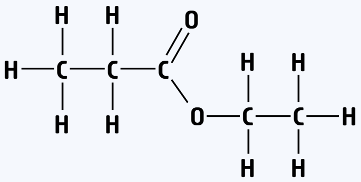


Figure 14 The ester molecule is visualised as consisting of a carboxylate group, originating from a carboxylic acid, (highlighted in **red** with a **green** background) where the **H** atom of the carboxylic acid has been replaced with an **alkyl** group (**blue**).

The stem name for an ester is derived from the parent carboxylic acid (in this example ethanoic acid). The acid suffix (-oic acid) is replaced with **-oate** and the attached alkyl group is named as a prefix (in this case **propyl**). Thus the name for the ester shown is **propyl ethanoate**.

Table 9 Structure and nomenclature of selected esters.

Name	Structural formula	Condensed structural formula
methyl methanoate		$HCOOCH_3$
ethyl methanoate		$HCOOCH_2CH_3$
methyl ethanoate		CH_3COOCH_3
ethyl propanoate		$CH_3CH_2COOCH_2CH_3$

The presence of the ester group **—COO—** creates a **degree of polarity** at the central part of an ester molecule. This allows esters to interact by **dipole-dipole** forces as well as by **dispersion** forces. Hydrogen bonding does **not** occur between ester molecules. As a result, their **boiling points** are similar to aldehydes and ketones but lower than alcohols and carboxylic acids of a similar molar mass. Lower molar mass esters are volatile liquids (readily evaporate) with strong **pleasant fruity odours**. Octyl ethanoate, for example gives oranges their distinctive odour, while pentyl pentanoate, ethyl butanoate and pentyl hexanoate all contribute to the characteristic odour of bananas.

The presence of the polar **—COO—** group influences the solubility of esters. (See Table 10.) Esters of low molecular size are reasonably soluble in polar solvents. As with other polar organic substances, their solubility in polar solvents decreases as their molar mass increases. Esters are useful as **solvents** and for adding fruity and floral odours in foods and cosmetics. Higher molar mass esters are solids with a waxy feel. Beeswax for example contains the ester triacontyl palmitate [$CH_3(CH_2)_{14}COOCH_2(CH_2)_{28}CH_3$]) while lanolin is a mixture of high molecular mass esters from wool. The leaves of most plants have a protective wax coating consisting of various high molar mass esters.

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Attempt Set 16 # 12.

Table 10 The **solubility** of esters in water.

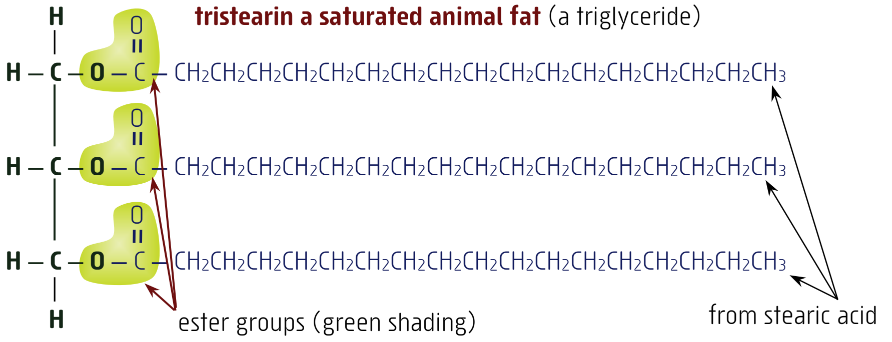
	Solubility in water g ester/100 g H_2O
ethyl methanoate	10.5
ethyl ethanoate	8.7
ethyl propanoate	1.7
ethyl butanoate	0.49

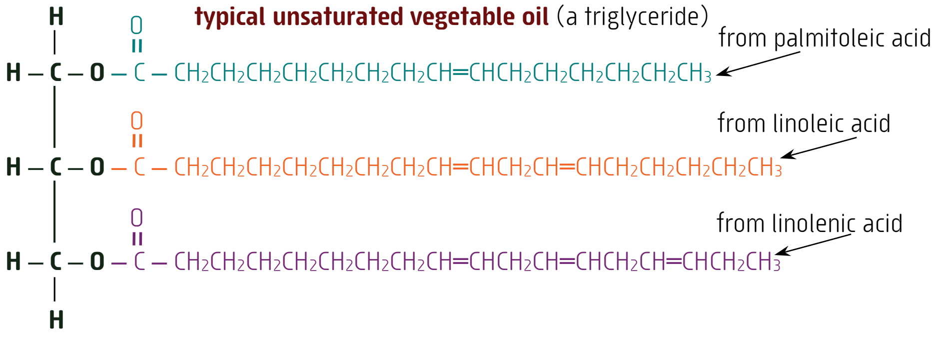
The **solubility** of esters in water is influenced by their **polarity** and their ability to form **hydrogen bonds** with water molecules. This can happen as a lone pair of electrons from the electronegative oxygen atom of the ester group can form a hydrogen bond with one of the hydrogen atoms from a water molecule. In a similar way esters can form hydrogen bonds with other solvents like alcohols, carboxylic acids and amines. The effect of polarity and hydrogen bonding on solubility reduces as the molecular mass of the ester increases.

11.10 Fats and oils

Triglycerides are an important group of **esters** commonly known as **fats** and **oils**. These esters can be visualised as being formed from a **glycerol** molecule (propane-1,2,3-triol) that has become attached to **three fatty acid molecules** by the elimination of three water molecules. (See esterification reactions p136.)

Figure 15 **Tristearin** is a **triglyceride** found in **animal fat**. It is an ester that serves as an energy store in animals. The **blue** sections originate from the fatty acid stearic acid $CH_3(CH_2)_{16}COOH$.





Most **animal triglycerides** are solids called fats. As these do not usually contain double bonds they are said to be saturated.

Liquid triglycerides like vegetable oils usually contain one or more **double bonds** in the carbon chains. These are said to be **unsaturated** or **polyunsaturated** (averaging more than one double bond per carbon chain).

Where plant oils contain a double bond, the chain is arranged in the ***cis*** form, never the ***trans*** form. (See Fig 16). The presence of double bonds in the *cis* configuration is one reason why plant triglycerides are liquids. The bent shape of the *cis* isomer reduces dispersion forces and prevents the efficient packing of molecules that is needed to form a solid phase.

Omega-3 fatty acids are unsaturated fatty acids with a double bond between the **third** and **fourth** carbon from the methyl ($-CH_3$) end of the carbon chain. The omega-3 fatty acid α-linolenic acid is an essential fatty acid that humans can not synthesise and so need to include sources of it in their diet. Eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) are two other essential, omega-3 fatty acids. Fish (especially fatty fish) are a good source of both EPA and DHA.

While vegetable oils are known to be a healthy part of a balanced diet and suitable for many types of cooking, they are unsuitable for baking products like biscuits and cakes. This is partly because they remain **liquid** in the finished product and so drain from it rather than remaining suspended as a solid. As well as this, the unsaturated fats from plants tend to have a short shelf life and are likely to spoil or go rancid. **Hydrogenation** of vegetable oils has long been used as a solution to this problem. The hydrogenation process converts unsaturated liquid vegetable oils into more versatile **solid products** like **shortening** and **margarine**. Hydrogenation involves an **addition reaction** where hydrogen atoms add to some of the double bonds in the carbon chains of the fat molecules (triglycerides). This reduces the degree of unsaturation and produces a **solid fat** suitable for use in baking or spreading.

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One unintended effect of the hydrogenation process is an **undesirable side reaction** involving the conversion of some of the ***cis*** double bonds of the triglyceride carbon chains into the ***trans*** form. Although the *trans* isomers are unsaturated, their linear geometry increases dispersion forces and allows their molecules to pack more efficiently than the *cis* form. As a result, *trans* fats solidify more readily than the *cis* isomers. Dieticians believe the consumption of these *trans* isomers poses a risk to the health of our cardiovascular system. (See Fig 16.)

Three different **triglyceride** molecules: **A** represents tristearin, a **saturated** fat; **B** is the triglyceride ester of oleic acid, a **monounsaturated *cis*** ester and **C** is the ***trans*** version of **B**. Notice the distinctly **non-linear shape** of the ***cis*** isomer, **B**.

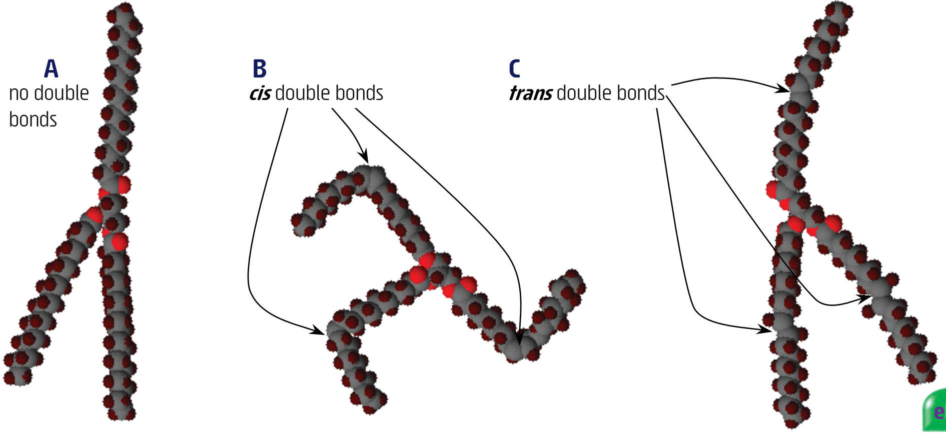

Figure 16 Vegetable oils are essentially liquid because of the *cis* isomerism of the double bonds in their carbon chains. The **bent shape** of the ***cis*** isomer (**B**) reduces dispersion forces and prevents the efficient packing of fat molecules that is needed to form a solid phase.

The **linear shape** of ***trans*** isomers (**C**) means they pack more efficiently and have stronger dispersion forces. Thus triglycerides with *trans* carbon chains more readily form solids at room temperature.

It is generally accepted amongst nutritionists that the presence of ***trans* fats** in our diet should be avoided as these are strongly associated with an increased risk of cardiovascular diseases.

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Attempt Set 16 # 13.

11.11 Alpha (α) amino acids

As the name suggests, **amino acids** contain both the amino functional group (**—NH₂**) and the carboxylic acid functional group (**—COOH**). Many different types of amino acid are possible; however, it is the **alpha (α) amino acids** (Fig 17) that are most important in living systems. They are the building blocks of which **proteins** are made. In humans, proteins produce tissue like muscle, skin, hair, ligaments and tendons. Some proteins may function as antibodies to protect against infection or hormones like insulin that control biological process. Other proteins act as enzymes; biological catalysts that speed up metabolic processes (chemical reactions) in the body. Haemoglobin is a protein involved in transport of oxygen and carbon dioxide in the body.

Proteins and **polypeptides** are unbranched polymers formed from the combination of multiple α-amino acid molecules (monomers). (See 14.7 p151.) An individual protein molecule may be formed from several thousand α-amino acid molecules that join in a specific sequence. Although a great variety of amino acids are possible, in nature there are 20 different common α-amino acids that are found to produce the great variety of proteins used by all living things.

In an amino acid the acid functional group (—COOH) is always located on a primary carbon (ie a terminal carbon) while the amino group may be located on any other carbon atom within the molecule. **Alpha (α) amino acids** however, always have the amino group, **—NH₂** attached to the carbon atom next to the **—COOH** functional group. This carbon is referred to as the α

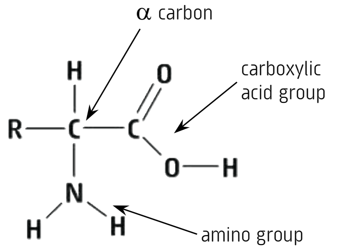


Figure 17 The general structure of an **α-amino acid**.

R represents a carbon chain or cyclic functional group (or a single H atom as in glycine). All 20 common α-amino acids found in living systems have this structure, except for one, proline which has an extra bond between the N atom and the R group. (See Appendix 6.)

Table 11 Structure and name of selected α
emphasises the structural similarity of the different α-amino acids. A complete table of commonly occurring α-amino acids can be found in the appendix section.

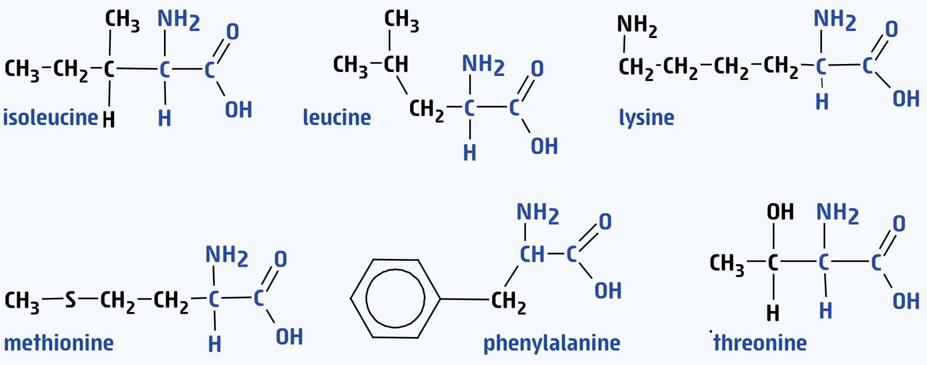
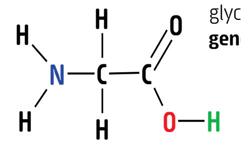
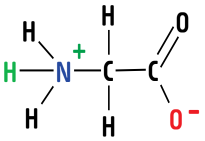


Figure 18 While it is sometimes convenient to represent α
molecular form this does not show their true structure. In the solid state and in aqueous solution α
called **zwitterions**.

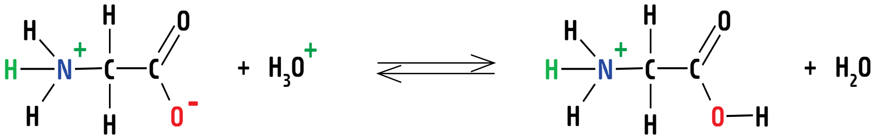

glycine
general form


glycine
zwitterion form

Although α-amino acids are often drawn as shown in Figure 17 and Table 11 these representations do not reflect their true structure. In the solid state and in aqueous solution α-amino acids are known to exist as a **dipolar ion** called a **zwitterion**. (See Fig 18.) This structure contains both a positive charge and a negative charge (not to be confused with the partial charges of a polar molecule) while being overall neutral. It is the presence of the weakly acidic –COOH group and a weakly basic $–NH_2$ group in the α-amino acid structure that causes the zwitterion to form. The **weakly acidic -COOH** group releases a proton (**H^+** ion) that is accepted by the **weakly basic $-NH_2$** group. The molecule then contains an **anionic $-COO^-$** group and a **cationic $-NH_3^+$** group. Overall the zwitterion is **neutral** in charge.

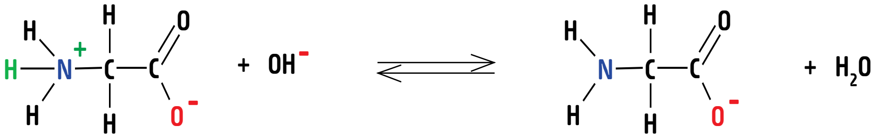
The formation of zwitterions explains why all of the α-amino acids are crystalline solids with relatively high melting points. In the solid state, instead of being held together by relatively weak intermolecular forces, zwitterions are attracted to one another by much stronger ionic interactions. Glycine for example, the smallest of the α-amino acids (NH_2CH_2COOH) remains solid at temperatures of up to around 262 °C at which point it decomposes rather than melts. As a comparison, the analogous carboxylic acid, ethanoic acid (CH_3COOH) has a melting point of 16.6 °C. Also, all of the α-amino acids are fairly soluble in water. If they were not dipolar ions then only the smaller examples would be expected to be soluble in water.

The zwitterion structure, (Fig 18) shows an α-amino acid molecule contains both a **weakly acidic** group, **$-NH_3^+$** (conjugate acid of $–NH_2$) and a **weakly basic** group **$-COO^-$** (conjugate base of –COOH). This means zwitterions are capable of behaving as acids (proton donors) or bases (proton acceptors) depending upon the pH of their surrounding solution. When placed into an acidic solution, ie one with a high concentration of $H_3O^+(aq)$ [ie $H^+(aq)$] the weakly basic $-COO^-$ group will gain a proton from solution to form the –COOH group. The resulting structure is no longer neutral but has an overall positive charge and is known as the cationic form. (See below.)


neutral **zwitterion** form

cationic form

Conversely if placed into a basic solution, ie one with a high concentration of $OH^-(aq)$ the weakly acidic $-NH_3^+$ group will lose a proton to form the $–NH_2$ group. The resulting structure has an overall negative charge and is known as the anionic form. (See below.)


neutral **zwitterion** form

anionic form

These reactions demonstrate the buffering potential of α-amino acids.

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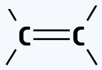
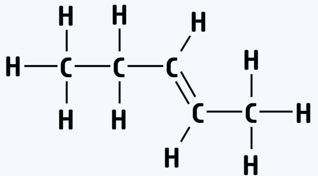
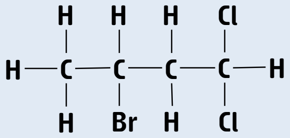
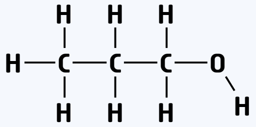
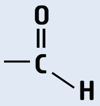
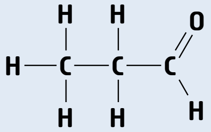
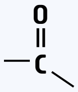
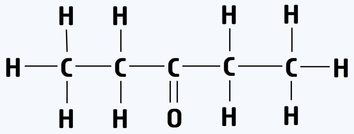
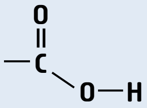
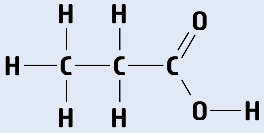
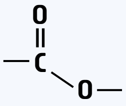
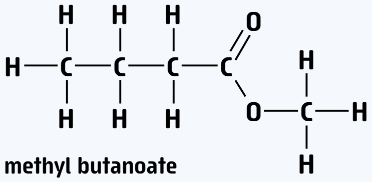
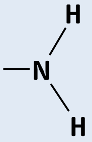
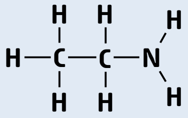
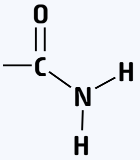
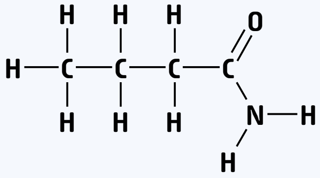
Attempt Set 16 # 14, 15 and 16.

11.12 Review: Organic nomenclature and functional groups

Functional groups (See Table 12.) are atoms or groups of atoms that give an organic molecule its particular characteristics. The nomenclature of organic compounds with functional groups follows the same rules as those previously outlined for alkanes. (See 10.6.) Importantly though, it is the **functional group** that has priority in determining the suffix and numbering of the stem. The presence of **halogen** (F–, Cl–, Br–, I–) or **alkyl** groups (methyl, ethyl etc) is indicated using numbers and prefixes as outlined previously.

Where two or more functional groups occur in the same molecule then the **principal functional group** is given priority. In the scope of this text and your coursework it is not anticipated that you are required to name organic compounds containing more than one functional group. However, where this does occur, the **order of priority** for the principal functional group (highest to lowest) is carboxylic acid (–COOH), amide ($–CONH_2$), aldehyde (–CHO), ketone (–CO–), alcohol (–OH), amine ($–NH_2$) and alkene (–C=C–).

Table 12 Common functional groups in organic compounds.

Structural formula	Simplified formula	Class of compound	Prefix or suffix to stem	Example
	$-CH=CH-$ or $-CHCH-$	alkene	–ene	 *trans*-pent-2-ene
$-F$ $-Cl$ $-Br$ $-I$		haloalkane	fluoro– chloro– bromo– iodo–	 3-bromo-1,1-dichlorobutane
$-O-H$	$-OH$	alcohol	–ol or hydroxy–(if not the principal functional group)	 propan-1-ol
	$-CHO$	aldehyde	–al	 propanal
	$-CO-$	ketone	–one	 pentan-3-one
	$-COOH$	carboxylic acid	–oic acid	 propanoic acid
	$-COO-$	ester	–oate	 methyl butanoate
	$-NH_2$	amine	–amine or amino– (if not the principal functional group)	 ethanamine
	$-CONH_2$	amide	–amide	 butanamide

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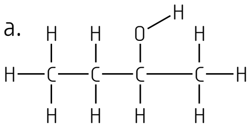
Complete Set 16.

Set 16 Organic chemistry: Functional groups

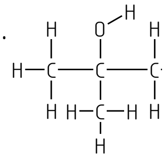
1. Draw **full structural formula** for the following alcohols and **classify** these as primary, secondary or tertiary alcohols. **Show all bonds**.
   a. butan-1-ol
   b. pentan-3-ol
   c. propan-2-ol
   d. 2-methylbutan-2-ol

2. Give the **IUPAC** name for the substances whose molecular structures are shown here.

a.



b.



3. A student named an alcohol from its structure. The name he suggested was **butan-3-ol**. Draw this structure and **explain** why the name is incorrect.

4. **Ethane** is a gas at room temperature with a boiling point of **-89 °C**. By comparison, ethanol is a liquid and has a boiling point of **78 °C**. **Account** for this difference in terms of **intermolecular forces**.

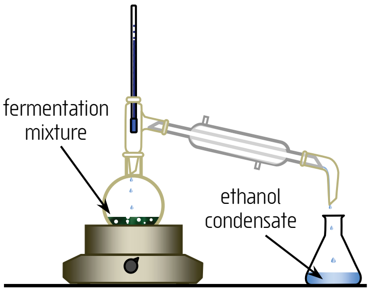
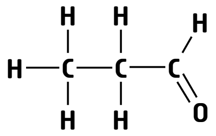


Figure 19 Distillation apparatus for separating ethanol from the fermentation mixture in Question 4.

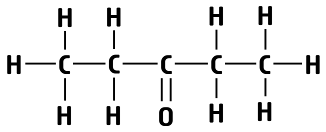
5. A student had prepared some **ethanol** by the **fermentation** of sugar with yeast. He planned to separate the ethanol from the resulting reaction mixture so that he could determine the yield of ethanol in his experiment. The student decided to do this by **distillation**, a technique used for separating liquids from a mixture by boiling it and condensing the resulting vapours. The following questions refer to this situation.
   a. The fermentation mixture will consist mainly of **ethanol** and **water**. **Explain** why these two liquids remain mixed together rather than forming separate layers.
   b. The best separation that can be achieved by the distillation process is **95.6%** pure ethanol, ie the distillate still contains 4.4% water. This is essentially due to the **hydrogen bonding** ability of water and ethanol. Draw a **labelled diagram** of a water molecule and an ethanol molecule to show how they interact this way.

6. Give the **IUPAC** name for substances with the following molecular structures.

a.



b.



c. **$CH_3COCH_2CH_3$**

d. **CH_3CHO**

7. With reference to **intermolecular forces**, **account** for the difference in **boiling point** of the listed substances.

Substance	**Condensed formula**	**Molar mass (g mol^{-1})**	**Boiling point (°C)**
butane	$CH_3CH_2CH_2CH_3$	58.1	-0.5
propan-1-ol	$CH_3CH_2CH_2OH$	60.1	97.2
propanal	CH_3CH_2CHO	58.1	47.9

8. Draw **full structural formula** for the following compounds. **Show all bonds**.
   a. CH_2BrCH_2COOH
   b. 2,2-dichloropentanoic acid
   c. 3-methylbutanoic acid

Remember! **Miscible** substances are soluble in one another in all proportions.

9. **Carboxylic acids**, like ethanoic acid, are **miscible** with water but other carboxylic acids, like palmitic acid [$CH_3(CH_2)_{14}COOH$], are virtually **insoluble** in water. **Explain** this difference in solubility in terms of molecular structure and **intermolecular forces**.

10. Draw structures for **ethanamine** and **pentan-1-amine**. Would these organic compounds be expected to **dissolve** in water? **Explain**.

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11. **Amines** and **amides** have some similarities and some significant differences. Draw the structural formula for **ethanamine** and **ethanamide** and answer the following questions about these two compounds.
    a. **Circle** the **hydrogen atoms** from each structure that are capable of hydrogen bonding.
    b. For both structures draw in all of the **lone pairs** that are capable of hydrogen bonding.
    c. Briefly explain why the **bond dipole** of the N-H bond is stronger in ethanamide than ethanamine, ie why the hydrogen atoms in ethanamide have a greater δ

°C) and ethanamide

(221 °C).

12. Three of the **esters** that contribute to the odour of ripe bananas are ethyl butanoate, pentyl hexanoate and pentyl pentanoate. Draw full **structural formulas** for these three esters.

13. **Palmitoleic** acid is a **monounsaturated fatty acid** found in human fat tissue. It is biosynthesised in the body from palmitic acid by the action of an enzyme called **delta-9 desaturase**. The wire frame structure (Fig 20) for these two substances is shown below. Answer the questions relating to this situation.

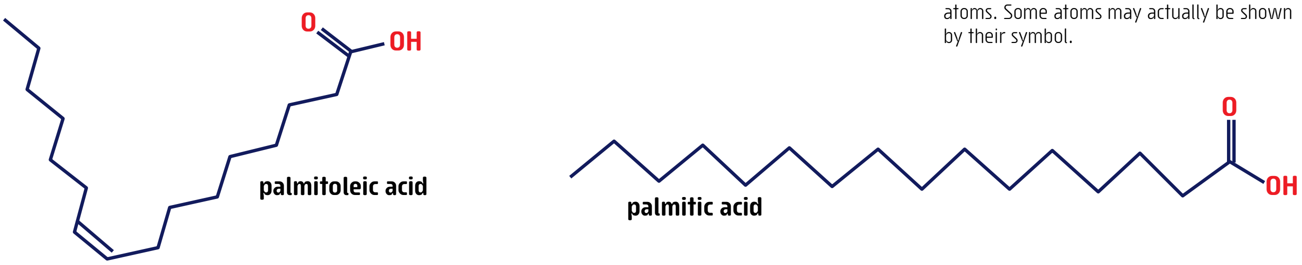


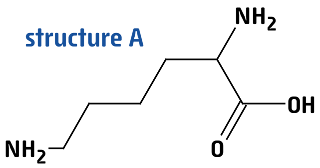
Figure 20 These **wire frame** models depict the monounsaturated fatty acid **palmitoleic acid** and **palmitic acid**. Each **junction** in the model shows the position of a **C** atom. Double bonds are shown as usual. Any missing atoms are assumed to be hydrogen atoms. Some atoms may actually be shown by their symbol.

    a. **Circle** the **carboxylic acid** functional group in each of the wire frame structures.
    b. Palmitoleic acid is a monounsaturated fatty acid. With reference to the wire frame structure explain the meaning of the term **monounsaturated**.
    c. Is palmitic acid a **fatty acid**? Is it **unsaturated**? **Explain**.
    d. The molecular formula of palmitic acid is $C_{16}H_{32}O_2$. From the wire frame structure determine the **molecular formula** of **palmitoleic acid**.
    e. Refer to the wire frame structures and their respective formula, $C_{16}H_{30}O_2$ and $C_{16}H_{32}O_2$, to help **describe** how palmitic acid has been changed in the biosynthesis of palmitoleic acid. Hence **suggest** how the name of the enzyme **delta-9 desaturase** describes its role in the conversion process.

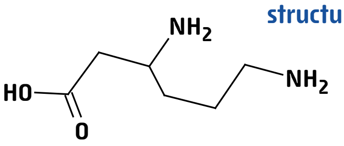
14. The amino acid known as **homoalanine** consists of a straight carbon chain with the molecular formula $C_4H_9NO_2$. Complete the following for this α-amino acid.
    a. Draw its **structural formula**. Ensure you show all atoms and bonds.
    b. What is meant by the α-carbon in an amino acid? Refer to your answer in (a).
    c. α-amino acids usually exist as a **zwitterion**. What is a zwitterion? Give the structural formula for the zwitterion of $C_4H_9NO_2$.

15. Which of the following structures represents an **alpha amino acid**? Explain why the other structure is not an alpha amino acid.

structure A



structure B

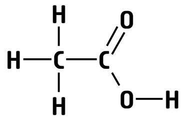


16. Like all alpha amino acids, **alanine** (CH_3CHNH_2COOH) normally exists in one of **three forms**. In the pure form or in a neutral solution it exists as a **zwitterion**. (See Fig 18.) In **acid** solutions the zwitterion changes to a **cationic** form. This happens as the weakly basic group **$-COO^-$** of the zwitterion accepts an H^+ ion from solution to form -COOH. The $-NH_3^+$ group remains unchanged. In a **basic** solution the zwitterion changes to the **anionic** form by donating an H^+ ion from the weakly acidic **$-NH_3^+$** group, to form a $-NH_2$ group. The $-COO^-$ group remains unchanged.

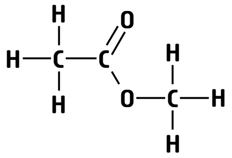
Draw four **structural diagrams** showing all bonds, atoms and charges for alanine (CH_3CHNH_2COOH) in the **zwitterion** form, the **cationic** form, the **anionic** form and one diagram showing its **general structure**.

17. Name the **functional group** in each of the following organic structures.

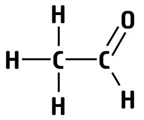
a.



b.



c.



d. $CH_3CH_2CH_2CONH_2$

e. $CH_2CHCH_2CH_3$

f. $CH_3COCH_2CH_3$

g. CH_3CH_2OH

h. $CH_3CH_2NH_2$

i. CH_3COOCH_3

18. Draw suitable **structural formula** for the following organic compounds.

a. 2,2-dimethylpentane
b. butanone
c. propyl ethanoate
d. butan-2-ol
e. 3-methylbutanoic acid
f. 3-methylbutan-1-ol
g. 2-ethylbutanamide
h. *cis*-2,3-dichloropent-2-ene
i. 3,3,3-tribromopropanoic acid
j. 2,4-dichloropentanal
k. ethyl methanoate
l. *trans*-1,2-diaminoethene
m. 2-aminopentanoic acid
n. pentan-3-one
o. 2-methylhexanal
p. butane-1,3-diamine
q. *cis*-but-2-ene
r. ethyl propanoate

Hint! Look for these clues for functional groups in semi-structural or condensed formula.

$CHCH_2$ at the chain end is an **alkene**.

CHCH within a chain is an **alkene**.

CH_2OH at the chain end is an **alcohol**.

$CHOHCH_2$ within a chain is an **alcohol**.

CHO at the chain end is an **aldehyde**.

COC within a chain is a **ketone**.

COOH at the end is a **carboxylic acid**.

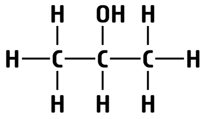
CH_2NH_2 at the chain end is an **amine**.

$CONH_2$ at the chain end is an **amide**.

COOC within a chain is an **ester**.

19. Give the **IUPAC** name for the following organic structures.

a.



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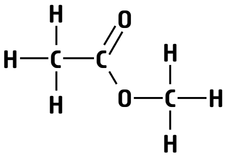

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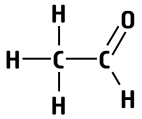

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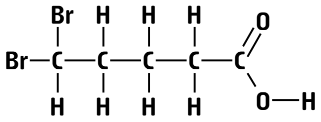

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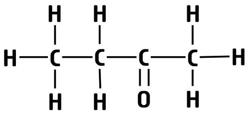

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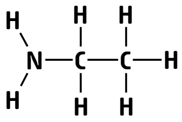
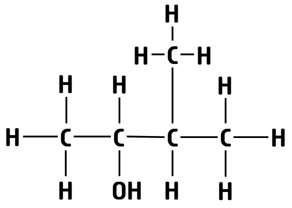


g.



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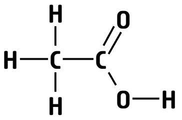
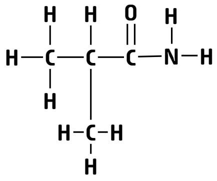


i.



j. $CH_3CH_2COOCH_2CH_3$

k. $CH_3COCH_2CH_2CH_3$

l. $CH_3CHOHCH_3$

m. CH_3CH_2CHO

20. **Name** the compounds described below.
    a. A **carboxylic acid** and an **ester** both of molecular formula $C_2H_4O_2$.
    b. The **tertiary alcohol** of molecular formula $C_4H_{10}O$.
    c. The **two esters** of molecular formula $C_3H_6O_2$.
    d. An **aldehyde** and a **ketone** of molecular formula C_3H_6O.

21. Sketch a molecule of the **omega-3 fatty acid docosahexaenoic acid**. Each molecule of this fatty acid has a straight chain of 22 carbon atoms with double bonds at carbon number 4, 7, 10, 13, 16 and 19. Remember carbon number 1 is the carboxylic acid functional group. All of the double bonds have a *cis* configuration. With reference to your structure **explain** why docosahexaenoic acid is referred to as a **polyunsaturated omega-3 fatty acid**. (See Fig 21.)

Figure 21 Docosahexaenoic acid (**DHA**) is an **omega-3 fatty acid** found in cold water fatty fish, seaweed and fish oil supplements. DHA is essential for the proper functioning of our brain as well as lowering our risk of heart disease. While our bodies do produce small amounts of DHA we need to supplement this from our diet. Western diets in particular tend to be deficient in omega-3 fatty acids.

All **omega-3** fatty acids have a double bond between the 3rd and 4th carbon atoms from the CH_3 end of the carbon chain, ie the end opposite to the -COOH functional group. Omega-3 fatty acids may have more than one double bond, ie may be polyunsaturated.

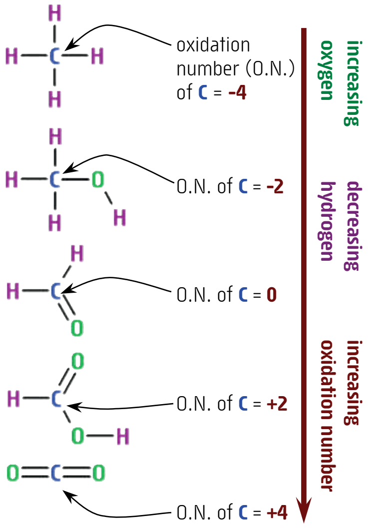
22. **Name** the eight isomeric **alcohols** of $C_5H_{12}O$. **Classify** these as **1°**, **2°** or **3°** alcohols.

23. **Propyl ethanoate** and **pentanoic acid** (common name valeric acid) are **isomers** of $\mathbf{C_5H_{10}O_2}$. Propyl ethanoate is a volatile liquid that finds application as a solvent for perfumes and wood lacquers. By comparison pentanoic acid is much less volatile and not suited to this use.
    a. **Suggest why** a **volatile** solvent is needed for perfumes and wood varnish.
    b. **Suggest** a reason in terms of intermolecular forces why pentanoic acid should be much **less volatile** than propyl ethanoate.

CHAPTER 12 | ORGANIC REACTIONS AND SYNTHESIS

12.1 Oxidation of organic compounds

Figure 1 The **oxidation number** of the **carbon atom** in these molecules increases (C is more oxidised) as the number of bonds to oxygen increases and/or the number of bonds to hydrogen decreases. Note, in these examples the oxidation number of **O = -2** and of **H = +1**.



Oxidation is defined as the loss of electrons. In an organic reaction this is often seen when a molecule **gains oxygen** or **loses hydrogen**. In either case, if a **carbon atom** in an organic molecule loses electrons or gains bonds to oxygen or loses bonds to hydrogen, then the carbon atom involved shows an increase in its **oxidation number**. (See Fig 1.) This increase in oxidation number confirms the carbon atom and hence the organic molecule has been oxidised.

Many organic compounds are indeed oxidised simply by being exposed to oxygen in the air. The traditional method of vinegar manufacture for example, involves the aerial oxidation of ethanol, from products like fermented fruit juices (eg wine or cider). Exposing the fermented juices to air (O_2) causes a slow oxidation reaction that converts CH_3CH_2OH (ethanol) to CH_3COOH (ethanoic acid), the key ingredient of vinegar. Notice the product, CH_3COOH has gained oxygen, lost hydrogen and its carbon atoms show an overall increase in oxidation number from -2 to 0. All of these changes are indicators of oxidation.

The combustion of ethanol; a sustainable fuel found in products like E10 and E85 (ie petrol with 10% and 85% ethanol respectively), also involves aerial oxidation. This is a much faster reaction where the fuel is vaporised, mixed with air and ignited. The equations below show the complete combustion of octane and ethanol, the major components of these fuels.

combustion of ethanol: $C_2H_5OH(l) + 3O_2(g) \rightarrow 2\mathbf{CO_2(g)} + 3H_2O(l) + \mathbf{1367\ kJ}$

combustion of octane: $2C_8H_{18}(g) + 25O_2(g) \rightarrow 16\mathbf{CO_2(g)} + 18H_2O(l) + \mathbf{10940\ kJ}$

In these combustion reactions the carbon present in the fuels (C_2H_5OH and C_8H_{18}) has gained oxygen, lost hydrogen and increased its oxidation number. Complete oxidation has occurred as the product, ie CO_2, has carbon in its highest possible oxidation state, ie +4, therefore no further oxygen could be added to it and no further hydrogen removed.

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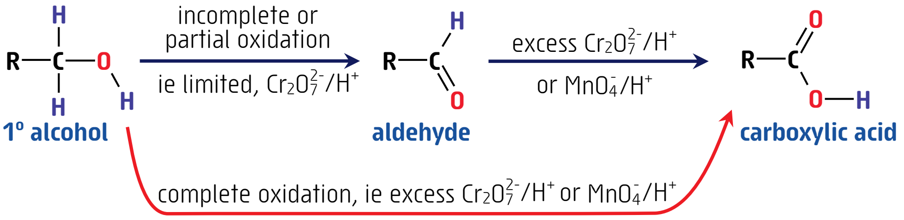
Attempt Set 17 # 1 and 2.

12.2 Synthesis by oxidation of alcohols

The oxidation of an alcohol by combustion, although useful for energy production, is of no use in organic synthesis. Combustion simply converts an organic compound into inorganic products like CO_2 and H_2O. However, in the laboratory the controlled oxidation of alcohols can be used to synthesise other organic compounds like **aldehydes**, **ketones** or **carboxylic acids**. This is achieved using oxidising agents like **acidified $KMnO_4(aq)$** or **acidified $K_2Cr_2O_7(aq)$**.

Using these reagents a **1° alcohol** can be made to undergo **complete oxidation** (*****see border note) to produce a **carboxylic acid** or **partial oxidation** to form an **aldehyde**. Achieving partial oxidation is difficult as there is a strong tendency for the aldehyde to be oxidised to a carboxylic acid as soon as it forms. Partial oxidation is favoured by using an excess of the alcohol with the weaker oxidising agent, acidified $K_2Cr_2O_7(aq)$. To prevent complete oxidation the mixture is heated sufficiently to distil off the aldehyde as soon as it forms. Conveniently an aldehyde will always have a lower boiling point than its parent alcohol.

* or destructive oxidation of an organic substance produces compounds like CO_2 and H_2O. These products are not organic compounds. In the context of organic reactions, **complete oxidation** generally refers to a reaction where at least one **organic product remains**.

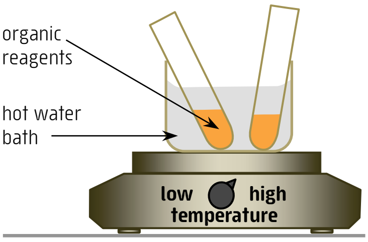


Heat is often used to increase the rate of these sometimes slow reactions. (See Fig 2).

Figure 2 **Caution** should be exercised when heating organic reagents as they are both **volatile** and **flammable**.

For this reason a Bunsen flame should not be used for heating. In a school laboratory situation it is most practical to use a **hot water bath** or an **electric heater** as a heating method.

Toxicity of these organic vapours must also be considered by checking **MSD** information.



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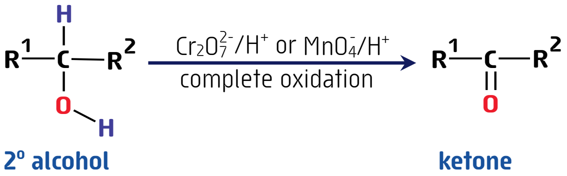
Ketones can be synthesised by the oxidation of a **2° alcohol**. (See below.) As ketones are resistant to further oxidation they are the final product of this reaction.



Tertiary alcohols are **resistant to oxidation** and hence show no reaction with acidified $KMnO_4(aq)$ or acidified $K_2Cr_2O_7(aq)$. Half-equations and full redox equations for the oxidation of organic reagents can be written in the usual way.

Attempt Set 17 # 3.

Example 1 Write a balanced half-equation for each of the reactions described below. Assume **acidic** conditions apply.

	Reaction 1	**Partial** oxidation of ethanol.	**Reaction 2** **Complete** oxidation of ethanol.
Show the reactant and its product.	$CH_3CH_2OH \rightarrow \mathbf{CH_3CHO}$	an **aldehyde** forms	$CH_3CH_2OH \rightarrow \mathbf{CH_3COOH}$ a **carboxylic acid** forms
Balance **oxygen** by adding H_2O.	$CH_3CH_2\mathbf{O}H \rightarrow CH_3CH\mathbf{O}$	**O** is already balanced	$CH_3CH_2OH + \mathbf{H_2O} \rightarrow CH_3COOH$
Balance **hydrogen** by adding H^+ ions.	$CH_3CH_2OH \rightarrow CH_3CHO + \mathbf{2H^+}$		$CH_3CH_2OH + H_2O \rightarrow CH_3COOH + \mathbf{4H^+}$
Balance **charge** by adding electrons.	$CH_3CH_2OH \rightarrow CH_3CHO + 2H^+ + \mathbf{2e^-}$		$CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 4H^+ + \mathbf{4e^-}$

Example 2 Write the redox equation for the **oxidation** of $\mathbf{CH_3CHO}$ by acidified $KMnO_4(aq)$.

Write the oxidation and reduction half-equations in the usual way.	$5e^- + MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$.............. ① $CH_3CHO + H_2O \rightarrow CH_3COOH + 2H^+ + 2e^-$ ..... ②
Multiply the coefficients of each half-equation so that **electrons** are **equalised** in both equations.	Multiply ① by 2... $\mathbf{10}e^- + \mathbf{2}MnO_4^- + \mathbf{16}H^+ \rightarrow \mathbf{2}Mn^{2+} + \mathbf{8}H_2O$ Multiply ② $CH_3CHO + \mathbf{5}H_2O \rightarrow \mathbf{5}CH_3COOH + \mathbf{10}H^+ + \mathbf{10}e^-$
Add the two half-equations and simplify the coefficients for any species on both sides of the equation.	$5CH_3CHO + 2MnO_4^- + \mathbf{6H^+} \rightarrow 5CH_3COOH + 2Mn^{2+} + \mathbf{3H_2O}$ Simplify the equation by eliminating $\mathbf{10e^-}$, $\mathbf{10H^+}$, and $\mathbf{5H_2O}$ from both sides of the equation.

As most organic reagents are colourless any **colour changes** occurring during these reactions are due to the oxidising agents. If $KMnO_4(aq)$ is used, it changes colour from **purple** (due to MnO_4^-) to **colourless** (Mn^{2+} is very pale pink). Using acidified $K_2Cr_2O_7(aq)$ gives a colour change from **orange** ($Cr_2O_7^{2-}$) to **green** (Cr^{3+}). If there is no colour change then this indicates no reaction has taken place.

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Complete Set 17.

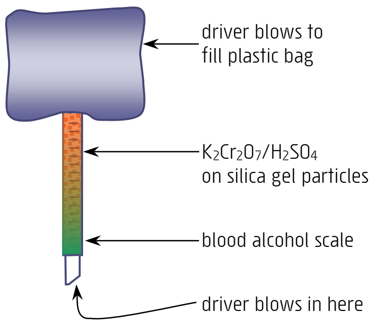
Set 17 Organic chemistry: Redox reactions

1. Write balanced equations for each of the following combustion reactions.
   a. The **complete** combustion of methanol, CH_3OH to form CO_2 and H_2O.
   b. The **incomplete** combustion of methanol, CH_3OH forming CO and H_2O.
   c. The **complete** combustion of butane, $CH_3CH_2CH_2CH_3$.
   d. The **complete** combustion of propan-2-ol, $CH_3CHOHCH_3$.
   e. The **complete** combustion of ethanoic acid, CH_3COOH.

2. Consider the combustion reactions from Question 1 and answer the following.
   a. Use oxidation numbers to show the complete combustion of methanol, CH_3OH as shown in Question 1(a) above is indeed a redox reaction.
   b. Use oxidation numbers to prove the reaction in Question 1(b) involves the **partial oxidation** of methanol, CH_3OH.

3. The following organic substances are treated with acidified potassium dichromate solution. If a reaction occurs, give the **condensed structural formula only**, for the expected organic product. Assume the reaction goes to completion unless stated.
   a. $CH_3CH_2CH_2OH$
   b. $CH_3CH_2CH_2CHO$
   c. CH_3CH_2COOH
   d. $CH_3CH_2CH_2OH$ (**incomplete oxidation**)
   e. $HOOCCH_2CH_2OH$
   f. $CH_3CHOHCH_3$
   g. 2-methylpentan-2-ol
   h. butanone
   i. pentane-1,3-diol

Figure 3 A simplified sketch of the original chemical **breathalyser**.



4. The original breathalyser, used for roadside alcohol screening of drivers in Western Australia, involved a chemical reaction that produced a colour change. A driver suspected of alcohol intoxication was required to blow through a small tube containing silica gel particles coated with a potassium dichromate/sulfuric acid mixture. They would blow until a small bag at the end of the tube was fully inflated. (See Fig 3.) The level of alcohol in the person's breath was determined by the extent of colour change occurring in the tube of crystals. The equation for the reaction is:

   $$3CH_3CH_2OH \quad + \quad 2Cr_2O_7^{2-} \quad + \quad 16H^+ \quad \rightarrow \quad 3CH_3COOH \quad + \quad 4Cr^{3+} \quad + \quad 11H_2O$$

   Answer the following questions about the operation of the breathalyser.

   a. What is the **role** of the **potassium dichromate** in this reaction and why is **sulfuric acid** present?
   b. **Explain** how the colour change in the tube of potassium dichromate is related to the **concentration** of **alcohol** in a driver's breath.
   c. Why is it important for a driver to blow sufficient breath to **fill the bag** at the end of the tube of crystals?
   d. Water is the major component in blood, making up around half of its total volume. What **physical properties** of ethanol (the alcohol in alcoholic beverages) enables it to be present in a person's **blood** and **breath** once they have consumed it?

5. Write a balanced **oxidation half-equation** for each of the following changes. In each case the reaction occurs in acidic conditions.

   a. The **complete** oxidation of ethanol, CH_3CH_2OH to form ethanoic acid, CH_3COOH.
   b. The **partial** oxidation of butan-1-ol, $CH_3CH_2CH_2CH_2OH$ forming butanal, $CH_3CH_2CH_2CHO$.
   c. The **complete** oxidation of propan-2-ol, $CH_3CHOHCH_3$ to produce propanone, CH_3COCH_3.
   d. Oxidation of propanal, CH_3CH_2CHO forming propanoic acid, CH_3CH_2COOH.

6. **Ethanol** is present in wines at around 12% by volume. Once a bottle of wine is opened and exposed to air it can become spoiled within a few days. This occurs by the action of various bacteria (acetobacters) and air (oxygen) and can soon give the wine an undesirable, distinct vinegary taste.

   a. What is the probable **source** of the **vinegary** taste in spoiled wine?
   b. What is the probable **role** of **oxygen** in the spoiling process?
   c. An Australian invention, known as the **wine cask**, is designed to solve this problem. In the wine cask, wine is stored in a flexible plastic bladder and released from the cask via a spout. As wine is released, the bladder volume decreases (collapses), preventing air from entering it. **Explain** why this invention prevents wine spoilage.

7. Give the **IUPAC name** for a precursor alcohol that could be oxidised to produce each of the listed compounds.

   a. CH_3CH_2COOH
   b. CH_3COCH_3
   c. $CH_3CH_2CH_2CHO$
   d. $CH_3CH_2COCH_3$
   e. $HOOCCH_2CH_2COOH$
   f. CH_3COCH_2COOH

8. For each of the situations described below, decide if a redox reaction will occur. If a reaction is expected, write a balanced **redox equation** to show this. Also describe what you would **observe** as each reaction takes place.

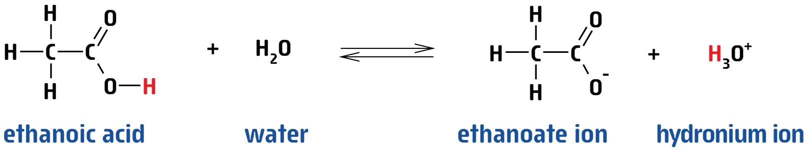
   a. Acidified potassium permanganate solution is added to **excess** propanal.
   b. Butan-2-ol is added to **excess** acidified potassium permanganate solution.
   c. Acidified potassium dichromate solution is added to methanol. Assume **complete** oxidation is the major reaction.
   d. 3-methylbutan-2-ol is added to **limited** acidified potassium dichromate solution.
   e. Acidified potassium dichromate solution is mixed with methanal.
   f. Acidified potassium dichromate solution is mixed and gently warmed with pentan-2-one.
   g. 2-methylbutan-2-ol is added to **limited** acidified potassium permanganate solution.
   h. Propan-1-ol and **excess** acidified potassium permanganate solution are mixed.
   i. Excess acidified potassium permanganate solution is added to propanoic acid.

Note: If a 1° alcohol is oxidised using a **limited** amount of **cold** oxidising agent then partial oxidation will be the major reaction, ie an aldehyde forms. **Excess** oxidising agent will certainly produce complete oxidation of a 1° alcohol, ie a carboxylic acid will be the product.

9. Use your knowledge of organic redox reactions to answer the following questions.
   a. Consider the four **isomeric alcohols** of molecular formula **C_4H_9OH**. Which of these is being described below? Give its IUPAC name.
      i. The alcohol that does **not** discolour an acidified potassium permanganate solution.
      ii. The two alcohols that **readily oxidise** to form a **carboxylic acid**.
      iii. The alcohol that oxidises to produce a **ketone**.
   b. Name the compound of molecular formula **C_3H_6O** which contains a **double bonded** oxygen atom and does **not** discolour an acidified potassium permanganate solution.
   c. Consider the following pairs of organic compounds. Name a **reagent** that when added to these substances, would **distinguish** each member of the pair. Note the **observation** expected for each substance.
      i. ethanol and ethanoic acid
      ii. propanone and propanal
      iii. 3-methylhexan-3-ol and 3-methylhexan-2-ol.

12.3 Carboxylic acids: Acid-base properties

As their name suggests, carboxylic acids are indeed **acidic** in nature. When dissolved in water they donate a proton to produce hydronium ions, H_3O^+ thus lowering pH. It is only the hydrogen atom of the carboxyl group, –COO**H** (in red) that shows acidic properties.



$CH_3COOH(aq)$ + $H_2O(l)$ $\rightleftharpoons$ $COO^-(aq)$ + $H_3O^+(aq)$

Table 1 K_a values for several straight chain carboxylic acids.

Acid name	Formula HA	$K_a = \frac{[H_3O^+][A^-]}{[HA]}$
methanoic acid	$HCOOH$	17.8×10^{-5}
ethanoic acid	CH_3COOH	1.75×10^{-5}
propanoic acid	CH_3CH_2COOH	1.38×10^{-5}
butanoic acid	$CH_3CH_2CH_2COOH$	1.48×10^{-5}
pentanoic acid	$CH_3CH_2CH_2CH_2COOH$	1.45×10^{-5}
hexanoic acid	$CH_3CH_2CH_2CH_2CH_2COOH$	1.41×10^{-5}

Carboxylic acids are typically **weak acids**, even the strongest of these, methanoic acid is considered a weak acid. The K_a values from Table 1 show ethanoic acid is the next strongest of these with the remaining longer chain carboxylic acids all being a little weaker in strength.

Their acidic nature means carboxylic acids and their solutions exhibit physical and chemical properties typical of acid solutions. Their solutions will turn **blue litmus red**, have a **sour** taste, produce **hydrogen gas** with reactive **metals**, are **neutralised** by a base and produce **carbon dioxide gas** with **carbonates** and **hydrogencarbonates**. (See below.)

$Zn(s) + 2CH_3COOH(aq) \rightarrow Zn(CH_3COO)_2(aq) + H_2(g)$

$NaOH(aq) + CH_3COOH(aq) \rightarrow COO(aq) + H_2O(l)$

$NiCO_3(s) + 2CH_3COOH(aq) \rightarrow Ni(CH_3COO)_2(aq) + H_2O(l) + CO_2(g)$

$Ni(HCO_3)_2(s) + 2CH_3COOH(aq) \rightarrow Ni(CH_3COO)_2(aq) + 2H_2O(l) + 2CO_2(g)$

The reaction with **sodium hydrogencarbonate** is sometimes used to distinguish a carboxylic acid from other organic compounds. Adding $NaHCO_3(aq)$ to a suspected carboxylic acid gives a **fizzing** reaction that produces the colourless, odourless gas carbon dioxide, $CO_2(g)$. Other commonly encountered organic compounds do not produce this result.

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Attempt Set 18 # 1, 2, 3 and 4.

Figure 4 Organic reagents are both **volatile** and **flammable**. Ideally a **refluxing** apparatus should be used to safely and efficiently heat these reagents.

A condenser prevents the loss of any volatile organic reagents by condensing vapours and returning the liquid to the reaction flask. An electric heating mantle is an added safety precaution against igniting any organic vapours that might escape. In a school laboratory situation it is often practical to use a **hot water bath** or an **electric heater** in place of the specialised heating mantle.

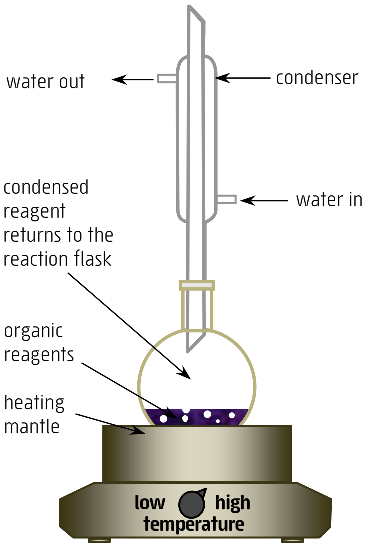

Figure 5 Do you like your soap **liquid**, **solid** or maybe **insoluble**?

Potassium salts produce low melting point liquid soaps. **Lithium** soaps are quite hard and high melting while **sodium** soaps are softer and used in typical bar soap. **Calcium** and **magnesium** soaps are **insoluble**. This explains why **hard water** (water containing Ca^{2+} and/or Mg^{2+}) renders soap inactive.

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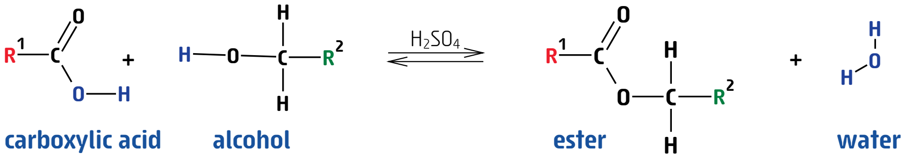
Attempt Set 18 # 8.

12.4 Esterification

Esterification is a reversible equilibrium reaction between an **alcohol** and a **carboxylic acid**. The reaction produces an **ester** and **water**. A general equation for esterification is shown here: R^1 and R^2 represent alkyl groups (carbon chains). The O and H atoms in **blue** show the water molecule originates from the -OH of the acid and the -H of the alcohol.



carboxylic acid **alcohol** **ester** **water**

Although esterification is slow under normal conditions, its rate can be increased by heating and using a catalyst. A strong acid like **sulfuric acid** is an effective catalyst for this reaction. If heating is used to increase the rate then it is best to use a refluxing apparatus (see Fig 4) as some of the reactants and products are both volatile and flammable. The **equilibrium** nature of this reaction means it does not go to completion and thus the yield of ester can vary according to the conditions used and the particular reaction involved. Typically there will be appreciable amounts of both reactants and products at equilibrium.

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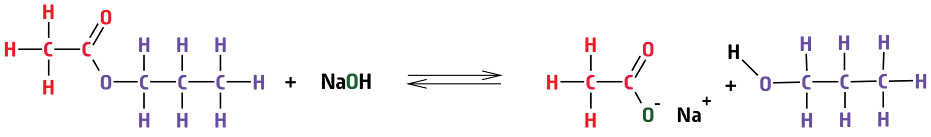
Attempt Set 18 # 5, 6 and 7.

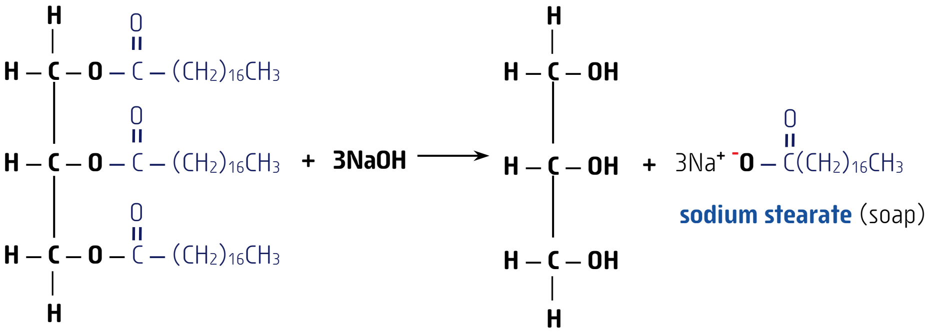
12.5 Ester hydrolysis and soap formation

The heating of an ester with a strong base, like sodium hydroxide, causes its **hydrolysis**. This converts the ester to the original alcohol and carboxylic acid from which it was made. The presence of a strong base in the reaction mixture means the carboxylic acid will be in the form of a salt. In this example the various atoms are **colour coded** to show how the reactants and products are related.



propyl ethanoate **sodium hydroxide** **sodium ethanoate** **propanol**

Ester hydrolysis is used in the manufacture of cleaning agents called **soaps**. Bar soap, like that used for personal hygiene, is a sodium salt of a fatty acid (Fig 5). Soaps like this have been manufactured from animal fats and vegetable oils since early human history. The earliest known evidence of soap making dates back to around 2800 BC in the ancient region of Babylon. An example of this reaction, known as **saponification**, uses the ester **tristearin** (an animal fat) to produce **sodium stearate** (a soap) and the by-product glycerol.



sodium stearate (soap)

tristearin (an animal fat) **glycerol** (propane-1,2,3-triol)

12.6 Structure and cleaning action of soaps and detergents

The **cleaning action** of soap is attributed to its unique structure that consists of a non-polar hydrocarbon chain plus a highly polar ionic group. (See Fig 6.) The ionic end is said to be **hydrophilic** (meaning water attracting) while the non-polar hydrocarbon chain is said to be **hydrophobic** (not attracted to water or literally 'water hating').

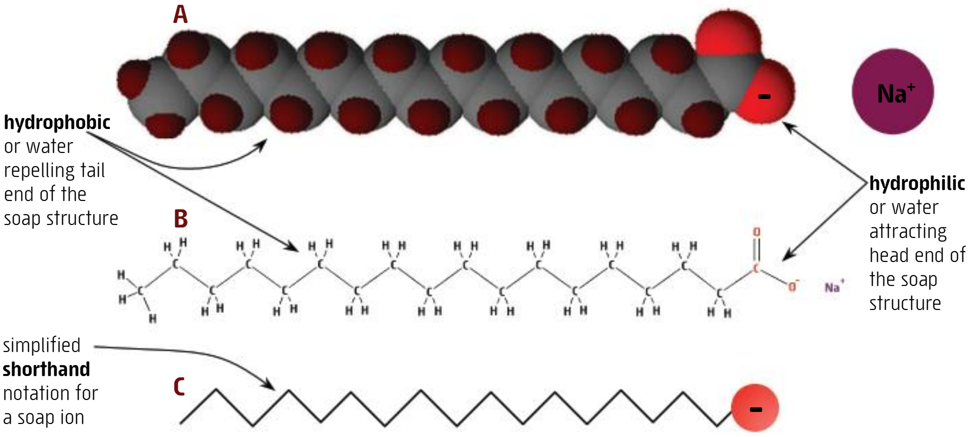
These structures (Fig 6) show the dual hydrophilic and hydrophobic nature of the soap sodium stearate.

Figure 6 The soap **sodium stearate** showing its 3D structure, **A**, structural formula, **B** and a simplified structure, **C**.

The hydrocarbon section of the soap ion is essentially non-polar. For this reason it is not attracted to water and is said to be **hydrophobic**.

The head, or ionic part of the soap ion is however, strongly attracted to the positive dipole of nearby water molecules. For this reason, this part of the soap ion is said to be **hydrophilic**.

The cleaning action of sodium stearate and soaps in general is a result of this dual hydrophilic-hydrophobic nature.



In water, soap or surfactant ions (as they are also known), are able to dissolve normally insoluble non-polar '**greasy**' materials. This happens as the **hydrophobic** tails (non-polar) of the soap ions are **attracted** to non-polar **greasy** material while the **hydrophilic** head end of the soap ions are **attracted** to **water** molecules. This results in soap ions forming small compact spherical structures known as **micelles**. The **inside** of the micelle contains the greasy non-polar substance ('the dirt') along with the hydrophobic tails of the soap ions.

The **outside** surface of the micelle is formed by the hydrophilic, water attracting ends of the soap ions. In this way soapy water is able to wash greasy materials from any surface while water alone would be unable to achieve this. (See Fig 7 below.)

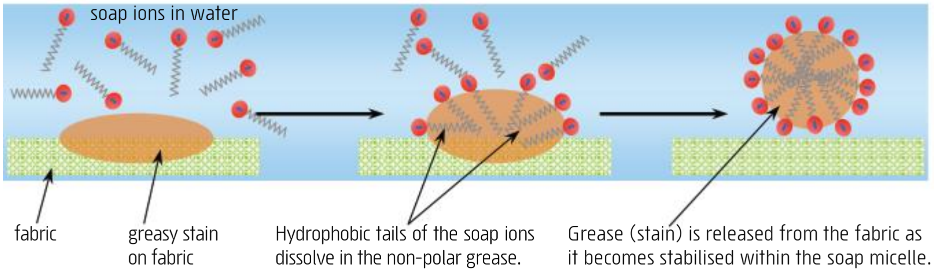


Figure 7 The **hydrophobic tails** of soap ions are attracted to one another and to **non-polar grease** molecules by dispersion forces. This attraction coupled with the attraction of the **hydrophilic** ends of the soap ions to water molecules (by ion-dipole forces) cause soap ions and grease to form **micelles**. As the non-polar grease is embedded inside the micelle it is able to be stabilised in water. In this way, the polar solvent water is able to 'dissolve' otherwise insoluble greasy non-polar substances.

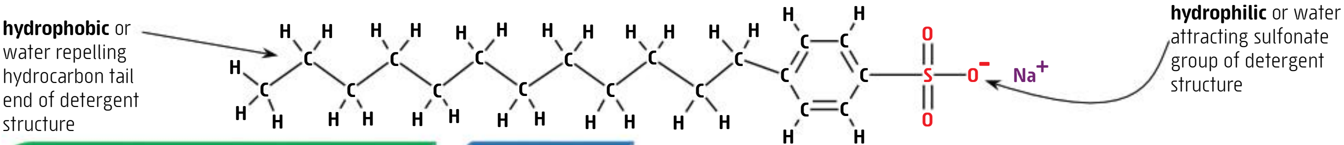
The cleaning action of soap is enhanced by agitation and using hot water. One factor that prevents the cleaning action of soap is the presence of **calcium ions**, Ca^{2+} or **magnesium ions**, Mg^{2+} in water. These ions react with soap ions in a precipitation reaction that forms an insoluble substance resembling a floating scum. Water containing these ions does not lather with soap and is known as **hard water**. The following equation shows how calcium ions, Ca^{2+} **precipitate** stearate soap ions, $CH_3(CH_2)_{16}COO^-$ removing them from solution.

$$Ca^{2+}(aq) \quad + \quad 2CH_3(CH_2)_{16}COO^-(aq) \quad \rightarrow \quad Ca(CH_3(CH_2)_{16}COO)_2(s)$$

Detergents are synthetic compounds that are similar to soap in both structure and cleaning action. However, unlike soaps, detergent ions do not form precipitates with Ca^{2+} or Mg^{2+} ions and so are able to function in hard water. They can also be produced more cheaply and in greater quantities, as animal fats or vegetable oils are not required. Detergents instead are manufactured from synthetic reagents like **sulfuric acid** and **petroleum products**.

As well as their ability to function in hard water detergents have a much stronger cleaning action. This makes them ideal for use in laundry powders and dish washing powders but less suitable for personal hygiene. Sodium **dodecylbenzenesulfonate** (Fig 8), an **anionic detergent**, is one of the most commonly used detergents.

Figure 8 Sodium dodecylbenzenesulfonate, a detergent, shows a similar dual **hydrophobic-hydrophilic** structure to that of soap.



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Complete Set 18.

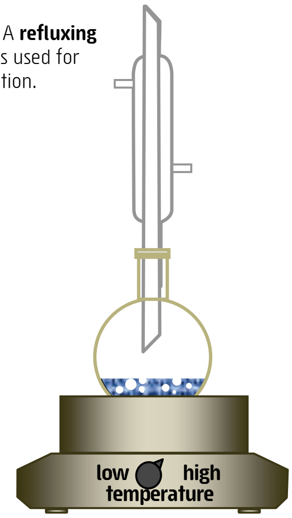
Set 18 Carboxylic acids, esterification and soaps

1. If **milk** is not refrigerated it will soon turn **sour**. Even refrigerated milk will eventually pass its use by date, curdle and go sour. The sour taste is due to the formation of lactic acid, a reaction product of the fermentation of lactose (a sugar) by lactobacteria.
   a. **Lactic acid** has the semi structural formula $CH_3CHOHCOOH$. **Explain** why its presence causes milk to taste sour.
   b. Does the formation of lactic acid in milk cause its **pH** to rise or fall? Write an **Arrhenius equation** to justify your answer.

2. The Formicinae subfamily of ants all have a specialised venom gland for the production of methanoic acid (also called formic acid). If threatened they can repel their attackers by spraying them with this acid. Another organic acid found in biological systems is propanoic acid. The respective acid dissociation constants for these acids are **methanoic acid**, $K_a = 1.78 \times 10^{-4}$ and **propanoic acid**, $K_a = 1.38 \times 10^{-5}$. The following questions refer to these two compounds.
   a. Write **Bronsted-Lowry** equations that account for the acidic properties of these acids in water.
   b. Would you describe propanoic acid as strong or weak? **Justify** your answer with reference to its **K_a** value.
   c. Which is the **stronger** of the two acids? **Justify** your answer.

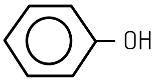
3. Write a balanced **molecular equation** for any reaction that may occur in each of the following experiments. Note a probable **observation** for each situation.
   a. A methanoic acid solution is added to a sodium hydroxide solution.
   b. A strip of magnesium ribbon is added to an ethanoic acid solution.
   c. Granules of calcium carbonate are added to a propanoic acid solution.
   d. Sodium hydrogencarbonate solution is added dropwise to an ethanoic acid solution.

Figure 9 A **refluxing** apparatus used for esterification.



4. A student adds a few drops of **concentrated $NaHCO_3(aq)$** to each of the following substances in the hope of distinguishing the two compounds. Will the tests be successful? **Explain**.
   a. CH_3CH_2COOH and $CH_3CH_2CH_2OH$
   b. CH_3CH_2CHO and $CH_3CH_2CH_3$
   c. $HCOOH$ and CH_3COOCH_3

5. **Esters** can be formed in the laboratory by refluxing together an alcohol and a carboxylic acid. (See Fig 9.)
   a. What is the **purpose** of adding **sulfuric** acid to the mixture?
   b. An ester is the organic product of this reaction. What is the **other product**?
   c. What is the advantage of using a **reflux** apparatus and **electric heating mantle** (Fig 9) for this type of reaction?

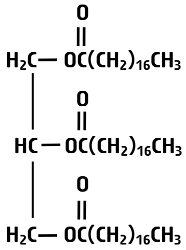
6. Draw **full structural formula** only, for the **ester** formed when the following pairs of reagents are combined and refluxed together in the presence of an acid catalyst.
   a. CH_3OH *and* CH_3COOH
   b. $CH_3(CH_2)_5COOH$ *and* CH_3CH_2OH
   c. $CH_3CH_2CH_2CH_2OH$ *and* CH_3CH_2COOH
   d. 

   and CH_3CH_2COOH

7. Write an **esterification equation** to show the reaction that happens in each of the following situations. **Name** the **ester** produced.
   a. CH_3OH and CH_3COOH are refluxed together with a sulfuric acid catalyst.
   b. CH_3CH_2OH is refluxed together with CH_3CH_2COOH and some sulfuric acid.
   c. Propanol and ethanoic acid are refluxed together with a suitable catalyst.

8. Xinyi and Kirsten performed an experiment on a sample of the ester propyl ethanoate. They added 35 mL of the ester to a conical flask along with 10 g of sodium hydroxide. The mixture was heated for 10 minutes.
   a. Describe a specific **safety hazard** associated with heating an ester. What safety **precautions** should Xinyi and Kirsten take to minimise this danger?
   b. What **precautions** should they take when using **solid sodium hydroxide** pellets? Explain your reasoning.
   c. Draw **structural formula** for the **products** expected from their reaction.

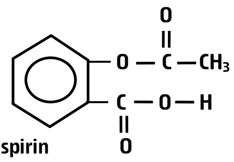
9. While pure water is normally a very poor solvent for non-polar substances like grease and oil, the addition of soap to water allows grease and non-polar materials to easily '**dissolve**' in water. A major ingredient of bar soap, as used in most bathrooms, is **sodium stearate**, $CH_3(CH_2)_{16}COONa$. It can be produced by the reaction of sodium hydroxide with the animal fat tristearin. (See structure at right.)
   a. Would you expect soap solutions to be **electrically conducting**? Explain with the aid of a **dissociation equation** using sodium stearate as an example.
   b. Draw the sodium stearate structure and identify its **hydrophobic** and **hydrophilic** parts and state the meaning of these two terms.
   c. Explain in terms of **intermolecular forces** and **ion-dipole forces**, why parts of the soap structure are hydrophobic while other parts are hydrophilic.
   d. Write a **balanced equation** for the conversion of tristearin to sodium stearate.
   e. **Explain** why the cleaning action of soaps is hampered by **hard water**. Use sodium stearate as an **example** to illustrate your answer.



tristearin

10. Synthetic **detergents** were first developed in the early part of the twentieth century. These compounds have many similarities with soap and yet have some important differences as well. Use your knowledge of soaps and detergents to answer the following questions.
    a. Detergents are referred to as synthetic whereas soaps are considered natural products. **Justify** this statement with reference to the raw materials used to make soap and detergent.
    b. Draw the structure for the dodecylbenzenesulfonate anion and identify its **hydrophobic** and **hydrophilic** parts.
    c. Soaps and detergents (eg dodecylbenzenesulfonate) have a very similar cleaning action. Describe their cleaning action and hence **justify** this claim with reference to the structure of soaps and detergents.
    d. **Explain** why the cleaning action of detergents is not affected by **hard water**.

11. Use your knowledge of **esterification reactions** to answer the following questions.
    a. Oranges owe their distinctive odour to the ester **octyl ethanoate**. What reagents could be used to synthesise this compound in the laboratory? **Describe** how the reaction could be performed.
    b. **Pentyl butanoate** and **pentyl ethanoate** are two of the esters that give bananas their distinct odour. Describe a method for synthesising these two esters.
    c. The structure of **aspirin** is shown at right. It can be synthesised using an esterification reaction. **Draw structures** for the two organic starting materials.



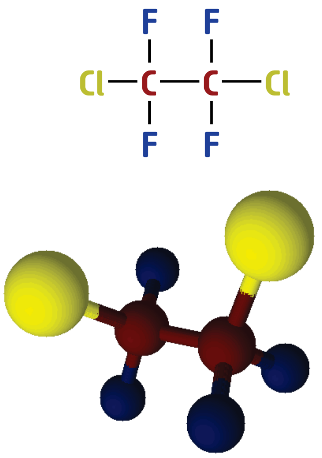
aspirin

CHAPTER 13 | EMPIRICAL FORMULA

13.1 Review: Empirical and molecular formulas

Some elements and compounds, such as organic compounds, have a molecular structure. These substances consist of numerous identical particles called molecules. Each molecule is a cluster of two or more atoms strongly bonded together by covalent bonds. A **molecular formula** shows the actual number of each type of atom in a single molecule of the substance. (See Fig 1.)

Figure 1 Freon 114 has the **molecular formula $C_2F_4Cl_2$**. This gives the **number** of each type of atom in a molecule of Freon.



CF_2Cl is the **empirical formula** for Freon. It shows the **atomic ratio** of C:F:Cl in Freon is 1:2:1.

An **empirical formula** by contrast only shows the types of atoms present in a substance and gives their simplest whole number atomic ratio. The empirical formula can be found from a molecular formula by dividing the subscripts of each element in the molecular formula by the lowest common denominator (LCD). (See Example 1)

Example 1 Determine the **empirical formula** for each of the molecular compounds.

Compound	Molecular formula	Divide by LCD	Empirical formula
dinitrogen tetroxide	N_2O_4	÷ by 2	NO_2
oct-3-enedioic acid	$C_8H_{12}O_4$	÷ by 4	C_2H_3O
glucose	$C_6H_{12}O_6$	÷ by 6	CH_2O
ammonia	NH_3	÷ by 1	NH_3
ethanoic acid	CH_3COOH	÷ by 2	CH_2O

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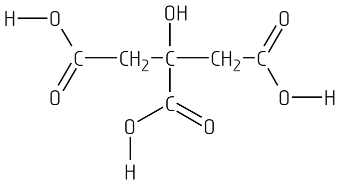
Attempt Set 19 # 1.

13.2 Calculating empirical formula from empirical data

The chemical composition of a compound, ie its composition by mass or its % composition by mass can be found by various experimental techniques. **Empirical data** like this can then be used to find the compound's **empirical formula**. Example 2 shows how empirical data on a compound's elemental composition by mass is used to find its empirical formula.

Figure 2 Citric acid is a weak organic acid occurring in many biological systems. Particularly high concentrations occur in citrus fruits like lemons and limes where it can constitute as much as 8 g/100 g of the dried fruit.

Each molecule of citric acid contains a single hydroxyl group (-OH) and three carboxyl groups (-COOH).



Example 2 Analysis of a 3.625 g sample of **citric acid** (Fig 2) showed it contained 1.360 g of carbon, 0.1522 g of hydrogen, with the remainder being oxygen. What is the **empirical formula** of citric acid?

$$m(O) = m(\text{citric acid}) - [m(C) + m(H)] = 3.625 - [1.360 + 0.1522] = 2.113\text{ g}$$

As the compound contains C, H and O only, then the sum of these masses must be 3.625 g.

C	H	O	
C	**H**	**O**	List each **element** in the sample.
1.360 g	0.1522 g	2.113g	List the **mass** of each element in the sample.
$\frac{1.360}{12.01}$	$\frac{1.522}{1.008}$	$\frac{2.113}{16.00}$	Find the **moles** of each element by dividing the mass of each element by its molar mass.
0.1132	0.1510	0.1321	
$\frac{0.1132}{0.1132}$	$\frac{0.1510}{0.1132}$	$\frac{0.1321}{0.1132}$	To find the **simplest mole ratio**, divide each molar amount by the smallest value, ie 0.1132.
1.000	1.333	1.166	Multiply all values by 6. (See below.)
6.000	8.000	6.997	**Round** to a whole number ratio. (See below.)

Thus the empirical formula is $\mathbf{C_6H_8O_7}$.

The simplest whole number mole ratio of C:H:O is 6:8:7. Thus the empirical formula is $C_6H_8O_7$.

Sometimes dividing by the smallest molar value does not produce a whole number ratio. If this happens, try multiplying the results by 2, 3, 4, 5 and so on. This involves a trial and error approach that should produce a whole number ratio. (See Example 2 above.)

When **rounding** the final ratio from your empirical formula calculation the numbers should be very close to whole numbers; how close depends upon the accuracy and precision of the data being processed. In this book you can round final empirical formula ratios that are within ±0.05 of being a whole number. For this reason it is important to carry at least 4 significant figures throughout your empirical formula calculation.

Attempt Set 19 # 2 and 3.

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Example 3 (below) shows how the elemental % composition by mass of a compound can be used to find its empirical formula.

Example 3 The analysis of a compound showed it contained 14.49% carbon, 47.05% potassium with the remainder being oxygen. Determine the compound's **empirical formula**.

$\%O = 100.00 - [\%C + \%K]$
$= 100.00 - [14.49 + 47.05]$
$= 38.46\%$

The compound contains C, K and O only. The sum of their % compositions must be 100%.

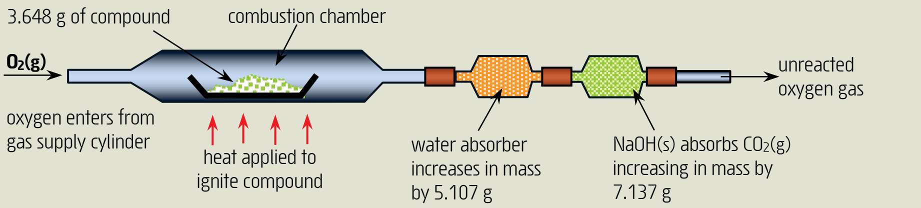
K	C	O	
K	C	O	List each **element** in the compound.
47.05%	14.49%	38.46%	List the **percentage** of each element in the compound.
47.05 g	14.49g	38.46 g	List the **mass** of each element per 100 g sample.
$\frac{47.05}{39.10}$ 1.203	$\frac{14.49}{12.01}$ 1.206	$\frac{38.46}{16.00}$ 2.404	To find the **moles** of each element in the 100 g sample divide the mass of each element by its molar mass.
$\frac{1.203}{1.203}$ 1.000	$\frac{1.206}{1.203}$ 1.003	$\frac{2.404}{1.203}$ 1.998	To find the **simplest mole ratio** and thus the empirical formula, divide all values by the smallest value, ie 1.203. Thus the simplest whole number mole ratio of K:C:O is 1:1:2.

Thus the empirical formula is KCO

Attempt Set 19 # 4 and 5.

Combustion analysis is an experimental technique used to find the empirical formula of a combustible compound. A carefully weighed sample of the compound is burnt in air and the combustion products, H_2O and CO_2 are captured and weighed. This data is used to determine the mass of carbon and hydrogen in the original sample. In this way the empirical formula of the compound can be determined. (See Example 4.)

Example 4 A 3.648 g sample of an unknown organic compound was completely burnt in an apparatus like the one shown here. The analysis of the combustion products showed 7.137 g of carbon dioxide and 5.107 g of water were produced. Find the compound's **empirical formula** if it contains the elements **carbon**, **hydrogen** and **nitrogen** only.



$n(CO_2) = \frac{m}{M} = \frac{7.137}{44.01} = 0.1622$ mol
$n(C) = n(CO_2) = 0.1622$ mol
$m(C) = n \times M = 0.1622 \times 12.01 = 1.948$ g

All of the **carbon** originally present within the 3.648 g sample of compound now resides within the 7.137 g of CO_2. Thus find the $n(CO_2)$ produced and use this to determine the moles and mass of carbon in the original 3.648 g sample.

$n(H_2O) = \frac{m}{M} = \frac{5.107}{18.016} = 0.2835$ mol
$n(H) = 2 \times n(H_2O) = 2 \times 0.2835 = 0.5669$ mol
$m(H) = n \times M = 0.5669 \times 1.008 = 0.5715$ g

All of the **hydrogen** originally present within the 3.648 g sample of compound now resides within the 5.107 g of H_2O. Thus find the $n(H_2O)$ produced and use this to determine the moles and mass of hydrogen in the original 3.648 g sample.

$m(N) = 3.648 - [m(C) + m(H)]$
$= 3.648 - (1.948 + 0.5715) = 1.129$ g

The sample contains C, H and N only and has a total mass of 3.648 g. Thus determine the mass of **nitrogen** in the sample.

C	**H**	**N**	List each **element** in the compound.
1.948g	0.5715 g	1.129 g	List the **mass** of each element in the 3.648 g sample.
$\frac{1.948}{12.01}$ 0.1622	$\frac{0.5715}{1.008}$ 0.5669	$\frac{1.129}{14.01}$ 0.08058	Find the **moles** of each element, ie divide the mass of each element by its molar mass.
$\frac{0.1622}{0.08058}$ 2.013	$\frac{0.5669}{0.08058}$ 7.036	$\frac{0.08058}{0.08058}$ 1.000	To find the **simplest mole ratio** and thus the empirical formula, divide all values by the smallest molar value, ie 0.08058. Thus the simplest whole number mole ratio of C:H:N is 2:7:1.

The empirical formula is $\mathbf{C_2H_7N}$.

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Attempt Set 19 # 6, 7 and 8.

13.3 Molecular formula determination

The **molecular formula** of a compound shows the actual number of each type of atom in one molecule of the compound. It is always a **whole number multiple** of its empirical formula. (See Fig 1 and Example 1.) Molecular formula can be found by comparing the empirical formula mass, **M_{ef}** to the molecular formula mass, **M**, ie by finding the ratio of **M/M_{ef}** (See Example 5.)

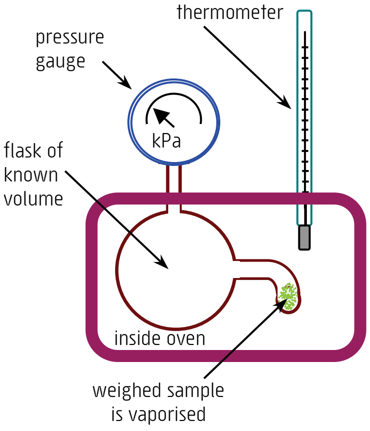
Example 5 The chlorofluorohydrocarbon known as **Freon 114** (Fig 1) has a molecular formula mass, M of 170.92 g mol^{-1} and an empirical formula of CF_2Cl. Determine its **molecular formula**.

M_{ef}(CF_2Cl) = 12.01 + 2 x 19.00 +35.45 = 85.46 g mol^{-1}	Find the empirical formula mass, **M_{ef}** from the given empirical formula CF_2Cl.
ratio(M/M_{ef}) = $\frac{M}{M_{(ef)}}$ = $\frac{170.92}{85.46}$ = 2.00 The molecular formula is **$C_2F_4Cl_2$**.	As the molecular formula mass, **M** is twice the empirical formula mass, **M_{ef}** then the molecular formula must be twice the empirical formula. Thus doubling the empirical formula subscripts gives the molecular formula $C_2F_4Cl_2$.

Attempt Set 19 # 9.

One experimental method for finding the **molecular formula mass**, **M** (also called the **molar mass**) of an unknown compound involves vaporising a weighed sample in a sealed flask of known volume. The temperature and pressure of the resulting vapour are measured and used along with the vapour volume and mass to experimentally find the molar mass. (See Fig 3 and Example 6.)

Figure 3 The **pressure**, **volume** and **temperature** of a **vaporised** sample can be found using this apparatus. The sealed flask is heated inside an oven until the compound has fully vaporised.



Example 6 A 3.429 g sample of an organic compound is vaporised and found to occupy a volume of 1.130 L at 101.3 kPa and 398 K. Determine the compound's **molecular formula** if its empirical formula is CH_2Cl.

P V = n R T ie **n** = $\frac{PV}{RT}$ = $\frac{101.3 \times 1.130}{8.3145 \times 398}$ = 0.03460 mol	Find the **moles** of gas using the ideal gas law.
n = $\frac{m}{M}$ ie **M** = $\frac{m}{n}$ = $\frac{3.429}{0.03460}$ = 99.13 g mol^{-1}	Determine the **molecular formula mass**.
M_{ef}(CH_2Cl) = 12.01 + 1.008 x 2 + 35.45 = 49.476 g mol^{-1}	Determine the empirical formula mass, **M_{ef}** from the given empirical formula CH_2Cl.
ratio(M/M_{ef}) = $\frac{M}{M_{(ef)}}$ = $\frac{99.13}{49.476}$ = 2.00 ∴the molecular formula is **$C_2H_4Cl_2$**	Compare the molecular formula mass, **M** and the empirical formula mass, **M_{ef}**. This result shows the molecular formula is twice the empirical formula.

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Complete Set 19.

Set 19 Empirical formula

1. Give the **empirical formula** of the following compounds.
   a. hydrogen peroxide, H_2O_2
   b. arginine, $C_6H_{14}N_4O_2$
   c. lactic acid, $CH_3CHOHCOOH$
   d. propane, C_3H_8

2. A 10.000 g sample of a gaseous hydrocarbon is decomposed to form 7.490 g residue of carbon. Assuming hydrogen is the only other element in this compound determine its **empirical formula**.

3. The characteristic odour of pineapple is largely due to an ester containing the elements **carbon**, **hydrogen** and **oxygen**. A 3.4330 g sample of the compound was analysed and found to contain 2.1300 g of carbon and 0.3575 g of hydrogen. Determine the **empirical formula** for the compound.

Not getting a whole number ratio?
Sometimes dividing by the smallest molar value does not produce a whole number ratio. If this happens, try multiplying the results by 2, 3, 4 or 5 and so on until a suitable whole number ratio is produced.

When rounding the final ratio from your empirical formula calculation you would expect the numbers to be very close to whole numbers, typically within ± 0.05 of being a whole number.

4. Two different **oxides** of **iron** can be identified; one contains 77.7% Fe by mass and the other 72.4% Fe. Determine the **empirical formula** of these two **iron oxides**. (See border note.)

5. A compound contains 40.27% potassium, 26.78% chromium and the remainder being oxygen. What is the compound's **empirical formula**?

6. The complete combustion of a 3.550 g sample of a hydrocarbon produced 11.14 g of carbon dioxide. Determine the **empirical formula** of the hydrocarbon. Remember, hydrocarbons contain the elements C and H only.

7. The **hydrocarbon** used in a common gas lighter was analysed by burning a 5.249 g sample of the gas and collecting the resulting water vapour in a cold trap. This produced 8.198 g of water. What is the **empirical formula** of this hydrocarbon?

8. A 3.996 g sample of an **organic compound** containing the elements **carbon**, **hydrogen** and **oxygen** was completely burnt in oxygen. This produced 7.974 g of carbon dioxide and 3.264 g of water. Determine its **empirical formula**.

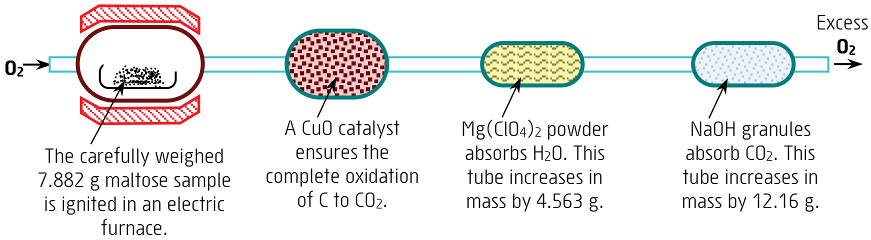
9. Use the given empirical formula and molar mass (molecular formula mass, M) to determine the **molecular formulas** of the listed compounds.

Compound	Empirical formula	Molar mass, M	Molecular formula
a. ascorbic acid	$C_3H_4O_3$ (vitamin C)	176 g mol^{-1}	?
b. cyclohexane	CH_2	84.16 g mol^{-1}	?
c. benzene	CH	78.1 g mol^{-1}	?

10. A 3.121 g sample of the gaseous compound in Question 7 (empirical formula C_2H_5) is released into a sealed container at STP. Under these conditions the sample occupied a volume of 1.217 L. Determine the compound's **molecular formula**.

11. The compound analysed in Q3 (EF = C_3H_6O) is a liquid at STP. In order to determine its molar volume a 6.182 g sample of it was vaporised at 135.0 °C and filled a 2.25 L container at a pressure of 80.2 kPa.
    a. What is its **molecular formula**?
    b. The compound is known to be an ester of butanoic acid. What is its **IUPAC** name?

12. **Maltose** is a carbohydrate with a similar chemical composition to sucrose. It contains the elements **carbon**, **hydrogen** and **oxygen**. A 7.882 g sample of maltose is analysed by combustion analysis using an apparatus similar to that shown here.



    a. Using the data presented here determine the **empirical formula** for maltose.
    b. Another 3.115 g sample of the maltose was vaporised and found to occupy a volume of 324.2 mL at 165.0 °C and 101.9 kPa. What is the **molecular formula** for maltose?

13. **α-amino acids** are the building blocks from which all proteins are made. **Alanine** is one such α-amino acid. It contains the elements **carbon**, **hydrogen**, **oxygen** and **nitrogen**. To determine its empirical formula a 2.170 g sample was completely burnt in oxygen. The resulting carbon dioxide and water were collected and found to weigh 3.219 g and 1.537 g respectively. The nitrogen contained in the sample was released during combustion and collected as nitrogen gas. When isolated, the nitrogen gas had a volume of 300.3 mL at 102.1 kPa and 302.5 K.

    a. Determine the **empirical formula** for alanine.

    b. Further analysis showed alanine has a molar mass of **88.7 g mol^{-1}**. Determine its molecular formula and draw the **structure** for this α-amino acid.

14. Two chemistry students, Brendon and Sarah were researching one of the chemical components of the **rhubarb** plant. They were able to extract a **white crystalline solid** from the plant's stem tissue. Using various analytical techniques Sarah determined that the crystalline solid contained **two carboxylic acid groups** per molecule. To find its empirical formula Brendon dried a sample of the crystalline solid to ensure any water of crystallisation was driven off then weighed 10.79 g of the dry solid. When completely **burnt** in excess oxygen it formed 10.60 g of carbon dioxide and 2.136 g of water.

    a. Given the compound contains only **carbon**, **hydrogen** and **oxygen**, determine its **empirical formula**.

    b. A further 1.851 g sample of the compound was dissolved in water and made up to 250.0 mL in a volumetric flask. 20.00 mL samples of this solution were titrated with 0.2021 mol L^{-1} NaOH(aq). On average 16.25 mL of NaOH(aq) was needed for equivalence. What is the **molecular formula**?

    c. Draw a possible **structure** for the compound.

15. A 4.406 g sample of a **hydrocarbon** is burnt in excess oxygen forming carbon dioxide and water. The resulting gases were bubbled through a solution of NaOH(aq) absorbing the $CO_2(g)$ as $Na_2CO_3(aq)$. Adding $Ca(NO_3)_2(aq)$ to this results in a precipitate of $CaCO_3(s)$. When washed and dried the $CaCO_3(s)$ has a mass of 31.34 g.

    a. Using this information determine the **empirical formula** of the hydrocarbon.

    b. Another 4.485 g sample of the compound was vaporised and found to occupy a volume of 1.754 L at 76.0 °C and 129.5 kPa. Determine its **molecular formula**.

    c. The unknown organic compound is found to quickly discolour a bromine water solution. Suggest four possible **IUPAC** names for the hydrocarbon.

Hint: Some empirical formula calculations involve the analysis of data from two **different mass samples**. In situations like this it is advisable to use the given data to find the percentage composition of each individual element in the different mass samples of the compound.
The percentage composition can then be used in the normal way to find the compound's empirical formula.

16. **Aspartame** is a compound used as an artificial **sweetener** in foods and beverages. It contains the elements **carbon**, **hydrogen**, **oxygen** and **nitrogen**. To determine its empirical formula a 7.335 g sample was completely burnt in oxygen. The resulting carbon dioxide and water were collected and found to weigh 15.36 g and 4.041 g respectively. A second 4.719 g aspartame sample was treated to convert the nitrogen it contained into ammonia (NH_3). The resulting ammonia was absorbed into 100.0 mL of 0.3559 mol L^{-1} HCl(aq). The excess HCl(aq) was then titrated to equivalence using 28.18 mL of 0.1249 mol L^{-1} NaOH(aq). Determine the **empirical formula** for aspartame.

CHAPTER 14 | MACROMOLECULES: POLYMERS AND PROTEINS

14.1 Macromolecules

Substances like synthetic **polymers** and biological compounds such as **polypeptides** and **proteins** consist of extremely large molecules called macromolecules. For example, ultra high molecular weight polyethene, a tough polymer used in artificial joints, has a molar mass in the range 3 to 6 million g mol^{-1}, while haemoglobin, a protein found in red blood cells, has a molar mass of 64458 g mol^{-1}. In this chapter we will examine the synthesis, structure and properties of such compounds.

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Table 1 Some commonly used **polymers** and their **recycling** identification codes.

Identification code	Polymer name and uses
1 PET	**Polyethylene terephthalate**: soft drink bottles, food jars, films, textile fibres for clothing and carpet (terylene®).
2 HDPE	**High density polyethene**: grocery bags, freezer bags, bottles for food and non-food items, pipes and wire coating.
3 PVC	**Polyvinyl chloride**: pipe, window frames, garden hose, floor coverings, electrical wire insulation, traffic cones.
4 LDPE	**Low density polyethene**: retail shopping bags, cling wrap, shrink wrap, squeeze bottes, electrical insulation.

The plastics identification code is a '1 to 7' numbering system that identifies the polymer composition of plastic containers. The industry coding system is an important element in the successful recycling of used plastics in Australia.

14.2 Polymers

Polymers are a versatile class of materials sometimes referred to as plastics or synthetics. They can be extruded or moulded into various shapes and are relatively inert during normal use. Plastic chairs, car parts, soft drink bottles, reticulation pipe and grocery bags for example, are made this way from polymers like polyvinyl chloride, polyethene and polyethylene terephthalate (PET). (See Table 1.)

Some polymers are suitable for producing strong threads called **fibres**. These can be woven to form a **fabric**. Most clothing and footwear use fabric made from synthetic polymers like nylon, polyester, polypropene and Lycra®. Other polymers such as Teflon® and Kevlar® are used to produce specialised fabric for items like breathable waterproof clothing and bulletproof vests.

Polymers like PET, HDPE and PVC are called **thermoplastics**. These polymers soften and melt when heated. Thermoplastics are easily **recycled** as they can be remelted and reshaped many times. Polymers that do not soften when heated are called **thermosetting** polymers. These polymers are shaped during manufacture and cannot be melted and reshaped. If heated excessively they simply char or in some cases they decompose to form their original monomers.

Polymers also occur widely in nature. They include substances like **polysaccharides**, **proteins**, **DNA** and **RNA**. These substances are vital to most life processes. Prior to the discovery of synthetic polymers, natural fibres like wool and silk (a protein) and cotton (a polysaccharide) were essential to the manufacture of fabrics for clothing.

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14.3 Polymerisation reactions

Polymers consist of long chain molecules made from smaller molecules known as **monomers**. An individual monomer molecule consists of only a few atoms; however, once joined together in the polymerisation process they produce molecules that typically have molar masses of several million grams per mole.

Polymer molecules may consist of **straight chains** of atoms or they may have **side chains** and sometimes chains are joined to other chains. This is known as **cross linking**. Elastomers like rubber contain some degree of cross linking between their polymer molecules. This gives the polymer elastic properties. However, the more cross linking there is the stiffer and less flexible is the resulting rubber. Manufacturing processes try to control all of these aspects of a polymer as they affect the polymer by altering important properties such as stiffness, hardness, density and appearance. Two distinct processes are used for producing polymers; **addition** polymerisation and **condensation** polymerisation.

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Figure 1 Polyethene and **polyvinyl chloride** (PVC) plastic films are durable and lightweight materials often used as an inexpensive option in greenhouse roofing. PVC black plastic sheeting is also used as a soil cover for minimising weeds, pests and for retention of water and heat in soil.

Attempt Set 20 # 1.

14.4 Addition polymerisation

Polyethene (also known as polyethylene) is a thermoplastic produced by the **addition polymerisation** of the **monomer** ethene. Addition polymerisation occurs if the monomer has a carbon to carbon **double bond** that can be eliminated during polymerisation. The loss of the double bond allows monomer molecules to join end on end. The following equation shows the addition polymerisation of ethene. A subscript **n** (an integer in the order of several thousand) shows the monomer is repeated **n** times in the polymer molecule polyethene.

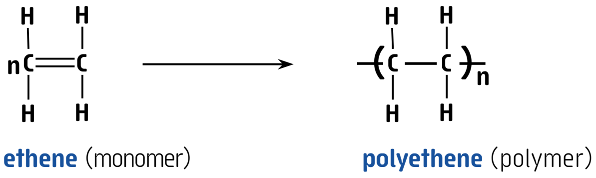


Figure 9 The equation (at left) shows the addition polymerisation of ethene. The subscript **n** (an integer in the order of several thousand) shows the monomer is repeated **n times** in the polymer molecule polyethene.

A **structural** formula (below left) and **space-filling** model (below right) show a **small section** of **polyethene** consisting of **four** monomer units (shown in alternating blue and red). In practice, a polyethene molecule may be formed from **several thousand** ethene monomer units but there is no exact number. The dashes and zigzag lines at the terminal ends of the models are a reminder that the structure extends beyond the sections shown here.

polyethene* section consisting of 4 monomer units

***Ethylene** is a commonly used name for ethene. The polymer is sometimes called polyeth**yl**ene.

Attempt Set 20 # 2.

Polyethene is currently the most widely used polymer with over 55 million tonnes produced worldwide in 2011. Depending upon the manufacturing conditions used, polyethene can be produced as high density polyethene (**HDPE**) or low density polyethene (**LDPE**).

The first commercial process for the polymerisation of ethene gas which is still used today, requires a very high pressure of 1000 to 3000 times atmospheric pressure, a temperature of around 200 °C and a peroxide catalyst to promote the reaction. The major reaction involves the progressive joining of ethene molecules to form a straight linear configuration. However, due to the nature of this reaction, a **side reaction** occasionally occurs where a small branch (usually four carbon atoms long) is created. This form of polyethene, with numerous **small side chains** situated along the main chain, is called **LDPE** (low density polyethene). The side chains in LDPE prevent its molecules from packing efficiently thus reducing the strength of its intermolecular dispersion forces and creating an **amorphous**, ie non-crystalline or irregular arrangement of its molecules. Consequently LDPE has a relatively low melting point of around 105 °C-115 °C, is soft, flexible and fairly weak. Its low melting point means it is not suitable for extended use at temperatures above 95 °C, such as with boiling water. (Remember, a polymer is not a pure substance. Its individual molecules vary in size, hence polymers do not have the well defined melting point typical of a pure substance.)

LDPE is suitable for making thin flexible films that can be used for food wrapping, garbage bags, tank and pond liners and as moisture barriers in construction. It is also suitable for moulding into soft flexible articles like squeeze bottles, toys, utensils, hoses and electrical wire and cable insulation.

In 1956 a new technique for the polymerisation of ethene was devised by **Karl Ziegler** from Germany and **Giulio Natta** from Italy. They were awarded the 1963 Nobel Prize in chemistry for their alternative technique. They had devised a new catalyst, now called a Zeigler-Natta catalyst, that enabled the process to be carried out at much lower pressures of only 1-4 times atmospheric pressure and temperatures of only 60 °C. Most importantly this polymerisation process, which occurs on the catalyst surface, results in mainly **long straight polymer chains** with very few side chains. This form of polyethene is called **HDPE** (high density polyethene). This more linear molecular shape allows a more efficient regular packing of HDPE molecules to produce a more crystalline polymer with stronger interaction by dispersion forces. (See Fig 2.) As a result, HDPE is quite a strong polymer (≈3-10 times stronger than LDPE), stiffer than LDPE (increased crystallinity leads to greater stiffness), slightly higher in density (0.94-0.97 g mL^{-1} for HDPE and 0.92–0.93 g mL^{-1} for LDPE) and has a higher melting point of around 120 °C-135 °C.

HDPE has similar applications to those of LDPE, keeping in mind it is stronger, more rigid and has a significantly higher working temperature. It can be moulded into items like food containers, chemical resistant containers like fuel tanks, toys, picnic ware, household and kitchenware, electrical cable insulation, pipes, carry bags and food wrapping material.

Another form of polyethene called 'Ultra High Molecular Weight Polyethene', **UHMWPE** (also known as high performance polyethene, HPPE) has molecules averaging around ten times the length of those in HDPE. When these molecules align, the collective strength of dispersion forces between them becomes very significant due to their very large molecular size. UHMWPE fibres are so tough they are used to make fabric for bulletproof vest panels. UHMWPE is also used as the bearing material in hip and knee replacement joints.

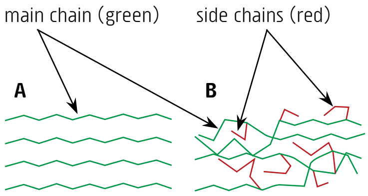


Figure 2

(A) 2D representation of the regular, ie **crystalline** arrangement of unbranched polyethene molecules in **HDPE**.

(B) The random entangled arrangement of branched polyethene molecules in **LDPE**.

(C) (below) A section of **HDPE** showing some molecules arranged in crystalline regions (regular alignment) and some molecules arranged in **amorphous** regions (tangled and irregular arrangement). Typically, 80-95% of HDPE consists of crystalline regions compared with only 40-55% in LDPE.

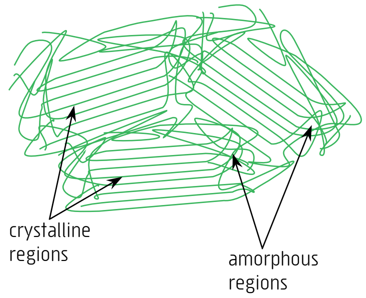
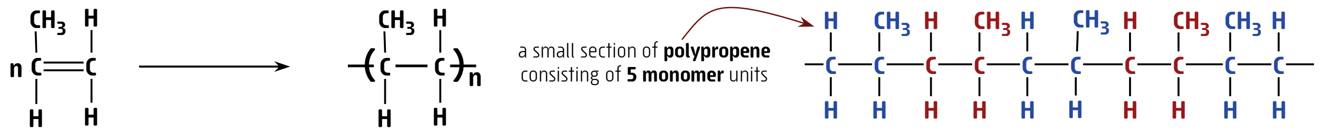


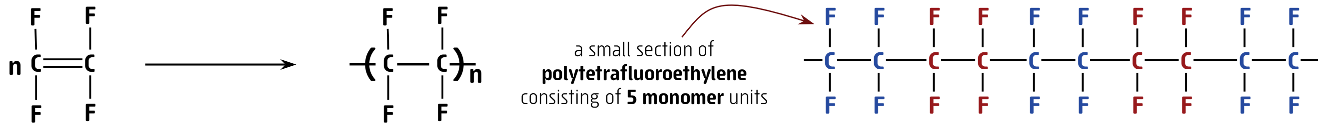
Figure 3 A variety of metals, ceramics and plastics are used in hip and knee implant devices. Of these materials metal-on-plastic (**polyethene**) is the longest tried combination. The convex femoral stem is made of metal (usually a cobalt chrome alloy) and the concave cup liner is made of plastic.

The current plastic of choice used in hip replacement implants is 'Ultra High Molecular Weight Polyethene', **UHMWPE**, a very stable and reliable polymer with a greatly reduced risk for wear.

Using different monomers enables a variety of different addition polymers to be produced. (See Table 2.) The equations below show the formation of two of these, **polypropene** and **polytetrafluoroethylene** (**PTFE** or commonly called **Teflon**®



propene (monomer) **polypropene** (polymer) **polypropene section consisting of 5 monomer units**



tetrafluoroethene (monomer) **polytetrafluoroethylene** (polymer) **PTFE section consisting of 5 monomer units**

The extensive presence of **fluorine atoms** in **PTFE** (Teflon®

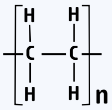
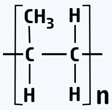
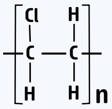
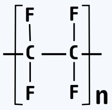
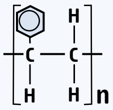
the C-H covalent bonds in PE, contributes to PTFEs greater resistance to chemical attack and its chemical stability, even at temperatures of up to 260 °C. The strongly bonded fluorine atoms resist bonding to (ie sticking to) or reacting with other chemical substances such as acids, water and oil or food products. This gives PTFE a non-stick, low friction surface.

PTFE has a variety of uses including non-stick coating (eg Teflon®

TM),

low friction bearings and gears and in reactor and plant equipment linings where highly corrosive substances are involved and resistance to chemical attack is essential.

Table 2 Some addition polymers.

Monomer	Polymer structure	Common name with indicative properties and uses
$CH_2{=}CH_2$ **ethene** (ethylene)		**polyethene or polyethylene** (LDPE and HDPE) LDPE has a low melting point (105 °C-115 °C), is soft, very flexible and insulating. It is used for packaging film, tubing, bottles, electrical cable insulation and toys. HDPE has a higher melting point (120 °C-135 °C), is tougher and more rigid. It is used for chopping boards, water pipes, toys, buckets and crates.
$CH_3CH{=}CH_2$ **propene** (propylene)		**polypropene or polypropylene** (PP) PP is a tough low density polymer (≈0.905 g mL^{-1}) suitable for making into thin films, packaging material, rope and carpet. It is moulded to form toys, chairs and furniture and car parts like bumpers or dashboards.
$CH_2{=}CHCl$ **chloroethene** (vinyl chloride)		**polyvinyl chloride or poly(chloroethene)** (PVC) PVC is normally a hard, stiff and brittle polymer suitable for moulding or extruding into construction products like window frames, pipes and gutters. Adding plasticisers to PVC increases its flexibility making it suitable for use as electrical cable insulation, floor tiles and as a soft fabric coating.
$CF_2{=}CF_2$ **tetrafluoroethene**		**polytetrafluoroethylene** (PTFE or Teflon®) PTFE is chemically very stable, non-stick, low friction, water and oil repellent, has a high melting point (for a polymer) and a high electrical resistance. Uses include inert non-stick coatings on cooking equipment, coatings on bearings and low friction surfaces, cable insulation and as a semi-permeable membrane in fuel cells.
$CH_2{=}CHC_6H_5$ **phenylethene** (styrene)		**polystyrene** (PS) PS is hard and brittle and can be moulded to form products like CD jewel boxes, petri dishes, toys and casings for electrical goods. PS can be produced as a low density 'expanded' solid (a foam) that is very soft and has excellent thermal insulation properties. Expanded PS is used for insulation, foam cups and as a packaging foam for fragile goods.

Attempt Set 20 # 3 and 4.

Figure 4 Plumbers apply a thin layer of PTFE tape to threaded connections. The **PTFE** film prevents the join from becoming chemically fused and helps form a watertight seal.

Polymer nomenclature

Individual polymers have a range of common names, abbreviated names, trade names as well as an IUPAC name.

Throughout this text common names have been adopted. The **IUPAC** name (bold) for some addition polymers is shown here along with a common name.

IUPAC name	common name(s)
polyethene	polyethylene, polythene
poly(propene)	polypropene, polypropylene
poly(chloroethene)	polyvinyl chloride
poly(1,1,2,2-tetrafluoroethylene)	polytetrafluoroethylene
poly(phenylethene)	polystyrene

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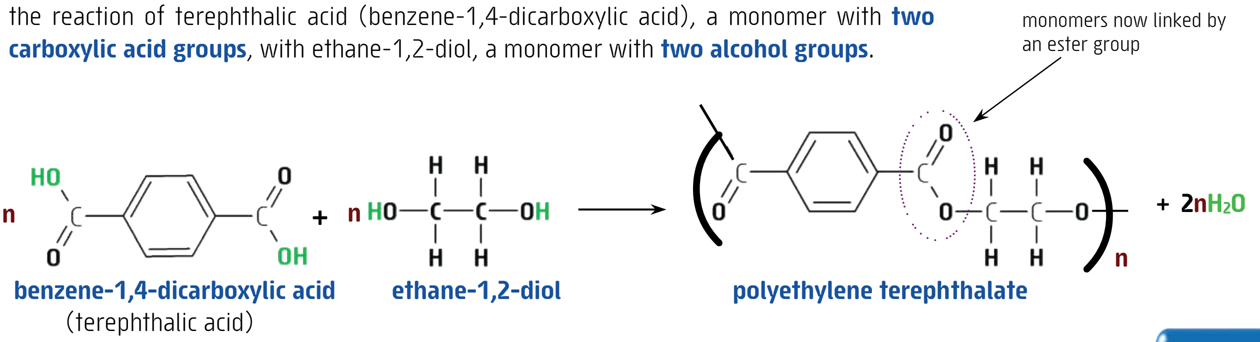
Attempt Set 20 # 5 and 6.

14.5 Condensation polymerisation

Condensation polymerisation involves the joining of individual monomer units by the loss of small molecules like H_2O or CO_2. Polyesters like **polyethylene terephthalate** (**PET**) also known as Dacron® or Terylene® are made this way. One method for making PET involves the reaction of terephthalic acid (benzene-1,4-dicarboxylic acid), a monomer with **two carboxylic acid groups**, with ethane-1,2-diol, a monomer with **two alcohol groups**.



Attempt Set 20 # 7.

The green highlighted atoms (**H** and **OH**) combine to form water thus leaving the remaining parts of the monomer molecules to join end on end, via **ester groups** (above circled).

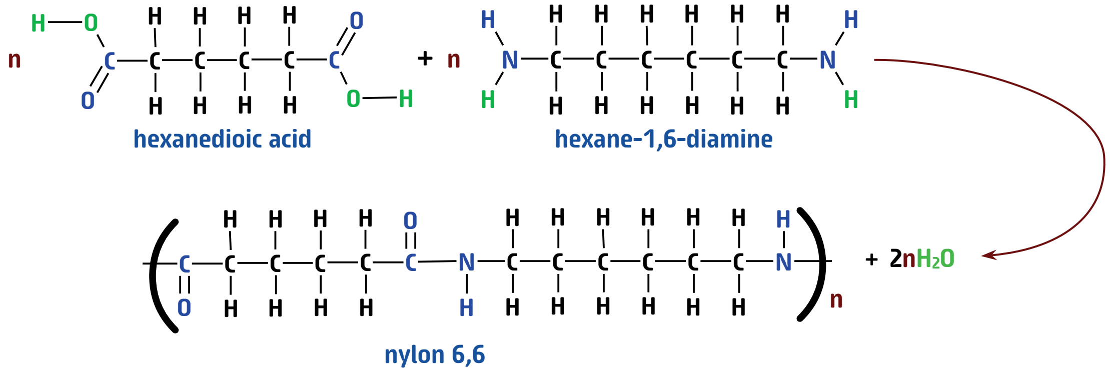
Polyester molecules like PET have a permanent net dipole around each of the ester groups. This means their molecules can attract and align by dipole-dipole forces as well as by dispersion forces. As with all polymers the degree of crystallinity (ordered alignment of molecules) in the bulk product has a major impact on its toughness and strength. The greater the crystallinity the stronger the finished product. The exceptional toughness and strength of PET **fibres** (**Dacron**® , called **Mylar**®

final shape. Polyester fibres made this way are exceptionally strong and resistant to creasing and wrinkling. These are typically mixed with natural cotton fibres to produce fabric for clothing. Fibre production is the major use of PET, accounting for around 60% of production.

Various forms of blow moulding are also used to produce bottles from PET. (See Fig 5.) Bottles produced this way are relatively stiff, strong and dimensionally stable. Their good gas barrier properties and chemical resistance make them ideal for bottling soft drinks and other carbonated beverages. PET bottles are easily recycled as the polymer can be remelted and regenerated as a fibre for use in products like carpet and clothing.

Figure 5 A PET drink bottle being formed in a stretch blow moulding machine. Note the initial shape of the '**preform**' bottle at the top right.

The polymer **nylon** is also produced by condensation polymerisation. Polymers like nylon are known are **polyamides** because of the repeating **amide linkages** they contain. These are formed by the condensation polymerisation of a **diamine** with a **dicarboxylic** acid. Nylon 6,6 for example comes from the condensation polymerisation of hexanedioic acid and hexane-1,6-diamine.



Attempt Set 20 # 8, 9 and 10.

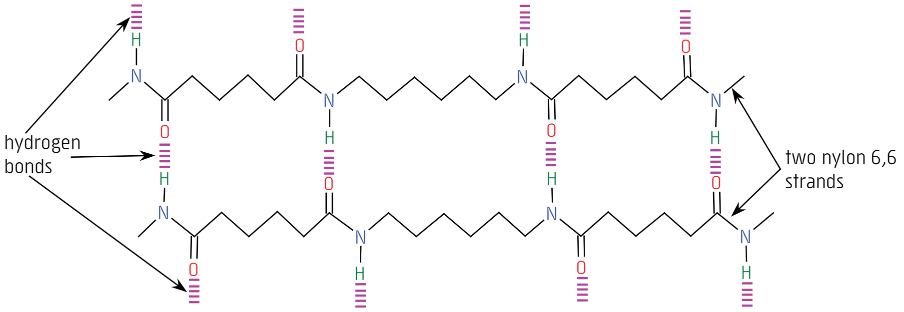
The 6,6 in the name nylon 6,6 refers to the number of carbon atoms in each of the monomers. Other nylons such as nylon 4,6, nylon 6,10 and nylon 6,12 are also commercially available. One special property of polyamides is their ability to form **hydrogen bonds** between the lone pair of electrons on the oxygen atom from a carbonyl group (-C=O) of one molecule and a hydrogen atom from the N-H group of another. This ability greatly increases the tensile strength and stiffness of nylon.

Figure 6 Dome tents like this are made of fabric consisting of strong polyester or polyamide fibres (eg nylon and Dacron®).

Polyamides like nylon 6,6 are ideal for making solid components like the gear wheels shown here.

As with polyesters, polyamides such as nylon can be converted into strong fibres suitable for weaving into fabric. This involves melting the raw nylon from the condensation process and **extruding** it through small holes in a plate called a spinneret to form nylon filaments. When cooled to room temperature these filaments are stretched (called cold-drawing) to about four times their original length. As with other polymers the stretching process greatly strengthens the fibre by helping individual molecules to untangle and align to form a more crystalline arrangement. As the polyamide molecules straighten and line up they form numerous hydrogen bonds with neighbouring polyamide molecules. The formation of these hydrogen bonds contributes to the strength and stiffness of polyamide fibres.

Figure 5 Extensive hydrogen bonds form as raw nylon fibres are stretched and the polyamide molecules align.



Nylon 6,6 is notable for being the world's first ever **synthetic fibre**. It was discovered by Wallace Carothers and his associates at the laboratories of DuPont in the US in 1934. Its first ever commercial use was as a replacement fibre for silk in stockings. The first pairs went on sale in Wilmington, Delaware, USA in October 1939. Today, nylon fibre is used in a diverse range of products including fabric for clothing and underwear, stockings, fishing line, rope, carpet, reinforcing fibres in tyres and fabric for parachute, seat belt and tent manufacture. Nylon fibres are used on their own or as a blend with other fibres where nylon adds strength and abrasion resistance to the finished product.

Nylon can also be extruded or moulded to produce a great variety of solid products including hoses, zip fasteners, skate wheels, gears, cams and bearings. Many of these applications rely on nylon's exceptional properties of high strength and ability to stretch under tension, wear and abrasion resistance, durability, low coefficient of friction and good chemical resistance. The presence of hydrogen bonding between nylon's polyamide chains plays an important role in enhancing these properties.

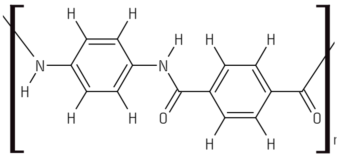


Figure 7 The repeating structure of **Kevlar**. Polyamides like this are known as **aramids**. These polymers produce exceptionally strong fibres, fabric and composite materials.

Kevlar (Fig 7) is a variation of nylon 6,6 where aromatic benzene rings replace the two carbon chain sections of the polyamide. Chemists at DuPont had hypothesised such a change would stiffen up the individual polymer chains and possibly produce a stronger product. Their interpretation of the effect of polymer structure on properties proved correct as Kevlar fibres (first introduced in 1960) proved to be incredibly strong, much stronger than nylon 6,6 fibres. Cables made of woven Kevlar are as strong as steel cables but only 20% the weight. Kevlar is now used for high performance ropes and cables, flame resistant clothing, sail cloth, bulletproof vests and sports gear.

Figure 8 The strength, durability and low density of many polymers is used to great advantage in sail boat construction. Here they have application in sail making and as a composite material (two or more materials bonded together) in hulls and superstructures.

Sails are most commonly constructed from a polyester fabric such as PET. This gives a durable, light weight and low cost sail. Higher performance sails can be made using Kevlar fabric; however, Kevlar has the disadvantage of being easily degraded on exposure to ultra violet light. Carbon fibre, though more expensive, is now the material of choice in high performance sailing. While carbon fibre is not a polymer the sail material typically consists of a carbon fibre woven fabric sandwiched between two films of polyester such as PET, ie Mylar® (or a PET co-polymer). Sails like this are black in colour due to their carbon content.

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Attempt Set 20 # 11 and 12.

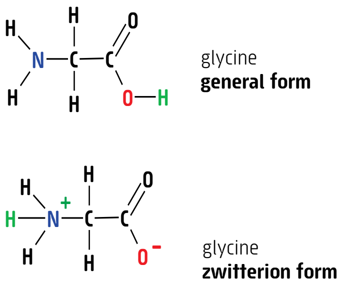
14.6 Proteins: Biological macromolecules

Proteins are very important molecular substances found in varying forms in **all living things**. In people, the protein **keratin** forms hair and fingernails while **haemoglobin** carries oxygen in the blood. **Actin** and **myosin** are the proteins that allow movement in the muscles. Other proteins in the human body act as **enzymes**, cellular **messengers**, **antibodies** and form vital cellular components.

There are 20 common **α-amino acids** (p125, Fig 9 and Appendix 6) that combine in various sequences to produce the myriad of protein materials used by all living things. People have the ability to manufacture a few of these amino acids but most are obtained from our **diet**. Consumed protein is 'depolymerised' by our digestive system to regenerate the original α-amino acids of which the proteins were made. In our cells the amino acid building blocks are reconstructed into the specific sequence for the proteins we require.

Proteins may contain from 50 to 2000 or more α-amino acid **residues** linked in a specific sequence. Messenger **RNA** produced from our own **DNA** is what specifies the particular sequence of amino acids needed for the manufacture of the unique proteins present in our bodies. Many diseases are believed to occur as a result of a single error in the sequencing of the α-amino acids in our proteins.

Figure 9 Glycine, one of the 20 commonly occurring α-amino acids found in biological systems.



A complete table of the naturally occurring α-amino acids can be found in Appendix 6.

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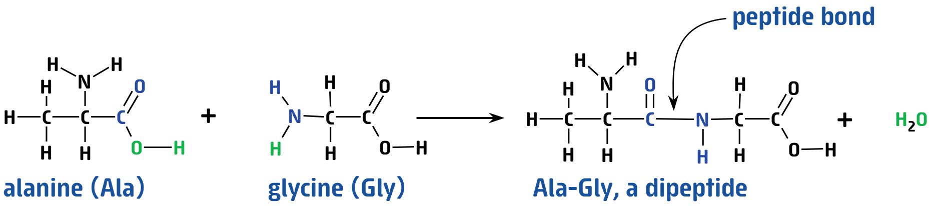
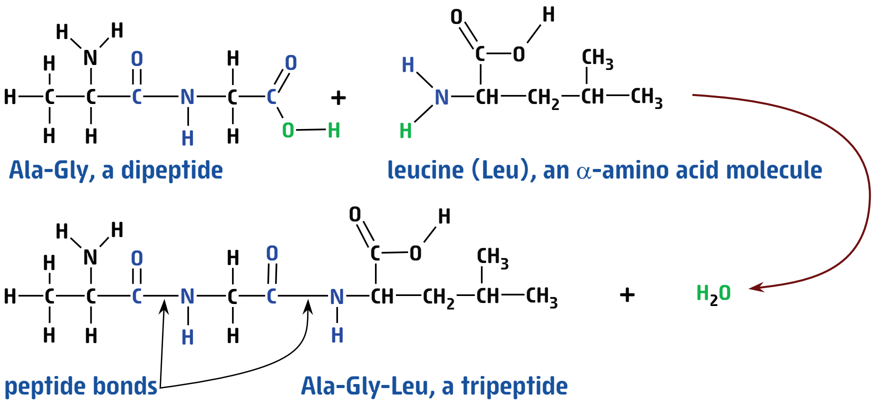
14.7 Formation of polypeptides and proteins

Proteins can be thought of as natural polymers formed from a combination of the naturally occurring **α-amino acid** molecules. As each α-amino acid molecule has a carboxylic acid group (-COOH) and an amine group (-NH_2) then any two of these molecules can join by the elimination of water (much like condensation polymerisation in nylon). The result, called a **dipeptide**, consists of two amino acid residues. The bonded amino acid molecules are called **residues** as in the polymerisation process each amino acid has lost an H, OH or the equivalent of H_2O from its formula. The equation below shows the formation of a dipeptide from the combination of the two α-amino acid molecules alanine and glycine (abbreviated Ala, Gly respectively). The atoms in blue highlight the location of the **peptide bond** (also called a **peptide linkage**), a characteristic feature of all polypeptides and proteins.

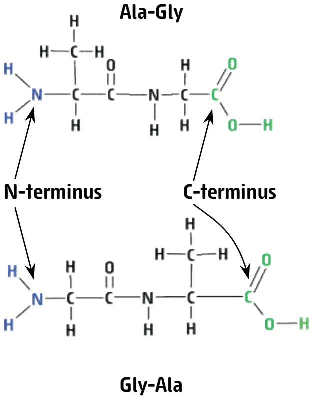


As the dipeptide molecule also has a carboxylic acid group (-COOH) and an amine group (-NH_2) then it can join to another α-amino acid molecule to form a **tripeptide**. The structure below represents the addition of leucine to form the tripeptide Ala-Gly-Leu.



In a similar way more and more α-amino acid molecules can add to the peptide chain producing what are known as **polypeptides**. When the number of α-amino acid molecules in a peptide chain is **large**, usually greater than 50, though there is no specific number, then it is known as a **protein**.

Figure 10 You will notice one end of a polypeptide has a remaining **-NH_2** group while the other end has a **-COOH** group. The end with the **-NH_2** group is called the **N-terminus** while the **-COOH** end is the **C-terminus**. When listing the sequence of amino acid residues in a polypeptide, called its **primary structure**, it is usual to start at the N-terminus end and finish at the C-terminus end. It is important to do this as Ala-Gly is a different dipeptide to Gly-Ala, see below.



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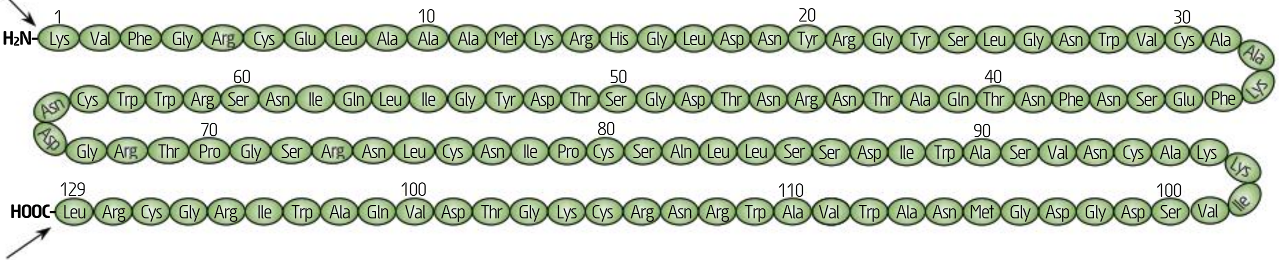
Attempt Set 20 # 13, 14 and 15.

14.8 Proteins: Structure and function

Individual protein molecules are characterised by their **specific sequence** of amino acid residues. Given there are 20 different commonly occurring α-amino acids and there can be 2000 or more in a particular protein then the number of different possible proteins is almost limitless. As an example, a relatively tiny protein chain containing only 60 residues will have 20^{60} different possible sequences of amino acid residues (20 being the available number of different common α-amino acids). It is this specific linear sequence of individual α-amino acid residues that is the protein's **primary structure**. The sequence is always listed from the **N-terminus** end of the protein. (See Fig 10 and 11.)

Figure 11 The protein **lysozyme** is an enzyme with mild antibacterial properties. It is found in tears, nasal secretions and the whites of bird eggs. In hen's eggs it destroys bacteria by catalysing the decomposition of certain carbohydrate chains that form part of the bacteria's tough cell wall. The primary structure of hen's lysozyme protein is shown here. The human version also contains 129 α-amino acid residues but has a slightly different sequence of α-amino acids.

N-Terminus, primary structure sequence starts here.



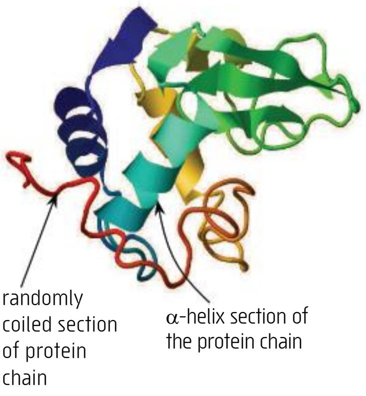
C-Terminus, primary structure sequence ends here.

Lysozyme **primary structure** = **Lys-Val-Phe-Gly-Arg-Cys-Glu-Leu-Ala-Ala-** a further 109 α-amino acid residues **-Val-Gln-Ala-Trp-Ile-Arg-Gly-Cys-Arg-Leu**

A protein's primary structure essentially determines how its chain will **fold** and **curl** in on itself to assume its final **three-dimensional** (**3D**) shape, known as its **conformation**. (See Fig 12.) This shape along with the sequence of amino acid residues it contains will govern the way the protein can interact with or fit onto other molecules and hence determine its **function**. The alteration of a single amino acid residue in a protein's primary structure can affect its final 3D (three-dimensional) structure and hence alter its function.

Three levels of structure can be identified as contributing to a protein's function. One aspect of this is the protein's **primary structure** (discussed above). Two other aspects are the secondary structure and tertiary structure. The **secondary structure** refers to the regular arrangement of various sections of the protein chain. Common protein secondary structures are the **α-helix**, a coiled section of the protein chain (Fig 13), and **β-pleated sheets**, adjacent chains bonded together to form a corrugated structure (Fig 14). Both of these structures are stabilised by **hydrogen bonding**.

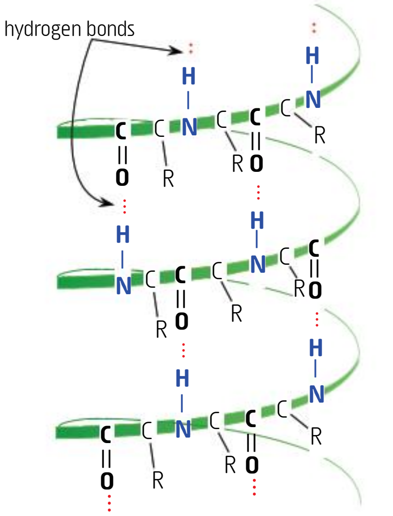
Figure 12 The primary structure of a protein molecule only gives the sequence of amino acids; it does not indicate its most important feature, its **3D shape**. This illustration shows the 3D structure of the egg white enzyme **lysozyme**. This was the first enzyme to have its 3D structure resolved. Using a technique called X-ray crystallography, David C. Phillips was able to solve the structure. His results were published in 1965 in the journal, ***Nature***.



The **α-helix** structure (Fig 13) is held in place by hydrogen bonds. These occur between a lone pair of electrons from the oxygen atom of a carbonyl group (-C=O) and the polar hydrogen atom of an amide group (-N-H). The amide group must be situated four residues further along the spiral from the carbonyl group. For this reason an α-helix structure is possible for some residue sequences but not for others. Hence protein molecules have sections with the α-helix structure interspersed with sections where the chain is randomly coiled or involved in some other form of interaction.

In 3D computer generated graphics, called ribbon diagrams, the α-helix structure is represented as a **coiled ribbon**. (See Fig 12.)

Figure 13 The protein **α-helix** structure showing selected atoms. The protein backbone is shown in green, with hydrogen bonds (**red**) between N-H groups and C=O groups. Various side chains (R) point outwards from the α-helix structure.



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β-pleated sheets (Fig 14) can occur with sections of the polypeptide chain where the α-amino acid residues have small (rather than large) side chains. Such sections of polypeptide (from the same protein chain or different protein chains) can fit closely alongside one another and become held in place by hydrogen bonding between the two polypeptide sections. In 3D computer generated graphics (ribbon diagrams) these are represented as **flat arrowed ribbons**. (See Fig 12 and 15.)

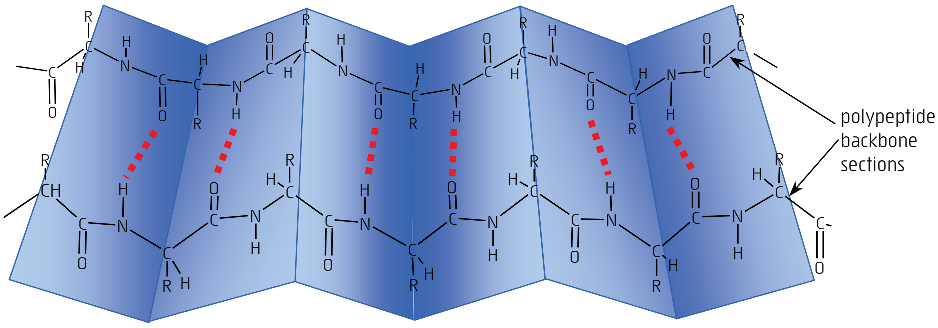
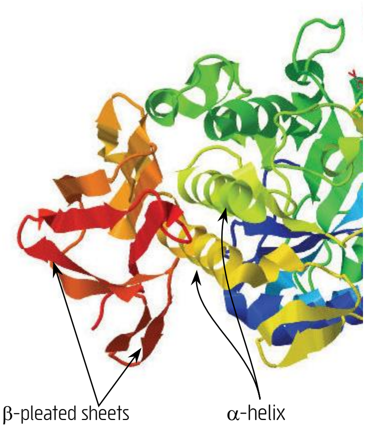


Figure 14 β **pleated** sheet structure. The two polypeptide sections are held in place by hydrogen bonds (red) between N-H groups and C=O groups from different sections of the same polypeptide chain or from different polypeptide chains. The hydrogen bonds lie within the plane of the sheet structure while the side chains (R) point above and below.

A protein's **tertiary structure** is its overall 3D shape that forms as a result of the main chain folding and bonding back on itself. Tertiary structure is due to various bonds that form between some of the **residue side chains** (R). These bonds include disulfide bridges, hydrogen bonds, dipole-dipole forces, dispersion forces and ionic bonds.

Figure 15 A diagrammatic view of part of the human saliva enzyme, alpha amylase. Various **secondary structural features** (α-helix and β-pleated sheets) as well as its overall **tertiary structure** can be seen.



A **disulfide bridge** consists of a covalent bond between two sulfur atoms from two **cysteine** residue side chains. When the cysteine residues align their **–SH** groups (one from each cysteine residue) each lose a hydrogen atom (oxidation) leaving the two sulfur atoms free to join by a covalent bond. The disulfide bridge then strongly holds together the two parts of the polypeptide chain thus contributing to the protein's tertiary structure. Sometimes **hydrogen bonding** can occur between the polypeptide **side chains**. This happens between side chains that contain groups like –OH, -COOH or –NH_2. While these interactions are weaker than disulfide bridges they still contribute to a protein's tertiary structure. Similarly, **dipole-dipole** forces and even **ionic bonds** can occur between residue side chains. (See Fig 16.)

Figure 16 Diagram showing various bonding forces between **side chains** of a **protein backbone** (in green). These bonds fold the protein molecule to produce its complex **tertiary structure**.

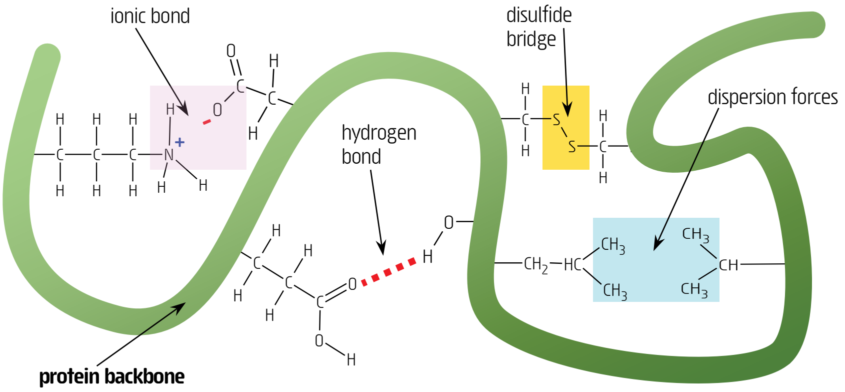
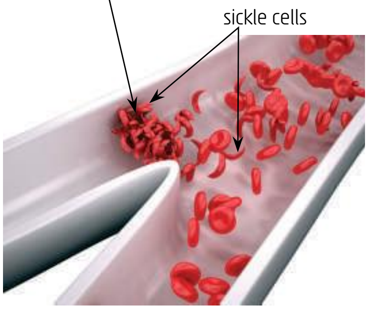


Figure 17 Normal blood cells have a donut-like shape. Abnormal sickle shaped red blood cells are caused by the replacement of a single amino acid residue in one protein chain of the haemoglobin molecule. One effect of this is to cause red blood cells to clump and clog capillaries.



The structure and function of a protein are both critically related to the specific sequence of amino acid residues in its primary structure. This determines the nature of its most stable secondary and tertiary structures. The genetic disorder called **sickle-cell anaemia** for example, is caused by the replacement of a single amino acid residue from a string of 146 residues in one of the protein chains found in haemoglobin. One glutamic acid (**Glu**) residue, which has a **highly polar side chain** (–COOH), is replaced with one valine (**Val**) residue, containing a **non polar side chain**. This single alteration changes the solubility of the protein chain thus affecting its shape and altering its functionality. These lower solubility haemoglobin molecules are called **HBs**. Red blood cells containing HBs become deformed in shape (sickle shaped) and tend to clog capillaries causing severe pain, physical weakness, organ deterioration and premature death. (See Fig 17.)

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Attempt Set 20 # 16 to 20.

14.9 The Protein Data Bank (PDB)

The **Protein Data Bank** (PDB) is an online archive of macromolecular structural data. The information stored in the PDB is contributed by scientists from around the world and is freely and publicly available to anyone. The PDB had its beginnings in 1971 but it was not until 2003 that the PDB became an international archive which is now overseen by an organisation called the **Worldwide Protein Data Bank** (wwPDB). The wwPDB has four member organisations from the USA, Japan and Europe, and as of 2014, it contains information for over 100 000 structures.

The wwPDB was formed in order to formalise and standardise the presentation and annotation of protein structural data. The four member organisations each act as a point for data deposition, processing and distribution; however, the wwPDB provides an overarching organisational structure and ensures a single uniform archive is maintained. The data stored in the PDB can be freely accessed and downloaded by anyone and this allows better **collaboration** and **communication** between scientists all over the world. Each PDB entry contains information about the **primary**, **secondary**, **tertiary** and **quaternary structure** of a protein, with the main focus on tertiary and quaternary structure.

The three dimensional structural information about a protein is useful for many different avenues of scientific research. This data can be used to examine things such as which amino acid residues are exposed in the structure and which are not, the positioning of alpha helices and beta pleated sheets within the protein, protein-protein interactions, as well as how proteins may bind with other small molecules. This information can be used to find potential inhibitors or binding partners for a protein. For instance, when looking at treatments for a disease, this may require development of a drug that blocks a particular binding site on a protein. (See Fig 18.) The structural information in the PDB can provide the information which may assist in designing such a drug.

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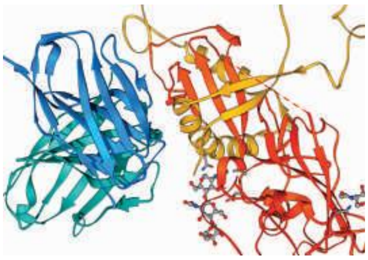
Figure 18 Researchers are looking hard for ways to fight infection by the dangerous **Ebola** virus both with drugs and with vaccines. The glycoprotein is a major target for vaccines, since it is on the surface of the virus and is accessible to antibodies.

The **partial** glycoprotein structure below includes neutralizing antibodies from a person who survived infection by the virus. It is hoped that vaccines will be able to elicit these types of antibodies in patients, protecting them from infection.



Full details of this protein can be found at the RCSB PDB website at **PDB 3csy**.

14.10 Enzymes: Biological catalysts

Many proteins found in living systems act as **catalysts** and are known as **enzymes**. As with inorganic catalysts like platinum and manganese dioxide, enzymes are able to speed up the rates of reactions by providing a reaction pathway of lower activation energy. However, unlike inorganic catalysts most enzymes (but not all) tend to be very specific in the reactions they catalyse and much faster acting. (See Fig 19.) Often it is their complex structure and particularly their specific conformation (shape) that allows a given reagent molecule (or molecules) called the **substrate**, to fit onto or 'dock' with a specific **active site** on the enzyme surface. It is for this reason that a particular enzyme will often only catalyse a specific reaction. This is known as **enzyme specificity**. Once in place the enzyme forms various weak intermolecular forces with the substrate thus holding it in place at the active site. While the substrate is in this position, bonds are more easily rearranged leading to the quick formation of products. Once the substrate has undergone chemical changes the new products disengage from the enzyme surface leaving the enzyme in its original form. This simple model for enzyme action is called the **lock and key model**. (See Fig 20.)

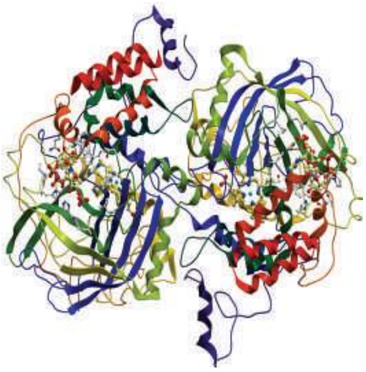
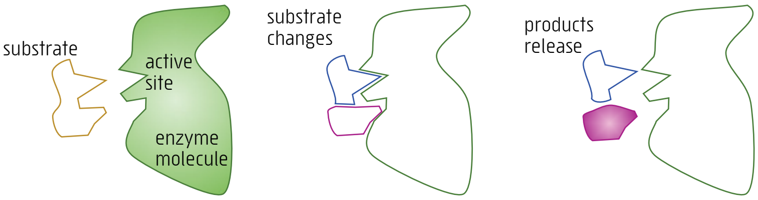


Figure 19 Hydrogen peroxide, **H_2O_2** occurs naturally in the human body as a **waste** product of many normal metabolic processes. As it is extremely toxic to cell tissue it must be removed rapidly before causing cell damage or death.

In the human body and the tissue of almost all living organisms an **enzyme** called **catalase** is responsible for the rapid catalytic decomposition of H_2O_2. Catalase is one of the **fastest acting catalysts known**. A single molecule can decompose several million H_2O_2 molecules per second. The model above shows the complex structure of the catalase molecule.

Figure 20 A diagrammatic representation of the **lock and key model** of enzyme action.



The substrate approaches an enzyme's active site.

Weak intermolecular forces keep the substrate in place while some bonds break and new ones form.

The changed substrate releases from the active site as the products are no longer bonded.

Some **industrial processes** use enzymes to speed up reactions that would otherwise require high temperature or pressure to achieve an economic rate. Due to their specificity there is also less chance of side reactions and unwanted by-products. In this way the use of enzymes can enhance the sustainability of chemical synthesis.

Unlike inorganic catalysts, enzyme activity (ie ability to increase rate) is sensitive to both **temperature** and **pH**. These conditions affect an enzyme's **conformation** (shape) and hence affect its catalytic properties. For this reason individual enzymes have a preferred operating range for both temperature and pH. Outside of this range the enzyme conformation is altered thus compromising its activity.

In an un-catalysed reaction, the rate always increases with increasing reactant concentration. In an enzyme catalysed reaction however, the rate does initially increase with increasing substrate (reactant) concentration until at some point there is no further increase in rate. At this point all of the active sites on the available enzyme molecules are occupied by substrate molecules undergoing their catalysed reaction. Increasing substrate concentration at this point has no effect on rate as substrate molecules must wait for active sites to become available. (See Fig 21)

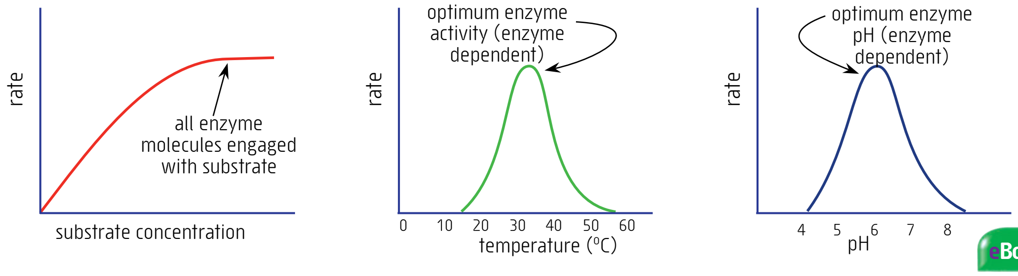


Figure 21 Optimal conditions of temperature and pH depend on the origin of the enzyme. Most enzymes have an optimal temperature of around 37 °C. Enzymes from bacteria living near deep sea thermal vents may have optimal temperatures closer to 100 °C.

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Complete Set 20.

Set 20 Polymers, polypeptides and proteins

1. The following passage is about macromolecules such as polymers, polypeptides and proteins. Use the terms shown to complete the passage.

   Macromolecules are very large molecules with a particularly high (a) ___________. Synthetic examples include (b) ___________ like polyethene, PET and Kevlar while polysaccharides, (c) ___________ and DNA are naturally occurring (d) ___________ examples.

   Synthetic polymers are a very useful class of macromolecule. They consist of very large molecules formed by the chemical combination of many small molecules called (e) ___________. Some polymers can be (f) ___________ to form various shaped objects like chairs, toys or bottles while others are suitable for extruding and drawing into (g) ___________ for making (h) ___________.

   Polymers that soften then melt when heated are known as (i) ___________. These are often easily recycled. (j) ___________ polymers are moulded during manufacture and not able to be reshaped by heating. Instead, heating causes them to char or decompose. The nature of polymer chains can also vary. Some have chains that are essentially (k) ___________ while others have chains with numerous (l) ___________. Others like rubber, form covalent bonds that link chains together. This is known as crosslinking and gives the polymer (m) ___________ properties.

fabric
side chains
thermoplastics
proteins
polymers
straight
elastic
molar mass
moulded
monomers
biological
thermosetting
fibres

2. The following equation shows the change that occurs during the **addition polymerisation** of **chloroethene**.

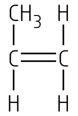
$$n\mathrm{CH_2{=}CHCl} \longrightarrow \mathrm{-\!\!\!(CH_2CHCl)\!\!\!-}_n$$

chloroethene polychloroethene

   a. **Explain** the significance of the letter **n** in the equation.
   b. **Sketch** a section of the polymer when **n=4**. Show all bonds and atoms.
   c. **Sketch** a section of polymer formed from the addition polymerisation of **2-methylpropene**. Show all bonds and atoms and include **three monomer** units in your structure. (See hint at right.)

Hint: Draw the full structural formula for the double bonded part of the monomer. This makes it much easier to visualise the repeating unit of the polymer structure. eg For **polypropene** write the monomer

like this



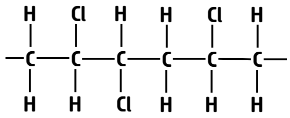
not this

$CH_3CH{=}CH_2$

Hint: When looking at a section of polymer it must be remembered that the individual monomer units may not have joined in the same orientation, ie they may have flipped top to bottom or left to right when joining the growing chain. During industrial polymerisation this orientation is usually controlled as it does affect polymer properties.

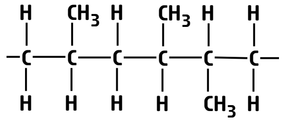
3. Small sections of several **addition polymer** molecules are shown here. The **wire frame** structure in (iii) does not show H or C atoms. Carbon atoms are understood to be present at each bond junction in the structure. Hydrogen atoms occupy any remaining spaces. (See hint at left.)

i



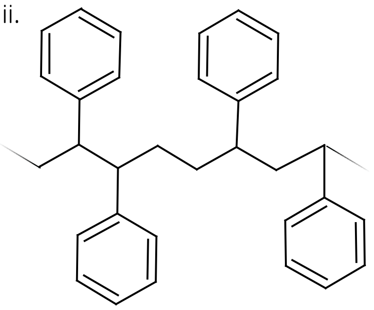
$$\begin{array}{cccccc} H & Cl & H & H & Cl & H \\ | & | & | & | & | & | \\ -C- & C- & C- & C- & C- & C- \\ | & | & | & | & | & | \\ H & H & Cl & H & H & H \end{array}$$

ii



$$\begin{array}{cccccc} H & CH_3 & H & CH_3 & H & H \\ | & | & | & | & | & | \\ -C- & C- & C- & C- & C- & C- \\ | & | & | & | & | & | \\ H & H & H & H & CH_3 & H \end{array}$$

iii.

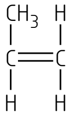


a. **Identify** the **monomer** that forms each of the above polymers and draw the **structural formula** for the monomer involved.

b. **Describe** the **change** that takes place during **addition** polymerisation that allows monomer units to join and form a polymer structure?

Remember: In an addition polymerisation equation always show the full structural formula for the double bonded part of the monomer. This makes it much easier to visualise the repeating unit of the final polymer molecule.

like this



$$\begin{array}{cc} CH_3 & H \\ | & | \\ C & = C \\ | & | \\ H & H \end{array}$$

not this

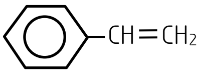
$CH_3CH{=}CH_2$

4. Write **equations** for the addition polymerisation of the following monomers. Assume suitable conditions of temperature, pressure and catalysts are provided.

a. $CH_2 = CH_2$

b. $CH_3CH = CH_2$

c.



(styrene)

d. chloroethene

e. 2-butene

5. **Crystallinity** in polymers can have a significant impact on the polymer's final properties. The conditions used during the polymer's manufacture and subsequent processing will determine its final crystallinity and hence its properties. Consider the various polymers of ethene, ie LDPE, HDPE and UHMWPE and answer the following.

   a. Use a **sketch** to help **explain** the meaning of **crystallinity** as it applies to a polymer.

   b. How are the molecules of **LDPE** different from those of **HDPE** and how does this difference affect their crystallinity and resulting properties of strength, density and melting point?

   c. What are some of the **distinguishing properties** of each of the different forms of polyethene (LDPE, HDPE and UHMWPE) and what are their associated uses?

6. The addition polymer **polytetrafluoroethylene** (PTFE) was accidently discovered by the scientist, Roy J. Plunkett in 1938, while investigating the apparent disappearance of the gas tetrafluoroethene from a supposedly full cylinder. Determined to solve the puzzle he cut open the cylinder to find its insides were coated with a waxy white material. The material, which turned out to be polytetrafluoroethylene, had some remarkable properties and today has many important uses. **Describe** some of the **properties** and **uses** of this polymer.

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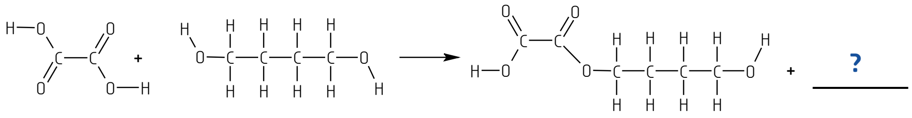
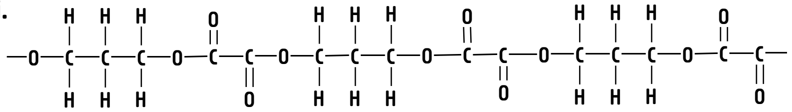
7. The following **partially completed equation** shows the condensation reaction of oxalic acid (HOOCCOOH) with butane-1,4-diol to form a dimer (two monomer units joined together).



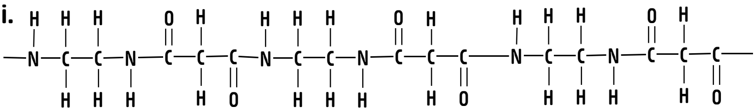
   a. **Complete** the equation by filling in the **missing product**.
   b. Write the **formula only** of the organic product that would be formed if another molecule of butane-1,4-diol were to attach to the dimer.
   c. What is the **name** of the **group of atoms** linking the monomers in the above dimer and trimer?
   d. If a polymer was to be produced by this reaction it would require **n** monomer units of oxalic acid. How many **monomer units** of butane-1,4-diol would be needed and how many **water molecules** would be formed?
   e. Use **brackets** around the repeating unit along with the subscript **n** to represent the **formula** for the polymer that would be produced from these monomers.

8. Small sections of several **condensation** polymer molecules are shown here.

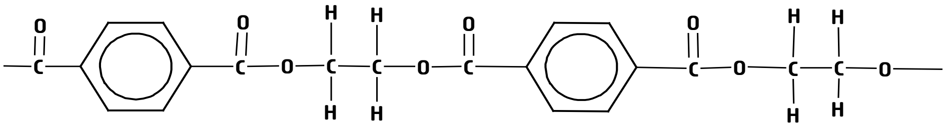
i.



ii.



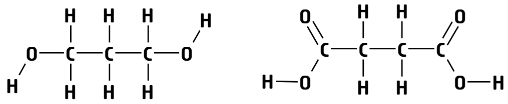
iii.



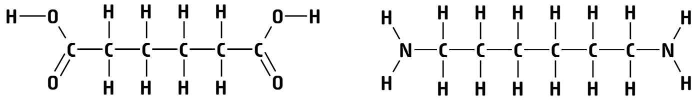
   a. What **change** occurs during **condensation** polymerisation that allows monomer units to join together to form a polymer?
   b. In each of the structures **circle** all of the **ester** groups and **amide** groups. Identify these polymer sections as belonging to a **polyester** or a **polyamide**?
   c. Identify the **monomers** that form each polymer and draw the **structural formula** for the monomers involved.

9. The following pairs of monomers undergo **condensation** polymerisation. Write **equations** to show this.

   a. propane-1,3-diol and butanedioic acid



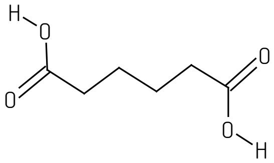
   b. hexanedioic acid and hexane-1,6-diamine (produces nylon-6,6)



   c. hexanedioic acid and butane-1,4-diol
   d. propane-1,3-diamine and octanedioic acid

10. For the polymers from Question 9(a) and 9(b), **draw a section** of polymer showing exactly **two complete repeating units**. Show all atoms and bonds.

Figure 22 Wire frame structures such as that for hexanedioic acid (below) do not show **H** or **C** atoms. Carbon atoms are understood to be present at each bond junction in the structure. Hydrogen atoms occupy any remaining spaces. Atoms other than carbon and hydrogen must be shown.



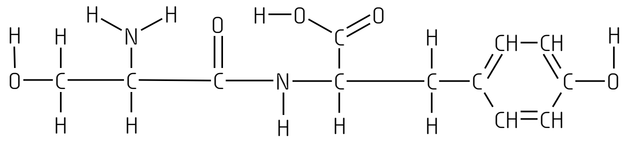
11. Polyamides like nylon 6,6 can form quite strong threads suitable for producing fabric. An important contributor to the strength of these threads is the presence of **hydrogen bonding**. Use a simplified wire **diagram** (Fig 22) to show where they form and **describe** how the fibre manufacturing process of cold-drawing enhances their presence.

12. Nylon and polyethylene terephthalate (PET) are two important condensation polymers. Note some of their particular **properties** and **uses**.

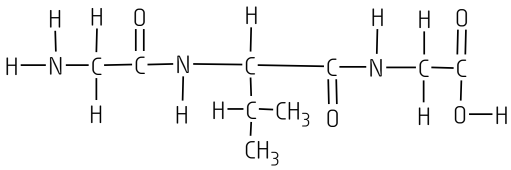
13. **Proteins**, **polypeptides** and α
    Briefly describe what they are and how they are related?

14. Consider the **dipeptide** and **tripeptide** molecules shown here.

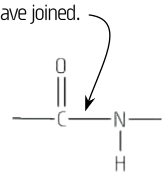
A dipeptide.



A tripeptide.



Hint: Look for the peptide bond indicated here. This shows where the two α-amino acid molecules have joined.



a. **Circle** and label the **peptide bonds** linking the amino acid residues in both peptides.
b. Identify the amino acids that formed each of the molecules and **draw** these.
c. **Describe** the type of **reaction** that produces these peptides from their amino acids and name the other **product** of the reaction.

15. The α-amino acids that form a polypeptide or protein are referred to as α-amino acid residues or just residues. **Why** is the term **residue** used rather than α-amino acid?

16. What is meant by the **primary structure** of a polypeptide or protein? Use the dipeptide and tripeptide from Question 14 to show your understanding of primary structure. Remember primary structure must be given starting at the N-terminus.

17. The α-helix is a **secondary structure** occurring in proteins. What **part** of the protein structure is involved in forming the α-helix and how does it keep its shape? A **very simple sketch** could be used to support your answer.

18. What are β α
    structure?

19. What is the **tertiary structure** of a protein? In your answer note:
    - the **parts** of the protein structure involved in forming the tertiary structure.
    - the types of **bonds** involved.
    - the **significance** of tertiary structure to a protein's function.

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20. The diagrammatic representation drawn here shows various components and structures of a **protein molecule**. The green line represents the **protein backbone**. The following questions refer to this structure.

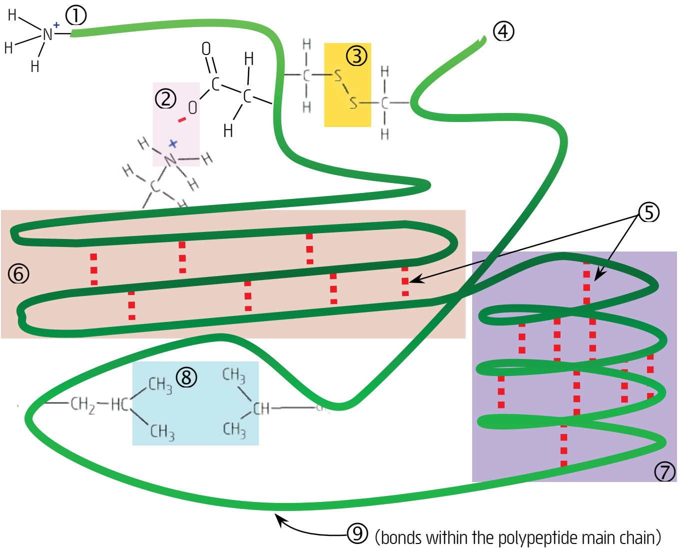
   a. Identify by **name** the various bonds numbered 2, 3, 5, 8 and 9. **Classify** each of these as contributing to the **primary**, **secondary** or **tertiary** structure of the protein.

   b. What does the structure at position 1 represent?

   c. What structure should be at position 4?

   d. Name the shaded structures at 6 and 7.

   e. Name the type of bond that can contribute to a protein's tertiary structure but it is not shown in this context in the diagram below.



21. The preparation of jams like strawberry jam involve heating the fruit in a sugar solution. In the process, sugar (sucrose, $C_{12}H_{22}O_{11}$) undergoes an **acid catalysed hydrolysis** reaction converting it to a much sweeter mixture of fructose and glucose. Honey bees achieve a similar reaction with the aid of an enzyme called **invertase**; no heating required! The reaction is shown here.

$$C_{12}H_{22}O_{11}(aq) + H_2O(l) \xrightarrow{\text{invertase}} 2C_6H_{12}O_6(aq)$$

sucrose — glucose/fructose (a mixture of isomers)

Figure 23 The preparation of jam from fruit involves the conversion of sugar (sucrose) to invert sugar; a mixture of glucose and fructose. Invert sugar is much sweeter than the original sucrose.

   a. In jam making the sugar mixture is **heated** to boiling and a little **acid**, eg lemon juice may be added. Briefly, how do these two conditions affect the hydrolysis of sucrose?

   b. Honey bees are able to achieve a similar reaction using the enzyme invertase. What type of compound is the enzyme invertase and what is its role in the hydrolysis reaction?

   c. Invertase can be used in the laboratory to hydrolyse sucrose. In an investigation a student prepared three sucrose solutions of equal volume and concentration all containing the same amount of **invertase**. The solutions were kept at different **temperatures** and then after 12 minutes the yield of glucose was determined. The results are shown in Table 3 at right. Account for the **lower yield** of glucose at:

      i. 8 °C

      ii. 90 °C

   d. The optimum pH range for the enzyme catalysed reaction is pH 4 to 5. What does this mean and what happens if the reaction pH is outside of this range?

Table 3 Glucose yield after 12 minutes using different temperatures.

Temperature	Percentage yield
8.0 °C	7
38 °C	82
90 °C	3

CHAPTER 15 | CHEMISTRY IN INDUSTRY

15.1 Chemical synthesis

People living in today's modern world rely heavily on a ready supply of many useful chemical substances, for example fertilisers for food supply, pharmaceuticals for our health, polymers and plastics for clothing and consumer items and fuels for transport and energy needs. These substances are **synthesised** or manufactured in chemical plants using readily available natural resources. The synthesis may be achieved by a **single chemical reaction**; as in the Haber process (15.9) for producing ammonia or it may involve a **reaction sequence**; such as in the production of sulfuric acid by the Contact process (15.10). Designing and operating a chemical plant involves the work of chemical engineers and industrial chemists who use well established chemical principles and knowledge as well as conducting ongoing research into new and better materials and chemical processes.

An important focus for industrial chemists is the development of a more **sustainable** chemical industry based on the principles of **green chemistry**. (See Fig 1.) This involves developing and using products and processes that do not harm human health or our natural environment. In general this includes avoiding the use of toxic materials or their release into the environment, using renewable resources, minimising energy consumption and using products and processes that are in balance with the Earth's own natural processes. Paul Anastas and John Warner (1998 'Green Chemistry: Theory and Practice') identified twelve commonly accepted principles of **green chemistry**.

Figure 1 **Bioethanol** synthesis from crops like agave and jatropha offer the potential of a '**greener**' more sustainable alternative to petroleum based fuels. **Biofuels** like this are a renewable resource whose use can be in balance with the Earth's carbon cycle. Their production does not involve hazardous substances or the use of high temperatures or pressures.

Importantly, crops like agave (below) and jatropha can be grown without irrigation and on less fertile soils not currently used for agriculture.

- **Prevention**:
- **Atom economy**:

  product.
- **Less hazardous chemical syntheses**:

  substances that possess little or no toxicity to human health and the environment.
- **Designing safer chemicals**:
- **Safer solvents and auxiliaries**:

  wherever possible and innocuous when used.
- **Design for energy efficiency**:

  impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure (ie that of the natural surroundings).
- **Use of renewable feedstocks**:

  economically practicable.
- **Reduce derivatives**:

  keep the overall process as simple as possible).
- **Catalysis**:

  Design for degradation:

  in the environment.
- **Real-time analysis for pollution prevention**:

  formation of hazardous substances.
- **Inherently safer chemistry for accident prevention**:

  chemical accidents, including releases, explosions and fires.

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As well as addressing the principles of **green chemistry** the synthesis of a chemical must be optimised to maximise both **yield** and **rate** of production. Doing this achieves the best economic and environmental outcomes. This involves the application of **collision theory** and the principles of **equilibria**. The use of catalysts and especially **enzymes** (biological catalysts) can be very important in this regard. Enzymes tend to be specific in their action and so reduce or eliminate unwanted **side reactions** that may otherwise result in waste of reactants and unwanted reaction products that must be separated and disposed of. Enzymes also have the potential to reduce energy consumption in chemical reactions as they operate at much lower temperatures than traditional catalysts.

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Attempt Set 21 # 1, 2 and 3.

15.2 Biofuels

Biofuels like **bioethanol** and **biodiesel** are produced from **biomass** and are considered fossil fuel alternatives. Although their current contribution to total global fuel requirements is small (Table 1) their production is predicted to double by 2025 from 2012 levels. Replacing petroleum fuels with biofuels is consistent with the principles of green chemistry and a sustainable chemical industry for a number of reasons.

- Biofuels are a renewable resource while the petroleum they replace is not.
- Biofuels are essentially natural products and exposure to these is of limited or no consequence to human health or the natural environment. Petroleum based fuels however, are toxic and harmful when accidentally released into the environment.
- CO_2 emissions (a greenhouse gas) from biofuels can be in balance with the Earth's carbon cycle as the carbon in these fuels simply replaces atmospheric CO_2 absorbed by plants (during photosynthesis) as they produce the biomass originally used to make the fuel.
- Petroleum based fuels frequently contain sulfur. Their combustion releases **sulfur dioxide**, a respiratory irritant that impacts human health and also leads to acid rain which has environmental consequences. Petroleum based fuels typically require extra treatment to either remove or considerably reduce their sulfur content. Biofuels do not require supplementary treatment as their **sulfur content** is typically negligible.
- Biofuels burn cleaner, ie produce less particulate emissions (eg soot) than do petroleum based fuels. Biodiesel combustion however, is prone to producing slightly higher emissions of toxic nitrogen oxides (NOx).

Table 1 Global liquid fuel production (million barrels per day).

Year Fuel type	2009	2010	2011	2012
ethanol	1.323	1.521	1.490	1.470
biodiesel	0.312	0.345	0.425	0.431
***refined petroleum**	82.4	84.2	84.7	85.2

*Includes transport fuels like petrol, diesel and LPG. Source 'U.S. Energy Information Administration (EIA)'.

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Attempt Set 21 # 4.

15.3 Ethanol production

There are two commonly used methods for producing ethanol. The **acid catalysed addition** of water to ethene and the **enzyme catalysed fermentation** of sugars. The production of ethanol by fermentation has several 'green' advantages.

- Ethanol from **fermentation** is a **biofuel** as it is manufactured using biomass whereas ethanol from the **acid catalysed addition** of water to ethene is not a biofuel as ethene originates from fossil fuel sources.
- Fermentation uses **renewable resources** whereas manufacturing ethanol from ethene (derived from fossil fuels) uses non-renewable resources.
- Using **enzymes** in the fermentation process results in less energy use as well as reaction conditions and chemicals that are inherently safer. For example, fermentation is conducted at atmospheric pressure, ambient temperature (eg 25-37 °C) and a moderate pH whereas manufacture of ethanol from ethene uses a high pressure of 60-70 times atmospheric pressure, ≈300 °C and a corrosive acid catalyst, eg $H_3PO_4(l)$.

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Figure 2 Sugar cane harvesting in North Queensland. Molasses, a by-product of sugar refining, is used by the 'Wilmar BioEthanol' distillery at Sarina in North Queensland to produce around 60 million litres of bioethanol per year.

Ethanol uses include:

- A fuel replacement for petrol in blends such as E10 and E85 (ie 10% and 85% ethanol respectively).
- An industrial solvent for products like paints and varnishes.
- A solvent in some cosmetics and pharmaceuticals.
- An antiseptic in some hand sanitisers and mouthwashes.
- A feedstock for manufacturing other chemicals.

15.4 Ethanol: Synthesis by fermentation

The natural process of fermentation accounts for about 93% of world ethanol production. It has been used for thousands of years to produce **alcoholic beverages** (ie ones containing ethanol) such as wine from grape juice and beer from malted wheat. The process relies on **yeast** that produce enzymes capable of catalysing the conversion of plant carbohydrates such as **starch** or **sugar** into ethanol.

Figure 3 Distillation towers at a bioethanol plant.

Today a diverse range of agricultural crops such as corn, wheat and other cereals, sugar cane, beets and potatoes are used to produce ethanol by fermentation. Much of this ethanol is used as a motor fuel or fuel blend. Producing ethanol by fermentation relies on a suitable and readily available source of **cheap biomass** or **biomass waste**. In Brazil, India and northern Australia for example, sugar cane is the basis of the process while in Europe and the US corn, wheat or sugar beet are preferred.

In Northern Queensland for example, a sugar rich waste product of the sugar refining industry (called molasses syrup), is used to produce ethanol by fermentation. This process uses the catalytic activity of several enzymes produced by yeast. The two major chemical reactions occurring are:

- **Hydrolysis** of sucrose to glucose and fructose, (isomers of $C_6H_{12}O_6$). This reaction is catalysed by the yeast enzyme invertase or sucrase.
- **Fermentation** of the glucose/fructose mixture to ethanol and carbon dioxide. This is catalysed by the yeast enzyme zymase.

The commercial yeast ***Saccharomyces cerevisiae*** is used in the fermentation process. Its cells produce the enzymes **invertase** and **zymase**.

hydrolysis of sucrose:

$$\underset{\textbf{sucrose}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{\text{invertase}} \underset{\textbf{glucose/fructose}}{2C_6H_{12}O_6(aq)}$$

fermentation:

$$\underset{\textbf{glucose/fructose}}{C_6H_{12}O_6(aq)} \xrightarrow{\text{zymase}} \underset{\textbf{ethanol}}{2C_2H_5OH(aq)} + 2CO_2(g)$$

overall process:

$$\underset{\textbf{sucrose}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{\text{yeast enzymes}} \underset{\textbf{ethanol}}{4C_2H_5OH(aq)} + 4CO_2(g)$$

The specific conditions used during fermentation will vary depending upon the nature of the yeast chosen and the feedstock used. If **molasses** (a waste product of sugar refining) is used it requires dilution with water to produce a 10-15% sucrose solution. Warm conditions of about 25-37 °C (depending upon yeast) are employed with a pH in the range 3-5.

Like all proteins, **enzymes** are sensitive to both temperature and pH. They are readily denatured (structure and shape is altered) and made ineffective by high temperatures or unsuitable pH. As fermentation is an exothermic reaction, cooling is needed. This prevents overheating which would deactivate the enzymes. Heat exchangers are used for this purpose. A weakly acidic pH of 3-5 is chosen as this favours yeast growth and activity while inhibiting and killing unwanted bacteria.

In the initial phase of fermentation the yeast grows and reproduces quickly. During this period they respire aerobically and quickly deplete the available oxygen. By **excluding air** (oxygen) from the fermentation vat the mixture soon becomes anaerobic (no oxygen). The falling oxygen concentration is important as it forces yeast to respire anaerobically by converting glucose to ethanol rather than to water and carbon dioxide (aerobic respiration). **Nutrients** like diammonium hydrogenphosphate [$(NH_4)_2HPO_4$] may also be added to the mixture as they promote the initial growth and reproduction of yeast.

At an ethanol concentration of about 8-14%, fermentation ceases as the yeast becomes poisoned by the alcohol they have produced. Yeast is now separated from the fermentation mixture and **distillation** used to raise the alcohol concentration to 95% (by mass). Ethanol separation beyond 95.6% cannot be achieved by normal distillation as the ethanol-water mixture forms an azeotrope, a mixture with a constant composition and boiling temperature. Other methods can be used to produce 100% (anhydrous) ethanol.

Producing ethanol from starch products, eg wheat or corn, is a similar process but involves a different choice of enzymes and reaction conditions. A bioethanol plant at Nowra in southern NSW, for example, produces 300 million litres of ethanol annually using waste starch from flour processing. The starch is mixed with water and adjusted to pH ≈6. Heating this mixture to ≈90 °C in the presence of alpha amylase enzyme breaks down the starch to simpler sugars. This mixture is then cooled to about 33 °C. Glucoamylase enzyme and a yeast specifically designed for ethanol production is then added. The enzyme further breaks down the sugars to glucose and other simple sugars which are then fermented (as above) to ethanol and CO_2. Fermentation takes about 48 hrs to complete. Ethanol is retrieved as before by distillation and any remaining solids are dried to produce stockfeed.

Figure 4 Current research in the area of bioethanol production has recently commercialised technologies for producing ethanol from non-edible carbohydrates such as the fibrous or woody portions of plants (lignocellulose) including wood chips, straw, algae and **sugar cane bagasse** (above). Some of these processes involve enzymes and micro-organisms that convert lignocellulose into sugar prior to its fermentation into ethanol.

Cellulosic ethanol is now being produced on a commercial scale in Europe, US and Brazil. In October 2013, the world's largest cellulosic ethanol facility, producing 75 ML of cellulosic ethanol annually, was opened at Crescentino in Italy, below.

Biofuels produced this way are referred to as second generation biofuels. These technologies use a new range of biofuel feedstock such as waste from agriculture and forestry or from farming algae in saline lakes. This approach avoids the competition for traditional agricultural resources and may complement current agriculture by turning farming waste into valuable biofuel.

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Attempt Set 21 # 5 and 6.

15.5 Ethanol: Synthesis from ethene

This is a **quicker** method for producing ethanol for industrial use. It uses the **acid catalysed addition** of **water** to **ethene** and is easily adapted as a continuous process. By comparison, ethanol production by fermentation is usually performed as a batch process taking 2-3 days for the complete fermentation of each batch. Producing ethanol by the addition process is most viable where it can be part of an integrated system of petroleum production and refining.

The process involves passing a mixture of **steam** and **ethene** through a catalyst bed made of silica particles coated with pure **phosphoric acid**, $H_3PO_4(l)$ as the catalyst. This results in the following equilibrium.

$$CH_2CH_2(g) + H_2O(g) \rightleftharpoons CH_3CH_2OH(g) \qquad \Delta H = -45\text{ kJ}$$

A temperature of around 300°C and a pressure of 6-7 MPa (60-70 atm) is used. The **exothermic** nature of this reaction means products are favoured by a low temperature. Thus the chosen temperature is a **compromise** between maximising rate, ie a high temperature, and maximising yield, ie a low temperature. The high pressure favours both high yield and a fast rate while the use of a catalyst, $H_3PO_4(l)$ increases rate while having no effect on yield.

An ethene to water molar ratio of **1 : 0.6** is used despite the **stoichiometric** ratio of **1 : 1**. Steam is present as a limiting reagent as higher concentrations of steam result in the undesirable dilution and washing away of the phosphoric acid catalyst coating on the silica particles.

With these conditions, a conversion to ethanol of ≈5% occurs as the reagents quickly pass through the catalyst bed. By separating ethanol and continually **recycling** the unreacted ethene and steam, an overall yield of ≈95% is achieved. As with fermentation the resulting ethanol can be distilled to separate any water or other impurities it may contain.

Most of the ethanol produced by the addition of water to ethene is used as a feedstock for the manufacture of other industrial chemicals rather than as a fuel or beverage additive. It must be emphasised that ethanol produced this way does not have the environmental advantages of bioethanol as it is produced from **non-renewable petroleum** based resources (ethene) and its combustion does contribute to increasing atmospheric CO_2 concentration (a greenhouse gas).

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15.6 Biodiesel

Biodiesel is a liquid consisting typically of the **methyl** or **ethyl esters** of naturally occurring fatty acids, FAs. (See Fig 5.) It is used in Australia as a blend, eg B5, B20 or B100, ie pure biodiesel. Its production is almost entirely by the **base catalysed trans-esterification** of **triglycerides** (TGs) present in natural fats and oils. Typical feedstocks for the production of biodiesel include canola oil, soybean oil, palm oil, animal fats (tallow) or used cooking oil.

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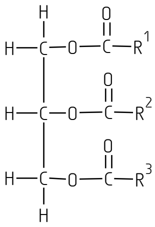
15.7 Biodiesel: Base catalysed transesterification of TGs

In this process the chosen feedstock is filtered to remove any **foreign matter** (especially in recycled cooking oil) and treated to remove **water** that may be present. Water must be excluded from the reaction mixture (or at least greatly minimised) as its presence results in an undesirable **side reaction** involving the conversion of esters, free fatty acids and TGs into **soap**. (See ester hydrolysis 12.5 p136.) Soap formation is undesirable as its production wastes valuable reagent and its presence in the final reaction mixture causes biodiesel and its co-product glycerol to form an **emulsion** making them much harder to separate.

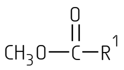
Once filtered and dried the oil is analysed for the presence of any naturally occurring free fatty acids, FFAs. (See Fig 5.) If the FFA content exceeds 4% then the oil must be treated to remove or greatly reduce the FFA content. If this is not done then later in the process when sodium hydroxide is added to the oil any FFAs in the mixture will be converted to soap.

Figure 5 **Biodiesel** typically consists of the methyl or ethyl ester of naturally occurring fatty acids. These are derived from triglycerides or free fatty acids.

In these general structures $\mathbf{R^1}$, $\mathbf{R^2}$ and $\mathbf{R^3}$ represent various carbon chains with typically greater than four carbon atoms each.

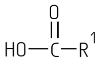


TG, a triglyceride molecule.



$CH_3O-\overset{O}{\overset{\|}{C}}-R^1$

FAME, a fatty acid methyl ester molecule, ie biodiesel.

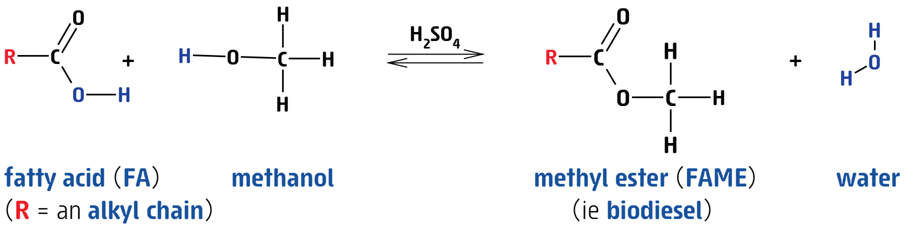


$HO-\overset{O}{\overset{\|}{C}}-R^1$

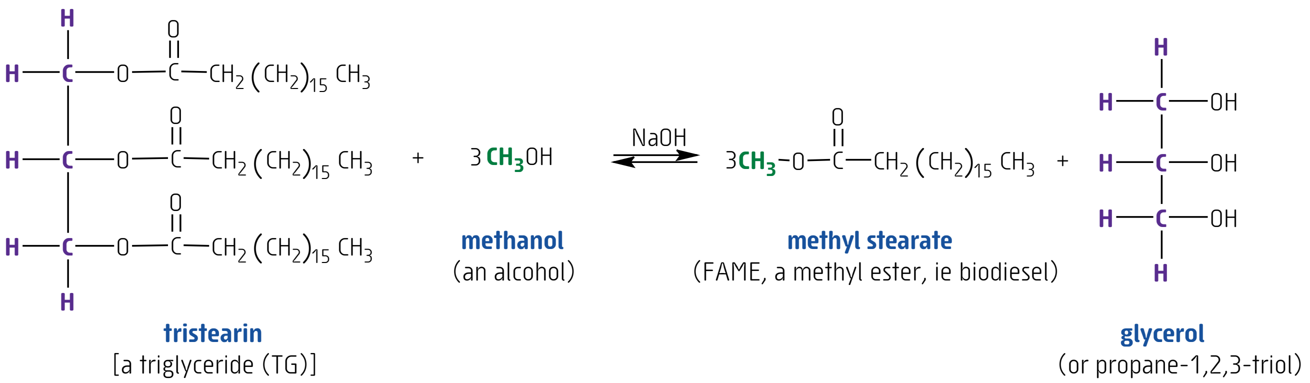
FA or **FFA**, a free fatty acid molecule.

By comparison, **petroleum based diesel** is a mixture of various hydrocarbons with around 8-21 carbon atoms per molecule and no oxygen content. The presence of oxygen in biodiesel contributes to its better combustion properties, such as producing less particulate pollution (soot) and carbon monoxide gas.

One method for dealing with FFAs is to treat the oil with methanol (or ethanol) and an acid catalyst (eg H_2SO_4) prior to transesterification. This converts the problem FFAs to methyl esters (or ethyl esters), ie biodiesel. This is a simple esterification reaction (see 12.4).



After suitable preparation the oil then undergoes **transesterification** to produce biodiesel. This is normally a very slow equilibrium process so a catalyst is used to achieve a reasonable rate. Most biodiesel production uses a strong base such as **sodium hydroxide** or **potassium hydroxide** to catalyse the reaction. To further increase the speed of reaction a moderate temperature (≈60 °C) is used. Typically methanol or ethanol (other alcohols may also be used) are mixed with the catalyst, eg NaOH, prior to mixing with the oil. The reaction mixture is contained within a sealed reaction vessel to prevent loss of the volatile alcohol, eg methanol BP = 64.7 °C. The resulting transesterification reaction using **methanol** and **tristearin** (an example of an animal fat, ie a TG) is shown below.



The required **stoichiometric ratio** of alcohol to TG is 3:1; however, the alcohol is added in a large **excess**, eg up to 6:1 (this varies) as its higher concentration in the reaction mixture favours a high equilibrium yield of biodiesel. Using the base catalysed process it is possible to achieve a biodiesel yield of 98%.

The reaction products, biodiesel and glycerol are essentially insoluble in one another hence once the reaction is complete they form **two separate layers**. Biodiesel is separated from the top layer while the denser glycerol forms a bottom layer. Most of the excess methanol, the base catalyst and any soap that may have formed remain in the glycerol layer with only small amounts in the biodiesel. The biodiesel is **washed** with warm water to remove any residual catalyst, methanol or soap it may contain. Finally the biodiesel is **dried** and ready for use in diesel/biodiesel blends or as pure biodiesel.

The glycerol layer is also treated to remove impurities and becomes a valuable co-product contributing significantly to the economics of this process. Any methanol recovered from the glycerol is recycled for use in the transesterification reaction.

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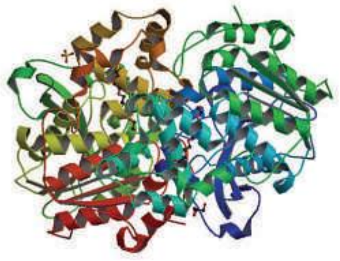
Figure 6 Lipase A from the yeast species candida antarctica.



Lipase enzymes from a variety of species, including candida antarctica, show great potential as catalysts for the transesterification of triglycerides in the production of biodiesel.

RCSB PDB (www.rcsb.org) PDB ID 3GUU.

15.8 Biodiesel: Lipase catalysed transesterification of TGs

Many alternative, potentially **greener** methods have been investigated as replacements for the traditional base catalysed transesterification of TGs. One such method replaces the traditional strong base catalyst (eg NaOH or KOH) with one of a group of **enzymes** (biological catalysts) known as **lipases**. (See Fig 6.) Lipases are naturally occurring enzymes found in the cellular material of almost all living things. Their normal biological role is to catalyse various reactions involving fats and oils. In biodiesel production, lipase can be used to catalyse the transesterification of fats and oils into biodiesel. Their use offers several **potential advantages** over traditional base catalysts. These include:

- An ability to operate at milder temperatures and milder pH.
- They tolerate feedstock high in FFAs so there is no the need for pre-treatment of FFAs.
- Lipase can simultaneously catalyse the transesterification of TGs and the esterification of FFAs into biodiesel. This simplifies the use of oils naturally high in FFAs.
- They do not cause side reactions, such as soap formation, that use up valuable reagents and complicate diesel separation.
- They simplify product purification and reduce the environmental problem of basic waste water disposal or treatment.
- They use significantly less energy as lower temperatures are involved and the products (biodiesel and glycerol) need less or no refining.

Despite these advantages there exists a number of **impediments** to the widespread use of lipase catalysed transesterification on an industrial scale. Firstly, compared to conventional base catalysts, lipase catalysts are **slower acting** and so a higher catalyst concentration is needed in order to achieve the faster reaction rates offered by traditional catalysts. Lipase catalysts are currently quite expensive and this impacts the **competitive economics** of using lipase instead of the cheaper traditional base catalysts like NaOH or KOH.

Furthermore, lipase recovery from within the final reaction mixture is difficult to achieve. Consequently fresh lipase must be used for each batch of biodiesel. This further adds to the cost of production. **Current research** in this area aims to find cheap and effective ways to recover the enzyme. One approach aims to find ways to bind the lipase catalyst onto a solid surface or other solid particles so that the **immobilised lipase** remains active while being easily retrieved for reuse at the end of the process.

Problems are also encountered if lipase is used in the presence of high concentrations of alcohol, especially methanol, or glycerol. Both of these reagents **inhibit** lipase and prevent its catalytic effect. This is especially problematic as glycerol is a product of transesterification and high methanol concentrations are typically used for maximising the equilibrium yield of biodiesel. Some possible solutions include the stepwise addition of alcohol to the reaction mixture or substituting methanol or ethanol in the transesterification step with different reagents like ethyl ethanoate. Research in the area of genetic modification of lipase could be the solution to developing methanol tolerant lipase catalysts.

Finding the optimum conditions for the industrial production of biodiesel by the lipase catalysed method is the subject of ongoing research. Importantly this method offers many potential advantages that encompass the principles of sustainability and green chemistry.

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15.9 The Haber process: Ammonia synthesis

Ammonia, NH_3 is a most important chemical raw material made industrially by the Haber process. In 2008 Australia produced 1.3 million tonnes of ammonia representing about 1% of total world production. Its major uses are as a feedstock for the production of other valuable substances. Fertiliser manufacture accounts for over 80% of ammonia consumption. Some of the materials produced from ammonia include:

- **fertilisers** like NH_4NO_3, $(NH_4)_2SO_4$, $(NH_4)_2HPO_4$ and urea $(NH_2)_2CO$
- **polymers** such as nylon and acrylic plastics
- **explosives** like trinitrotoluene (TNT), nitroglycerin, and NH_4NO_3
- **cleaning** agents for removing dirt and grease.

Ammonia is manufactured by the **Haber process** which utilises the equilibrium reaction of **nitrogen** with **hydrogen**:

$$N_2(g) \quad + \quad 3H_2(g) \quad \rightleftharpoons \qquad (g) \qquad \Delta H = \ -92kJ$$

While this reaction has a reasonable equilibrium **yield** of ammonia at room temperature and pressure, the **rate** of attainment of equilibrium is extremely low. Higher temperatures will increase the rate of reaction; however, this also reduces the equilibrium yield of NH_3. High pressure favours both a high rate of reaction and a high equilibrium yield of NH_3. However, using high pressure significantly increases construction and operating **cost** of the ammonia plant. For this reason excessively high pressures are uneconomic. As a consequence of these conflicting problems a **compromise** in conditions must be used in order to produce ammonia economically. (See Fig 8 and Table 2.)

Figure 7 Located at Karratha on the Burrup Peninsula in Western Australia is the world's single largest ammonia production plant. The plant produces 850,000 tonnes of ammonia annually.

An abundance of natural gas from the nearby North West Shelf was an important consideration in its location at Karratha as natural gas is used to produce the hydrogen required in the synthesis of ammonia. Image courtesy of Yara Pilbara Fertilisers Pty Ltd.

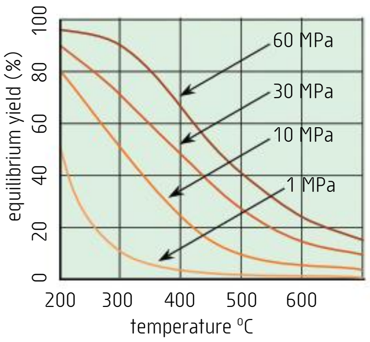

Figure 8 These four **equilibrium yield curves** show how the yield of ammonia reduces with increasing temperature and increases with greater pressure. The Haber process uses a compromise of moderate temperatures and high pressure so that a reasonable **rate** of attainment of equilibrium and equilibrium **yield** can both be achieved.

The economic production of ammonia is achieved by choosing reaction conditions that **maximise** the **rate** of attainment of equilibrium while still allowing a satisfactory equilibrium **yield** of ammonia without incurring excessive **cost**. It wasn't until 1909 that German chemist Fritz Haber demonstrated a set of conditions that allowed ammonia to be economically produced by this reaction. Today the actual process is carried out using a 3:1 molar mixture of $H_2(g)$ and $N_2(g)$ at a temperature of around 350-550 °C and a pressure of 15-35 MPa. A catalyst consisting of iron-iron oxide fused with MgO, Al_2O_3 and SiO_2 is also used. With these conditions a reasonable rate can be maintained with a yield of around 15-30% ammonia (depending upon the actual conditions used). Recycling unused $N_2(g)$ and $H_2(g)$ ensures an almost complete conversion of these gases to $NH_3(g)$. (See Fig 9.)

Figure 9 Stages in the Haber process for the synthesis of ammonia.

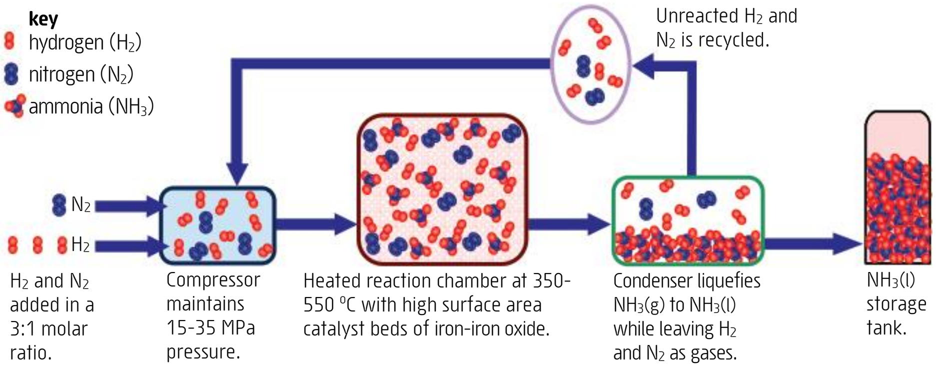

Table 2 Haber process: Applying the principles of reaction rate and equilibrium to maximise the rate of formation and yield of ammonia.

Condition used	Effect on rate	An explanation in terms of the Collision theory	Effect on yield	Using Le Chatelier's principle to account for the yield effects	Compromise
Moderate temperature 350 to 550 °C	increases rate of reaction	Reacting particles have a higher average kinetic energy, thus a greater percentage of collisions are successful (have energy greater than activation energy).	decreases yield, ie favours reactants	The equilibrium system opposes higher temperatures by absorbing heat, ie the endothermic reaction is favoured, causing the decomposition of $NH_3(g)$ to $N_2(g)$ and $H_2(g)$.	A moderate temperature is used so that a reasonable rate can be achieved without excessively decreasing equilibrium yield.
High pressure 15 to 35 MPa (≈ 150 to 350 atm)	increases rate of reaction	Higher pressure causes a higher concentration of reacting particles and this results in a greater rate of collisions.	increases yield, ie favours products	The equilibrium system opposes higher pressure by favouring the formation of fewer gas molecules, ie the formation of $NH_3(g)$.	High pressure favours high rate and equilibrium yield. However, cost limits the use of excessively high pressure.
Catalyst iron-iron oxide fused with MgO, Al_2O_3 and SiO_2	increases rate of reaction	The catalyst provides an alternative reaction path of lower activation energy, thus a greater percentage of collisions have energy greater than activation energy.	no effect on yield	Catalysts increase the rate of forward and reverse reaction equally, thus neither reaction is favoured.	The catalyst has no effect on the equilibrium yield. Its use significantly increases rate and thus lowers costs of production.

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Attempt Set 21 # 14 and 15.

15.10 Contact process: Sulfuric acid synthesis

Sulfuric acid is one of the world's most widely manufactured chemicals. Over half of world production is consumed in the manufacture of **phosphate fertilisers**. These fertilisers are essential in helping modern farms achieve high agricultural yields. Sulfuric acid is also an important raw material used in the manufacture of **detergents**, **explosives**, **other acids**, **polymers** and **pharmaceuticals**. It is also used in **metal extraction**, as a **catalyst** and as an **electrolyte** in the lead acid battery. Not surprisingly, its level of production is considered a strong indicator of a nation's industrial activity.

Today sulfuric acid synthesis is almost exclusively by the **Contact process**. This process uses the raw materials **sulfur**, **water** and **oxygen** (air), in a **reaction sequence** involving up to five separate chemical reactions. Three stages can be identified in the Contact process; production of **sulfur dioxide**, conversion of sulfur dioxide to **sulfur trioxide** and finally the conversion of sulfur trioxide to **sulfuric acid**.

Stage 1: Molten sulfur is burnt in dry air at around 1000 °C. At this stage only $SO_2(g)$ is formed, ie $SO_3(g)$ does not form even though excess oxygen is present.

$S(l) + O_2(g) \rightarrow SO_2(g) \quad \Delta H = -297\ kJ$............①

This highly exothermic reaction readily proceeds to completion and produces a considerable amount of heat energy. Typically the energy released in this reaction is used to generate steam used for operating a small onsite power station. Often sufficient electricity may be generated to satisfy the needs of the entire production facility. Using otherwise waste energy like this contributes to the sustainability (green principles) of sulfuric acid manufacture.

Many modern sulfuric acid plants are now found integrated alongside **metal sulfide ore smelters**. In this way, instead of burning sulfur to produce $SO_2(g)$, the sulfuric acid plant can use waste $SO_2(g)$ produced from the metal sulfide smelting process. Otherwise, if $SO_2(g)$ is released into the environment it causes acid rain whilst human exposure causes respiratory problems as well as irritation to the eyes, nose and throat. Utilising an otherwise toxic waste to make a valuable product is consistent with the principles of green chemistry.

Stage 2: Sulfur dioxide is converted to sulfur trioxide according to the following equilibrium reaction.

$2SO_2(g) + O_2(g) \rightleftharpoons \quad (g) \quad \Delta H = -198\ kJ$................②

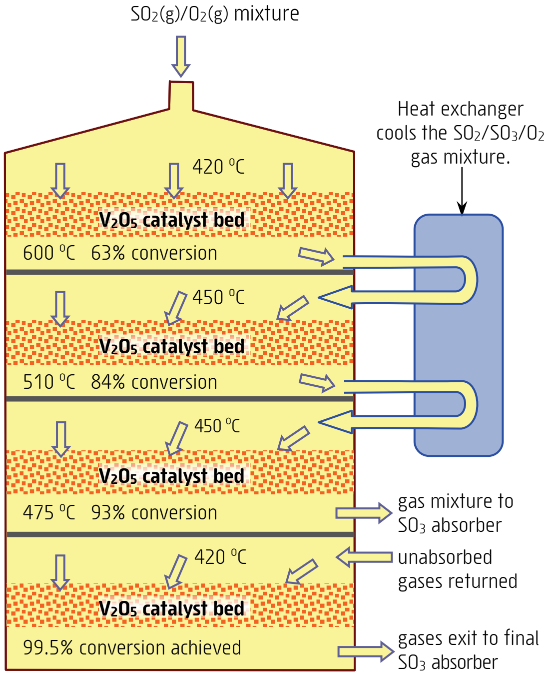
The formation of $SO_3(g)$ from $SO_2(g)$ is problematic as it is an **equilibrium reaction**. A **high yield** of $SO_3(g)$ is favoured by low temperature and high pressure. However, a low temperature slows the **reaction rate** and using high pressures introduces **excessive cost** into the manufacturing process.

In practice, a compromise temperature of around 450 °C is used along with a catalyst of vanadium(V) oxide, **V_2O_5**. These conditions give a satisfactory rate without excessively compromising yield.

As high pressure systems are expensive to maintain it is sufficient to use a pressure of 1-2 atmospheres. Maintaining a suitable excess of air (ie O_2) within the system, typically **1 mole O_2:1 mole SO_2** (ie around twice the stoichiometric requirement of O_2) also helps increase the equilibrium yield of $SO_3(g)$ from $SO_2(g)$.

The overall yield of SO_3 is further increased by extracting the product $SO_3(g)$ from the reaction mixture and recycling the unreacted $SO_2(g)$. Doing this several times gives an ultimate $SO_3(g)$ yield close to 100%. (See Fig 10.) Also as the formation of SO_3 is exothermic (see above) it is necessary to use heat exchangers to extract heat from the gas mixture thus preventing its temperature from rising excessively.

Figure 10 A four stage **catalytic converter** tower for the conversion of $SO_2(g)$ to $SO_3(g)$.



Stage 3: The conversion of sulfur trioxide and water to sulfuric acid is achieved **indirectly** by initially absorbing $SO_3(g)$ into $H_2SO_4(l)$ to produce an oily compound called oleum. Addition of water to oleum then produces 98% (18 $molL^{-}$ $_2SO_4(l)$.

producing oleum: $H_2SO_4(l) + SO_3(g) \rightarrow H_2S_2O_7(l)$ .... ③

adding water: $H_2O(l) + H_2S_2O_7(l) \rightarrow 2H_2SO_4(l)$ .... ④

overall $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(l)$.................... ⑤

This indirect method of adding water to $SO_3(g)$ is used as the direct addition of water to $SO_3(g)$ only results in a low yield and a difficult to manage mist of $H_2SO_4(l)$ particles.

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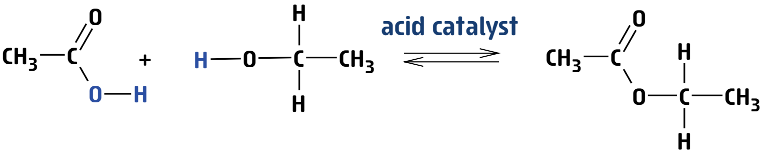
Attempt Set 21 # 16 and 17.

15.11 Manufacture of ethyl ethanoate

The ester ethyl ethanoate (ethyl acetate) is a volatile liquid with a strong fruity odour. It is naturally produced by many ripening fruits and is largely responsible for the distinctive odour of ripe bananas and pineapples. Commercially it is a very useful **solvent** and is considered one of the **least toxic** of all the industrial organic solvents. (See Fig 11.)

Industrial production of ethyl ethanoate is largely by the **esterification** of ethanoic acid with ethanol in the presence of an acid catalyst (eg sulfuric acid), known as the Fischer esterification reaction.

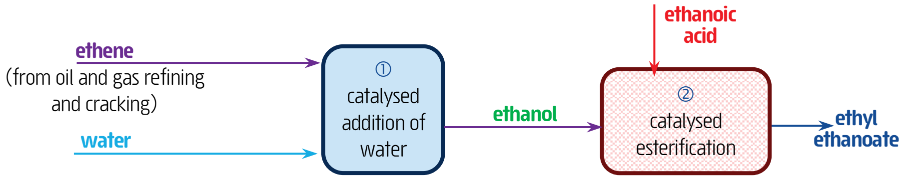
Figure 11 Ethyl ethanoate is used as a solvent in **nail polish remover**, adhesives, varnishes and printing inks, in the extraction and purification of antibiotics, the manufacture of polyester and BOPP (biaxially oriented polypropylene) film and in the preparation of synthetic fruit essences, flavours and perfumes.



This is a readily reversible process and at equilibrium there exist significant concentrations of all four liquid reagents in the **homogeneous** reaction mixture, eg 65% yield at 298 K.

Of the two reagents ethanoic acid is the more expensive so by using an excess of the cheaper reagent, ethanol, the yield of ethyl ethanoate can be increased while maximising the consumption of ethanoic acid. Also, by continually removing the products as they form it is possible to achieve a 95% conversion of reagents into products.

The flow diagram below shows how the production of ethyl ethanoate can be part of a larger synthesis route that includes the synthesis of ethanol from ethene. (See 15.5.)



Acid catalysed addition: $CH_2CH_2(g) + H_2O(g) \rightleftharpoons CH_3CH_2OH(g)$ .... ①

$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l)$ ... ②

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15.12 Quantities in chemical synthesis

An application of the principles of **stoichiometry** (Chapter 9) are central to the successful synthesis of any chemical substance. Generally the amounts used in a synthesis will be the stoichiometric amounts dictated by the balanced equation. This ensures there will be no wastage of either reagent. In some situations, such as those involving equilibrium reactions, it may be desirable to use an excess of a cheaper reagent in order to increase the **yield** of the desired product by maximising consumption of the more expensive reagent. (See border note.)

While industrial chemists generally try to maximise yield it may not always be possible or practical to achieve 100% yield, especially when working with equilibrium reactions. In such cases the yield might be low; however, by separating the unreacted reagents and recycling these through the chemical plant it is often possible to achieve close to 100% conversion of reagents into the desired product.

Factors that can lead to a reduced yield are:

- Loss of reagent due to unwanted side reactions that unnecessarily consume reagents.
- Physical loss of product, eg due to the inability to completely separate or purify the product from the final reaction mixture.
- Equilibrium reactions that do not go to completion.
- Presence of impurities in the reagents meaning the amount of reagent added is less than the amount measured.

The **theoretical yield** (maximum yield) of a chemical reaction gives the amount of product that would be formed when the limiting reagent is fully consumed. The **actual yield** of a given product is typically less than the theoretical yield.

The comparison of actual yield to the theoretical gives the **percentage yield** of a reaction.

$$\%\ \text{yield} = \frac{\text{actual yield x 100}}{\text{theoretical yield}}$$

See 9.8 page 98-99.

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Complete Set 21.

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Set 21 Industrial synthesis

1. Use the list of terms to **complete** the following passage about **chemical synthesis**.

   Useful chemical compounds like fertilisers, pharmaceuticals, plastics and dyes can be industrially (a) __________ in chemical plants. The manufacture or synthesis of these compounds may involve a single (b) __________ or it may require the construction of a reaction (c) __________ that involves (d) __________ chemical reactions. In either case the industrial chemist will choose reaction conditions that take into account the principles of reaction (e) __________ and chemical (f) __________. Conditions are chosen to maximise (g) __________ and (h) __________ while minimising (i) __________. Sometimes this may require a (j) __________ in conditions used.

   Another very important consideration in the development of new methods of chemical synthesis and for the improvement of established processes is the application of the principles of (k) __________ chemistry. The general goals of green chemistry are to:

   - Eliminate the use of or environmental release of (l) __________ substances.
   - Design processes that use (m) __________ resources and minimise (n) __________ use.
   - Use processes that are in balance with the Earth's (o) __________ processes.
   - Maximise the (p) __________ economy of industrial reactions.

   A comprehensive list of the (q) __________ principles of green chemistry are used by industrial chemists and chemical engineers as a guide in the design of 'greener' methods of chemical synthesis.

green
yield
chemical reaction
renewable
equilibrium
natural
compromise
atom
sequence
synthesised
reaction rate
twelve
cost
toxic
energy
several
rate

2. One of the twelve principles of **green chemistry** aims to achieve **maximum atom economy** in a synthesis process. This means that in a given chemical reaction as much as possible of the reactants (mass) should be incorporated into the desired product. Atom economy can expressed as a percentage of the mass of reactants that are incorporated in the desired product. (See border note.) Use this idea to find the atom economy (as a percentage) for each of the two industrial methods used to synthesise ethanol and hence compare the two processes in terms of their atom economy.

   ethanol synthesis by fermentation: $C_6H_{12}O_6(aq) \rightarrow 2C_2H_5OH(aq) + 2CO_2(g)$

   ethanol synthesis by addition: $CH_2CH_2(g) + H_2O(g) \rightleftharpoons C_2H_5OH(g)$

Calculating atom economy.
Example: Determine the atom economy for the synthesis of the nitrogen fertiliser **urea**, $\mathbf{(NH_2)_2CO}$ from NH_3 and CO.

$$2NH_3 + CO_2 \rightarrow (NH_2)_2CO + H_2O$$

$$\%\text{atom economy} = \frac{m[\text{desired product}] \times 100}{m[\text{reactants}]}$$

$$= \frac{m[(NH_2)_2CO] \times 100}{m[NH_3] + m[CO_2]}$$

$$= \frac{60.062 \times 100}{2 \times (17.034) + 12.01 + 2 \times 16.00}$$

$$= 76.93\%$$

3. The use of **catalysts**, especially **enzymes** wherever possible in chemical synthesis, is another important principle of green chemistry. What are the advantages of catalysts in general and why are enzymes preferred?

4. Biofuels are said to be a **renewable** energy source whose combustion **does not** contribute to raising the Earth's atmospheric carbon dioxide concentration. Give **two examples** of biofuels and **elaborate** on these two claims.

5. A **bioethanol** production facility at Sarina in northern Queensland produces around 60 million litres of ethanol annually. This is achieved by the **hydrolysis** and **fermentation** of waste sugars present in molasses from sugar refining. Two chemical steps in the production process are the hydrolysis of sucrose to glucose and fructose followed by the fermentation of the glucose/fructose mixture to ethanol. These reactions are **exothermic** and the reaction mixtures must be kept **cool** (≈37 °C) through the use of heat exchangers.

   a. Write equations for the **hydrolysis** and **fermentation** reactions.

   b. Both of these reactions can be extremely **slow**. How is their **rate increased** in the fermentation process?

   c. Normally a high temperature is an advantage in chemical synthesis as this increases reaction rate. **Explain** why the fermentation process uses a heat exchange process to keep the exothermic fermentation reaction cool, ie ≈37 °C.

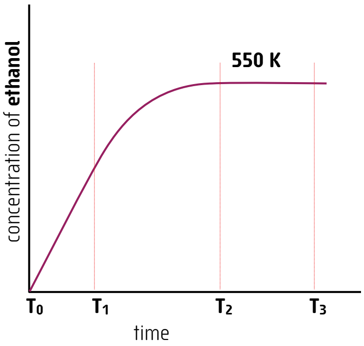
Continued next page.

d. Yeast used in the fermentation process are living organisms. These normally obtain the energy they require from the **aerobic respiration** of sugars. Write a chemical equation for the aerobic respiration of sugar and explain why it can be an **undesirable side reaction** in the fermentation process. What conditions are used to prevent aerobic respiration?

e. Fermentation typically **stops** once the ethanol concentration reaches a maximum of ≈**14%**. Why are higher concentrations of ethanol not achievable solely by fermentation?

6. While the ethanol production plant at Sarina in northern Queensland uses **molasses** from sugar refining, a similar plant at Dalby in southern Queensland uses **red sorghum** while one in Nowra (NSW) uses **waste starch** from wheat processing. What do these feedstock have in common and why are different ones used at different production facilities around Australia?

Figure 12 Change in ethanol concentration over time for the addition of water to ethene at 550 K. All reagents are in the **gas** phase.



7. Another method for the industrial production of **ethanol** involves the acid catalysed addition of water to ethene as shown here.

$$CH_2CH_2(g) + H_2O(g) \rightleftharpoons CH_3CH_2OH(g) \qquad \Delta H = -45\ kJ$$

The graph at left (Fig 12) shows the change in concentration of ethanol over time as equimolar amounts of ethene and water are reacted in a sealed flask at **550 K**. Initially there is no ethanol present in the reaction mixture.

a. **What** is the significance, in terms of **reaction rates**, of the graph's steep slope between T_0 and T_1?

b. Why does the graph remain level from T_2 to T_3? **Explain** in terms of **reaction rates** and **equilibrium**.

c. **Sketch** similar curves using the same set of axes at left for the same reaction mixture placed into a sealed flask:

(i) at the **higher** temperature of 650 K.
(ii) at 550 K but in the presence of a **catalyst**.

8. The following questions refer to the equation in Question 7 for the industrial manufacture of ethanol by the **acid catalysed addition** of water to ethene.

a. The industrial synthesis of ethanol by this reaction is conducted at a pressure of around 60-70 atm. How does this choice of pressure affect the **rate** of attainment of equilibrium. Use your knowledge of **collision theory** to justify your answer.

b. Write the **equilibrium constant expression** (K_c) for this reaction.

c. Refer to your equilibrium constant expression to help **justify** why a higher total pressure must increase the equilibrium **yield** of ethanol.

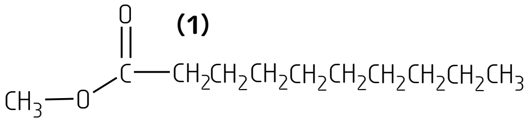
d. **Explain** why the temperature used for this process is said to be a **compromise**.

e. What other reaction condition other than temperature or pressure is used to increase the rate of attainment of this equilibrium reaction.

9. The manufacture of ethanol by **fermentation** is more consistent with the principles of **green chemistry** than is its production by the acid catalysed **addition of water to ethene**. **Support** this statement with reference to points such as energy use, renewable feedstock, production or use of toxic substances, inherent safety risks due to production method and atom economy.

10. Examine the structures shown here and answer the questions that follow.

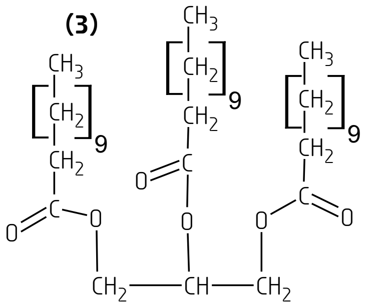
(1)



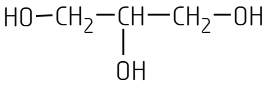
$CH_3-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

(2)

(3)

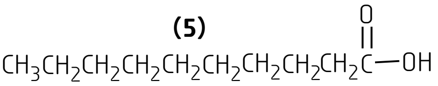


(4)



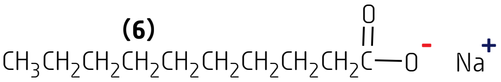
$HO-CH_2-\underset{\underset{\displaystyle OH}{|}}{CH}-CH_2-OH$

(5)



$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}-OH$

(6)



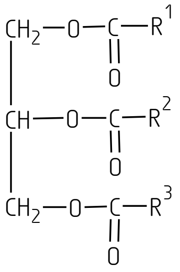
$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}-O^- \quad Na^+$

Which structure or structures drawn above could represent the following substances.

a. animal fat	b. a free fatty acid	c. a triglyceride	d. biodiesel
e. glycerol	f. a carboxylic acid	g. a soap	h. an enzyme

11. Biodiesel is mainly produced by the **base catalysed transesterification** of various fats and oils.
    a. Write an **equation** for the transesterification process and describe the reaction **conditions** used. Use methanol and tristearin or a general TG formula (Fig 13) in your equation.
    b. The alcohol used for transesterification is typically **methanol** or **ethanol**. It is common to use an **excess** of alcohol in this equilibrium reaction. What is the advantage of doing this?
    c. How is biodiesel obtained from the final reaction mixture and what further treatment of the biodiesel may be required?
    d. What other potentially valuable products are obtained from the final mixture?

Figure 13 For convenience, the general formula shown here can be used to represent a triglyceride, TG. **R^1**, **R^2** and **R^3** represent various carbon chains.



12. The production of biodiesel by **base catalysed transesterification** is a fairly energy intensive process and also prone to unwanted side reactions. In particular, the presence of water or free fatty acids (FFAs) in the fat or oil is a problem. These must be removed prior to transesterification otherwise they cause various undesirable reactions.
    a. What **unwanted products** may form if FFAs are present during transesterification and why is their formation a **problem**?
    b. Fats and oils used in transesterification often contain some **free fatty acids**, FFAs (ie free long chain carboxylic acids). Write an equation for the reaction of a 12 carbon FFA (lauric acid, ie dodecanoic acid) with sodium hydroxide and **justify** the statement '**soap** formation can be an unwanted side reaction in the transesterification of fats and oils with a high FFA content'.
    c. The presence of **water** during the transesterification process can also cause NaOH to **hydrolyse** any esters or triglycerides present. Write an **equation** showing the hydrolysis (saponification, see 12.5) of a **diesel methyl ester**. You may use a general notation for your methyl ester.

13. Researchers are exploring ways to commercially produce biodiesel by transesterification using **lipase** instead of a base like NaOH or KOH. What is lipase and what are the **expected benefits** of producing biodiesel this way?

14. The synthesis of ammonia by the **Haber process** involves the following equilibrium.

$N_2(g) + 3H_2(g) \rightleftharpoons \qquad (g) + 92\ kJ$

In this industrial process there needs to be a compromise of conditions used. What are the **conditions used** in the Haber process and how do these conditions affect equilibrium **yield** and **rate** of attainment of equilibrium? In your answer you should refer to any **compromise** in conditions used.

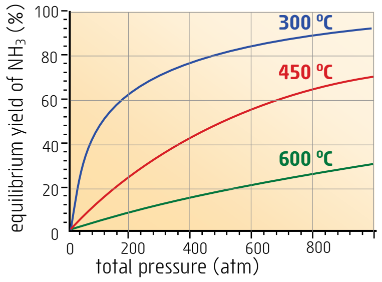


Figure 14 Variation of equilibrium yield of NH_3 with pressure at various temperatures.

15. The graphical curves in Fig 14 show how the equilibrium yield of ammonia in the **Haber process** changes with pressure at a variety of temperatures.

a. **Determine** the equilibrium yield of ammonia at: (i) 300 °C and 600 atm.
(ii) 600 °C and 600 atm.

b. **Account** for the lower **yield** at the **higher temperature**. In your answer you should refer to changes in the **equilibrium constant** or to the effect of temperature changes on the forward and reverse reaction **rates**.

c. A particular ammonia plant synthesises ammonia by the Haber process using conditions of 200 atm and 450 °C. What is the equilibrium **yield** at these conditions? **How** can the plant achieve close to 100% conversion of nitrogen and hydrogen into ammonia using these conditions?

16. The synthesis of sulfuric acid by the **Contact process** involves a **sequence** of four chemical reactions. Write an equation for each of the four reactions and add these to show the overall reaction occurring in the Contact process. Also state which of these reactions readily go to completion and which is (or are) an equilibrium reaction(s).

17. In 2010 around 200 million tonnes of sulfuric acid was produced worldwide, equivalent to around 30 kg per person. One step in the chemical synthesis of sulfuric acid by the **Contact process** is an equilibrium reaction involving the conversion of sulfur dioxide and oxygen to sulfur trioxide.

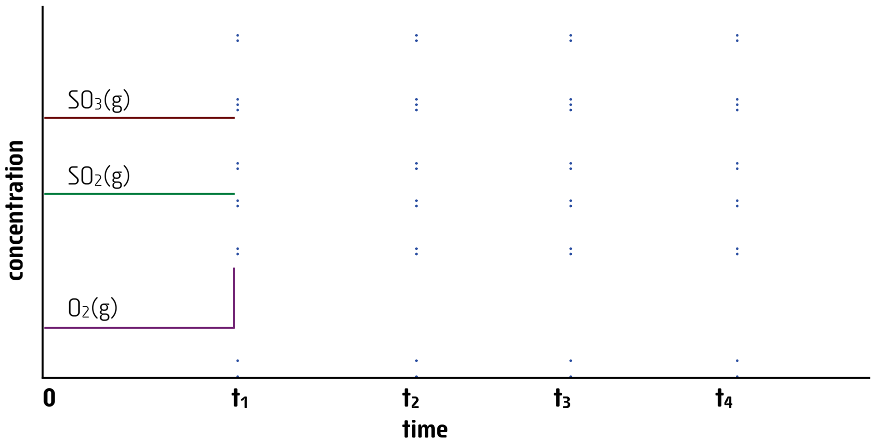
$2SO_2(g) + O_2(g) \rightleftharpoons \qquad (g) \quad \Delta H = -198\ kJ$

a. The graph below shows the concentration of the three gases SO_2, O_2 and SO_3 in an equilibrium mixture. At time **t_1** some **$O_2(g)$** is injected into the system. This is also shown on the graph. Equilibrium is re-established in the gas mixture at time **t_2**. Complete the graph up to time **t_3** to show how the gas concentrations change.

b. The system continues at equilibrium from **t_2** until time **t_3**. At time **t_3** the **pressure** of the system is **halved** by **doubling** its **volume**. Show how the concentration of each of the gases changes until equilibrium is once again established at time **t_4**.

c. What conditions of **temperature** and **pressure** would be most favourable for attaining a **high equilibrium yield** of $SO_3(g)$? Are there any **problems** with the use of these conditions? Consider reaction **rate** and **economic** issues. Explain.

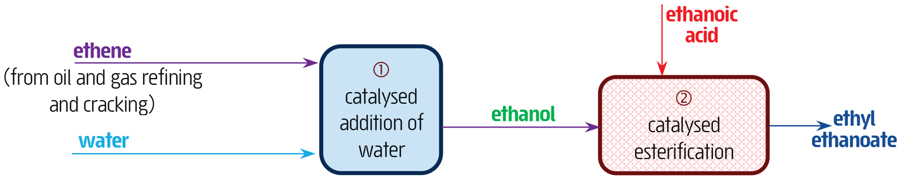
d. What are the actual **conditions used** in the Contact process for this reaction? How do these conditions affect equilibrium **yield** and **rate** of attainment of equilibrium? In your answer refer to any **compromise** in conditions used.



18. The **alcohol** (ethanol) present in beer is a product of the **anaerobic** fermentation of sugars like glucose by yeast. A typical full strength beer will contain 4.8% alcohol by volume. This is equivalent to an ethanol concentration of 38 g L^{-1}.
    a. Determine the **mass** of alcohol present in a 375 mL can of full strength beer.
    b. Write an **equation** for the fermentation of glucose ($C_6H_{12}O_6$) and determine the **minimum mass** of glucose that must be present in order to generate the required amount of ethanol for a single can of beer.
    c. What **volume** of **carbon dioxide gas** measured at 273 K and 100 kPa (ie at STP) would be produced along with the ethanol?

19. **Ethyl ethanoate** is a valuable solvent and a feedstock used in the manufacture of other compounds. It can be produced by the **Fischer** esterification process ②
    ethanol used to produce ethyl ethanoate can itself be manufactured by the **acid catalysed addition of water to ethene** ①

    shown here.



Acid catalysed addition: $CH_2CH_2(g) + H_2O(g) \rightleftharpoons CH_3CH_2OH(g)$........................... ①

$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l)$ .. ②

    a. In a one hour period a particular plant puts through its reactor 1255 kg of steam mixed with 2541 kg of ethene. One of these reagents is present in excess. Determine the **limiting reagent**.
    b. What is the **theoretical** (maximum) **mass** of ethanol that can be produced from this combination of reagents?
    c. The **actual yield** of ethanol on the first run of these reagents through the reactor is 167.8 kg of ethanol. What is the first run **percentage yield** of ethanol?
    d. By separating ethanol from the reaction mixture and **recycling** the **unreacted ethene gas** with fresh steam it is possible to achieve a 96% conversion of the original 2541 kg of ethene to ethanol.
        (i) Despite the efforts of recycling the unreacted ethene, the final ethanol yield is still less than 100%. **Describe three possible reasons** why a 100% yield cannot be achieved.
        (ii) What **maximum mass** of ethyl ethanoate can be expected from this amount of ethanol when it reacts with excess ethanoic acid if the Fischer esterification reaction has a 94% yield?

20. The majority of **biodiesel** in use today is produced by the **base catalysed transesterification** of various fats and oils. Prior to transesterification a 2550 kg batch of oil is analysed for its free fatty acid content. It is determined to contain 8.45% by mass **FFAs** and thus requires pre-treatment to convert the FFAs to methyl esters. This is achieved using excess methanol, CH_3OH and an acid catalyst like H_2SO_4. You may assume the average molar mass of the FFAs is found to be 200.3 g mol^{-1}.
    a. Use a general formula of an **FFA** to write a **balanced equation** for its acid catalysed reaction with methanol.
    b. What **minimum mass** of methanol should be used to treat the FFAs?
    c. Both of the **products** of this reaction are significant in the biodiesel manufacturing process. In this context what is the **significance** of each of the **reaction products**?

21. An appropriately prepared batch of **palm oil** has been dried and is free of any FFAs. The batch of oil has a mass of 4.855 tonnes and will be treated with **ethanol**, C_2H_5OH and **KOH** to produce biodiesel. You may assume the average molar mass of the triglyceride molecules in the palm oil to be 833 g mol^{-1}.

    a. Use a **general formula** for the triglyceride molecule to write a **balanced equation** for the formation of biodiesel.

    b. Instead of using the stoichiometric ratio of **3 mol C_2H_5OH : 1 mol triglyceride** it is decided to use a molar ratio of **6 mol C_2H_5OH : 1 mol triglyceride** thus using a large excess of ethanol. What **mass** of **ethanol** should be used with the batch of palm oil?

    c. The reaction **yield** is 97% for the conversion of the triglycerides to biodiesel. Determine the **mass** of **biodiesel** obtained assuming the average molar mass of the biodiesel molecules to be 293 g mol^{-1}.

22. One step in the manufacture of **sulfuric acid** by the **Contact process** is the combustion of sulfur in dry air to produce sulfur dioxide, SO_2. The reaction is conducted in a furnace where molten sulfur is sprayed into the furnace and mixed with dry air at a temperature of around 1000 °C.

    a. Write an **equation** for the combustion process.

    b. Every minute the furnace receives 138 kg of molten sulfur and 357 kL of air measured at 157 kPa and 45.0 °C. Remember, air contains only 20.95% oxygen gas by volume, ie 1.00 L of air contains 0.2095 L of oxygen. Is there **sufficient air** for the complete combustion of sulfur in the furnace? Show your working.

    c. Given the combustion reaction **yield** is 99.5% determine the **volume** of sulfur dioxide produced **each minute**. Assume the gas is measured at **STP**.

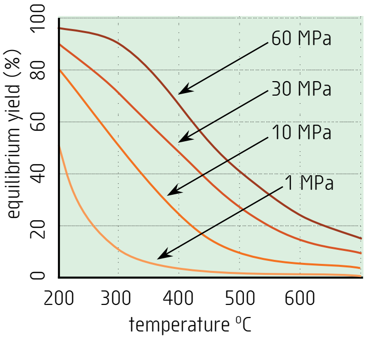


Figure 15 Equilibrium yield curves for the Haber process.

23. **Ammonia** manufacture by the **Haber process** involves the direct reaction of gaseous hydrogen and nitrogen to produce ammonia. The yield curve at left shows the equilibrium yield of ammonia at various conditions of temperature and pressure. In a particular plant, hydrogen and nitrogen are pumped into a catalytic reaction vessel at a pressure of 30.0 MPa and a temperature of 450.0 °C. The flow rates of the gases into the heated reaction chamber are 9.55 kL min^{-1} for nitrogen and 28.50 kL min^{-1} for hydrogen.

    a. Write an **equation** for the Haber process.

    b. Determine the **limiting reagent** for the gaseous reaction mixture entering the heated reaction chamber. You may assume the gases both enter the chamber at 30.0 MPa and a temperature of 450 °C.

    c. Use the graph in Fig 15 to determine the **equilibrium yield** of ammonia at the given conditions.

    d. Determine the **mass** of **ammonia** that forms each **minute** under the given conditions. You may assume the reactants reach equilibrium in this time.

    e. The **ultimate** equilibrium yield of the Haber process is close to 100%. **How** is this achieved considering the low equilibrium yield indicated in the yield curve at left?

A

- **Relative atomic masses** used in all calculations are consistent with data from the periodic table on the back inside cover.
- **Numerical answers** are rounded to the appropriate number of **significant figures** using the rules outlined in Appendix 1.
- Where **partial working** has been evaluated, answers are given with the appropriate number of significant figures, however, the complete number is carried forward into later parts of a calculation. It is recommended that you also **carry full numerical figures** until completion of a calculation.
- Answers are often accompanied by **extra information** that may be helpful to assist understanding but does not form part of the answer.

Set 1 Review: Reaction rate and energy change

1. The system consists of the reactants and products, ie the copper coil, silver nitrate solution, the deposit of pure silver and resulting solution of copper nitrate. The surroundings include the test tube, surrounding air and any other materials outside of the system itself.

2. a. The products have lower enthalpy than the reactants.

b. During this chemical change the temperature of the system, ie the reaction mixture, rises. This happens when the reaction releases heat. Heat is produced as the amount of stored chemical potential energy in the products [Ag(s) and $CuSO_4$(aq)] is less than that in the reactants [Cu(s) and $AgNO_3$(aq)]. As energy must be conserved, the lost chemical potential energy is balanced by an increase in particle kinetic energy, ie temperature rises. As the system is now hotter than its surroundings heat now flows out of the system into the surroundings. The loss of heat from the reacting system means its enthalpy (total energy) decreases.

c. Energy must always be conserved and since energy is released by the system (surroundings are heated) it follows that the products of the reaction must have less potential energy than the reactants. (The difference being transferred as heat to the surroundings.) A system loses energy when stronger bonds are formed as stronger bonds correspond to a lower potential energy. Thus it follows the products must have stronger bonds than the reactants.

3. a. Exothermic. The temperature of the system rises as the reaction releases 572 kJ of heat for every two moles of H_2(g) consumed. The heat released means particle kinetic energy increases which is why the temperature rises.

b. Exothermic. The temperature of the system rises as for every mole of $C_6H_{12}O_6$ consumed the reaction converts 2870 kJ of chemical potential energy (bond energy) into heat. The heat raises the temperature of the reaction mixture and is ultimately lost to the surroundings thus causing the enthalpy of the chemical system to decrease.

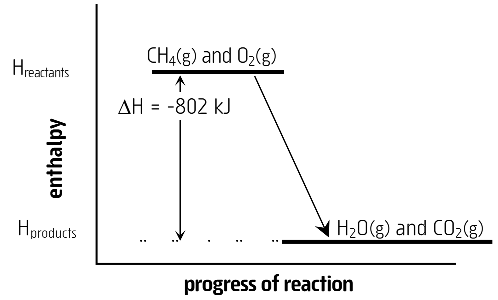
c. Endothermic. The temperature of the system initially falls as for every mole of H_2O(s) that melts the reaction converts 6.0 kJ of 'heat' (particle kinetic energy) within the system into enthalpy in the form of increased bond energy. However, as the system is now colder than the surroundings, heat will flow into it until it returns to the surrounding temperature.

d. Endothermic. The temperature of the system falls as for every mole of C_2H_5OH(l) that evaporates the reaction converts 43 kJ of heat from within the system into enthalpy in the form of increased bond energy. The loss of heat from within the system means particle kinetic energy decreases which is why its temperature falls.

4. a. This reaction causes a temperature rise. This happens when enthalpy decreases and the reaction releases an equivalent amount of heat to the surroundings. Thus the reaction is exothermic.

b. $CH_4(g) + 2O_2(g) \rightarrow 2H_2O(g) + CO_2(g)$

c. $CH_4(g) + 2O_2(g) \rightarrow 2H_2O(g) + CO_2(g) + 802\ kJ$



d. $CH_4(g) + 2O_2(g) \rightarrow 2H_2O(g) + CO_2(g)$ $\Delta H = -802$ kJ

As this reaction is exothermic (heat produced) then enthalpy must be lost. Thus ΔH has a negative value to signify this. [Remember: $\Delta H = H_{products} - H_{reactants}$]

5. a. molecules
b. randomly
c. collide
d. electron clouds
e. repel
f. kinetic energy
g. activation energy
h. orientation
i. activated complex
j. breaking
k. forming
l. decompose
m. reactants
n. hydrogen bromide

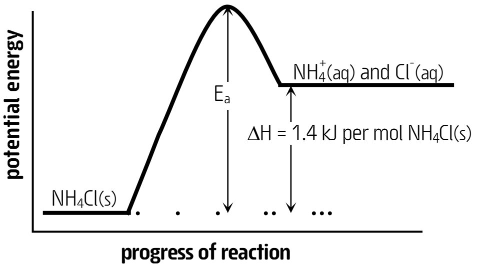
6. a. Endothermic. This reaction causes temperature to fall. This happens when a reaction converts heat from within the reacting system into enthalpy in the form of increased bond energy. Heat then flows into the system from the warmer surroundings.

b. $NH_4Cl(s) \rightarrow NH_4^+(aq) + Cl^-(aq)$

c. $NH_4Cl(s) + 1.4\text{ kJ} \rightarrow NH_4^+(aq) + Cl^-(aq)$

d. $NH_4Cl(s) \rightarrow NH_4^+(aq) + Cl^-(aq)$ $\Delta H = 1.4$ kJ

e.

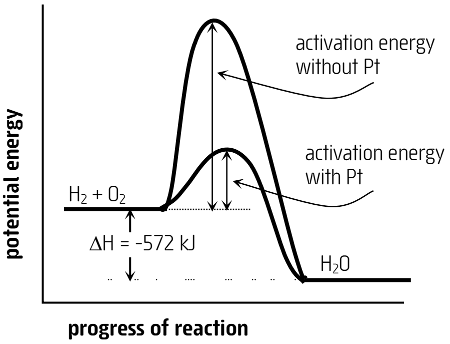


7. The initial rate of reaction at ① depends upon the concentration of HCl (2.5 mol L^{-1}), the temperature (19 °C) and the surface area of the single piece of $CaCO_3$. As the reaction is exothermic it causes a temperature rise in the reaction mixture resulting in the increased rate observed early in the reaction at ②. Towards the end of the reaction at ③ very little of the $CaCO_3$ remains and so its surface area is significantly reduced. This would have the effect of reducing the rate of reaction. Also as the reaction progresses the consumption of HCl causes its concentration to decrease. This would also have the effect of gradually reducing the reaction rate. Thus towards the end of the reaction at ③ the reduced HCl concentration and reduced surface area of the piece of $CaCO_3$, have the effect of decreasing the rate of reaction despite the higher temperature.

8. a. In the presence of platinum, Pt the rate of reaction of H_2 with O_2 increased. Also the Pt appeared not to be consumed. ('No evidence of chemical change.') This can happen if Pt is acting as a catalyst. A catalyst allows a reaction to occur by a different pathway of lower activation energy without the catalyst being consumed*****. Thus with Pt present, a greater percentage of collisions between H_2 and O_2 have collision energy ≥ activation energy and are successful in forming products. [*****Actually, the catalyst is consumed in one step of the reaction, however, an equal amount of it is produced in another so that overall it is not consumed.]

[Note: The enthalpy change for the reaction as written is $\Delta H = -572$ kJ. Alternatively it may be given as $\Delta H = -286\text{ kJ mol}^{-1}(H_2O)$.]

b.



c. i. Lightning will cause a significant rise in temperature of any H_2 and O_2 in its immediate vicinity. This higher temperature means particles will on average have a higher kinetic energy. Upon collision the particles are more likely to have a collision energy exceeding the activation energy. Thus the rate of reaction increases due to an increase in the percentage of collisions with energy ≥ activation energy.

As the reaction is exothermic heat released from the reaction of H_2 with O_2 in the vicinity of the spark heats the nearby gas mixture. This then causes the higher reaction rate to spread throughout the entire H_2/O_2 gas mixture.

ii. According to the collision theory, reacting particles must first collide if a reaction between them is to occur. Since the gas inside the buoyancy cells is pure hydrogen then there is no possibility for a collision between H_2 and O_2 molecules, hence no possibility of reaction, ie pure hydrogen can't ignite on its own.

9. a. Laura could measure the mass or volume of one of the reactants or products at various time intervals during the reaction. For this reaction it would be easy to monitor the volume of $CO_2(g)$ produced. The gas could be collected by the downward displacement of water (p10 Fig 20) and the volume collected could be recorded at various time intervals during the reaction. Another technique could involve measuring the total mass of the reaction vessel at particular time intervals during the reaction. This would require carrying out the reaction in an open conical flask. As the reaction proceeds $CO_2(g)$ is formed and escapes from the flask and leads to a mass loss equal to the mass of $CO_2(g)$ produced. A further method, although more problematic, would involve monitoring the changing mass of the piece of marble. This would require the piece of $CaCO_3$ to be periodically removed, dried and weighed and the weight and time recorded.

b.	**Alteration**	**Independent variable and predicted effect on rate**	**Using the collision theory to justify your prediction**
i	**Heat the reaction mixture to 55 °C.**	temperature and increase rate	This higher temperature means particles will on average have a higher kinetic energy. Upon collision the particles are more likely to have a collision energy exceeding the activation energy. Thus the rate of reaction increases due to an increase in the percentage of collisions with energy ≥ activation energy. [Note: An increase in temperature also produces a **small** increase in collision rates as the particles in the reacting system are moving faster. This is a **minor** effect and does **not** explain the large increase in rate that happens with a small increase in temperature.]
ii	**Use 0.10 mol L^{-1} HNO_3.**	concentration and increase rate	Using a higher concentration of HNO_3 increases the concentration of reacting species (hydrogen ions, H^+). This leads to an increase in the rate of collisions between the reacting particles (H^+ ions and $CaCO_3$ particles) and the subsequent increase in reaction rate.
iii	**Use smaller pieces of $CaCO_3(s)$**	surface area and increase rate	Smaller pieces of $CaCO_3$ (same total mass) means an increase in the surface area of $CaCO_3$. This increases the rate of collisions between hydrogen ions (solution phase) and $CaCO_3$ particles (solid phase). Thus reaction rate increases.
iv	**Refrigerate the mixture to 2 °C.**	temperature and decrease rate	This is a lower temperature than originally used. Thus the particles will have lower kinetic energy and the percentage of collisions with energy ≥ activation energy decreases. Consequently the rate of reaction reduces. [Note: The small decrease in collision rates due to the slower moving particles is a **minor** effect that does **not** explain the large decrease in rate that happens with a small decreases in temperature.]

10. a.

$$Cl(g) + O_3(g) \rightarrow ClO(g) + O_2(g) \quad ①$$

$$ClO(g) + O(g) \rightarrow Cl(g) + O_2(g) \quad ②$$

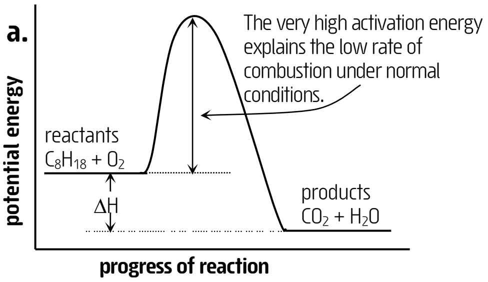
Combining both equations: $Cl(g) + O_3(g) + ClO(g) + O(g) \rightarrow ClO(g) + O_2(g) + Cl(g) + O_2(g)$

When simplified: $\mathbf{O_3}(g) \qquad (g) \qquad \mathbf{2O_2}(g)$

b. Cl(g) atoms are acting as a catalyst. Catalysts are substances that increase the rate of reaction without being consumed. (*****See note in part (b).] As can be seen here, Cl(g) atoms are able to speed up the reaction rate and are not actually consumed despite being involved in the reaction process.

c. A catalyst allows a reaction to occur by a different pathway of lower activation energy without the catalyst being consumed* atoms present, a greater percentage of collisions have energy ≥ activation energy and are successful in forming products. The Cl(g) atoms increase the reaction rate without appearing to be consumed in the reaction. [* however, an equal amount of it is produced in another ②. The activation energy of each of these two reactions ① and ② is lower than the activation energy for the single step reaction.]

11. a.



b. A fine mist of fuel (C_8H_{18}) means smaller droplets of fuel which means an increase in the surface area of liquid fuel that is in contact with air (O_2). This increases the rate of collisions between C_8H_{18} (in the liquid phase) and O_2 molecules (in the gas phase). Thus the reaction rate increases.

c. Reducing the fuel/air volume by a factor of ten times increases the gas pressure. This means a higher concentration of O_2 molecules (10x) which leads to a higher rate of collision between C_8H_{18} (in the liquid phase, ie droplets) and O_2 molecules (in the gas phase). Thus the reaction rate increases.

d. i. The spark will cause a significant rise in temperature of any $C_8H_{18}(l)$ and $O_2(g)$ in its immediate vicinity. The higher temperature means molecules near the spark, will on average, have a higher kinetic energy. Collision between O_2 molecules in the gas phase and C_8H_{18} molecules in the liquid phase are more likely to have a collision energy exceeding activation energy. Thus the rate of reaction increases due to an increase in the percentage of collisions with energy ≥ activation energy.

ii. The combustion reaction between C_8H_{18} and O_2 is very exothermic. Heat released from the exothermic combustion reaction in the vicinity of the spark, heats the nearby gas mixture and raises its temperature. This subsequent rise in temperature (due to combustion in the immediate vicinity of the spark) then causes the higher reaction rate to spread (by raising temperature) throughout the entire C_8H_{18}/O_2 gas mixture. [Highly exothermic reactions like this can become extremely fast in a very short period of time and are said to be explosive.]

e. Air drawn into the combustion cylinders contains both N_2 and O_2 gas. During combustion, the temperature inside the cylinders is much higher than in the atmosphere and so N_2 and O_2 molecules will on average have a higher kinetic energy than they do in air. Thus collisions between N_2 and O_2 molecules are more likely to have an energy exceeding activation energy and the rate of formation of NO increases. The higher pressure inside the cylinders (≈ 10x atmospheric) also leads to a higher rate of collisions between N_2 and O_2 molecules, further increasing the rate of formation of NO. The high temperature spark produced by the spark plug is also known to be a significant contributor to NO production.

Set 2 Chemical equilibrium

1. A single arrow is shown in the equation for the combustion of myricyl palmitate, $C_{46}H_{92}O_2$, this indicates this reaction goes to completion. Reactions that go to completion are typically not reversible. This means the products of this reaction are unlikely to reform the reactants. Possibly the reverse reaction has a very high activation energy compared to the forward reaction.
The reaction for the dissolving of carbon dioxide gas, $CO_2(g)$ in soft drink is a reversible reaction as indicated by the double arrows. Quite possibly the activation energy for the forward and reverse reaction are both low. Thus in this reaction the product may easily decompose to reform the original reactants.

2. a. Matter in the form of iodine vapour is shown escaping from the system (beaker and its contents). Thus this is an open system.

b. Matter in the form of hydrogen gas will escape from this system (beaker and its contents) as quickly as it is being produced. Thus this is an open system.

c. Systems like this are a reasonable approximation of a closed system. All of the reactants in this system are confined to the aqueous phase within the test tube. Thus none of the reactants can readily escape from the system. Over a long period of time there will be a loss of water from the system (test tube and its contents) due to its evaporation. Hence in this regard the open test tube (over a long period of time) would be considered an open system.

d. This change is occurring in a closed system. Matter cannot enter or leave the system (vial and its contents). Heat energy is able to enter this system as this is permissible for a closed system.

3. a. evaporation **b.** dry **c.** closed system **d** escape **e.** condense **f.** rate **g.** equal
h. dynamic equilibrium **i.** forward/reverse **j.** reverse/forward **k.** macroscopic **l.** static

4. a. Sucrose dissolving: $C_{12}H_{22}O_{11}(s) \longrightarrow C_{12}H_{22}O_{11}(aq)$. Sucrose crystallising: $C_{12}H_{22}O_{11}(aq) \longrightarrow C_{12}H_{22}O_{11}(s)$
b. $C_{12}H_{22}O_{11}(s) \rightleftharpoons C_{12}H_{22}O_{11}(aq)$

c. A closed system is one from which matter can neither enter nor leave but energy can. This system is a reasonable approximation of a closed system when considering a short timeframe (ie days but not months). All of the reactants in this system are confined to the aqueous phase within the beaker. Thus none of the reagents, sucrose or sucrose solution, can readily escape from the system. Over a long period of time however, there will be a loss of water from the system (beaker and its contents) due to evaporation. Hence in this regard the open beaker is only an approximation of a closed system.

d. i This system is at equilibrium as the solution is saturated, ie even though some solid remains, over time no more appears to dissolve and the concentration of glucose will not change. Hence the rate of glucose dissolving will equal the rate of glucose crystallising.

ii This system is not in equilibrium as the solution is unsaturated for the temperature of 25 °C. Hence the rate of glucose dissolving will be greater than the rate of glucose crystallising. This continues until the glucose concentration reaches 4.0 mol L^{-1}.

iii This system is not in equilibrium as the solution is supersaturated due to the lower temperature. (With few exceptions, all solids are less soluble at a lower temperature.) Hence the rate of glucose crystallising will be greater than the rate of glucose dissolving. This continues until the glucose solution is no longer supersaturated.

5. **a.** reactants
b. products
c. reverse
d reversible
e. rate
f. equal
g. dynamic
h. ①
i. $H_3O^+(aq)$ and $CH_3COO^-(aq)$
j. ②
k. constant

6. **a.** $NO_2(g)$ was initially added. This is evident as the initial rate of the reverse reaction, ② is high while the initial rate of the forward reaction, ① is zero. As the rate of a reaction increases with concentration it must follow that the concentration of $N_2O_4(g)$ is initially either very low or zero.

b. From time t_1 onwards the rates of the forward and reverse reactions are equal and the system is said to be in equilibrium.

c. According to the collision theory the rate of a reaction depends upon the rate of collisions between its reacting particles. As the concentration of a reactant increases so does the rate of collisions between its particles and hence the rate of reaction. For this reason the forward reaction rate, ① will immediately increase upon the addition of extra $N_2O_4(g)$. Since there is no initial change to the concentration of $NO_2(g)$, the reverse reaction rate does not immediately change.
[Note: Subsequent to the immediate change in the concentration of $N_2O_4(g)$, the concentration of $NO_2(g)$ will begin to rise as more of it is formed due to the faster rate of reaction ①. This will then lead to an increase in the rate of the reverse reaction ②, ie the increase in the rate of reaction ② is not immediate.]

7. **a.** $K_c = \frac{[H^+][CN^-]}{[HCN]}$ **b.** $K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$ **c.** $K_c = \frac{1}{[Pb^{2+}][I^-]^2}$ **d.** $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$ **e.** $K_c = [H^+][OH^-]$ **f.** $K_c = \frac{[Ca^{2+}][CO_2]}{[H^+]^2}$

8. **a.** i. products favoured ii. reactants favoured iii. neither favoured

b. A weak acid is one that only partially ionises when dissolved in water. In solution weak acids are mostly in the form of molecules. The low value of K_c shows the ionisation equilibrium for ethanoic acid favours reactants, ie molecules rather than products (ions) thus confirming ethanoic acid is a weak acid.

c. A strong acid is one that mainly forms of ions when dissolved in water. The higher value of K_c for the ionisation equilibrium of nitric acid ($K_c = 23$) shows it favours products, ie the formation of ions, more strongly than nitrous acid ($K_c = 5.1 \times 10^{-4}$). Thus nitric acid is the stronger acid of the two acids.

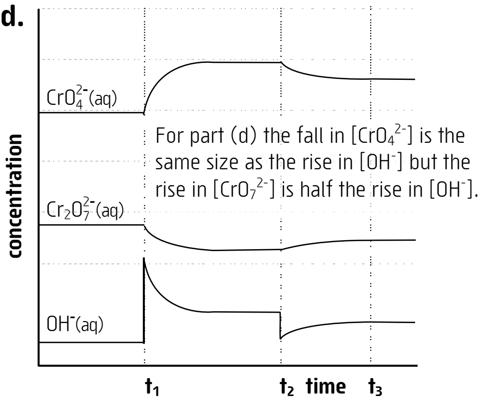
d. The very small value of K_c indicates a low concentration of products at equilibrium. Thus the concentration of both $Pb^{2+}(aq)$ and $I^-(aq)$ are very low indicating the solubility of $PbI_2(s)$ must be very low.

9. **a.** colour
b. 'cancel out'
c. temperature/pressure
d temperature/pressure
e. concentration
f. no longer
g. imposed change
h. imposed
i. partially counteracts

10. a. Le Chatelier's principle states, "If a system is at equilibrium and a change in conditions is imposed on the system then the system will re-establish a new equilibrium in such a way as to partially counteract the imposed change". In this example the imposed change is the increased hydroxide ion, OH^-(aq) concentration. The system counteracts this by favouring the forward reaction ①. This reduces both the hydroxide ion, OH^-(aq) concentration and the dichromate ion, $Cr_2O_7^{2-}$(aq) concentration. When the system returns to equilibrium at time t_2 the imposed change (ie increased hydroxide ion, OH^-(aq) concentration) will have been partially counteracted as well as reducing the dichromate ion, $Cr_2O_7^{2-}$(aq) concentration.

b. The balanced equation for the forward reaction shows that for every two moles of hydroxide ion, OH^-(aq) consumed only one mole of dichromate ion, $Cr_2O_7^{2-}$(aq) is consumed. As the two ions are in the same solution volume then It follows that the molar concentration of the dichromate ions, $Cr_2O_7^{2-}$(aq) will fall by only half the molar concentration of the hydroxide ions, OH^-(aq) as only half as much is consumed.

c/d.



For part (d) the fall in $[CrO_4^{2-}]$ is the same size as the rise in $[OH^-]$ but the rise in $[CrO_7^{2-}]$ is half the rise in $[OH^-]$.

e. The concentration of $H_2O(l)$ remains constant (at 55.5 mol L^{-1}) throughout the experiment. As its concentration is constant it is not included in the graph.

11. a. Colour is a macroscopic property of a system and must be constant for a system to be at equilibrium. So after the addition of a large amount of the ammonia solution the passage states, "**The mixture eventually becomes a constant dark blue colour**." This means the macroscopic property of colour is once again constant, implying the system is at equilibrium.

b. Le Chatelier's principle states, "If a system is at equilibrium and a change in conditions is imposed on the system then the system will readjust to form a new equilibrium in such a way as to partially counteract the imposed change". In this example the imposed change is the increased ammonia (NH_3) concentration. The system counteracts this by favouring the forward reaction. This reduces both the ammonia, NH_3 and Cu^{2+}(aq) (light blue colour) concentrations while increasing the concentration of the dark blue $[Cu(NH_3)_4]^{2+}$(aq). When the system returns to equilibrium the imposed change (increased NH_3 concentration) will have been partially counteracted.

c. Adding concentrated ammonia solution to the equilibrium system increases the concentration of NH_3(aq). This increases the rate of collisions between NH_3(aq) molecules and Cu^{2+}(aq) ions and by the collision theory this increases the rate of the forward reaction ①. Initially this change has no effect on the rate of the reverse reaction ② as the concentration of $[Cu(NH_3)_4]^{2+}$(aq) has not been altered. Thus initially the dark blue $[Cu(NH_3)_4]^{2+}$(aq) is being produced faster than it is being consumed and subsequently its concentration increases while the concentration of NH_3(aq) and Cu^{2+}(aq) decreases. Eventually though, the rate of the forward reaction ① slows as the concentrations of both NH_3(aq) molecules and Cu^{2+}(aq) ions slowly decreases. Also the rate of the reverse reaction ② begins to increase due to the increasing concentration of $[Cu(NH_3)_4]^{2+}$(aq). At some point the rate of the forward and reverse reactions are again equal and the system has returned to equilibrium. When this happens the concentration of Cu^{2+}(aq) ions will have decreased, the concentration of NH_3(aq) molecules will have decreased partly back to their original value and the concentration of $[Cu(NH_3)_4]^{2+}$(aq) ions will have increased.

d. Adding HCl(aq), initially reduces the concentration of NH_3(aq) as some of it reacts with the added HCl(aq) producing ammonium ions [NH_3(aq) + H^+(aq) $\rightleftharpoons$ NH_4^+(aq)]. As a result of this imposed change the equilibrium re-establishes itself in such a way that partially replaces the reduced NH_3(aq) concentration. To do this the equilibrium favours the reactants. Thus when the new equilibrium is established the $[Cu^{2+}]$ will be higher than before adding HCl(aq). The NH_3(aq) concentration will have been partially increased towards its original value while the $[Cu(NH_3)_4]^{2+}$ will be lower than before adding HCl(aq).

e. As stated in the question, adding concentrated HCl(aq) solution to the equilibrium system decreases the concentration of NH_3(aq). This decreases the rate of collisions between NH_3(aq) molecules and Cu^{2+}(aq) ions and by the collision theory this decreases the rate of the forward reaction ①. Initially this change has no effect on the rate of the reverse reaction ② as the concentration of $[Cu(NH_3)_4]^{2+}$(aq) has not yet been affected. Thus after adding HCl(aq) solution the dark blue $[Cu(NH_3)_4]^{2+}$(aq) is being consumed faster than it is being produced and so its concentration slowly decreases while the concentration of NH_3(aq) and Cu^{2+}(aq) slowly increase. Eventually though, the rate of the forward reaction ① speeds up as the concentrations of both NH_3(aq) molecules and Cu^{2+}(aq) ions begin to increase. Also the rate of the reverse reaction ② begins to decreases due to the slowly falling concentration of $[Cu(NH_3)_4]^{2+}$(aq). At some point the rate of the forward and reverse reactions are again equal and the system has returned to equilibrium. When this happens the concentration of Cu^{2+}(aq) ions will have increased, the concentration of NH_3(aq) molecules will have also increased but this is still lower than its original value and the concentration of $[Cu(NH_3)_4]^{2+}$(aq) ions will have decreased.

12. a. Halving the gas volume causes the pressure to double.

b. Products are favoured. Le Chatelier's principle states, "If a system is at equilibrium and a change in conditions is imposed on the system then the system will re-establish a new equilibrium in such a way as to partially counteract the imposed change". In this example the imposed change is an increased pressure inside the reacting system. The system counteracts this by favouring the forward reaction, ie favouring the products, the side with fewer moles of gas. This effectively consumes 3 moles of gas for every 1 mole of gas produced, thus causing a net reduction in the moles of gas inside the system, resulting in a lower pressure. When the system returns to equilibrium the imposed change (increased pressure) will have been partially counteracted.

c. The CO gas partial pressure immediately doubles to 110 kPa (volume was halved). Its partial pressure then begins to decrease, rapidly at first, then decreasing more slowly until the partial pressure is once again constant. The new constant partial pressure will be higher than 55 kPa but lower than 110 kPa.

13.a. favours products **b.** favours reactants **c.** favours products **d.** favours products **e.** cooled **f.** cooled

14. a. Small equilibrium constant values generally imply the equilibrium process strongly favours the reactant(s). Thus at equilibrium in this situation the concentration of products, H^+(aq) and OH^-(aq) is very low.

b. The reaction as written is endothermic, ie left to right. This can be deduced as K_w increases in value as temperature increases. This is consistent with an endothermic equilibrium. For an exothermic equilibrium K_w decreases with increasing temperature.

c. i As can be seen K_w increases with increasing temperature. This means the equilibrium favours products at a higher temperature. Thus the concentration of both H^+(aq) and OH^-(aq) increase at the higher temperature.

ii All reactions proceed at a faster rate when temperature is increased. Thus both reactions ① and ② proceed at a faster rate at 50 °C. However, the rate of the endothermic reaction ① increases more than the rate of the exothermic reaction ②.

Equilibrium system and alteration	Imposed change	Predicting the change in equilibrium position using LCP
15. a. $HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$		
i. A small amount of concentrated HCl(aq) is added to the system.	concentration of H^+(aq) is increased	**Favours reactants.** Equilibrium shifts to the left. This consumes some of the added H^+(aq) and hence partially counteracts the imposed change, ie the raised H^+(aq) concentration.
ii. Some concentrated NaOH(aq) is added to the equilibrium system.	concentration of H^+(aq) is decreased	**Favours products**. Equilibrium shifts to the right to form some H^+(aq), thus partially counteracting the imposed change, ie the lowered H^+(aq) concentration.

Continued next page.

b. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + 92\ kJ$		
i. The system volume is reduced.	pressure is increased	**Favours products**. This reduces the amount of gas in the system as 4 moles of gas are consumed, for every 2 moles of gas formed. This causes a reduction in the system's pressure, thus partially counteracting the imposed change, ie the raised pressure.
ii. The system is heated.	temperature is increased	**Favours reactants**. This favours the reverse reaction as it is endothermic. As a result heat energy is consumed and converted to enthalpy. The loss of heat causes temperature to fall thus partially counteracting the imposed change, ie the raised temperature.
c. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)\ \Delta H = -198\ kJ$		
i. The system volume is increased.	pressure is reduced	**Favours reactants**. This increases the amount of gas in the system as 3 moles of gas are produced for every 2 moles of gas consumed. This leads to an increase in the system's pressure thus partially counteracting the imposed change, ie the reduced pressure.
ii. Some $O_2(g)$ is added into the system.	concentration (partial pressure) of $O_2(g)$ increased	**Favours products**. Equilibrium shifts to the right. This consumes some of the added $O_2(g)$. Thus partially counteracting the imposed change, ie the raised $O_2(g)$ partial pressure/concentration.
iii. The system is cooled.	temperature is lowered	**Favours products**. This favours the forward reaction as it is exothermic. As a result enthalpy is converted to heat energy. The extra heat energy raises the system's temperature thus partially counteracting the imposed change, ie the lowered temperature.
d. $CaCO_3(s) + 179\ kJ \rightleftharpoons CaO(s) + CO_2(g)$		
i. Extra $CaCO_3(s)$ is added to the system.	no imposed change	**No effect**. Chemical equilibria do not respond to changes in the amounts of solids or liquids in a system.
ii. The system is cooled.	temperature is lowered	**Favours reactants**. This favours the reverse reaction as it is exothermic. As a result enthalpy is converted to heat energy. The extra heat energy raises the system's temperature thus partially counteracting the imposed change, ie the lowered temperature.
iii. Some $CaO(s)$ is removed from the system.	no imposed change	**No effect**. Chemical equilibria do not respond to changes in the amounts of solids or liquids in a system.

16. a. i. The system colour will change from blue to pink.

ii. The addition of $AgNO_3(aq)$ causes a sudden decrease in the concentration of $Cl^-(aq)$. This happens as $Cl^-(aq)$ precipitates from solution along with the added $Ag^+(aq)$ to form $AgCl(s)$. The concentration of the other species is Initially unchanged. The reduced $Cl^-(aq)$ concentration means the rate of collisions between $Cl^-(aq)$ and $Co(H_2O)_6{}^{2+}(aq)$ decreases and thus by the collision theory so does the rate of the forward reaction. As the concentration of the products is not initially affected this reaction proceeds at the same rate as before $AgNO_3(aq)$ was added. The reduced forward rate means the products are now being formed slower than they are being used. Consequently the concentration of the $Co(Cl)_4^{2-}(aq)$ begins to fall while the concentration of $Cl^-(aq)$ and $Co(H_2O)_6{}^{2+}(aq)$ begins to rise. As a consequence of the now changing concentrations the forward reaction rate begins to increase while the reverse reaction rate begins to decrease.

At some point the rates of these two reactions are again equal, the system has now re-established equilibrium. When equilibrium is eventually re-established the $Cl^-(aq)$ ion concentration will be lower than it was before the addition of $AgNO_3(aq)$ but higher than it was just after the addition of the $AgNO_3(aq)$. The concentration of $Co(H_2O)_6^{2+}(aq)$ will be higher than before the addition of $AgNO_3(aq)$ while the concentration of $Co(Cl)_4^{2-}(aq)$ will be lower than before the addition of $AgNO_3(aq)$.

b. i. The system colour change from pink to blue suggests the equilibrium has readjusted to favour products, ie the blue $Co(Cl)_4^{2-}$(aq) is favoured by heating.

ii. Only temperature changes will affect K_c. A higher temperature increases the value of K_c for endothermic reactions and lowers K_c for exothermic reactions. In this experiment the higher temperature favoured the products meaning K_c increased. (Remember only temperature changes affect K_c.) Thus the forward reaction (as written) is endothermic.

17. a. ①: A high yield of H_2(g), ie the product, is favoured by high temperature and low pressure.

②: A high yield of H_2(g), ie the product, is favoured by low temperature and pressure will make no difference.

b. ①: A high rate of attainment of equilibrium, ie fast reaction rates, is favoured by high temperature, high pressure and the use of a suitable catalyst.

②: A high rate of attainment of equilibrium, ie fast reaction rates, is favoured by high temperature, high pressure and the use of a suitable catalyst.

c. When chemical engineers design industrial chemical processes, they choose reaction conditions that achieve a high yield (ie maximum conversion of reactants to products) and a fast rate of reaction at minimum cost. Doing this makes the process economically viable. Sometimes a compromise in the conditions of temperature and pressure must be used. In the steam reforming process ① high temperature and high pressure give a high rate of formation of H_2(g). However, high pressure will cause the equilibrium yield to be low as high pressure favours the formation of reactants. Thus a compromise must be found where the pressure is neither too high nor too low so that an acceptable yield and an acceptable rate can be maintained in the process. It may be favourable to use a lower pressure thus sacrificing high rate in order to achieve a higher yield. Using excessively high pressure can also be unfavourable as it will incur extra cost in both plant construction and its ongoing operation. Catalysts are a desirable way to increase rate without compromising yield or compromising operating costs. [The actual industrial conditions are: High temperature of 700-1100 °C with a Ni catalyst giving a yield of around 65-75%.]

18. a. Hypoxia (altitude sickness) is a disorder caused by a lack of oxygen reaching body tissues. The uptake of oxygen in the lungs is an equilibrium process where haemoglobin molecules (Hb) combine with oxygen molecules O_2(g) producing oxyhaemoglobin HbO_2(aq). The low oxygen partial pressure at the summit of Mount Kilimanjaro, around 10 kPa compared to 20 kPa at sea level means the equilibrium for the uptake of oxygen in the lungs shifts more to the left causing oxyhaemoglobin HbO_2(aq) concentration to fall. Low oxyhaemoglobin HbO_2(aq) concentration means there is less HbO_2(aq) reaching the body cells and so less oxygen is available to body tissues. This results in the symptoms of hypoxia.

b. After a period of time at high altitude, the body adjusts by producing more haemoglobin molecules (Hb) thus increasing its concentration in the blood. An increased concentration of haemoglobin molecules (Hb) shifts the equilibrium process for the uptake of oxygen to the right favouring a higher oxyhaemoglobin HbO_2(aq) concentration. A higher oxyhaemoglobin HbO_2(aq) concentration means the blood now carries a more normal concentration of oxygen to body cells and hypoxia no longer occurs.

19. a. HF(aq) $\rightleftharpoons$ F^-(aq) + H^+(aq) $K_c = 6.8 \times 10^{-7}$. The very low value of K_c implies the equilibrium for the ionisation of hydrogen fluoride favours HF(aq) with only a very low concentration of products, F^-(aq) and H^+(aq). The low H^+(aq) concentration shows that HF is a weak acid.

b. HF in its molecular form is able to be absorbed through the skin (see paragraph 2) and diffuse into body tissue. Its ionisation to F^-(aq) and H^+(aq) only begins to happen as F^-(aq) and Ca^{2+}(aq) [present in blood serum] react to form insoluble CaF_2, shown in equation ②. The precipitation of CaF_2 reduces the F^-(aq) concentration thus reducing the rate of the reverse reaction in the ionisation of HF equilibrium, ie reduces the rate of recombination of F^-(aq) and H^+(aq) to reform HF(aq). As the forward reaction for the ionisation of HF(aq) is now proceeding faster than the reverse reaction (it has slowed down) then the concentration of HF(aq) begins to decline while the concentration of F^-(aq) and H^+(aq) begin to rise. Even though the reducing concentration of HF(aq) slows down the rate of the forward reaction, the reverse reaction rate can never catch up with the forward reaction rate because F^-(aq) is constantly precipitating along with Ca^{2+}(aq) to form insoluble CaF_2(s). Thus this reaction cannot reach equilibrium and ultimately all of the HF(aq) will become ionised forming F-(aq) and H^+(aq). The F^-(aq) precipitates as insoluble CaF_2(s) while the elevated H^+(aq) concentration will cause tissue burns deep within the body.

c. As elaborated in Part b, the complete ionisation of HF only happens as it penetrates deep into body tissue. The release of hydrogen ions deep within body tissue will then cause tissue damage (burns) typical of a strong acid.

d. The ionisation of HF produces fluoride ions that precipitate calcium ions (present in blood serum) as insoluble $CaF_2(s)$. This reduces the concentration of calcium ions in blood serum and affects the equilibrium between blood calcium and bone calcium ①. The reduced blood calcium concentration reduces the rate of its uptake into bone tissue by the reverse reaction in equilibrium ①. Meanwhile the release of calcium from bone tissue in equilibrium ① continues at a normal rate. As a consequence, bone calcium dissolves from bone tissue faster than it is being replaced. This leads to bone destruction. This imbalance in reaction rates in equilibrium ① will continue as long as blood calcium continues to be depleted by its precipitation in reaction②.

20. **a.** carbon dioxide
b. anthropogenic
c. temperature
d. coral bleaching
e. food and habitat
f. ocean acidification
g. equilibrium
h. $CO_2(aq)$
i. carbon sink
j. $H^+(aq)$ concentration
k. $CO_3^{2-}(aq)$ concentration
l. calcifying
m. calcareous plankton

21. a. Wind and wave action allow atmospheric carbon dioxide to dissolve in seawater, ie: $CO_2(g,\ atmosphere) \rightleftharpoons CO_2(aq,\ ocean)$. This is an equilibrium process where the rate at which $CO_2(g,\ atmosphere)$ enters the ocean has for thousands of years been in balance with the rate at which $CO_2(aq,\ ocean)$ returns to the atmosphere. However, the atmospheric carbon dioxide concentration is known to be rising, due to anthropogenic causes, and this is causing an increase in the rate at which CO_2 dissolves in sea water. This in turn is causing a new equilibrium to be established where the oceanic concentration of $CO_2(aq,\ ocean)$ will increase until this system returns to equilibrium.

b. Dissolved $CO_2(aq,\ ocean)$ maintains an equilibrium with carbonic acid, $CO_2(aq,\ ocean) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$. Due to the increasing $CO_2(aq,\ ocean)$ concentration [part (a)] the rate of the forward reaction, ie formation of $H_2CO_3(aq)$ is currently greater than the rate of the reverse reaction, ie formation of $CO_2(aq,\ ocean) + H_2O(l)$. As a result of this current imbalance in reaction rates, the concentration of $H_2CO_3(aq)$ is steadily rising.

Another equilibrium also exists between the weak acid $H_2CO_3(aq)$ and the hydrogencarbonate ion: $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$. The rising concentration of $H_2CO_3(aq)$ is causing an increase in the rate of formation of $H^+(aq)$ and $HCO_3^-(aq)$. The rising $H^+(aq)$ concentration is responsible for the falling ocean pH.

22. The higher atmospheric concentration of $CO_2(g)$ does result in an increase the concentration of $CO_2(aq,\ ocean)$ which goes on to increase the $H_2CO_3(aq)$ concentration. Higher $H_2CO_3(aq,\ ocean)$ also results in higher concentrations of both $H^+(aq)$ and $HCO_3^-(aq)$ as outlined here: $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$. However, while this process produces equal molar amounts of $H^+(aq)$ and $HCO_3^-(aq)$ the factor increase in the $H^+(aq)$ concentration is a lot greater than for $HCO_3^-(aq)$. This happens as the $H^+(aq)$ concentration is initially extremely low ($\approx 6.3 \times 10^{-9}$ mol L^{-1}), much lower than the $HCO_3^-(aq)$ concentration ($\approx 1.9 \times 10^{-3}$ mol L^{-1}). The net effect of this is to cause the equilibrium reaction between carbonate ions and hydrogencarbonate ion, ie $HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$ to shift to the left. This happens as the reverse reaction speeds up more because the concentration of $H^+(aq)$ has increased by a greater factor than the concentration of $HCO_3^-(aq)$. This change reduces the natural ocean concentration of $CO_3^{2-}(aq)$.

Set 3 Review: Acid-Base properties

1. Solution A: **Acidic**. The universal indicator colour indicates a pH of around 3-5. Solutions of pH less than 7 are acidic.

Solution B: **Inconclusive**, the solution could be acidic, basic or neutral. Solution conductivity is a property of acidic, basic and neutral salt solutions.

Solution C: **Basic.** The strong pungent odour is most probably due to the formation of ammonia, NH_3. Only basic solutions produce the pungent odour of ammonia gas with an ammonium salt. Thus the solution is not neutral or acidic.

Solution D: **Inconclusive**, the solution is basic or neutral. The solution cannot be acidic as this would have turned the blue litmus to red. However, the solution may be basic or neutral as neither of these solution would change the colour of blue litmus.

Solution E: **Neutral**. The solution cannot be basic as this would have turned the red litmus blue. It is not acidic as this would have produced a colourless gas (hydrogen) with the reactive metal magnesium. A neutral solution does not change the colour litmus or react with magnesium.

Solution F: **Acidic**. Acidic solutions produce a colourless gas (carbon dioxide) with carbonates. Neither neutral nor basic solutions do this.

2. **a.** $3HNO_3(aq) + Fe(OH)_3(s) \rightarrow Fe(NO_3)_3(aq) + 3H_2O(l)$ A brown solid dissolves producing a pale brown solution.

b. $2HCl(aq) + CaO(s) \rightarrow CaCl_2(aq) + H_2O(l)$ A white solid dissolves producing a clear colourless solution.

c. $KOH(aq) + NH_4NO_3(aq) \rightarrow KNO_3(aq) + NH_3(g) + H_2O(l)$
Two colourless solutions produce a colourless gas with a pungent irritating odour.

d. $2H_3PO_4(aq) + 3Ca(OH)_2(s) \rightarrow Ca_3(PO_4)_2(s) + 6H_2O(l)$
The colourless solution and white solid appear unchanged.

e. $3H_2SO_4(aq) + 2Al(s) \rightarrow Al_2(SO_4)_3(aq) + 3H_2(g)$
A silvery grey solid dissolves producing a colourless solution and a colourless, odourless gas.

f. $K_2CO_3(s) + 2HCl(aq) \rightarrow 2KCl(aq) + H_2O(l) + CO_2(g)$
The white solid dissolves producing a colourless, odourless gas.

g. $CuO(s) + 2HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + H_2O(l)$ The black solid dissolves forming a blue solution.

h. $CO_2(g) + 2KOH(aq) \rightarrow K_2CO_3(aq) + H_2O(l)$
The colourless, odourless gas dissolves forming a colourless solution.

3. **a.** $CuO(s) + 2H^+(aq) \rightarrow Cu^{2+}(aq) + H_2O(l)$ A black solid dissolves and a blue solution is formed.

b. $HCO_3^-(aq) + H^+(aq) \rightarrow CO_2(g) + H_2O(l)$
The colourless mixture fizzes to produce a colourless, odourless gas.

c. $NH_4Cl(s) + OH^-(aq) \rightarrow NH_3(g) + H_2O(l) + Cl^-(aq)$
The white solid dissolves producing a colourless gas with a strong pungent odour.

d. $NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(g) + H_2O(l)$
Two colourless solutions form a colourless gas with a strong pungent odour.

e. $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$
A grey solid dissolves producing a colourless solution and bubbles of a colourless odourless gas.

f. $Cu(OH)_2(s) + 2H^+(aq) \rightarrow Cu^{2+}(aq) + 2H_2O(l)$
The cloudy blue suspension dissolves resulting in a clear blue solution.

g. $Al_2O_3(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2O(l)$
The white solid dissolves producing a clear colourless solution.

h. $CO_2(g) + 2OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l)$
The colourless, odourless gas dissolves producing a clear colourless solution.

i. $CaCO_3(s) + 2H^+(aq) + SO_4^{2-}(aq) \rightarrow CaSO_4(s) + CO_2(g) + H_2O(l)$
A colourless, odourless gas forms. Some white solid still remains.

j. $NH_3(g) + H^+(aq) \rightarrow NH_4^+(aq)$
A colourless pungent gas rapidly dissolves to give a colourless solution.

k. $CuCO_3(s) + 2H^+(aq) \rightarrow Cu^{2+}(aq) + H_2O(l) + CO_2(g)$
A green solid dissolves forming a clear blue solution and a colourless, odourless gas.

4. Vinegar contains a dilute solution of the weak acid ethanoic acid. Since kettle scale is essentially $CaCO_3(s)$ then vinegar would be suitable for removing it as ethanoic acid will dissolve $CaCO_3$ to form soluble $Ca(CH_3COO)_2$ along with gaseous CO_2 and water. All three products will either wash off or escape from the kettle surface, ie $CaCO_3(s) + 2CH_3COOH(aq) \rightarrow Ca^{2+}(aq) + 2CH_3COO^-(aq) + CO_2(g) + H_2O(l)$. Also as vinegar is a dilute solution of a weak acid (ethanoic acid) it is unlikely to harm any metallic components inside the kettle.

5. Rust converter contains the weak acid phosphoric acid. Since rust is essentially $Fe_2O_3(s)$ then phosphoric acid will react with rust converting it to insoluble $FePO_4(s)$ and water, ie $Fe_2O_3(s) + 2H_3PO_4(aq) \rightarrow 2FePO_4(s) + 3H_2O(l)$. Thus the layer of surface rust has been converted to a $FePO_4$ layer. [Note: The iron phosphate layer has the advantage of being impervious to water and oxygen; the agents causing rusting, while iron oxide is porous to these agents.]

6. Both of these nitrogen fertilisers contain ammonium compounds. These compounds react with bases like CaO (a basic oxide) to produce ammonia gas $NH_3(g)$, water and a calcium salt:
eg $2NH_4NO_3(s) + CaO(s) \rightarrow 2NH_3(g) + Ca(NO_3)_2(s) + H_2O(l)$.
This results in the loss of ammonium ions, the intended source of nitrogen for promoting crop growth. Also, mixing these compounds is hazardous as it will produce large volumes of the toxic gas ammonia, NH_3.

7. All three major components of marbelite and plaster are basic compounds that are insoluble in water. These insoluble compounds can react with acidic solutions, ie solutions of low pH to produce soluble compounds. (See equations below.) As a consequence the marbelite or plaster surface will slowly dissolve to become pitted and rough as described.
$CaO(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2O(l)$
$Ca(OH)_2(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + 2H_2O(l)$
$CaCO_3(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + CO_2(g) + H_2O(l)$

Set 4 Theories of acid-base behaviour

1. a. Lavoisier had conducted experimental work on the oxides of elements like carbon, phosphorus and sulfur. He observed the oxides dissolved in water to produce solutions with acidic properties. This led Lavoisier to propose that it was the presence of oxygen in a compound that gave it acidic properties.

b. Certain compounds of the group 1 and 2 elements were known to be strongly basic. Using electrolysis, Davy was able to show these compounds were all oxides. Thus contrary to Lavoisier's theory of acidity, these oxygen containing compounds were strongly basic not acidic. He also showed the strongly acidic compound, muriatic acid (HCl) did not contain oxygen.

c. Using electrolysis, Davy showed the strong acid 'muriatic acid' (hydrochloric acid) contained only hydrogen and chlorine. Experimentation by others showed more acids, eg HCN, HBr and HI did not contain oxygen but did contain hydrogen. This led Davy to propose that the presence of hydrogen in a compound would give it acidic properties.

d. Davy's theory could not account for the lack of acidity of some known hydrogen containing compounds, eg CH_4. Von Liebig and others had observed that metals reacted with acids to produce hydrogen gas. Liebig proposed a modified version of Davy's theory that acids were substances which contained 'replaceable' hydrogen.

2. a. H or OH
b. $H^+(aq)$ or $OH^-(aq)$
c. ions
d. ionises
e. $H^+(aq)$
f. $OH^-(aq)$
g. $FeCl_3$ or $Cr(NO_3)_3$
h. Na_2CO_3

3. a. The Arrhenius theory describes an acid as a substance that will ionise in solution producing $H^+(aq)$ ions, eg: $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$. A base is a substance that will dissociate in solution releasing $OH^-(aq)$ ions, eg: $Ba(OH)_2(s) \rightarrow 2OH^-(aq) + Ba^{2+}(aq)$. Thus $Ba(OH)_2$ is defined as a base and HCl as an acid.

b. According to Arrhenius, a strong acid is more fully ionised in aqueous solution than a weak acid. Hence for the same concentration a stronger acid, like HCl produces a higher $H^+(aq)$ concentration and stronger acidic properties than a weak acid like CH_3COOH. This is shown using a single arrow, → for complete ionisation (ie all of the acid molecules are present in solution as ions) or double arrows, $\rightleftharpoons$ for partial ionisation (only some of the acid molecules are present in solution in the form of ions).

4. When $NH_3(g)$ dissolves in water it reacts with water in a proton transfer reaction as shown here: $NH_3(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$. In this way ammonia behaves as a Brønsted-Lowry base, ie it acts as a proton acceptor. In the process it produces hydroxide ions making the resulting solution basic.

5. a. $\underset{\textbf{base}}{NH_3(aq)} + \underset{\textbf{acid}}{H_2O(l)} \rightleftharpoons OH^-(aq) + NH_4^+(aq)$

b. $\underset{\textbf{acid}}{H_3PO_4(aq)} + \underset{\textbf{base}}{H_2O(l)} \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq)$

c. $\underset{\textbf{base}}{H_2O(l)} + \underset{\textbf{acid}}{HNO_2(aq)} \rightleftharpoons NO_2^-(aq) + H_3O^+(aq)$

d. $\underset{\textbf{base}}{HCOO^-(aq)} + \underset{\textbf{acid}}{H_2O(l)} \rightleftharpoons HCOOH(aq) + OH^-(aq)$

6. In each case the Bronsted-Lowry equation is written first followed by an Arrhenius equation where appropriate.

a. $HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$ $\qquad$ $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$

b. $CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$ $\qquad$ $CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$

c. $NH_3(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$ $\qquad$ Not applicable.

d. $H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq)$ $\qquad$ $H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq)$ (Single ionisation, as stated.)

e. $H_2SO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HSO_4^-(aq)$ $\qquad$ $H_2SO_4(aq) \rightarrow H^+(aq) + HSO_4^{2-}(aq)$ (Single ionisation, as stated.)

f. $H_2SO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HSO_3^-(aq)$ $\qquad$ $H_2SO_3(aq) \rightleftharpoons H^+(aq) + HSO_3^-(aq)$

g. $CH_3NH_2(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + CH_3NH_3^+(aq)$ $\qquad$ Not applicable.

Note: CH_3NH_2 has a similar behaviour to that of NH_3 as in **c**.

7. **a.** 1.0 mol L^{-1} HNO_3 has the highest $H^+(aq)$ concentration. Ethanoic acid is a weak acid and only partially ionises in aqueous solution. By comparison nitric acid is a strong acid and is completely ionised in aqueous solution thus producing a higher $H^+(aq)$ concentration for the same acid concentration.

b. Both 1.0 mol L^{-1} $NH_3(aq)$ and 1.0 mol L^{-1} $NaOH(aq)$ form basic solutions. As ammonia is a weak base it produces a low concentration of $OH^-(aq)$ ions. $NaOH(s)$ produces the most strongly basic solution as it completely dissociates producing a higher $OH^-(aq)$ ion concentration.

c. 1.0 mol L^{-1} $HCl(aq)$ produces the most acidic solution as its solution has a $H^+(aq)$ concentration of 1.0 mol L^{-1}. The 0.10 mol L^{-1} $HCl(aq)$ solution forms an acidic solution having an $H^+(aq)$ concentration of only 0.10 mol L^{-1}.

8. **a.** proton transfer
b. donates
c. proton acceptor
d. proton
e. ammonium ion
f. water
g. reversible
h. conjugate acid
i. conjugate base
j. partially
k. products
l. single arrow

9. **a.** $NH_3(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$
base acid **conjugate base** **conjugate acid**

b. $H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq)$
acid base **conjugate acid** **conjugate base**

c. $H_2O(l) + HNO_2(aq) \rightleftharpoons NO_2^-(aq) + H_3O^+(aq)$
base acid **conjugate base** **conjugate acid**

d. $HCOO^-(aq) + H_2O(l) \rightleftharpoons HCOOH(aq) + OH^-(aq)$
base acid **conjugate acid** **conjugate base**

10. **a.** $Cl^-(aq)$ **b.** $SO_4^{2-}(aq)$ **c.** $PO_4^{3-}(aq)$ **d.** NH_3

11. **a.** $CH_3COOH(aq)$ **b.** $H_2O(l)$ **c.** $NH_4^+(aq)$ **d.** $H_2PO_4^-(aq)$

12. **a.** When oxalic acid has just been added: The rate of the forward reaction is greater than the rate of the reverse reaction. (Initially the concentration of the products is extremely low, effectively zero so the reverse reaction rate is initially very slow, negligible.)
At equilibrium: The rate of the forward reaction is equals the rate of the reverse reaction. (By definition this is the condition for equilibrium. At this point the concentration of all of the species has reached a point where the forward and reverse reactions are occurring at the same rate.)

b. K_a is significantly less than 1. This implies the equilibrium favours the reactants.

c. A moderate acid. A strong acid would be more fully ionised at equilibrium and thus produce a higher concentration of products and a larger value of K_a.

d. If some sodium hydroxide is added to the equilibrium system it has an immediate effect of consuming hydrogen ions and thus reducing the concentration of $H_3O^+(aq)$. Consequently the rate of the reverse reaction slows down. Thus temporarily the forward reaction rate is greater than the reverse rate. Thus $H_2C_2O_4(aq)$ is temporarily being consumed faster than it is being produced and both $H_3O^+(aq)$ and $HC_2O_4^-(aq)$ are being produced faster than they are being consumed. This has the effect of lowering the concentration of $H_2C_2O_4(aq)$ and raising the concentration of $HC_2O_4^-(aq)$. When equilibrium is re-established the concentration of $H_2C_2O_4(aq)$ will be lower and the concentration of $HC_2O_4^-(aq)$ will be higher than before adding the $NaOH(aq)$.

13. a. $K_a = \dfrac{[H_3O^+][NO_3^-]}{[HNO_3]}$ $\qquad$ $K_a = \dfrac{[H_3O^+][HCO_3^-]}{[H_2CO_3]}$

b. K_a for HNO_3 is 20 while K_a for H_2CO_3 is 4.5×10^{-7}. The much higher value of K_a for HNO_3 means a higher equilibrium concentration of products, ie it produces a higher concentration of hydrogen ions. Thus HNO_3 is the stronger acid as it is more fully ionised.

c. The nitric acid solution will have the higher concentration of hydrogen ions. This is evident as nitric acid has a much larger K_a meaning the products of its proton transfer reaction (which include hydrogen ions) are more strongly favoured at equilibrium than those of H_2CO_3.

14. HNO_3 and CH_3COOH are monoprotic acids, ie capable of donating a single hydrogen ion. H_2SO_4 is a polyprotic acid or more specifically it is diprotic meaning it can donate two hydrogen ions per sulfuric acid molecule.

15. a. Acid strength from strongest to weakest: $H_3PO_4(aq)$ $H_2PO_4^-(aq)$ $HPO_4^{2-}(aq)$.

b. The acid species become progressively more negative in charge as more protons; which have a positive charge; are donated from the acid. The higher negative charge makes it increasingly difficult for the subsequent species, $H_2PO_4^-(aq)$ then $HPO_4^{2-}(aq)$, to lose a proton. Instead, due to the attraction of opposite charges, there is an increasing tendency for the subsequent conjugate species (**-**) [ie $H_2PO_4^-(aq)$ and $HPO_4^{2-}(aq)$] to attract a proton (+ -Lowry bases.

c. Base strength from strongest to weakest: $PO_4^{3-}(aq)$ $HPO_4^{2-}(aq)$ $H_2PO_4^-(aq)$

16. a. water **b.** $OH^-(aq)$ **c.** $H_2CO_3(aq)$ **d.** proton **e.** $H_3O^+(aq)$ **f.** $SO_4^{2-}(aq)$ **g.** hydrolysis

17. a. strong acid:
$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$

b. neutral

c. strong acid:
$HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$

d. neutral

e. neutral

f. weak acid:
$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$

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

h. neutral

i. weak acid:
$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq)$

j. weak acid:
$H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$

k. weak base:
$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + H_2PO_4^-(aq)$

l. weak base:
$PO_4^{3-}(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HPO_4^{2-}(aq)$

m. neutral

n. strong acid:
$H_2SO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HSO_4^-(aq)$

o. weak acid:
$HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$

p. weak base:
$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + CH_3COOH(aq)$

q. weak acid:
$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$

r. weak acid:
$H_2CO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HCO_3^-(aq)$

s. weak base:
$HCO_3^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + H_2CO_3(aq)$

t. weak base:
$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HCO_3^-(aq)$

18. a. basic, ie pH > 7 due to CO_3^{2-}

b. neutral

c. acidic, ie pH < 7 due to NH_4^+

d. neutral

e. acidic, ie pH < 7 due to HSO_4^-

f. neutral

g. basic, ie pH > 7 due to CH_3COO^-

h. basic, ie pH > 7 due to S^{2-}

i. neutral

j. basic, ie pH > 7 due to HCO_3^-

k. basic, ie pH > 7 due to HPO_4^{2-}

l. neutral

19. a. The neutralisation products of this reaction are water and sodium ethanoate. As sodium ethanoate is weakly basic, due to the CH_3COO^- ion, then the final 'neutralised' reaction mixture will have a pH greater than 7.

b. The neutralisation product of this reaction is ammonium nitrate. As ammonium nitrate is weakly acidic, due to the NH_4^+ ion, then the final 'neutralised' reaction mixture will have a solution pH below 7.

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20. As H_2SO_3 is a weak acid, its ionisation equilibrium reaction, $H_2SO_3(aq) \rightleftharpoons H^+(aq) + HSO_3^-(aq)$, strongly favours H_2SO_3 molecules. Only a low concentration of H^+ ions and HSO_3^- ions will be present. If a base like NaOH(aq) is added to this solution then the few $H^+(aq)$ ions that are present will be consumed by the reaction with OH^- ions [$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$]. This causes the imposed change of a dramatically lowered H^+ ion concentration. According to Le Chatelier's principle, this imposed change (lowering the H^+ ion concentration due to the addition of the base) results in the ionisation equilibrium shifting to the right to partially counteract it. As this happens, more $H_2SO_3(aq)$ becomes ionised producing more $H^+(aq)$. Adding more NaOH(aq) causes this process to continue until eventually all of the weak acid H_2SO_3 has been ionised as a result of the added base, NaOH. Continuing to add NaOH will cause the further ionisation of $HSO_3^-(aq)$ ions, ie $HSO_3^-(aq) \rightleftharpoons H^+(aq) + SO_3^{2-}(aq)$ until only $SO_3^{2-}(aq)$ remains.

21. a. When $Na_2O(s)$ is placed into water it readily dissolves and dissociates: $Na_2O(s) \rightarrow 2Na^+(aq) + O^{2-}(aq)$. The resulting $O^{2-}(aq)$ ions are a very strong base that immediately accept hydrogen ions from water, ie: $O^{2-}(aq) + H_2O(l) \rightarrow 2OH^-(aq)$. **Overall:** $Na_2O(s) + H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq)$.

b. The solution essentially becomes a NaOH(aq) solution.

22. a. A diprotic acid is one that has two potentially ionisable hydrogen atoms in each molecule of acid. The complete ionisation of 1 mole of a diprotic acid like H_2SO_4 will produce two moles of hydrogen ions.

b. Single ionisation of sulfuric acid: $H_2SO_4(aq) \rightarrow H^+(aq) + HSO_4^-(aq)$ ....①
The single ionisation of the strong acid H_2SO_4 goes to completion.

Single ionisation of carbonic acid: $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$......②
The single ionisation of the weak acid H_2CO_3 is partial.

The single ionisation of sulfuric acid in water ① is a complete reaction with no H_2SO_4 molecules remaining in solution. A single arrow (→) indicates this. By comparison the single ionisation of carbonic acid ② is an equilibrium process that favours the reactants, ie a high concentration of $H_2CO_3(aq)$ molecules with very few ions being formed. A double arrow ($\rightleftharpoons$) emphasises this.

c. A dilute acid, like carbonic acid in soft drink, is one with a small amount of acid in a large volume of solution, eg 0.1 mol L^{-1} H_2CO_3 or 0.1 mol L^{-1} H_2SO_4. A concentrated acid has a high ratio of acid to solution, eg sulfuric acid in battery acid has a concentration of 4.5 mol L^{-1}.

d. A solution of sulfuric acid of the same low concentration as a solution of carbonic acid will have a much higher hydrogen ion concentration than the carbonic acid solution. This is due to sulfuric acid being a much stronger acid than carbonic acid. Being fully ionised, H_2SO_4 produces a much higher hydrogen ion concentration than a H_2CO_3 solution of the same concentration. The effects of the higher $H^+(aq)$ ion concentration could produce skin burns or mouth ulceration. Not recommended!

23. a. First ionisation of carbonic acid: $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$ ..... ①
Second ionisation: $HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$ .... ②

b. Carbonic acid is a weak acid. All of the H^+ ions it produces come from the single ionisation of $H_2CO_3(aq)$. The resulting $HCO_3^-(aq)$ ions are weakly basic and have a tendency to accept protons from water or other acids rather than donating them. Thus the second ionisation ② can be considered not to occur in a carbonic acid solution.

c. Each subsequent member of the series has one less H atom in the formula and its charge increases by 1**-**, ie the equivalent of each member having one less H^+.

d. There is a tendency for the species to become less acidic and more basic as more protons are lost. Thus the first member of the series, $H_2CO_3(aq)$ is a weak acid, the next, $HCO_3^-(aq)$ is a very weak base and the last, $CO_3^{2-}(aq)$ is a moderate base.

e. Yes, there is a tendency for any polyprotic acid species, subsequent to donating a proton, to become less acidic and more basic. For example $H_2SO_4(aq)$ is a strong acid, $HSO_4^-(aq)$ is a weak acid and, $SO_4^{2-}(aq)$ is neutral. (Specifically, $SO_4^{2-}(aq)$ is very, very weakly basic when in water.)

24. a. Although a pH of 5-6 is slightly acidic, this is not considered acid rain as it is quite normal for rainfall to have this range of pH due to natural levels of atmospheric CO_2.

b. SO_3 dissolves in water (rainfall) to produce sulfuric acid, ie $SO_3(g) + H_2O(l) \rightleftharpoons H_2SO_4(aq)$.

c. The acid produced from SO_3 (sulfuric acid, H_2SO_4) is a strong acid that fully ionises when dissolved in rain water. This results in a much higher rain water H^+ ion concentration than is produced by the weak acid $H_2CO_3(aq)$. Consequently even when $SO_3(g)$ is present at a lower atmospheric concentration than $CO_2(g)$ it may have a greater effect on rainfall pH than CO_2.

Set 5 pH in water and aqueous solutions

1. a. $K_w = c(H^+) \times c(OH^-) = 1.0 \times 10^{-14}$ however, in neutral water $c(H^+) = c(OH^-)$ thus:

K_w can be written as: $K_w = [c(H^+)]^2$

so at 25 °C: $c(H^+) = \sqrt{K_w} = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}$ mol L^{-1}

and at 50 °C . $c(H^+) = \sqrt{K_w} = \sqrt{5.5 \times 10^{-14}} = 2.3 \times 10^{-7}$ mol L^{-1}

b. The water is still considered neutral as $c(H^+) = c(OH^-)$.

c. Clearly $c(H^+)$ is not necessarily 1.0×10^{-7} mol L^{-1} in a neutral sample of water. The water temperature affects its ionisation equilibrium so that at higher temperatures the $c(H^+)$ can increase while the water is still considered neutral [as $c(H^+) = c(OH^-)$].

Numerical answers are rounded to the proper number of **significant figures** using the rules outlined in Appendix 1. For **your convenience**, where **partial working** has been evaluated this is shown with the correct number of significant figures, however, the complete number is carried forward into later parts of a calculation. It is recommended that you **carry full numerical figures** until completion of a calculation. Your **final answer** should be rounded to the proper number of significant figures.

2. All reactions proceed at a faster rate when temperature is increased. Thus both reactions ① and ② proceed at a faster rate at 50 °C. However, at the higher temperature the rate of the endothermic reaction ① increases more than the rate of the exothermic reaction ②. Thus at the higher temperature the equilibrium system favours the products. Hence the concentration of both $H^+(aq)$ and $OH^-(aq)$ increase and as $K_w = c(H^+) \times c(OH^-)$ then K_w increases with increasing temperature.

3. The electrical conductivity of any solution will increases with increasing ion concentration. In pure water the concentration of H^+ and OH^- ions due to its autoionisation is extremely low (in pure water both are 1.0×10^{-7} mol L^{-1} at 25 °C). Thus even though ions are present their concentration is so low that the conductivity of pure water is negligible.

4. a. $\mathbf{c(H^+)} = c(HNO_3) = \mathbf{0.159\ mol\ L^{-1}}$ *and* $\mathbf{c(OH^-}$ $\dfrac{K_w}{c(H^+)} = \dfrac{1 \times 10^{-14}}{0.159} = \mathbf{6.29 \times 10^{-14}\ mol\ L^{-1}}$ (3SF)

b. $\mathbf{c(H^+)} = 2 \times c(H_2SO_4) = 2 \times 1.50 \times 10^{-2}$ mol L^{-1} = $\mathbf{3.0 \times 10^{-2}\ mol\ L^{-1}}$

and $\mathbf{c(OH^-}$ $\dfrac{K_w}{c(H^+)} = \dfrac{1 \times 10^{-14}}{3.0 \times 10^{-2}} = \mathbf{3.3 \times 10^{-13}\ mol\ L^{-1}}$ (2SF)

c. $\mathbf{c(OH^-}$ $\mathbf{1.33\ mol\ L^{-1}}$ *and* $\mathbf{c(H^+)} = \dfrac{K_w}{c(OH^-)} = \dfrac{1 \times 10^{-14}}{1.33} = \mathbf{7.52 \times 10^{-15}\ mol\ L^{-1}}$ (3SF)

d. $\mathbf{c(OH^-}$ $_2]$ = $\mathbf{9.44 \times 10^{-4}\ mol\ L^{-1}}$ *and* $\mathbf{c(H^+)} = \dfrac{K_w}{c(OH^-)} = \dfrac{1 \times 10^{-14}}{9.44 \times 10^{-4}} = \mathbf{1.06 \times 10^{-11}\ mol\ L^{-1}}$ (3SF)

5. a. **pH** = $-\log c(H^+) = -\log 0.085 =$ **1.1** (2SF) **b.** **pH** = $-\log c(H^+) = -\log 8.2 \times 10^{-6} =$ **5.1** (2SF)

c. $c(H^+) = \dfrac{K_w}{c(OH^-)} = \dfrac{1 \times 10^{-14}}{3.37} = 2.97 \times 10^{-15}$ mol L^{-1} *and* **pH** = $-\log c(H^+) = -\log 2.97 \times 10^{-15} =$ **14.5** (3SF)

d. $c(H^+) = \dfrac{K_w}{c(OH^-)} = \dfrac{1 \times 10^{-14}}{7.70 \times 10^{-5}} = 1.30 \times 10^{-10}$ mol L^{-1} *and* **pH** = $-\log c(H^+) = -\log 1.30 \times 10^{-10} =$ **9.89** (3SF)

6. a. $c(H^+) = c(HCl) = 4.62 \times 10^{-2}$ mol L^{-1} *and* **pH** = $-\log c(H^+) = -\log 4.62 \times 10^{-2} =$ **1.34** (3SF)

b. $c(H^+) = 2 \times c(H_2SO_4) = 2 \times 9.47 \times 10^{-3} = 1.89 \times 10^{-2}$ mol L^{-1}
and **pH** = $-\log c(H^+) = -\log 1.89 \times 10^{-2} =$ **1.72** (3SF)

c. $c(OH^-) = 3 \times c[Al(OH)_3] = 3 \times 5.8 \times 10^{-4} = 1.74 \times 10^{-3}$ mol L^{-1}

and $c(H^+) = \frac{K_w}{c(OH^-)} = \frac{1 \times 10^{-14}}{1.74 \times 10^{-3}} = 5.7 \times 10^{-12}$ mol L^{-1}

so **pH** = $-\log c(H^+) = -\log 5.7 \times 10^{-12} =$ **11** (2SF)

7. a. pH = $-\log c(H^+)$

$2.2 = -\log c(H^+)$

$-2.2 = \log c(H^+)$

inverse log $-2.2 = c(H^+)$

$c(H^+)$ = 6.3×10^{-3} mol L^{-1} (2SF)

alternatively
$c(H^+) = 10^{-pH}$
$= 10^{-2.2}$
$= 6.3 \times 10$ mol L

b. pH = $-\log c(H^+)$

$0.82 = -\log c(H^+)$

$-0.82 = \log c(H^+)$

inverse log $-0.82 = c(H^+)$

$c(H^+)$ = 1.5×10^{-1} mol L^{-1} (2SF)

alternatively
$c(H^+) = 10^{-pH}$
$= 10^{-0.82}$
$= 1.5 \times 10$ mol L

c. pH = $-\log c(H^+)$

$8.1 = -\log c(H^+)$

$-8.1 = \log c(H^+)$

inverse log $-8.1 = c(H^+)$

$c(H^+)$ = 7.9×10^{-9} mol L^{-1} (2SF)

alternatively
$c(H^+) = 10^{-pH}$
$= 10^{-8.1}$
$= 7.9 \times 10$ mol L

8. a.

HCl solution	**CH_3COOH solution**
pH = $-\log c(H^+)$ *ie* $1.0 = -\log c(H^+)$	pH = $-\log c(H^+)$ *ie* $2.9 = -\log c(H^+)$
$-1.0 = \log c(H^+)$ *ie* inverse log $-1.0 = c(H^+)$	$-2.9 = \log c(H^+)$ *ie* inverse log – 2.9 = $c(H^+)$
$c(H^+)$ = 1.0×10^{-1} mol L^{-1}	**$c(H^+)$ = 1.3×10^{-3} mol L^{-1}**

b. Ethanoic acid is a weak acid, ie K_a is small. In solution its ionisation equilibrium favours the molecular form, ie it remains mostly as molecules and so produces a low $c(H^+)$. Hydrochloric acid is a strong acid, ie K_a is large. It undergoes complete ionisation thus produces a much higher $c(H^+)$.

9.

For a solution of pH 0	**For a solution of pH -1**	**For a solution of pH -2**
pH = $-\log c(H^+)$	pH = $-\log c(H^+)$	pH = $-\log c(H^+)$
$0 = -\log c(H^+)$	$-1.0 = -\log c(H^+)$	$-2.0 = -\log c(H^+)$
$-0 = \log c(H^+)$	$1.0 = \log c(H^+)$	$2.0 = \log c(H^+)$
inverse log $-0 = c(H^+)$	inverse log $1.0 = c(H^+)$	inverse log $2.0 = c(H^+)$
$c(H^+)$ = 1 mol L^{-1}	**$c(H^+)$ = 10 mol L^{-1}**	**$c(H^+)$ = 100 mol L^{-1}**

A pH of 0 or -1 is quite possible as these correspond to **H^+**(aq) concentrations of **1 mol L^{-1}** and **10 mol L^{-1}** [eg 1 mol L^{-1} HCl(aq) and 10 mol L^{-1} HCl(aq)]. A pH of -2 is not plausible as this would require an H^+(aq) concentration of **100 mol L^{-1}**. No known acid has a sufficient solubility to produce such a high H^+(aq) concentration.

10. It is evident that a one unit change in pH means a 10 times change in hydrogen ion concentration. A two unit change in pH results in a 100 times change in hydrogen ion concentration. This is true for all solutions including E to H.

H^+(aq) mol L^{-1}	pH
0.1	1
0.01	2
0.001	3
0.0001	4

H^+(aq) mol L^{-1}	pH
0.32	0.4948
0.032	1.4948
0.0032	2.4948
0.00032	3.4948

11. A neutralisation reaction will occur between these two substances. By finding the $n(OH^-)$ and $n(H^+)$ added, it is possible to determine the amount of excess reagent, (OH^-) or (H^+). The excess reagent then determines the pH of the final mixture.

$n(NaOH) = \frac{m}{M} = \frac{4.65}{39.998} = 0.116$ mol *and* $n(OH^-) = n(NaOH) = 0.116$ mol

also $n(HCl) = cV = 0.335 \times 0.626 = 0.210$ mol *and* $n(H^+) = n(HCl) = 0.210$ mol

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

OH^-(aq) is the limiting reagent, thus: $n(H^+ \text{ used}) = n(OH^-) = 0.116$ mol

$n(H^+ \text{ excess}) = n(H^+ \text{ added}) - n(H^+ \text{ used}) = 0.210 - 0.116 = 0.094$ mol (3DP as addition rules apply, ie 2SF)

$c(H^+) = \frac{n(H^+)}{V(\text{mixture})} = \frac{9.4 \times 10^{-2}}{0.626} = 0.15$ mol L^{-1} (2SF) *and* **pH** = $-\log c(H^+) = -\log 0.15 =$ **0.82** (2SF)

Set 6 Understanding buffers

1. **a.** concentration
b. weak acid
c. conjugate
d. acid
e. $CH_3COOH(aq)$
f. $CH_3COO^-(aq)$
g. $H_3O^+(aq)$
h. fall
i. left
j. consuming
k. reduction
l. neutralise
m. right
n. replacing

2. **a.**

Buffer A		Buffer B		Buffer C	
weak acid	conjugate weak base	weak acid	conjugate weak base	weak acid	conjugate weak base
CH_3COOH	CH_3COO^-	NH_4^+	NH_3	$H_2PO_4^-$	HPO_4^{2-}

b. Buffer A: $CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$
Buffer B: $NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$
Buffer C: $H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$

c. When the strong acid HCl(aq) is added to the NH_4^+/NH_3 buffer system, it imposes a higher $H_3O^+(aq)$ concentration on the system. By LCP, the equilibrium system will act to minimise the imposed change, ie oppose the raised $H_3O^+(aq)$ concentration. Referring to the equation for buffer B (above), the equilibrium now favours the left hand side, ie the consumption of $H_3O^+(aq)$ and formation of $NH_4^+(aq)$. As a result the $NH_4^+(aq)$ concentration begins to rise while the concentration of both $NH_3(aq)$ and $H_3O^+(aq)$ begin to fall. When equilibrium is re-established, the $H_3O^+(aq)$ concentration is very slightly higher than before the addition of HCl(aq) but it has been significantly reduced back towards its original concentration before the acid was added.

d. When the pellet of NaOH(s) is added to the buffer in C it has the effect of neutralising any $H_3O^+(aq)$ present [ie $H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2H_2O(l)$] in the buffer system. Subsequently the equilibrium system will act to minimise the imposed change, ie the reduced $H_3O^+(aq)$ concentration. Referring to the equation for buffer C, the equilibrium now favours the formation of the products, ie $H_3O^+(aq)$ and $HPO_4^{2-}(aq)$. As a result the $H_2PO_4^-(aq)$ concentration begins to fall while the concentration of both $H_3O^+(aq)$ and $HPO_4^{2-}(aq)$ begin to rise. When equilibrium is re-established the $H_3O^+(aq)$ concentration would have increased partly back towards its original concentration before the NaOH(s) was added.

3. The acid-base equilibrium for the CH_3COOH/CH_3COO^- buffer system can be represented by the following equation:
$CH_3COO^-(aq) + H^+(aq) \rightleftharpoons CH_3COOH(aq)$......................①

When a strong acid is added to the CH_3COOH/CH_3COO^- buffer system, it imposes a higher $H^+(aq)$ concentration on the system. By LCP, the equilibrium system will act to minimise the imposed change, ie oppose the raised $H^+(aq)$ concentration. Referring to equation ①, the equilibrium now favours the consumption of $H^+(aq)$ and formation of $CH_3COOH(aq)$. As a result the $CH_3COOH(aq)$ concentration begins to rise while the concentration of both $CH_3COO^-(aq)$ and $H^+(aq)$ begin to fall. When equilibrium is re-established, the $H^+(aq)$ concentration is very slightly higher but it has been partly reduced back towards its original concentration before the acid was added.

When some strong base is added to the CH_3COOH/CH_3COO^- buffer system it will lower the $H^+(aq)$ concentration [$H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l)$]. The equilibrium system will act to minimise the imposed change, ie a lowered $H^+(aq)$ concentration. Referring to equation ①, the equilibrium now favours the formation of the reactants [$CH_3COO^-(aq)$ and $H^+(aq)$]. As a result the $CH_3COOH(aq)$ concentration begins to fall while the concentration of both $CH_3COO^-(aq)$ and $H^+(aq)$ begin to rise. When equilibrium is re-established the $H^+(aq)$ concentration would have increased partly back towards its original concentration before the base was added.

4. **a.** buffer capacity
b. pH change
c. weak base
d. weak acid
e. pH
f. depleted
g. strong acid
h. concentration

5. Buffer capacity is the ability of a buffer solution to neutralise excess added acid or base without the buffer pH appreciably changing. Buffer A has a higher buffer capacity than buffer B. The same weak acid and base is present in each of the buffer solutions A and B, however, buffer A has ten times the buffer capacity of buffer B. This is because it contains a ten times the amount of the weak acid and weak base. Buffer A contains 1.0 mol of the weak acid CH_3COOH and 1.0 mole of the weak base CH_3COO^- compared to buffer B which contains 0.10 mol of the weak acid CH_3COOH and 0.10 mole of the weak base CH_3COO^-. For this reason buffer A can neutralise approximately ten times as much added acid or base as buffer B.

6. a. The formation of carbonic acid in rainwater: $CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

b. Hydrogen ions released by the strong acids in acid rain can lower a lake's pH. The presence of hydrogencarbonate ions $HCO_3^-(aq)$ in the lake water can partially minimise this by consuming almost all of the extra $H^+(aq)$ released by the strong acids: $HCO_3^-(aq) + H^+(aq) \rightleftharpoons H_2CO_3(aq)$. The extent of this buffering effect depends upon the amount or concentration of HCO_3^- in the lake water. For the buffering effect to work there must be a significant concentration of HCO_3^-. This ensures HCO_3^- is not completely depleted or significantly reduced in concentration as it consumes the added acid.

c. Small amounts of insoluble $CaCO_3(s)$ can dissolve in water: $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$. The presence of $CO_3^{2-}(aq)$ ion will buffer the effect of strong acids from acid rain by neutralising the $H^+(aq)$ ions produced: $2H^+(aq) + CO_3^{2-}(aq) \rightleftharpoons H_2CO_3(aq)$ or $H^+(aq) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq)$. Furthermore as the carbonate ion concentration is diminished by its reaction with excess acid in the lake water so the dissociation equilibrium for the dissolving of $CaCO_3(s)$ [above] moves to the right producing more $CO_3^{2-}(aq)$. This helps to maintain the water's buffer capacity.

7. a. Vigorous exercise will raise the $CO_2(aq)$ concentration in muscle tissue and surrounding blood. This happens as the increased energy demand (due to the vigorous exercise) leads to an increased rate of respiration, $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$, accompanied by an increased rate of formation of CO_2. The resulting increase in $CO_2(aq)$ concentration leads to an increased blood concentration of $H_2CO_3(aq)$ and an increased blood concentration of $H^+(aq)$ thus lowering blood pH. This can be understood in terms of Le Chatelier's principle and the following equilibria:

$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$......... ① *and* $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$.......... ②

As the blood concentration of $CO_2(aq)$ rises, the equilibrium ① shifts to the right minimising this imposed change, ie minimising the elevated $CO_2(aq)$ concentration. This leads to an increased $H_2CO_3(aq)$ concentration. Equilibrium ② then shifts to the right consuming $H_2CO_3(aq)$ and minimising the effect of its increased concentration. This leads to a higher blood $H^+(aq)$ concentration and thus a lower blood pH.

b. An increased breathing rate leads to a faster rate of loss of $CO_2(aq)$ from blood circulating in the lungs. This reduces blood $CO_2(aq)$ concentration. As a consequence the blood $H_2CO_3(aq)$ concentration will also decrease followed by a decrease in the $H^+(aq)$ concentration and rising blood pH. These changes can be understood in terms of Le Chatelier's principle and the following two equilibria:

$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$......... ① *and* $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$ ....②

As the blood concentration of CO_2 falls (due to a faster breathing rate), equilibrium ① shifts to the left minimising this imposed change, ie minimising the falling blood $CO_2(aq)$ concentration. This also results in a decreased $H_2CO_3(aq)$ concentration. Equilibrium ② then shifts to the left producing more $H_2CO_3(aq)$ and minimising the effect of its reducing concentration. As reaction ② shifts to the left, it leads to a lower $H^+(aq)$ concentration resulting in higher blood pH.

c. Respiratory alkalosis is a condition where blood pH rises excessively. This means blood $H^+(aq)$ concentration falls below normal levels. It can be remedied by breathing into a paper bag. Doing this reduces $CO_2(aq)$ loss from blood circulating in the lungs. This leads to higher blood $CO_2(aq)$ concentration which ultimately reduces blood pH back to normal levels. These changes can be understood in terms of Le Chatelier's principle and the following three equilibria:

$CO_2(g,\text{ lung cavities}) \rightleftharpoons CO_2(aq,\text{ blood capillaries})$............① $CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$...........②

and $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$.............③

Breathing into a paper bag means the exhaled air is breathed back into the lungs. Breathing in exhaled air causes a rise in $CO_2(g)$ concentration inside the lung ($CO_2(g)$ concentration in exhaled air is ≈100x higher than in normal air). This imposed change of rising $CO_2(g)$ concentration inside the lungs causes equilibrium ① to shift to the right thus partially counteracting the elevated $CO_2(g)$ concentration. As a consequence $CO_2(aq,\text{ blood capillaries})$ also rises causing elevated blood $CO_2(aq)$ concentration. Equilibrium ② now responds by favouring the products and thus minimising the elevated $CO_2(aq)$ concentration. This then results in an increased $H_2CO_3(aq)$ concentration. Equilibrium ③ now shifts to the right minimising the effect of the increasing $H_2CO_3(aq)$ concentration. As equilibrium reaction ③ shifts to the right it also raises $H^+(aq)$ concentration thus reducing blood pH back to a more normal level.

Set 7 Volumetric analysis: Acid-base titrations

1. **a.** concentration
   b. standard solution
   c. volume
   d. pipette
   e. conical flask
   f. burette
   g. dropwise
   h. excess
   i. equivalence point
   j. indicator
   k. end point
   l. approximation

2. **a. i.** n[Na_2CO_3] = cV = $1.50 \times 10^{-1} \times 0.2500 = 3.75 \times 10^{-2}$ mol (Volume must be in L, ie 250.0 mL = 0.2500 L.)
   and **m[Na_2CO_3]** = nM = $3.75 \times 10^{-2} \times 105.99$ = **3.97 g** (3SF)

   ii. n($H_2C_2O_4$) = cV = $0.250 \times 0.500 = 0.125$ mol Note: Volume must be in L, ie 500.0 mL = 0.5000 L.
   also n($H_2C_2O_4.2H_2O$ added) = n($H_2C_2O_4$ in solution) = 0.125 mol
   and **m($H_2C_2O_4.2H_2O$)** = nM = 0.125×126.068 = **15.8 g** (3SF)

   b. Obtain some $Na_2CO_3(s)$ and dry this in an oven at around 260-270 $^{\circ}C$ for half an hour, then allow it to cool in a desiccator. Weigh accurately, approximately 3.97 g of the anhydrous $Na_2CO_3(s)$ into a clean dry 100 mL beaker. Add approximately 20 mL of distilled water from a wash bottle to the $Na_2CO_3(s)$ and dissolve using a stirring rod to swirl the mixture. Obtain a 250.0 mL volumetric flask and clean it with detergent if needed, then finally rinse the flask with distilled water. It does not need to be dry. Carefully transfer the Na_2CO_3 solution to the volumetric flask using a stirring rod to ensure transfer without loss of solution. Ensure the stirring rod and beaker are rinsed several times with distilled water from a wash bottle. The rinsings are also added to the flask. Finally make the solution volume in the flask up to the mark. Use a wash bottle to add distilled water and ensure the bottom of the meniscus is in line with the neck marking on the volumetric flask. Ensure the solution in the volumetric flask is well mixed. Rinse a clean storage bottle with some of your primary standard solution and discard the rinsings. Label the storage bottle and transfer the remainder of the primary standard solution to the storage bottle.

3. **a.** Typically, a primary standard must:
   - be able to be obtained in a very pure form consistent with its chemical formula
   - be sufficiently stable so that on exposure to air it does not readily change its water content or react with other gases (like CO_2) in the air
   - have a relatively high molar mass.

   Sodium hydroxide is not a primary standard as it is unable to be obtained in a suitably pure form. It frequently contains variable amounts of water and readily absorbs water from the atmosphere as well as reacting with $CO_2(g)$ present in air. [ie $2NaOH(s) + CO_2(g) \rightarrow H_2O(l) + Na_2CO_3(s)$]

   b. Hydrochloric acid cannot be prepared as a primary standard as HCl is a gas. Obtaining a pure dry sample of known mass and dissolving this in a specific volume of solution presents many technical difficulties. Instead, a solution of approximately the desired concentration can be obtained and titrated with a primary standard solution like $Na_2CO_3(aq)$ of a known concentration. This allows the hydrochloric acid concentration to be determined accurately. The resulting solution of hydrochloric acid of accurately known concentration is called a secondary standard. Secondary standard solutions are those whose concentration has been found by titration against a primary standard solution. Inevitably there is greater uncertainty or error present in the calculated concentration of a secondary standard solution than a primary standard. This is due to the greater number of measurements and procedures involved in finding the concentration of the secondary standard.

   c. n(Na_2CO_3) = $\frac{m}{M} = \frac{3.25}{105.99} = 3.07 \times 10^{-2}$ mol *and* **c(Na_2CO_3)** = $\frac{n}{V} = \frac{3.07 \times 10^{-2}}{0.2500}$ = **0.123 mol L^{-1}** (3SF)

   d. $Na_2CO_3(s)$ has a tendency to absorb water from the atmosphere. If the unknown amount of water present in the $Na_2CO_3(s)$ is not removed it will introduce a random error into its measured mass. Heating removes any absorbed water and allowing it to cool in a desiccator, which has a dry atmosphere, prevents it from reabsorbing moisture.

   e. A 250.0 mL volumetric flask is used to prepare the solution. It can be cleaned with detergent if needed. Once cleaned, its final rinse is with distilled water. It does not need to be dry.

4. $3NaOH(aq) + H_3PO_4(aq) \rightarrow Na_3PO_4(aq) + 3H_2O(l)$

   n(H_3PO_4) = c V = $2.95 \times 10^{-2} \times 29.55 \times 10^{-3} = 8.72 \times 10^{-4}$ mol (3SF)

   n[NaOH] = $\frac{3}{1} \times$ n(H_3PO_4) = $\frac{3 \times 8.72 \times 10^{-4}}{1} = 2.62 \times 10^{-3}$ mol (3SF)*****

$$\textbf{c[NaOH]} = \frac{n}{V} = \frac{2.62 \times 10^{-3}}{20.00 \times 10^{-3}} = \mathbf{0.131\ mol\ L^{-1}} \quad (3SF)$$

***Numerical answers** are rounded to the proper number of **significant figures** using the rules outlined in Appendix 1. For **your convenience**, where **partial working** has been evaluated this is shown with the correct number of significant figures, however, the complete number is carried forward into later parts of a calculation. It is recommended that you **carry full numerical figures** until completion of a calculation. Your **final answer** should be rounded to the proper number of significant figures.

5. a. A pipette is used to transfer the 25 mL aliquot of vinegar solution. The pipette is rinsed and cleaned with detergent, if needed, then rinsed with distilled water. The final rinse of a pipette is with the reagent to be measured, ie in this case some of the vinegar solution.

b. $CH_3COOH(aq) + NaOH(aq) \rightarrow NaCH_3COO(aq) + H_2O(l)$

n(NaOH used in the titration) = c V = $0.928 \times 23.40 \times 10^{-3} = 2.17 \times 10^{-2}$ mol (3SF)

$$n(CH_3COOH \text{ used in the titration}) = \frac{1*}{1} \times n(NaOH) = 2.17 \times 10^{-2} \text{ mol} \quad (3SF)$$

$$\mathbf{c(CH_3COOH)} = \frac{n}{V} = \frac{2.17 \times 10^{-2}}{25.00 \times 10^{-3}} = \mathbf{0.869\ mol\ L^{-1}} \quad (3SF)$$

***Exact** numbers such as the **coefficients** from a balanced equation may appear to have only one significant figure, however, they actually have unlimited significant figures. Hence they place no restriction on the number of significant figures appearing in the final answer. See the appendix section for rules on using significant figures.

6. a. $\mathbf{2NaOH}(aq) + \mathbf{H_2C_2O_4}(aq) \rightarrow \mathbf{Na_2C_2O_4}(aq) + \mathbf{2H_2O}(l)$

b. n(NaOH) = c V = $0.1195 \times 26.25 \times 10^{-3} = 3.137 \times 10^{-3}$ mol (4SF)

$$n(H_2C_2O_4) = \frac{1*}{2} \times n(NaOH) = \frac{3.137 \times 10^{-3}}{2} = 1.568 \times 10^{-3} \text{ mol} \quad (4SF)$$

$$\mathbf{c(H_2C_2O_4)} = \frac{n}{V} = \frac{1.568 \times 10^{-3}}{25.00 \times 10^{-3}} = \mathbf{6.274 \times 10^{-2}\ mol\ L^{-1}} \quad (4SF)$$

7. a. Assuming the operator is experienced and competent (as stated) and does not introduce any extra operator errors and the primary standard is correctly prepared then the unavoidable sources of random error include:

- The volume of the 250 mL volumetric flask will have a small random error in the range of ± 0.15 mL to ± 0.3 mL. (Class B, see Table 1.)
- The digital mass balance reading will have an error in the last displayed digit, ie at least ± 0.005 g.
- Even though the operator is experienced it may be assumed that due to limitations in the techniques of rinsing and transferring solutions that a very small amount of the 2.13 g of primary standard might not be successfully transferred to the volumetric flask.

b. The final rinse of the reagent bottle with distilled water is a rinsing error. The presence of any remaining droplets of distilled water in the storage bottle results in a slight dilution of the added primary standard. The final rinse of the storage bottle should be with some of the prepared primary standard solution that is going to be stored in it. The rinsing solution is then discarded. Primary standard solution can now be stored in the storage bottle. Any droplets of solution that remained after rinsing will not cause a dilution as these drops have essentially the same composition as the prepared primary standard solution.

c. The presence of an unknown amount of distilled water in the storage bottle caused a small but unknown dilution of the Na_2CO_3 primary standard solution. Thus a slightly greater volume of base (Na_2CO_3(aq) is less concentrated than it is thought to be) will be needed to achieve equivalence with the 20.00 mL of approximately 0.1 mol L^{-1} HCl solution. This reduces the accuracy of the titre results that are obtained, ie they are all a bit higher than they should be. The set of results may still be precise, ie all titre values can still be within a narrow acceptable range, but they will be inaccurate, ie they are all a bit too high. Thus accuracy is affected but not precision.

d. All of the titre values are higher than they should be as the base (added from the burette) is slightly more dilute than expected. This has the effect of making the HCl solution appear more concentrated than it actually is, ie it takes a greater volume of base to neutralise it than it should. Thus the true concentration of the HCl(aq) is a little less than the experimentally determined value of 0.109 mol L^{-1}.

Continued next page.

[Alternatively: The larger titre volume (**V**) causes the calculated n(Na_2CO_3) used to be larger than it should as n(Na_2CO_3) = c x **V**. Thus the n(HCl) thought to be present in the 20.00 mL aliquots is larger as n(HCl) = 2 x n(Na_2CO_3). Finally this gives rise to a larger than expected c(HCl) as c(HCl) = n(HCl) ÷ 20.00 x 10^{-3}.]

8. a. $\mathbf{2HCl}(aq) + \mathbf{Na_2CO_3}(aq) \rightarrow \mathbf{2NaCl}(aq) + \mathbf{H_2O}(l) + \mathbf{CO_2}(g)$

b. Precision is an important consideration in a titration. A measuring cylinder is typically only precise enough to measure 20 mL to 2 SF, ie 2.0 x 10^1 mL, while a pipette is precise to at least 4 SF, ie 20.00 mL. A burette is similarly precise for measuring volume, though is not suitable for measuring specific volumes such as 20.00 mL. It is better suited to measuring accurate variable volumes.

c. n(Na_2CO_3) = c V = 0.1907 x 16.50 x 10^{-3} = 3.147 x 10^{-3} mol (4SF)

$n(HCl) = \frac{2}{1} \times n(Na_2CO_3) = \frac{2 \times 3.147 \times 10^{-3}}{1} = 6.293 \times 10^{-3}$ mol (4SF) As the coefficient of HCl is twice that of Na_2CO_3.

$\mathbf{c(HCl)} = \frac{n}{V} = \frac{6.293 \times 10^{-3}}{20.00 \times 10^{-3}} = \mathbf{0.3147\ mol\ L^{-1}}$ (4SF)

d. $\mathbf{c_o(HCl)} = \frac{c_nV_n}{V_o} = \frac{0.3147 \times 1000.0}{25.00} = \mathbf{12.59\ mol\ L^{-1}}$ As 25.00 mL of concentrated solution was diluted to a new volume of 1000.0 mL.

9. a. $\mathbf{2HCl}(aq) + \mathbf{Na_2CO_3}(aq) \rightarrow \mathbf{2NaCl}(aq) + \mathbf{H_2O}(l) + \mathbf{CO_2}(g)$

b. At equivalence both HCl(aq) and Na_2CO_3(aq) are fully consumed. The presence of the acidic product CO_2(g) means the solution will be acidic at equivalence. Thus a suitable indicator is methyl orange. This changes yellow to red at pH 4.4 - 3.1 thus the end point will be an orange colour.

c. $n(Na_2CO_3 \text{ in } 250\text{ mL}) = \frac{m}{M} = \frac{1.288}{105.99} = 1.215 \times 10^{-2}$ mol

and $c(Na_2CO_3) = \frac{n}{V} = \frac{1.215 \times 10^{-2}}{0.2500} = 4.861 \times 10^{-2}$ mol L^{-1}

n(Na_2CO_3 used in the titration) = c V = 4.861 x 10^{-2} x 20.62 x 10^{-3} = 1.002 x 10^{-3} mol (4SF)

$n(\text{HCl used in the titration}) = \frac{2}{1} \times n(Na_2CO_3) = \frac{2 \times 1.002 \times 10^{-3}}{1} = 2.005 \times 10^{-3}$ mol (4SF)

$\mathbf{c(\text{diluted HCl})} = \frac{n}{V} = \frac{2.005 \times 10^{-3}}{20.00 \times 10^{-3}} = \mathbf{0.1002\ mol\ L^{-1}}$ (4SF)

d. As 25.00 mL of the approximately 10 mol L^{-1} acid was diluted to 2.000 L then:

$\mathbf{c_o(\text{HCl undiluted})} = \frac{c_nV_n}{V_o} = \frac{0.1002 \times 2000.0}{25.00} = \mathbf{8.018\ mol\ L^{-1}}$ Use the same units for V_n and V_o, eg mL or L.

10. The following is a detailed description of a titration procedure for standardising a sodium hydroxide solution. You will notice the NaOH solution is first diluted to around one fifth its original concentration. This is important as the original concentration of NaOH(aq) is such that a 20 mL aliquot of NaOH would require around 100 mL of sulfuric acid solution for equivalence. A burette only holds 50 mL. Alternatively 20 mL of sulfuric acid would require only around 4 mL of sodium hydroxide solution. In either case this would incur considerable measurement errors.

The dilution:

- Obtain a 20.00 mL pipette and clean this first with detergent followed by distilled water from a wash bottle.
- Pour 50 mL of the NaOH solution into a clean, dry, 100 mL beaker. The beaker must be dry and free of distilled water (or pre-rinsed with NaOH solution) otherwise the NaOH solution concentration will change.
- Using a pipette filler, draw around 10 ml of the NaOH solution into a clean pipette. Remove the filler and use the NaOH solution to rinse around the inside of your pipette ensuring any water drops are rinsed with solution. This must be done prior to filling with a measured aliquot of NaOH otherwise the measured volume of NaOH solution would become diluted by any water in the pipette.
- Obtain a 100.0 mL volumetric flask and clean this first with detergent followed by distilled water from a wash bottle.

Continued next page.

- Using the pipette and pipette filler draw 20.00 mL of NaOH solution from the 100 mL beaker. Ensure the bottom level of the meniscus is in line with the pipette marking when the tip of the pipette is held out of the solution. This must be done as the level of solution inside the pipette changes as the end of the pipette is drawn from the solution. The tip of the pipette should be allowed to touch the side of the beaker to ensure any adhering drop of NaOH solution is discarded.
- Discharge the 20.00 mL aliquot of NaOH solution from the pipette into the previously prepared 100.0 mL volumetric flask. When draining is complete, ensure the solution at the tip of the pipette is allowed to touch the inside of the volumetric flask and allow free draining for a further 20 seconds. Some solution will remain in the tip of the pipette. This is normal when the pipette has been properly discharged. Do not force the discharge of this remaining solution into the volumetric flask.
- Fill the volumetric flask with distilled water. Use a wash bottle to add the final amount of water. Watch the meniscus at eye level ensuring the bottom of the meniscus lines up with the marking on the volumetric flask. Thoroughly mix the solution and transfer this to a clean labelled storage bottle. The storage bottle should first be rinsed with some of the diluted NaOH solution and the rinse solution discarded.

The titration:

- Obtain a 20.00 mL pipette and clean this with detergent followed by distilled water from a wash bottle.
- Pour 50 mL of the diluted NaOH solution into a clean, dry, 100 mL beaker. The beaker must be dry (or pre-rinsed with the diluted NaOH solution) otherwise the NaOH solution concentration will change.
- Using a pipette filler draw around 10 ml of the diluted NaOH solution into a clean pipette. Remove the filler and use the NaOH solution to rinse around the inside of your pipette ensuring any water drops are rinsed with solution. This must be done prior to filling with a measured batch of diluted NaOH otherwise the measured NaOH solution concentration would become further diluted by any water in the pipette.
- Obtain four conical flasks and clean these first with detergent followed by distilled water from a wash bottle. These do not need to be dry, however, they must **not** be rinsed with reagent.
- Using the cleaned pipette and pipette filler draw 20.00 mL of diluted NaOH solution from the 100 mL beaker. Ensure the bottom level of the meniscus is in line with the pipette marking when the tip of the pipette is held out of the solution. This must be done as the level of solution inside the pipette changes as the end of the pipette is drawn from the solution. The tip of the pipette should be allowed to touch the side of the beaker to ensure any adhering drop of NaOH solution is discarded.
- Discharge the 20.00 mL of NaOH solution from the pipette into one of the conical flasks. When draining is complete, ensure the solution at the tip of the pipette is allowed to touch the inside of the conical flask and allow free draining for a further 20 seconds. Some solution will remain in the tip of the pipette. This is normal when the pipette has been properly discharged. Do not force this remaining solution into the conical flask. Repeat for 3 other flasks.
- Obtain a burette and clean this with detergent followed by distilled water from a wash bottle.
- Pour 10 mL of sulfuric acid solution into the burette and rinse around the inside of your burette and burette tap ensuring all water drops are rinsed with sulfuric acid solution. Discharge the rinsing solution. This rinsing must be done prior to filling with sulfuric acid otherwise the sulfuric acid solution would become diluted by any water present in the burette.
- Secure your burette with a stand and clamp and fill it with sulfuric acid solution to beyond the top of the scale. Discharge some sulfuric acid from the burette into a 250 mL beaker. Ensure the solution in the tap has been discharged and that no air bubbles are present. Ensure no drops of solution adhere to the tip and that the solution's meniscus is within the scale range.
- Add two to three drops of phenolphthalein indicator solution to one of the flasks containing 20.00 mL of NaOH solution. Do not add too much indicator as this will affect your results.
- Take a reading of the volume of sulfuric acid inside the burette. Ensure you read the bottom of the meniscus at eye level to ensure there is no parallax error. Record your reading in a suitable data table.
- Using an appropriate tap grip (eg pistol grip) discharge the solution from the burette into the conical flask of NaOH solution and indicator. Keep the flask swirling. When the pink colour shows signs of going colourless, begin to add the sulfuric acid solution more slowly.

Continued next page.

- Before the end of the titration rinse down the inside of the flask with distilled water from a wash bottle. Continue adding solution dropwise until the solution just goes permanently colourless. This is the end point of the titration. Stop adding solution and take a final burette reading. Record this value.
- Repeat this process until at least three consistent results are obtained for the titre volume. For a classroom situation this should be within ± 0.2 mL. Average your titre volumes discarding, any inconsistent data and use this to calculate the concentration of sulfuric acid in the usual way.

11. a. Use an acid-base indicator. Since the products (K_2SO_4 and H_2O) of the titration are neutral the equivalence point will also be neutral. A suitable indicator is one changing colour around pH 7, eg phenolphthalein (changes from colourless to pink at pH = 8.3-10).

b. Average volume of KOH = $\dfrac{39.25 + 39.30 + 39.35}{3}$ = 39.30 mL (4SF)

The titre values of 39.25mL, 39.30 mL and 39.35 mL are within ± 0.20 mL. These values are consistent with the expected collective scale reading errors for the burette and pipette marking. The 39.95 mL titre is inconsistent with the other values and its variation is probably due to random mistakes in technique or procedure, eg continuing to add reagent after the end point colour change. This value is excluded from the average.

c. $n(KOH) = c\,V = 1.029 \times 39.30 \times 10^{-3} = 4.044 \times 10^{-2}$ mol (4SF)

$2KOH(aq) + H_2SO_4(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$

$n(H_2SO_4) = \dfrac{1}{2} \times n(KOH) = \dfrac{4.044 \times 10^{-2}}{2} = 2.022 \times 10^{-2}$ mol

$c(H_2SO_4) = \dfrac{n}{V} = \dfrac{2.022 \times 10^{-2}}{25.00 \times 10^{-3}} = 0.8088$ mol L^{-1} (4SF)

Alternatively: Find $n(H_2SO_4)$ in 250 mL by ratio, this gives $n(H_2SO_4)$ in the original 50 mL.

$n(H_2SO_4$ in 250 mL Flask$) = \dfrac{250}{25} \times 2.022 \times 10^{-2} = 0.2022$ mol L^{-1}

$c(H_2SO_4$ in 50 mL of battery acid$) = \dfrac{0.2022}{0.05000} = 4.044$ mol L^{-1}

As 50.00 mL of battery acid was diluted to a new volume of 250.0 mL then:

$\mathbf{c_o(H_2SO_4)} = \dfrac{c_nV_n}{V_o} = \dfrac{0.8088 \times 250.0}{50.00} = \mathbf{4.044}$ **mol** $\mathbf{L^{-1}}$ All volumes in the dilution formula must have the same units, eg mL have been used here.

d. The solution density is 1.21 g mL^{-1} thus 1 mL of solution has a mass of 1.21 g.

Assume a 1.00 L volume of H_2SO_4 solution then: $m(H_2SO_4$ solution$) = 1000 \times 1.210$ g = 1210 g

$n(H_2SO_4$ in 1 L$) = c \times V = 4.044 \times 1.0 = 4.044$ mol *and* $m(H_2SO_4$ in 1 L$) = n \times M = 4.044 \times 98.086 = 396.7$ g

$\mathbf{c_{ppm}(H_2SO_4)} = \dfrac{m(H_2SO_4 \text{ in } 1.00L)}{m(1.00 \text{ L of } H_2SO_4 \text{ solution})} \times 1 \times 10^6 = \dfrac{396.7 \times 10^6}{1210} = \mathbf{3.28 \times 10^5}$ **ppm** (3SF)

12. a. The product CO_2 is acidic so the equivalence point will also be acidic. A suitable indicator is one changing colour in the weakly acidic region, eg methyl orange (red for pH ≤ 3.1 and yellow for pH ≥ 4.4). End point colour will be orange.

b. $n(HCl) = c\,V = 0.985 \times 7.15 \times 10^{-3} = 7.04 \times 10^{-3}$ mol (3SF)

$n(NaHCO_3) = \dfrac{1}{1} \times n(HCl) = 7.04 \times 10^{-3}$ mol (3SF) Since the stoichiometric coefficient is 1 for both $NaHCO_3$ and HCl.

$\mathbf{c(NaHCO_3)} = \dfrac{n}{V} = \dfrac{7.04 \times 10^{-3}}{20.00 \times 10^{-3}} = \mathbf{0.352}$ **mol** $\mathbf{L^{-1}}$ (3SF) This gives the concentration of the 250.0 mL solution prepared from impure $NaHCO_3(s)$.

c. $n(NaHCO_3$ in 250 mL solution$) = cV = 0.352 \times 250.0 \times 10^{-3} = 8.80 \times 10^{-2}$ mol

m($NaHCO_3$ in 250 mL solution) $= n \times M = 8.80 \times 10^{-2} \times 84.008 =$ **7.40 g**

(remember to carry the full value **7.396 g** into latter parts of the calculation)

d. $m(H_2O$ in 8.76 g sample$) = m($sample$) - m(NaHCO_3$ in sample$) = 8.76 - 7.40 = 1.36$ g

%(H_2O in 8.76 g sample) $= \dfrac{m(H_2O \text{ in sample})}{m(\text{impure sample})} \times 100 = \dfrac{1.36 \times 100}{8.76} =$ **15.6 % by mass H_2O** (3SF)

13. $Ca(OH)_2(aq) + 2HCl(aq) \rightarrow CaCl_2(aq) + 2H_2O(l)$

$n(HCl) = c\,V = 3.190 \times 10^{-2} \times 20.31 \times 10^{-3} = 6.479 \times 10^{-4}$ mol (4SF)

$n[Ca(OH)_2$ in 20.00 mL$] = \dfrac{1}{2} \times n(HCl) = \dfrac{6.479 \times 10^{-4}}{2} = 3.239 \times 10^{-4}$ mol (4SF)

$m[Ca(OH)_2 \text{ in 20 mL}] = n \times M = 3.239 \times 10^{-4} \times 74.096 = 2.400 \times 10^{-2}$ g

solubility [$Ca(OH)_2$ in g L^{-1}] $= \dfrac{m[Ca(OH)_2 \text{ in saturated solution}]}{V(\text{of saturated solution in L})} = \dfrac{2.400 \times 10^{-2}}{20.00 \times 10^{-3}} =$ **1.200 g L^{-1}** (4SF)

14. a. As the titration product CO_2 is weakly acidic and CH_3COO^- is weakly basic, then the equivalence point is probably near neutral. A suitable indicator is one changing colour around pH 7, eg phenolphthalein (changes from colourless to pink at pH = 8.3-10).

b. $n(Na_2CO_3 \text{ in 500 mL}) = \dfrac{m}{M} = \dfrac{1.416}{105.99} = 1.336 \times 10^{-2}$ mol

and $c(Na_2CO_3) = \dfrac{n}{V} = \dfrac{1.336 \times 10^{-2}}{0.5000} = 2.672 \times 10^{-2}$ mol L^{-1}

Exclude 24.85 mL as it is clearly inconsistent with the other results hence:

Average volume of $Na_2CO_3 = \dfrac{23.50 + 23.75 + 23.85 + 23.60}{4} = 23.68$ mL (4SF)

$n(Na_2CO_3 \text{ used in the titration}) = c\,V = 2.672 \times 10^{-2} \times 23.68 \times 10^{-3} = 6.326 \times 10^{-4}$ mol (4SF)

$n(CH_3COOH \text{ used in the titration}) = \dfrac{2}{1} \times n(Na_2CO_3) = \dfrac{2 \times 6.326 \times 10^{-4}}{1} = 1.265 \times 10^{-3}$ mol (4SF)

$c(\text{diluted } CH_3COOH) = \dfrac{n}{V} = \dfrac{1.265 \times 10^{-3}}{25.00 \times 10^{-3}} = 5.061 \times 10^{-2}$ mol L^{-1} (4SF)

Since 50.00 mL of supermarket vinegar was diluted to 1000.0 mL then:

c_0(CH_3COOH in the undiluted vinegar) = $\dfrac{c_nV_n}{V_0} = \dfrac{5.061 \times 10^{-2} \times 1000.0}{50.00} =$ **1.012 mol L^{-1}**

c. Assume 1.00 L of vinegar solution. As 1 mL of this solution has a mass of 1.060 g (ie a density of 1.060 g mL^{-1}) then 1.00 L of solution has a total mass of 1060 g. Determine the moles of vinegar in this 1.00 L of solution.

$n(CH_3COOH \text{ in 1 L}) = c \times V = 1.012 \times 1.000 = 1.012$ mol

and $m(CH_3COOH \text{ in 1 L}) = n \times M = 1.012 \times 60.05 = 60.78$ g

c%(CH_3COOH) $= \dfrac{m(CH_3COOH \text{ in 1.00 L})}{m(1.00 \text{ L of vinegar solution})} \times 100 = \dfrac{60.78 \times 100}{1060} =$ **5.734 %** (4SF)

15. Using the titration data determine the moles of the excess HNO_3 in the diluted 250.0 mL of solution.

$NaOH(aq) + HNO_3(aq) \rightarrow NaNO_3(aq) + H_2O(l)$

$n(NaOH \text{ used in titration}) = c\,V = 0.3152 \times 32.95 \times 10^{-3} = 1.039 \times 10^{-2}$ mol

thus $n(HNO_3 \text{ remaining in 20.00 mL sample}) = n(NaOH \text{ used in titration}) = 1.039 \times 10^{-2}$ mol

$n(HNO_3 \text{ remaining in 250.0 mL}) = n(NaOH \text{ in 20.00 mL}) \times \dfrac{250.0}{20.00} = 1.039 \times 10^{-2} \times \dfrac{250.0}{20.00} = 0.1298$ mol (4SF)

Determine the amount of HNO_3 that reacted with the metal M.

$n(HNO_3 \text{ originally in the 125.0 mL sample}) = c\,V = 2.107 \times 0.1250 = 0.2634$ mol HNO_3 originally present

$n(HNO_3 \text{ reacting with metal M}) = n(HNO_3 \text{ originally in 125 mL}) - n(HNO_3 \text{ remaining in the diluted 250 mL})$
$= 0.2634 - 0.1298 = 0.1336$ mol

Determine the moles of the metal M that must have reacted with HNO_3 and hence determine its molar mass.

$n(\text{metal M}) = \dfrac{3}{16} n(HNO_3) = \dfrac{3 \times 0.1336}{16} = 2.504 \times 10^{-2}$ mol From the given equation.

also, since $n(\text{metal M}) = \dfrac{m}{M}$ *then* **M(Metal M)** $= \dfrac{m}{n} = \dfrac{2.972}{2.504 \times 10^{-2}} =$ **118.7 g mol^{-1}**

The metal M could be tin (molar mass 118.7).

16. Use the titration data to determine the moles of NaOH remaining in the 500.0 mL solution.

$2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$

$n(H_2SO_4) = c\,V = 0.1120 \times 38.48 \times 10^{-3} = 4.310 \times 10^{-3}$ mol

thus n(NaOH remaining in 20.00 mL) = $2 \times n(H_2SO_4) = 8.620 \times 10^{-3}$ mol

n(NaOH remaining in 500.0 mL) = n(NaOH remaining in 20.00 mL) x $\dfrac{500.0}{20.00}$

$= 8.620 \times 10^{-3} \times \dfrac{500.0}{20.00} = 0.2155$ moL (4SF)

Determine the amount of NaOH from the 500.0 mL of solution that reacted with the monoprotic acid $C_6H_8O_6$.

n(NaOH originally in the 500.0 mL sample) = $c\,V = 4.640 \times 10^{-1} \times 500.0 \times 10^{-3} = 0.2320$ mol NaOH (4SF)

n(NaOH reacting with $C_6H_8O_6$) = n(NaOH originally present in 500 mL) - n(NaOH remaining in 500 mL)

= 0.2320 - 0.2155 = 0.0165 mol NaOH (answer to four decimal places, ie 3SF)

Determine the amount of $C_6H_8O_6$ that must have reacted with NaOH from the solution.

As $C_6H_8O_6$ is a monoprotic acid it forms the $C_6H_7O_6^-$ ion: ie $NaOH(aq) + C_6H_8O_6(aq) \rightarrow NaC_6H_7O_6(aq) + H_2O(l)$

$n(C_6H_8O_6) = \dfrac{1}{1} \times n(NaOH) = 1.65 \times 10^{-2}$ mol *and* **$m(C_6H_8O_6)$** $= n \times M = 1.65 \times 10^{-2} \times 176.12 =$ **2.91 g** (3SF)

Thus the 3.55 g vitamin C tablet contains 2.91 g of $C_6H_8O_6$ (to 3SF).

17. a. The general formula, H**B** represents a monoprotic acid. **B** is used as a generic symbol for the anion of the acid, ie **B** could be Cl^-, CH_3COO^-, NO_3^- and so on, thus: $Ba(OH)_2(aq) + 2HB(aq) \rightarrow BaB_2(aq) + 2H_2O(l)$

$n[Ba(OH)_2] = c\,V = 6.070 \times 10^{-1} \times 16.97 \times 10^{-3} = 1.030 \times 10^{-2}$ mol (4SF)

n[H**B** in 20.00 mL] = $\dfrac{2}{1} \times n([Ba(OH)_2]) = \dfrac{2 \times 1.030 \times 10^{-2}}{1} = 2.060 \times 10^{-2}$ mol (4SF)

n[H**B** in 100.0 mL] = $\dfrac{100.0}{20.00} \times 2.060 \times 10^{-2} = 1.030 \times 10^{-1}$ mol *ie* n[H**B** in 11.80 g] = 1.030×10^{-1} mol

also, since n(H**B**) = $\dfrac{m}{M}$ *then* **M(HB)** = $\dfrac{m}{n} = \dfrac{11.80}{1.030 \times 10^{-1}} =$ **114.6 g mol⁻¹** (4SF)

b. If the acid were diprotic then $n[H_2B$ in 20.00 mL$] = n[Ba(OH)_2]$ and so the $n[H_2B]$ would be halved and its molar mass would doubled to 229.2 g mol^{-1}.

18. Methyl red has a strong colour change from red, pH<4.4 to yellow pH>6.2. The indicator has been placed into the conical flask, along with NaOH(aq), so its initial colour is yellow (pH>6.2). Adding acid from the burette eventually causes the indicator colour to turn red when the reaction mixture pH falls below 6.2. This happens rapidly as the reaction approaches equivalence.

The colour change is caused by a change in the predominant indicator form from its basic form, *Ind* , which is yellow, to its acid form, **H***Ind* , which is red. This change is due a shift in the indicator's acid-base equilibrium position: $HInd(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Ind^-(aq)$. This happens, as by LCP, a rising $[H_3O^+]$ causes the indicator's acid-base equilibrium to shift left, ie minimising the imposed change and favouring formation of the red H*Ind*(aq) form. Note, the end point colour is orange as this shows there is a reasonable concentration of both H*Ind*(aq) and Ind^-(aq) meaning the mixture pH is between pH 4.4 and pH 6.2.

Set 8 Oxidation numbers and redox reactions

1. **a.** 0
b. 0
c. 0
d. 0
e. 0
f. 0
g. +2
h. -2
i. +2
j. +1
k. +1, -2
l. +1, -1
m. +4, -1
n. +3, -2
o. -2, +1
p. +1, -1 (a peroxide)
q. +1, -1 (a hydride)
r. +3, -2, +1

2. **a.** +2
b. +4
c. -4
d. -3
e. +5
f. +4
g. +3
h. +4
i. +1
j. +5
k. -3
l. +7
m. +4
n. +6
o. +6
p. +3
q. +2
r. -3

3. **a.** protons
b. zero
c. positively
d. oxidised
e. increases
f. reduces (ie decreases)
g. redox
h. oxidised
i. reduced
j. reducing agent
k. oxidant

4. **a.** **i.** chlorine **ii.** sodium **iii.** Cl_2(g) **iv.** Na(s)
b. not redox, no change in oxidation numbers
c. **i.** hydrogen **ii.** zinc **iii.** H^+(aq) **iv.** Zn(s)
d. not redox, no change in oxidation numbers
e. not redox, no change in oxidation numbers
f. **i.** oxygen **ii.** hydrogen **iii.** O_2(g) **iv.** H_2(g)
g. **i.** copper* **ii.** copper * **iii.** Cu^+(aq) **iv.** Cu^+(aq)
h. **i.** oxygen* **ii.** oxygen* **iii.** H_2O_2(l) **iv.** H_2O_2(l)
i. **i.** hydrogen **ii.** calcium **iii.** H_2O(l) **iv.** Ca(s)
j. not redox, no change in oxidation numbers
k. not redox, no change in oxidation numbers
l. **i.** nitrogen **ii.** copper **iii.** NO_3^-(aq) **iv.** Cu(s)
m. **i.** chromium **ii.** carbon **iii.** $Cr_2O_7^{2-}$(aq) **iv.** HCHO(l)
n. not redox, no change in oxidation numbers
o. **i.** nitrogen* **ii.** nitrogen* **iii.** NO_2(g) **iv.** NO_2(g)

*Reactions like (g), (h) and (o), where the same species is the oxidising agent and the reducing agent, are known as disproportionation reactions.

5. **a.** Respiration is a redox reaction as it involves both oxidation and reduction. The element C from $C_6H_{12}O_6$ is oxidised as its oxidation number changes from 0 in $C_6H_{12}O_6$ to +4 in CO_2. Also, oxygen is reduced from an oxidation state of 0 in O_2 to -2 in both CO_2 and H_2O.

b. Combustion is a redox reaction as it involves both oxidation and reduction. The element C is oxidised as its oxidation number changes from -4 in CH_4(g) to +4 in CO_2. Also, oxygen is reduced from an oxidation state of 0 in O_2 to -2 in both CO_2 and H_2O.

c. Incomplete combustion is a redox reaction as it involves both oxidation and reduction. The element C is oxidised as its oxidation number changes from an average of ≈-1.91 (actually 1@ -3, 44@-2 and 1@+3) in $C_{46}H_{92}O_2$(s) to 0 in C(s). Also, oxygen is reduced from an oxidation state of 0 in O_2 to -2 in H_2O.

d. Corrosion is a redox reaction as it involves both oxidation and reduction. The element Fe is oxidised as its oxidation number changes from 0 in Fe(s) to +3 in $Fe(OH)_3$. Also, oxygen is reduced from an oxidation state of 0 in O_2 to -2 in $Fe(OH)_3$.

Set 9 Balancing half equations and redox reactions

1. **a.** $Fe(s) \rightarrow Fe^{3+}(aq) + 3e^-$
b. $Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-$
c. $Cl_2(g) + 2e^- \rightarrow 2Cl^-$
d. $2H^+(aq) + 2e^- \rightarrow H_2(g)$ (Note: H must be balanced.)
e. $2Hg(l) \rightarrow Hg_2^{2+}(aq) + 2e^-$ (Note: Hg must be balanced.)

2. **a.** $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$
b. $H_2SeO_3(aq) + 4H^+(aq) + 4e^- \rightarrow Se(s) + 3H_2O(l)$
c. $PbO_2(s) + 4H^+(aq) + 2e^- \rightarrow Pb^{2+}(aq) + 2H_2O(l)$
d. $S(s) + 3H_2O(l) \rightarrow H_2SO_3(aq) + 4H^+(aq) + 4e^-$
e. $NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$
f. $2NO_3^-(aq) + 4H^+(aq) + 2e^- \rightarrow N_2O_4(g) + 2H_2O(l)$
g. $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

3. a. i. A metal-metal ion displacement reaction.

ii. A salmon pink deposit forms on a silvery grey metallic surface while the solution changes from blue to colourless.

b. i. A halogen-halide ion displacement reaction.

ii. The pale yellow solution turns an orange colour.

c. i. An acid-metal reaction.

ii. A silvery solid dissolves as colourless bubbles of gas form on its surface. The solution remains colourless.

d. i A metal-metal ion displacement reaction.

ii. A dark green solution turns colourless as a shiny grey metallic material dissolves and forms a dull grey coating.

4. a. i. $2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$ .... **(x1)**

ii. $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$ .... **(x1)**

iii. $Cl_2(g) + 2Br^-(aq) \rightarrow Br_2(aq) + 2Cl^-(aq)$

b. i. $Al(s) \rightarrow Al^{3+}(aq) + 3e^-$ .... **(x2)**

ii. $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ .... **(x3)**

iii. $2Al(s) + 3Cu^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Cu(s)$

c. i. $Cr(s) \rightarrow Cr^{3+}(aq) + 3e^-$ .... **(x4)**

ii. $Sn^{4+}(aq) + 4e^- \rightarrow Sn(s)$ .... **(x3)**

iii. $4Cr(s) + 3Sn^{4+}(aq) \rightarrow 3Sn(s) + 4Cr^{3+}(aq)$

d. i. $Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-$ .... **(x3)**

ii. $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ .... **(x1)**

iii. $Cr_2O_7^{2-}(aq) + 3Sn^{2+}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 3Sn^{4+}(aq) + 7H_2O(l)$

e. i $CH_3OH(aq) + H_2O(l) \rightarrow HCOOH(aq) + 4H^+(aq) + 4e^-$ .... **(x5)**

ii. $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$ .... **(x4)**

iii. $5CH_3OH(aq) + 4MnO_4^-(aq) + 12H^+(aq) \rightarrow 5HCOOH(aq) + 4Mn^{2+}(aq) + 11H_2O(l)$

f. i. $Tl^+(aq) \rightarrow Tl^{3+}(aq) + 2e^-$ .... **(x5)**

ii. $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$ .... **(x2)**

iii. $2MnO_4^-(aq) + 5Tl^+(aq) + 16H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5Tl^{3+}(aq) + 8H_2O(l)$

g. i. $Cr^{2+}(aq) \rightarrow Cr^{3+}(aq) + e^-$ .... **(x6)**

ii. $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$ .... **(x1)**

iii. $Cr_2O_7^{2-}(aq) + 6Cr^{2+}(aq) + 14H^+(aq) \rightarrow 8Cr^{3+}(aq) + 7H_2O(l)$

h. i. $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^-$ .... **(x3)**

ii. $NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)$ .... **(x2)**

iii. $3Ni(s) + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3Ni^{2+}(aq) + 2NO(g) + 4H_2O(l)$

i. i. $VO^{2+}(aq) + H_2O(l) \rightarrow VO_2^+(aq) + 2H^+(aq) + e^-$ .... **(x2)**

ii. $Cl_2(aq) + 2e^- \rightarrow 2Cl^-(aq)$ .... **(x1)**

iii. $2VO^{2+}(aq) + Cl_2(aq) + 2H_2O(aq) \rightarrow 2VO_2^+(aq) + 2Cl^-(aq) + 4H^+(aq)$

5. a. $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

The shiny grey solid dissolves forming a colourless solution and a colourless, odourless gas.

b. $Cl_2(aq) + 2I^- \rightarrow 2Cl^- + I_2(aq)$ A pale yellow solution turns a brown colour.

c. $Cr_2O_7^{2-}(aq) + 3S^{2-}$ $^+(aq) \rightarrow 2Cr^{3+}(aq) + 3S(s) + 7H_2O(l)$

An orange coloured solution turns green as a yellow precipitate forms.

d. $Cl_2(g) + Sn^{2+}(aq) \rightarrow 2Cl^-(aq) + Sn^{4+}(aq)$ A pale yellow-green gas dissolves forming a colourless solution.

e. $Fe(s) + 2H^+(aq) \rightarrow Fe^{2+}(aq) + H_2(g)$

The shiny grey solid dissolves forming a pale green solution and a colourless, odourless gas.

f. $Br_2(aq) + 2I^- \rightarrow 2Br^- + I_2(aq)$ An orange solution turns a brown colour.

g. $2NO_3^-(aq) + Cu(s) + 4H^+(aq) \rightarrow 2NO_2(g) + Cu^{2+}(aq) + 2H_2O(l)$

A shiny salmon pink solid dissolves producing a blue solution and a dense brown gas.

h. $2H_2O_2(aq) \rightarrow O_2(g) + 2H_2O(l)$ A colourless solution produces a colourless, odourless gas.

6. a. $Ba(s) + 2H^+(aq) \rightarrow Ba^{2+}(aq) + H_2(g)$ [The colourless gas is due to $H_2(g)$, $Ba^{2+}(aq)$ ions are colourless.]

b. $Fe(s) + Cu^{2+}(aq) \rightarrow Fe^{2+}(aq) + Cu(s)$
[The steel wool, Fe(s) becomes oxidised to pale green $Fe^{2+}(aq)$ while blue $Cu^{2+}(aq)$ ions are reduced to solid copper metal, ie the salmon pink deposit that forms on the steel wool surface.]

c. $Cl_2(g) + 2I^- \rightarrow 2Cl^- + I_2(aq)$
[The colour change of the solution from colourless to brown suggests I^- $_2$(aq) [brown in an aqueous solution]. Thus $Cl_2(g)$ must be reduced, most probably to the colourless Cl^- ion.]

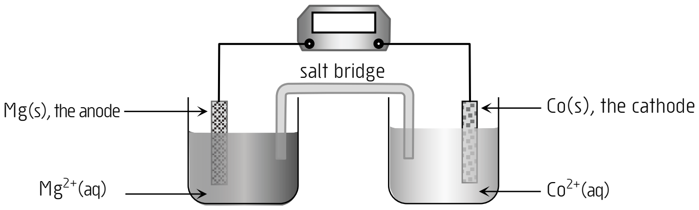
d. $MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$
[Acidified potassium permanganate is an oxidising agent where purple permanganate ions, $MnO_4^-(aq)$ are reduced to very pale pink (almost colourless) $Mn^{2+}(aq)$ ions. The formation of the pale brown solution indicates $Fe^{2+}(aq)$, which is a pale green colour, has been oxidised to $Fe^{3+}(aq)$ which is a pale brown colour.]

e. $5H_2C_2O_4(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$
[The colour change, purple to colourless and the acid conditions suggest $MnO_4^-(aq)$ [purple] has been reduced to the $Mn^{2+}(aq)$ [colourless or very pale pink]. The colourless gas is the oxidation product of $H_2C_2O_4(aq)$, ie $CO_2(g)$.]

Set 10 Understanding galvanic cells

1. a. galvanic cells
b. redox reaction
c. electric current
d. direct contact
e. reduction
f. cathode
g. electrode
h. anode
i. redox
j. oxidation
k. used
l. salt bridge
m. positive ions
n. net charge

2.



3. a. $Ag^+(aq) + e^- \rightarrow Ag(s)$ **b.** $H_2(g) \rightarrow 2H^+(aq) + 2e^-$ **c.** $H_2(g)|H^+(aq)||Ag^+(aq)|Ag(s)$.

d. To measure consistent standard reduction potentials all aqueous species involved in the redox process, both reactants and products, must be present at a concentration of 1.0 mol L^{-1} and any gaseous reactants or products must be present at a pressure of 100 kPa. Thus for standard conditions, a 1.0 mol L^{-1} $H^+(aq)$ solution and a hydrogen gas pressure of 100 kPa is needed.

e. The platinum surface acts as a catalyst that lowers the activation energy for the oxidation of $H_2(g)$. It also acts as an electron conductor for electrons travelling from the anode half-cell to the cathode half-cell.

f. The oxidation of hydrogen at the anode does contribute to the overall redox potential of 0.80 V. However, by definition the oxidation of hydrogen in a standard half-cell is defined as having a potential of exactly 0 V. Doing this allows a reduction potential to be determined for any given test species with reference to the oxidation of $H_2(g)$ being exactly 0 volts.

4. a. 1.36 V **b.** 0.34 V **c.** 0.43 V **d.** -0.96 V **e.** -0.34 V **f.** -1.51 V

5. a. i. strongest $Cl_2(g)$ $Br_2(l)$ $I_2(s)$ weakest
ii. strongest acidified MnO_4^- $Cl_2(g)$ acidified $Cr_2O_7^{2-}$ weakest
iii. strongest $Ag^+(aq)$ $Cu^{2+}(aq)$ $H^+(aq)$ weakest
b. i. strongest Ca(s) Ni(s) Cu(s) weakest
ii. strongest $I^-(aq)$ $Br^-(aq)$ $Cl^-(aq)$ weakest

6. a. Reaction will occur as written, ie is spontaneous as the E^{o}_{cell} = + 0.48 V. Alternatively, with reference to the SRP table, the oxidising agent $Cu^{2+}(aq)$ [left side of SRP] is above the reducing agent Sn(s) [right side of SRP], thus the reaction is spontaneous.

b. Reaction will not occur as written, ie not spontaneous as the E^{o}_{cell} = - 0.82 V. Alternatively, with reference to the SRP table, the oxidising agent $I_2(s)$ [left side of SRP] is below the reducing agent $Cl^{-}(aq)$ [right side of SRP], thus the reaction is not spontaneous.

c. Reaction will occur as written, ie is spontaneous as the E^{o}_{cell} = + 0.82 V. Alternatively, with reference to the SRP table, the oxidising agent $Cl_2(g)$ [left side of SRP] is above the reducing agent $I^{-}(aq)$ [right side of SRP], thus the reaction is spontaneous.

d. Reaction will occur as written, ie is spontaneous as the E^{o}_{cell} = + 1.68 V. Alternatively, with reference to the SRP table, the oxidising agent $H^{+}(aq)$ [left side of SRP] is above the reducing agent Al(s) [right side of SRP], thus the reaction is spontaneous.

e. Reaction will not occur as written, ie not spontaneous as the E^{o}_{cell} = - 0.80 V. Alternatively, with reference to the SRP table, the oxidising agent $H^{+}(aq)$ [left side of SRP] is below the reducing agent Ag(s) [right side of SRP], thus the reaction is not spontaneous.

f. Reaction will not occur as written, ie is not spontaneous as the $E^{\ominus}_{cell}$ = -0.34 V. Alternatively, with reference to the SRP table, the oxidising agent $H^{+}(aq)$ [left side of SRP] is below the reducing agent Cu(s), [right side of SRP] thus the reaction is not spontaneous.

g. Reaction will occur as written, ie is spontaneous as the E^{o}_{cell} = + 0.15 V. Alternatively, with reference to the SRP table, the oxidising agent $MnO_4^{-}(aq)$ [left side of SRP] is above the reducing agent $Cl^{-}(aq)$ [right side of SRP], thus the reaction is spontaneous.

7. a. Hydrogen gas is a colourless, odourless gas that is less dense than air. Its low density allows it to be collected in an inverted test tube. To do this, place the reaction mixture into a test tube and place an empty inverted test tube over the reaction mixture. After the reaction is complete a lighted match can be brought up to the open end of the inverted test tube to test for hydrogen gas. If the gas is hydrogen then a loud pop can be heard as the gas ignites.

b. The metals Ni, Sn, Al and Zn should all produce hydrogen as the oxidising agent $H^{+}(aq)$ [left side of SRP] is above each of the various reducing agents Ni(s), Sn(s), Al(s) and Zn(s) [right side of SRP]. The metals Cu and Ag will not produce hydrogen as the oxidising agent $H^{+}(aq)$ [left side of SRP] is below the reducing agents Cu(s) and Ag(s) [right side of SRP].

c. Nitrate ions [$NO_3^{-}(aq)$] in an acidic solution [$H^{+}(aq)$ ions present] are a much stronger oxidising agent than hydrogen ions. This is evident as nitrate ions are higher up on the left side of the SRP table and have a higher reduction potential (+0.96 V). Under standard conditions the reduction of nitrate ions in an acidic solution results in the formation of nitrogen monoxide (NO). Thus $NO_3^{-}(aq)$ ions are reduced in preference to $H^{+}(aq)$ ions and the gas produced is NO(g) rather than $H_2(g)$. Further, as nitrate ions are a stronger oxidising agent, then both Cu(s) and Ag(s) are able to be oxidised.

$NO_3^{-}(aq) + 4H^{+}(aq) + 3e^{-} \quad NO(g) + 2H_2O(l) \quad E^{o} = + 0.96\ V$

8. a. Reaction with Sn: $Sn(s) + Cu^{2+}(aq) \rightarrow Sn^{2+}(aq) + Cu(s)$ E^{o}_{cell} = +0·48 V so reaction will occur. Alternatively, with reference to the SRP table, the oxidising agent $Cu^{2+}(aq)$ [left side of SRP] is above the reducing agent Sn(s) [right side of SRP], thus the reaction is spontaneous.

Reaction with Ag: $2Ag(s) + Cu^{2+}(aq) \rightarrow 2Ag^{+}(aq) + Cu(s)$ E^{o}_{cell} = -0·46 V so reaction will not occur. Alternatively, with reference to the SRP table, the oxidising agent $Cu^{2+}(aq)$ [left side of SRP] is below the reducing agent Ag(s) [right side of SRP], thus the reaction is not spontaneous.

Conclusion: This test will work.

b. Reaction with Co: $Co(s) + 2H^{+}(aq) \rightarrow Co^{2+}(aq) + H_2(g)$ $E^{o}_{cell} = +0{\cdot}28$ V so this reaction will occur. Alternatively, with reference to the SRP table, the oxidising agent $H^{+}(aq)$ [left side of SRP] is above the reducing agent Co(s) [right side of SRP], thus the reaction is spontaneous.

Reaction with Ni: $Ni(s) + 2H^{+}(aq) \rightarrow Ni^{2+}(aq) + H_2(g)$ $E^{o}_{cell} = +0{\cdot}24$ V so this reaction will occur. Alternatively, with reference to the SRP table, the oxidising agent $H^{+}(aq)$ [left side of SRP] is above the reducing agent Ni(s) [right side of SRP], thus the reaction is spontaneous.

Conclusion: The test, as described, will not distinguish the metals, however, the metals may be distinguished as nickel produces a green solution of $Ni^{2+}(aq)$ while cobalt forms a pink solution of $Co^{2+}(aq)$.

c. Reaction with Zn: $Zn(s) + Ni^{2+}(aq) \rightarrow Zn^{2+}(aq) + Ni(s)$ $E^{o}_{cell} = +0{\cdot}52$ V so this reaction will occur. Alternatively, with reference to the SRP table, the oxidising agent $Ni^{2+}(aq)$ [left side of SRP] is above the reducing agent Zn(s) [right side of SRP], thus the reaction is spontaneous.

Reaction with Pb: $Pb(s) + Ni^{2+}(aq) \rightarrow Pb^{2+}(aq) + Ni(s)$ $E^{o}_{cell} = -0{\cdot}11$ V so this reaction will not occur. Alternatively, with reference to the SRP table, the oxidising agent $Ni^{2+}(aq)$ [left side of SRP] is below the reducing agent Pb(s) [right side of SRP], thus the reaction is not spontaneous.

Conclusion: This test will work.

9. a. $2Cr(s) + 3Cu^{2+}(aq) \rightarrow 2Cr^{3+}(aq) + 3Cu(s)$

b. Cell voltage = $E^{o}_{red} + E^{o}_{ox} = 0.34 + 0.74 = 1{\cdot}08$ Volts

c. A number of factors contribute to lower than expected cell voltages. If solution concentrations, temperature and gas pressures are not standard as reflected in the table of Standard Reduction Potentials then voltages may be higher or lower than expected. Even if conditions are standard, cells may become polarised very quickly if they actually deliver current. This happens as the concentrations of various ions immediately at the electrode surface rapidly fall or rise as the cell operates. Standard cell potential should only be measured when the cell is not delivering current.

d. Anode: Cr(s) electrode. Cathode: Cu(s) electrode.

e. Cathode: Solution changes from blue to colourless (or blue colour fades). The electrode increases in mass as a shiny salmon pink deposit forms.
Anode: Dissolves and decreases in mass as the surrounding solution turns a deeper green colour.

f. Electrons move through the external conductor from the Cr(s) electrode (anode) to the Cu(s) electrode (cathode).

g. Positive ions (eg Cr^{3+}) move from the $CrCl_3(aq)$ cell through the salt bridge to the $CuSO_4(aq)$ cell.

Negative ions (eg SO_4^{2-}) move from the $CuSO_4(aq)$ cell through the salt bridge to the $CrCl_3(aq)$ cell.

[Remember: Cations (+) move toward the cathode and anions (-) move toward the anode.]

10.a. i. Anode: Ni(s) electrode. Cathode: Cu(s) electrode.

ii. $Ni(s) \rightarrow Ni^{2+}(aq) + 2e^{-}$

iii. $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$

iv. $Ni(s) + Cu^{2+}(aq) \rightarrow Ni^{2+}(aq) + Cu(s)$ Expected EMF is 0.58 Volts.

v. Anode: Ni(s) electrode dissolves and loses mass while the surrounding solution becomes a deeper green colour.
Cathode: Cu(s) electrode gains mass as a salmon pink deposit forms here. The surrounding solution slowly loses its blue colour.

vi Electrons move, via the external circuit, from the nickel electrode, through the voltmeter, to the copper electrode.

vii Sulfate ions, $SO_4^{2-}(aq)$ move through the salt bridge towards the anode, Ni(s) electrode while nickel ions, $Ni^{2+}(aq)$ and copper ions, $Cu^{2+}(aq)$ move towards the cathode, Cu(s).

b. **i.** Anode: Pb(s) electrode. Cathode: Ag(s) electrode.

ii. $Pb(s) \rightarrow Pb^{2+}(aq) + 2e^-$

iii. $Ag^+(aq) + e^- \rightarrow Ag(s)$

iv. $2Ag^+(aq) + Pb(s) \rightarrow 2Ag(s) + Pb^{2+}(aq)$ Expected EMF is 0.93 Volts.

v. Anode: Pb(s) electrode dissolves and loses mass while the surrounding solution remains colourless.
Cathode: Ag(s) electrode gains mass as a silvery metallic deposit forms here.

vi Electrons move via the external circuit from the lead electrode through the voltmeter to the silver electrode.

vii $NO_3^-(aq)$ ions move through the salt bridge towards the anode, Pb(s) while $Pb^{2+}(aq)$ ions and $Ag^+(aq)$ ions move towards the cathode, Ag(s).

c. **i.** Anode: Zn(s) electrode. Cathode: Co(s) electrode.

ii. $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

iii. $Co^{2+}(aq) + 2e^- \rightarrow Co(s)$

iv. $Co^{2+}(aq) + Zn(s) \rightarrow Co(s) + Zn^{2+}(aq)$ Expected EMF is 0.48 Volts.

v. Anode: Zn(s) electrode dissolves and loses mass while the surrounding solution remains colourless.
Cathode: Co(s) electrode gains mass as a silvery metallic deposit forms here. The surrounding solution slowly loses its pink colour.

vi Electrons move via the external circuit from the zinc electrode through the voltmeter to the cobalt electrode.

vii $SO_4^{2-}(aq)$ ions move through the salt bridge towards the anode, Zn(s) while $Zn^{2+}(aq)$ ions and $Co^{2+}(aq)$ ions move towards the cathode, Co(s).

Set 11 Electrolysis

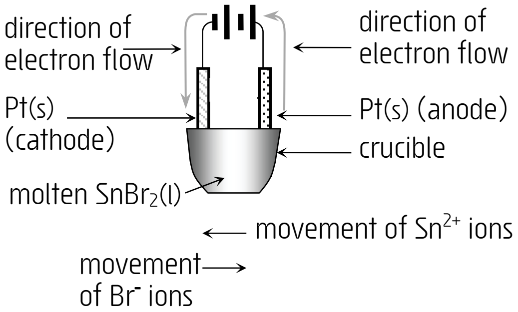
1. **a.** **Electrode A**: Electrons move away from electrode A, passing into the conducting wire as they move towards the positive terminal of the power supply.
Electrode B: Electrons move away from the negative terminal of the power supply as they move into the conducting wire towards electrode B.
Electrode C: Electrons move away from the negative terminal of the power supply as they move into the conducting wire towards electrode C.
Electrode D: Electrons move away from electrode D, passing into the conducting wire as they move towards the positive terminal of the power supply.

b. A: oxidation B: reduction C: reduction D: oxidation

c. **Electrode A**: Chloride ions (Cl^-) migrate towards electrode A.
Electrode B: Copper ions (Cu^{2+}) migrate towards electrode B.
Electrode C: Potassium ions (K^+) migrate towards electrode C.
Electrode D: Bromide ions (Br^-) migrate towards electrode D.

d. Cell (I) cathode is electrode B. Cell (II) cathode is electrode C.

2. **a.**



b. Cathode half-reaction: $Sn^{2+}(l) + 2e^- \rightarrow Sn(l)$

Note: Tin is shown in the liquid phase as it melts at 232 °C. The cell temperature is most probably well above this temperature as the salt $SnBr_2$ melts at 216 °C.

Anode half-reaction: $2Br^- \rightarrow Br_2(g) + 2e^-$

c. Wear **safety glasses**. These should always be worn when heating any substance. In this experiment the $SnBr_2(l)$ is heated to above 200 °C. There is always a danger of the molten salt exploding or splashing into the eye. Only conduct this experiment in a **fume hood** or an appropriately ventilated area. Bromine gas is produced at the anode. It is a corrosive gas and can irritate or burn the eyes, respiratory system and skin. Use **tongs** and avoid directly touching any of the hot apparatus like the tripod or crucible containing the molten salt. This will prevent painful skin burns. Use a **bench mat**. Whenever heating a substance a bench mat should be placed underneath the heating equipment. This protects the bench from heat damage.

3. a. **Cathode** half-reaction: $Na^+(l) + e^- \rightarrow Na(l)$

Observation: A silvery liquid forms at this electrode.

Anode half-reaction: $2Br^-(l) \rightarrow Br_2(g) + 2e^-$

Observation: A red gas is seen to form here.

b. **Cathode** half-reaction: $Mg^{2+}(l) + 2e^- \rightarrow Mg(l)$

Observation: A silvery liquid forms at this electrode.

Anode half-reaction: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

Observation: A pale yellow-green gas forms here.

c. **Cathode** half-reaction: $Al^{3+}(l) + 3e^- \rightarrow Al(l)$

Observation: A silvery liquid forms at this electrode.

Anode half-reaction: $2O^{2-}(l) \rightarrow O_2(g) + 4e^-$

Observation: A colourless gas forms here.

d. **Cathode** half-reaction: $Cu^{2+}(l) + 2e^- \rightarrow Cu(l)$

Observation: A salmon pink deposit forms at this electrode.

Anode half-reaction: $2I^-(l) \rightarrow I_2(g) + 2e^-$

Observation: A purple gas is seen to form here.

4. a. The electrolyte must be maintained in a molten state for electrolysis to work. The melting points of sodium chloride and calcium chloride respectively are 801 °C and 772 °C. The melting point of the $CaCl_2$ and NaCl mixture is quoted in the question as being 580 °C. As can be seen the mixture melts at a lower temperature than either of the pure components. This is a common property of mixtures and is known as freezing point depression. Thus economic and environmental advantages are achieved by adding $CaCl_2$ to the electrolyte as less energy is required to maintain the lower temperature of 580 °C needed to keep the electrolyte in a molten state.

b. **Sodium ions** (Na^+) move through the molten electrolyte towards the steel cathode. **Chloride** ions (Cl^-) move through the molten electrolyte towards the carbon anode.

c. **Cathode** half-reaction: $Na^+(l) + e^- \rightarrow Na(l)$ **Anode** half-reaction: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

d. If the presence of water prevents the reduction of sodium ions then water itself must be reduced. This would result in the formation of hydrogen gas at the cathode instead of sodium metal. [Clearly this must be the case, if Na^+ ions were reduced to Na metal then this highly reactive metal would react with water producing H_2 gas and OH^- ions.]

5. a. **Anode:** The species present in the electrolyte include: $H_2O(l)$, $Zn^{2+}(aq)$ and $Br^-(aq)$. Using a table of standard reduction potentials the possible anode (oxidation) half-reactions are:

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $E^o_{ox} = -1.23$ V *and* $2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$ $E^o_{ox} = -1.08$ V.

Of the two possible half-reactions, the oxidation of bromide ions is most favourable (ie most positive E^o_{ox}).

Cathode: Using SRP data the possible cathode (reduction) half-reactions are:

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E^o_{red} = -0.83$ V *and* $Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$ $E^o_{red} = -0.76$ V.

Of the two possible half-reactions the reduction of zinc ions is most favourable (ie most positive E^o_{red}).

b. **Anode:** The species present in the electrolyte include: $H_2O(l)$, $Cu^{2+}(aq)$, $Sn^{2+}(aq)$, and $Cl^-(aq)$. Using a table of standard reduction potentials the possible anode (oxidation) half-reactions are:

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $E^o_{ox} = -1.23$ V *and* $2Cl^-(aq) \rightarrow Cl_2(aq) + 2e^-$ $E^o_{ox} = -1.36$ V.

Of the two possible half-reactions, the oxidation of water is most favourable (ie most positive E^o_{ox}).

Cathode: Using SRP data the possible cathode (reduction) half-reactions are: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E^o_{red} = -0.83$ V *and* $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E^o_{red} = +0.34$ V *and* $Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$ $E^o_{red} = -0.14$ V.

Of the three possible half-reactions, the reduction of copper ions is most favourable (ie most positive E^o_{red}).

6. **a.** **i.** $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

ii. $2I^-(aq) \rightarrow I_2(s) + 2e^-$

iii. Cathode: The blue solution becomes pale (loses its colour) as the cathode gains mass while developing a salmon pink coating.
Anode: The blue solution surrounding the anode becomes increasingly brown in colour.

b. **i.** $Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$

ii. $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

iii. Cathode: The green solution becomes pale (loses its colour) as the cathode increases in mass and gains a grey coating.
Anode: A colourless gas forms here.

c. **i.** $2H^+(aq) + 2e^- \rightarrow H_2(g)$

ii. $2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$

iii. Cathode: A colourless gas forms here.
Anode: The colourless solution surrounding the anode turns an orange colour.

d. **i.** $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

ii. $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

iii. Cathode: Bubbles of colourless gas form here.
Anode: Bubbles of colourless gas also form here.

Set 12 Electrochemistry in action

1. The 'International Partnership for Hydrogen and Fuel Cells in the Economy' is an organisation consisting of eighteen countries dedicated to fostering global cooperation on research and development, common standards and infrastructure development relating to a hydrogen economy and fuel cell technology.

2. The dry cell is an example of a primary cell. Cells like this contain a fixed amount of oxidant and reductant. Once these reagents are used up the cell no longer produces a voltage and is said to be 'flat'. Primary cells cannot be recharged and so are discarded once they go flat. Secondary cells are galvanic cells that can be recharged. The recharging process involves applying a DC voltage to the cell. This regenerates the oxidant and reductant originally present in the charged cell. The lead-acid cell is an example of a secondary cell. In a fuel cell, like the hydrogen-oxygen fuel cell, the oxidant and reductant are continuously fed into the cell. Fuel cells have a very long life and can theoretically operate without limit as long as the oxidant and reductant are supplied into the cell.

3. **a.** Primary cells like these contain a fixed amount of oxidant and reductant and once this is consumed they are not able to be recharged.

b. In both cases the oxidising agent is $MnO_2(s)$ and the reducing agent is metallic Zn.

c. **i.** NH_4Cl is the electrolyte providing ions for the salt bridge. Also the acidic NH_4^+ ions provide protons needed in the reduction of MnO_2.

ii Ammonium ions are weakly acidic, ie $NH_4^+(aq) \rightleftharpoons H^+(aq) + NH_3(aq)$ thus giving the electrolyte paste a low pH. The resulting $H^+(aq)$ ions are in contact with zinc and hence oxidise it, ie $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$. This reaction slowly consumes the zinc and decreases the dry cell's shelf life.

d. The zinc anode in a dry cell is a single solid sheet rolled into the shape of a can, as opposed to the cylindrical plug of powdered zinc used in the alkaline cell.

e. The anode half-reaction is identical in both cells: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ can only occur at the zinc surface then the higher Zn surface area in the alkaline cell (Zn powder as opposed to Zn foil) promotes a faster rate of oxidation in the alkaline cell. This allows for a higher rate of production of electrons in the alkaline cell and hence a higher current flow. (Current is a measure of the number of electrons flowing in a conductor per second.)

f. $NH_3(aq)$ forms as a by-product of the reduction of MnO_2. As ammonia is a gas at room temperature, it can be released from solution to form ammonia gas: $NH_3(aq) \rightleftharpoons NH_3(g)$. Two changes occurring in a cell as it operates are; a temperature rise and a rise in the concentration of $NH_3(aq)$. Both of these effects favour the formation of more $NH_3(g)$.

4. AgO/Zn button batteries may be considered toxic in the environment as some brands contain small amounts of mercury. These should be recycled appropriately. Lithium cells do not contain toxic components but they are potentially dangerous (explosive and a fire hazard) as they may contain unreacted lithium metal, a strong reducing agent. They should be fully discharged prior to disposal. Dry cells and alkaline cells are not considered to contain toxic materials. Neither Zn nor Mn is considered toxic at low concentration.

5. a. Alkaline cells use zinc as the reducing agent while lithium is the reducing agent in a lithium cell.

b. Oxidation half-equation for Zn: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $E^0 = 0.76$ V

Oxidation half-equation for Li: $Li(s) \rightarrow Li^+(aq) + e^-$ $= 3.05$ V

The higher oxidation potential for Li means the lithium cell should produce a higher cell voltage, around 2.29 V higher at standard conditions. [Note: The actual operating voltage of a primary lithium cell is given as 3.0 V compared to 1.5 V for an alkaline cell.] The higher cell voltage contributes to the higher energy available from a primary lithium cell.

c. Two moles of lithium has a mass of 13.8 g [m(Li) =n M = 2 x 6.94 = 13.8 g]. By comparison one mole of zinc has a mass of 65.38 g. Thus to produce the same size electric current (amps) for the same length of time a smaller mass of lithium is required, approximately 4.7x less. This factor alone gives the lithium cell a higher energy density. [Other factors contributing to the overall energy density of a cell include available cell voltage and cell design. Typically a primary lithium cell has an energy density 2-3x that of an alkaline cell.]

d. Lithium cells must not contain water as the electrolyte solvent, as lithium reacts spontaneously with water producing hydrogen gas and lithium hydroxide.

6. Lead-acid batteries are classed as a hazardous waste as they contain lead and concentrated (4.5 mol L^{-1}) sulfuric acid. Lead and its compounds are acutely and chronically toxic. They should be recycled rather than carelessly released into the environment. Sulfuric acid is a hazardous, corrosive substance that must be recycled or neutralised before releasing into the environment.

7. a. The Pb(s) and $PbO_2(s)$ of the anode and cathode respectively, are present in a powdered, high surface area form. Both oxidation of Pb and reduction of PbO_2 can only take place on their surface where the solid makes contact with the electrolyte. For this reason a high surface area allows a high rate of oxidation and reduction, ie a high rate of production and consumption of electrons. This allows the cell to produce a high current.

b. One mole of lead has a mass of 207.2 g, by comparison one mole of zinc has a mass of 65.38 g. Thus to produce the same amount of electron flow, a much higher mass of lead is required, approximately 3.2x more compared to zinc. This factor alone gives the lead-acid cell a much lower energy density than an alkaline cell. [Other factors contributing to the overall energy density of a cell include available cell voltage and cell design. Typically an alkaline cell has an energy density ≈ 3x that of a lead-acid cell.]

c. Secondary cells like the lead-acid accumulator are able to be recharged when they go 'flat'. That is the oxidant and reductant can be regenerated within the cell by applying a suitable DC electric current. Being rechargeable means the lead acid accumulator can undergo many discharge-recharge cycles over a period of several years before eventually failing to recharge and requiring replacement.

d. A lead-acid cell has a single anode and cathode producing a voltage of around 2.0 V. Several of these arranged in series (+ terminal joined to - terminal) produce a battery of greater voltage, eg 4 volts, 6 volts, 8 volts and so on.

8. a. Recharge half-reaction occurring at the discharge anode: $PbSO_4(s) + 2e^-$ $Pb(s) + SO_4^{2-}(aq)$

Recharge half-reaction occurring at the discharge cathode: $PbSO_4(s) + 2H_2O(l) \rightarrow PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^-$

b. Anode: Originally consists of Pb(s), the reductant. During discharge this changes to $PbSO_4(s)$ and after recharge it is converted back to Pb(s).

Cathode: Originally consists of $PbO_2(s)$, the oxidant. During discharge this changes to $PbSO_4(s)$ and after recharge it is converted back to $PbO_2(s)$.

After recharge, the oxidising agent, $PbO_2(s)$ and reducing agent Pb(s) are regenerated at the anode and cathode respectively thus recharging the cell.

c. The increased enthalpy comes from the electrical energy of the electric current used to recharge the cell.

d. The oxidation process occurring during recharge; see part (a), produces 4 moles of $H^+(aq)$ for every mole of $PbSO_4(s)$ oxidised. Thus pH decreases, ie $c(H^+)$ increases.

e. An unwanted side reaction occurring during recharge involves the decomposition of water into oxygen gas and hydrogen gas. The overall process consumes water as shown here: $2H_2O(l) \rightarrow O_2(g) + 2H_2(g)$. Due to the loss of water the electrolyte level may decrease over time.

f. The unwanted decomposition of water into oxygen gas and hydrogen gas during recharge of lead-acid batteries can produce an explosive mixture of $O_2(g)$ and $H_2(g)$. This would be especially dangerous in a confined and unventilated space where the gases may accumulate and ignite explosively.

9. The lithium-ion cell is rechargeable, as is the lead-acid cell. It has a long shelf life once charged and requires no maintenance. The lead-acid cell by comparison may require addition of water to the electrolyte from time to time. The Li-ion cell's most important feature is its exceptional energy density, currently 3-5 times that of the lead-acid cell. (This varies depending upon the type of Li-ion cell.) This makes it ideal for all types of transport applications where the overall mass of the battery system must be kept as low as possible while maximising the available electrical energy. Furthermore the Li-ion cell does not have the toxicity issues of Pb and the corrosion problems of the H_2SO_4 electrolyte of the lead-acid battery.

10. Fuel cells differ from primary cells and secondary cells in that they do not store the oxidising or reducing agent. Instead these reactants are constantly fed into the cell to generate electricity. Chemical by-products of the cell reactions are expelled from the cell as it operates. Commercial fuel cells have been designed to use a variety of fuels like hydrogen, methanol or reformed hydrocarbons.

11. a. Overall redox reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ The waste product $H_2O(l)$ can be used as drinking water, saving valuable payload.

b. The oxidising agent is $O_2(g)$ as it gains electrons changing oxidation number from 0 to -2. $H_2(g)$ is the reducing agent as it loses electrons changing oxidation number from 0 to +1.

c. The net reaction in the hydrogen-oxygen fuel cell is identical to that occurring during the combustion of hydrogen gas in oxygen.

12. a. The overall reactions occurring in the PEMFC are identical to those in the alkaline fuel cell. In both cases $H_2(g)$ is oxidised and $O_2(g)$ reduced forming $H_2O(l)$ as the only product.

b. i. The polymer electrolyte or proton exchange membrane (PEM) acts as the electrolyte and electrode separator. The PEM allows protons (H^+) to transfer from the anode to the cathode. It also prevents $H_2(g)$ or $O_2(g)$ from moving across the membrane between the anode and cathode.

ii The PEM is a solid polymer rather than a liquid as is the electrolyte in the alkaline fuel cell. The PEM is not corrosive as is the concentrated sodium hydroxide solution of the alkaline fuel cell. The solid PEM can be extremely thin, which is not possible with a liquid electrolyte and consequently allows a very compact, flexible design.

c. Platinum nanoparticles act as a catalyst by lowering the activation energy for the electrode half-reactions. The use of a catalyst like this increases the efficiency of enthalpy conversion into electrical energy so that less of the available enthalpy is converted to heat and more as electrical energy. The small particle size (nanoparticles) gives the solid platinum a high surface area thus allowing greater contact with both hydrogen and oxygen at the respective electrodes. This increases the reaction rate for each of the half-reactions thus increasing the rate of electron supply and allowing a greater current to be produced.

13. a. High temperatures (150-220 °C) increase the conductivity of the liquid H_3PO_4 electrolyte by favouring its dissociation into H^+ and $H_2PO_4^-$ ions. These temperatures also help to reduce poisoning of the catalytic electrode surfaces by reducing the absorption of impurities like CO(g) onto these surfaces.

b. i. Only 40% of the available enthalpy change from the conversion of hydrogen and oxygen into water is converted into electrical energy. The remaining 60% is most probably converted into heat energy.

ii Greater energy efficiency is achieved through cogeneration as what would otherwise be waste heat (produced by the PAFC) is used for other useful purposes such as central heating in buildings.

iii PAFCs are favoured for stationary power systems, such as emergency power plants for buildings and hospitals, as these applications are most able to take advantage of the cogeneration benefits of PAFC systems. In such applications, overall efficiency of energy utilisation can rise to 85% and this helps to make these more expensive systems, cost competitive.

c. Both systems produce an electric current by using the reaction of hydrogen with oxygen to produce water. The PEMFC requires very pure hydrogen as its lower operating temperature makes it prone to catalytic poisoning. The electrode surfaces of both systems use carbon as a conductor and platinum particles as a catalyst to improve the efficiency of electrical generation. The electrolyte in the PAFC is liquid phosphoric acid while the PEMFC uses a thin solid polymer material. The thin solid electrolyte polymer allows the PEMFC to have a very compact design. In both cases the electrolyte material conducts protons (H^+ ions) from the anode to the cathode while preventing direct contact between the oxidant, $O_2(g)$ and reductant, $H_2(g)$. Cogeneration options for the PAFC mean it has greater overall energy conversion efficiency than a PEMFC.

14. a. Hydrogen is not a fuel source as no natural supply of hydrogen gas occurs on earth. Hydrogen must be produced from other fuel sources like petroleum, hydro, wind, solar or nuclear. Thus it can be considered a carrier of the stored energy originally present in the source used to produce it. (See note p86.)

b. The favoured method of hydrogen production at present is the steam reforming of petroleum products like methane. Some of the reactions involved in this process include: $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ (This exothermic reaction provides the energy needed to drive the following endothermic reactions.)

$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$ and $H_2O(g) + CO(g) \rightarrow CO_2(g) + H_2(g)$.

These equations show how steam reforming of methane to produce hydrogen gas can result in production of the greenhouse gas CO_2. (See p86.)

c. Sustainable hydrogen production could involve the electrolysis of water using electrical energy derived from renewable sources like solar, wind or hydro power. Using this method there is no direct production of $CO_2(g)$ and the resulting hydrogen is not contaminated with CO, as happens with the steam reforming of methane. Thus hydrogen produced by electrolysis does not cause the catalytic poisoning of platinum electrodes. Oxygen is also a valuable by-product of this process. Nuclear power could also be an option for H_2 production, though this is strictly not a renewable or inexhaustible option, at present. Furthermore current nuclear power technology has its own associated environmental problems.

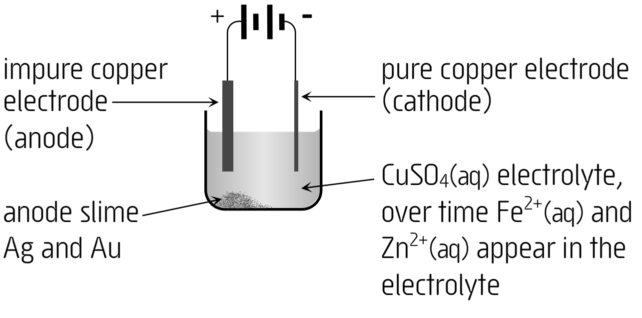
15. a. Overall redox reaction: $2CH_3OH(aq) + 3O_2(g) \rightarrow 4H_2O(l) + 2CO_2(g)$

b. Oxygen is the oxidising agent, its O.N. changes from 0 to -2. Methanol is the reducing agent, the O.N. of carbon in CH_3OH changes from -2 to +4.

c. The DMFC uses the fuel methanol, which is a liquid at room temperature while H_2/O_2 fuel cells use gaseous hydrogen as the fuel. Using liquid methanol alleviates the need for complex, pressurised storage and delivery systems needed for H_2/O_2 fuel cells. The DMFC sources the oxidant (oxygen) directly from the atmosphere so no storage system is needed for this gas either.

d. An energy source must be extractable or readily available from the Earth eg coal, petroleum, hydroelectricity and so on. Methanol is not available as an energy source, instead it must be manufactured from other energy sources. Typically methanol is manufactured from methane (the major component of natural gas) and water. Thus methanol can be considered an energy carrier of the energy originally present in the source (typically methane) used to produce it.

16. a. A simple electrolysis cell for electrorefining of impure copper.



b. The anode half-reactions involve the oxidation of copper, iron and zinc:

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

$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

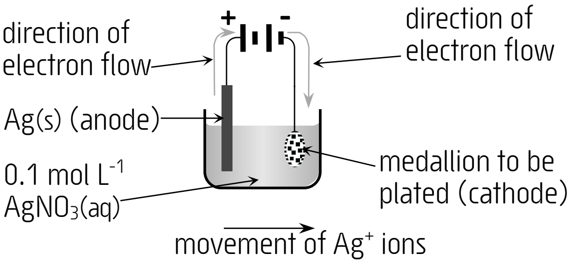
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

c. The cathode half-reaction involves the reduction of $Cu^{2+}(aq)$ only.

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

[The other metal ions that are released from the dissolving copper anode (eg Zn^{2+} and Fe^{2+}) remain in solution as these ions are not as easily reduced as are Cu^{2+} ions.]

17. a. A simple electrolysis cell for electroplating silver onto a copper medallion.



b. Cathode half-reaction:
$Ag^+(aq) + e^- \rightarrow Ag(s)$
Observation: A silvery solid forms here.

Anode half-reaction:
$Ag(s) \rightarrow Ag^+(aq) + e^-$
Observation: The silvery electrode loses mass as it dissolves.

18. a. The ions in solid Al_2O_3 are not mobile. In molten Al_2O_3 the Al^{3+} and O^{2-} ions are mobile. For the process of electrolysis to work the ions in the electrolyte must be mobile. This allows the positive Al^{3+} ions to move towards the negative electrode and the negative O^{2-} ions can move towards the positive electrode. This way the positive and negative ions can be reduced and oxidised respectively.

b. Cathode half-reaction: $Al^{3+}(l) + 3e^- \rightarrow Al(l)$

c. As can be seen in the oxidation half equation, carbon changes in oxidation number from 0 (in C) to +4 (in CO_2) while the oxidation number for oxygen remains unchanged at -2. This shows that carbon is in fact oxidised. Further, as carbon becomes oxidised to carbon dioxide the carbon anode will slowly lose mass until it is completely consumed. Thus the carbon anodes must be periodically replaced.

Set 13 Stoichiometry: Quantities in chemical change

1. a. $\mathbf{n(C)} = \frac{3}{2} \times n(Al) = \frac{3 \times 36}{2} = \mathbf{54\ mol}$ (2SF) *****

The coefficients in the equation show the molar amount of C is 1.5 times (3/2) that of Al_2O_3.

b. $\mathbf{n(CO_2)} = \frac{3}{4} \times n(Al) = \frac{3 \times 5.9}{4} = \mathbf{4.4\ mol}$ (2SF) *****

The coefficients in the equation show the molar amount of CO_2 is 0.75 times (3/4) that of Al.

c. The stoichiometric equation shows that for every 4 moles of Al (108 g of it) extracted from Al_2O_3, 3 moles of CO_2 gas (132 g of it) is also produced. This does not take into account any CO_2 gas resulting from mining, transportation and energy production required to operate the process. Thus the consumption of 1.0 kg of Al (37 mole of it) by the construction industry has an upstream greenhouse emission of at least 1.2 kg (28 mole) of $CO_2(g)$.

2. a. $n(C_6H_{12}O_6) = \frac{m}{M} = \frac{155}{180.16} = 0.860$ mol (3SF)

The molar amount of $C_6H_{12}O_6$ can be used to find the amount of C_2H_5OH produced.

$\mathbf{n(C_2H_5OH)} = \frac{2}{1} \times n(C_6H_{12}O_6) = \frac{2 \times 0.86}{1} = \mathbf{1.72\ mol}$ (3SF) *****

***Coefficients** from a balanced equation are **exact** numbers and as such have an unlimited number of significant figures. These place no restriction on the number of significant figures appearing in the final answer. See the appendix section for rules on using significant figures.

b. $\mathbf{n(CO_2)} = \frac{2}{1} \times n(C_6H_{12}O_6) = \frac{2 \times 16}{1} = \mathbf{32\ mol}$ (2SF)

$\mathbf{m(CO_2)} = n \times M = 32 \times 44.01 = \mathbf{1400\ g}$ **or** $\mathbf{1.4 \times 10^3\ g}$ (2SF)

c. Producing 2 moles of ethanol from glucose releases 2 moles of CO_2 gas to the atmosphere. However, the production of glucose by plants through photosynthesis absorbs even more CO_2 from the atmosphere than fermentation replaces. Actually the production of 1 mole of glucose by photosynthesis absorbs 6 mole of CO_2 from the atmosphere. It must be noted that the complete combustion of the ethanol will ultimately return all of the CO_2, originally absorbed by plants, back into the atmosphere. This results in zero net change of atmospheric CO_2 levels.

3. **a.** $\mathbf{n(CO_2)} = \frac{V_{(STP)}}{22.71} = \frac{195 \times 10^{-3}}{22.71} = \mathbf{8.59 \times 10^{-3}\ mol}$ (3SF)

Remember, volume must be in litres (L), ie 195 mL = 195×10^{-3} L.

b. $PV = nRT$ *ie* $\mathbf{n(CO_2)} = \frac{PV}{RT} = \frac{103.2 \times 195 \times 10^{-3}}{8.3145 \times (27 + 273.15)} = \mathbf{8.06 \times 10^{-3}\ mol}$ (3SF)

Ensure R has the value 8.3145 when pressure is in kPa, temperature in K and volume in L.

4. $n(O_2) = \frac{V_{(STP)}}{22.71} = \frac{6.5}{22.71} = 0.29\ mol$ (2SF)

As the gas volume is measured at STP and 1.00 mole of gas has a volume of 22.71 L at these conditions.

$n(H_2O_2) = \frac{2}{1} \times n(O_2) = 0.57\ mol$ *and* $\mathbf{m(H_2O_2)} = n \times M = 0.57 \times 34.02 = \mathbf{19\ g}$ (2SF)

5. **a.** $n(C_8H_{18}) = \frac{m}{M} = \frac{34.9 \times 10^3}{114.224} = 306\ mol$ (3SF) *and* $n(CO_2) = \frac{16}{2} \times n(C_8H_{18}) = \frac{16 \times 306}{2} = 2.44 \times 10^3\ mol$

$PV = nRT$ *ie* $\mathbf{V(CO_2)} = \frac{nRT}{P} = \frac{2.44 \times 10^3 \times 8.3145 \times 308.15}{102} = \mathbf{6.14 \times 10^4\ L}$ (3SF)

b. $n(O_2) = \frac{25}{2} \times n(C_8H_{18}) = \frac{25 \times 306}{2} = 3820\ mol$ (3SF)

$\mathbf{V(O_2)} = \frac{nRT}{P} = \frac{3.82 \times 10^3 \times 8.3145 \times 308.15}{102} = \mathbf{9.59 \times 10^4\ L}$ (3SF)

c. $\mathbf{V(air)} = \frac{V(O_2)}{\%\ O_2\ in\ air} \times 100 = \frac{100 \times 9.59 \times 10^4}{21} = \mathbf{4.6 \times 10^5\ L}$ (2SF)

Remember: Numerical answers are rounded to the proper number of **significant figures** using the rules outlined in **Appendix 1**. For **your convenience**, where **partial working** has been evaluated this is shown with the correct number of significant figures, however, the complete number is carried forward into later parts of a calculation. It is recommended that you **carry full numerical figures** until completion of a calculation. Your **final answer** should be rounded to the proper number of significant figures.

6. **a.** $2NaHCO_3(s) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l) + 2CO_2(g)$

b. $n(H_2SO_4) = cV = 4.80 \times 20.5 = 98.4\ mol$

and $n(NaHCO_3) = 2 \times n(H_2SO_4) = 197\ mol$ (3SF)

$\mathbf{m(NaHCO_3)} = n \times M = 197 \times 84.008 = \mathbf{1.65\ 10^4\ g}$ (3SF)

c. $Na_2CO_3(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + H_2O(l) + CO_2(g)$

$n(H_2SO_4) = cV = 4.80 \times 20.5 = 98.4\ mol$

and $n(Na_2CO_3) = n(H_2SO_4) = 98.4\ mol$ (3SF)

$\mathbf{V(Na_2CO_3)} = \frac{n}{c} = \frac{98.4}{4.30} = \mathbf{22.9\ L}$ (3SF)

7. **a.** Water is a molecular compound whose molecules are highly polar. Ions within an ionic compound, like NaCl, are strongly attracted to the molecular dipoles of water. Positively charged sodium ions will be strongly attracted to the negative dipole (δ^-) of the oxygen atom of a water molecule. Similarly the negatively charged chloride ions are attracted to the positive molecular dipole (δ^+) of the hydrogen atoms in a water molecule. This type of interaction is known as ion-dipole attraction and explains why ionic substances can be hygroscopic.

b. **% NaCl in table salt** $= \frac{m[NaCl]}{m[table\ salt]} \times 100 = \frac{24.9 \times 100}{25.6} = \mathbf{97.3\%}$ (3SF)

The impurity is most likely an anti-caking agent, eg $CaSiO_3$. (Unlikely to be water as the sample was freshly removed from its packaging.)

c. $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

$n(AgCl) = \frac{m}{M} = \frac{7.68}{143.35} = 5.36 \times 10^{-2}\ mol$ *and* $n(NaCl) = n(Cl^-) = \frac{1}{1} \times n(AgCl) = 5.36 \times 10^{-2}\ mol$

$m(NaCl) = n \times M = 5.36 \times 10^{-2} \times 58.44 = 3.13\ g$ (3SF)

% NaCl in table salt $= \frac{m[NaCl] \times 100}{m[table\ salt]} = \frac{3.13 \times 100}{3.25} = \mathbf{96.3\%}$ (3SF)

8. $\% \text{ Au in ore body} = \dfrac{m[\text{Au}]}{m[\text{ore body}]} \times 100$

thus **m(Au)** $= \dfrac{m[\text{ore body}] \times \%\text{Au}}{100} = \dfrac{2.5 \times 10^{12} \times 2.3 \times 10^{-4}}{100} = \mathbf{5.8 \times 10^{6}\ g}$ (2SF)

Remember, convert tonnes to grams thus 1.00 tonne = 1.00×10^{6} g.

9. a. % yield ethanol $= \dfrac{\text{actual yield} \times 100}{\text{theoretical yield}} = \dfrac{49.3 \times 100}{107} = \mathbf{46.1\%}$ **(3SF)**

b. Unwanted side reactions (such as aerobic respiration of glucose to CO_2 and H_2O) may have consumed some of the glucose producing alternative products. The glucose may not have been 100% pure (eg it may have contained some water) or the ethanol might not have been fully recovered from the mixture (eg some may have evaporated and been lost to the atmosphere or some may have remained in the reaction mixture). The yeast may have died (due to alcohol toxicity or some other reason) before the reaction was complete.

10. a. The independent and dependent variables are; moles of copper used and moles of silver produced respectively. Thus a suitable hypothesis could be, 'When copper metal reacts with a silver nitrate solution, the moles of silver produced should be twice the moles of copper used.'

b. The shiny salmon pink solid dissolves and loses mass as it gains a silvery metallic deposit. The solution will change from colourless to blue.

c. m(Cu consumed) = m(Cu coil before) - m(Cu coil after) = 15.53 - 14.69 = 0.84 g (2DP)

m(Ag formed) = m(filter paper + silver residue) - m(filter paper) = 3.78 - 1.08 = 2.70 g (2DP)

$n(\text{Cu}) = \dfrac{m}{M} = \dfrac{0.84}{63.55} = 1.3 \times 10^{-2}$ mol *and* $n(\text{Ag}) = \dfrac{m}{M} = \dfrac{2.70}{107.9} = 2.50 \times 10^{-2}$ mol

mole ratio $= \dfrac{n(\text{Ag formed})}{n(\text{Cu used})} = \dfrac{2.50 \times 10^{-2}}{1.3 \times 10^{-2}} = \mathbf{1.9}$ (2SF)

d. The expected ratio is 2 compared to the experimental ratio of 1.9. Keeping in mind the possible sources of error in the experiment it is reasonable to expect less than a 100% yield or recovery of silver. Some silver may be lost in the filtration process or some copper may have remained unreacted. Also as the mass measurements are only valid to 2 decimal places (2DP) then the calculated mass of Cu consumed (0.84 g) is only reliable to 2DP and in this case only 2 significant figures (2SF). Thus the final answer is only reliable to 2SF. This means you can expect errors in the second digit of the final calculated ratio of 1.9. With this in mind it is reasonable to conclude that the student's results do support the hypothesis as stated as the result of 1.9 is sufficiently in agreement with the expected result of 2, considering the expected degree of error.

e. **n(Ag)** $= \dfrac{2}{1} \times n(\text{Cu}) = \dfrac{2 \times 1.3 \times 10^{-2}}{1} = \mathbf{0.026\ mol}$(2SF) Coefficients in the equation show the molar amount of Ag formed is 2 times (2/1) that of Cu consumed.

m(Ag) = n x M = 0.026 x 107.9 = 2.9 g (2SF) ie **theoretical yield of silver is 2.9 g**

f. **% yield Ag** $= \dfrac{\text{actual yield} \times 100}{\text{theoretical yield}} = \dfrac{2.7 \times 100}{2.9} = \mathbf{95\%}$ (2SF)

g. The measured mass of silver was less than expected. This could be due to experimental technique, if for example, not all of the silver produced was transferred to the filter paper; some of it may have remained on various apparatus. This would result in a lower value for the mass of Ag formed. Alternatively the mass of copper reacting with $AgNO_3$ may have appeared higher than it actually was. If the copper had not been cleaned properly before use it would have been coated in CuO. During the reaction the surface coating of CuO would have been lost from the Cu coil but not contributed to the formation of silver. Hence the mass of Cu reacting with $AgNO_3$ would seem higher than it actually was. There are also significant measurement errors associated with the determination of the mass of copper used as the calculated value is only reliable to 2SF.

11. a. **m(CO_2 formed)** = m(flask + HCl sol'n + 5 tablets before react'n) - m(flask + HCl sol'n + 5 tablets after react'n)

= (157.98 + 26.85) - 172.60 = **12.23 g** (2DP as addition and subtraction rules apply)

b. $MgCO_3(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l) + CO_2(g)$

$n(CO_2) = \frac{m}{M} = \frac{12.23}{44.01} = 0.2779$ mol (4SF) *and* $n(MgCO_3) = \frac{1}{1} \times n(CO_2) = \frac{0.2779}{1} = 0.2779$ mol

m($MgCO_3$) = n x M = 0.2779 x 84.32 = **23.43 g** (4SF)

c. **%purity $MgCO_3$ =** $\frac{m(MgCO_3) \times 100}{m(tablets)} = \frac{23.43 \times 100}{26.85} =$ **87.27%** (4SF)

d. Using five antacid tablets reduces the measurement error thus increasing reliability of the experimental results. If one tablet had been used then its mass (5.37 g) can only be found to 3SF instead of 4SF (26.85 g) for five tablets. Thus using only one tablet would have increased the measurement error and reduced the reliability of the final answer to 3SF.

12. a. Calcite is insoluble in water and it does not react with water thus its mass will not change when left in water alone. It loses mass when left in a vinegar solution as it reacts with ethanoic acid to produce a gas (CO_2) and a soluble salt, $Ca(CH_3COO)_2$ which then dissolves in solution. Consequently the calcite crystal will lose mass when left in vinegar for a period of time.

b. A monoprotic acid has one acidic hydrogen per acid molecule and a weak acid only partially ionises in water. This can be shown for ethanoic acid using double arrows and an ionisation equation, ie

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

c. **m($CaCO_3$ consumed)** = m(calcite before) - m(calcite after) = 27.7 - 20.2 = **7.5 g** (1DP ie 2SF)

$n(CaCO_3) = \frac{m}{M} = \frac{7.5}{100.09} = 7.5 \times 10^{-2}$ mol *and* $n(CH_3COOH) = \frac{2}{1} \times n(CaCO_3) = 0.15$ mol (2SF)

m(CH_3COOH) = n x M = 0.15 x 60.052 = **9.0 g** (2SF)

d. From 12c the mass of CH_3COOH in 120 mL of solution is 9.0 g (2SF). Also as the vinegar solution has a density of 1.01 g mL^{-1} then the 120 mL of **vinegar solution** has a mass of (120 x 1.01) g ie **121 g** (3SF). Thus:

% purity CH_3COOH in vinegar = $\frac{m(CH_3COOH) \times 100}{m(vinegar)} = \frac{9.0 \times 100}{121} =$ **7.4%** (2SF)

e. **c(CH_3COOH)** = $\frac{n}{V} = \frac{0.15}{0.120} =$ **1.2 mol L^{-1}** (2SF)

f. All of the dissolved calcite was attributed to its reaction with CH_3COOH, however, as vinegar contains other acids (eg tartaric acid, malic acid and citric acid) then some of the lost calcite was actually due to a reaction with these acids. This assumption then would make it appear as though there was more ethanoic acid in the vinegar than there actually was, making its calculated concentration (above) higher than it actually is.

13. % Fe_2O_3 in ore body= $\frac{m[Fe_2O_3]}{m[ore\ body]} \times 100$

thus $m(Fe_2O_3) = \frac{m[ore\ body] \times \%Fe_2O_3}{100} = \frac{1.00 \times 10^6 \times 97}{100} = 9.7 \times 10^5$ g (2SF)

Remember, convert tonnes to grams thus 1.00 tonne = 1.00×10^6 g.

$n(Fe_2O_3) = \frac{m}{M} = \frac{9.7 \times 10^5}{159.7} = 6.1 \times 10^3$ mol *and* $n(Fe) = \frac{2}{1} \times n(Fe_2O_3) = 1.2 \times 10^4$ mol (2SF)

m(Fe) = n x M = $1.2 \times 10^4 \times 55.85 = 6.8 \times 10^5$ g (2SF)

% yield Fe = $\frac{actual\ yield \times 100}{theoretical\ yield}$

Continued next page.

thus **actual yield** = $\dfrac{\%\text{yield Fe x theoretical yield}}{100} = \dfrac{98 \times 6.8 \times 10^5}{100}$ = **6.6×10^5 g Fe** (2SF)

14. a. $3BaCl_2(aq) + 2H_3PO_4(aq) \rightarrow Ba_3(PO_4)_2(s) + 6HCl(aq)$

b. $n(Ba_3(PO_4)_2) = \dfrac{m}{M} = \dfrac{25}{601.84} = 4.2 \times 10^{-2}$ mol (2SF)

and $n(H_3PO_4) = \dfrac{2}{1} \times n(Ba_3(PO_4)_2) = \dfrac{2 \times 4.2 \times 10^{-2}}{1} = 8.3 \times 10^{-2}$ mol (2SF)

$V(H_3PO_4)$ = $\dfrac{n}{c} = \dfrac{8.3 \times 10^{-2}}{4.50}$ = **1.8×10^{-2} L or 18 mL** (2SF)

c. Although $Ba_3(PO_4)_2$ is insoluble some of it may remain dissolved in solution. Also some losses will occur in recovering and collecting the final product.

d. The volume of H_3PO_4 used should be greater by a factor of 100/85 so that the theoretical yield of H_3PO_4 is greater by a factor of 100/85. Taking 85% of this greater yield will produce the required 25 g of $Ba_3(PO_4)_2$.

$V(H_3PO_4)$ actually required = $\dfrac{100}{85} \times 1.85 \times 10^{-2}$ = **2.2×10^{-2} L or 22 mL** (2SF)

15. a. In these two linked reactions Cu_2S is the common reagent. Leaving the equation coefficients as they are ensures the moles of Cu_2S produced in equation ① is equal to the moles of Cu_2S used in equation ②. Add the two equations and simplify the result.

$2CuFeS_2 + 4O_2 \rightarrow Cu_2S + 2FeO + 3SO_2$ ..... ①

$Cu_2S + O_2 \rightarrow 2Cu + SO_2$ .... ②

Combining both equations: $2CuFeS_2 + 4O_2 + Cu_2S + O_2 \rightarrow Cu_2S + 2FeO + 3SO_2 + 2Cu + SO_2$

When simplified: **$2CuFeS_2 + 5O_2 \rightarrow 2FeO + 4SO_2 + 2Cu$**

b. $\%\ CuFeS_2 = \dfrac{m(CuFeS_2) \times 100}{m(\text{ore})}$

$\therefore\ m(CuFeS_2) = \dfrac{\%(CuFeS_2) \times m(\text{ore})}{100} = \dfrac{96.4 \times 1 \times 10^6}{100} = 9.64 \times 10^5$ g (3SF)

$n(CuFeS_2) = \dfrac{m}{M} = \dfrac{9.64 \times 10^5}{183.54} = 5.25 \times 10^3$ mol (3SF)

and $n(Cu) = \dfrac{2}{2} \times n(CuFeS_2) = 5.25 \times 10^3$ mol

m(Cu) = n x M = $5.25 \times 10^3 \times 63.55$ = **3.34×10^5 g** *or* **334 kg** (3SF)

c. SO_2 is a pollutant as it is an acidic gaseous oxide. Expelled to the atmosphere, it will dissolve in rain to produce the weak acid sulfurous acid causing rainfall to become acidic. Acid rain affects the physical environment by damaging metallic, concrete and limestone structures. Inhaled as SO_2 this gas dissolves in the mucous lining (contains water) of the lungs, eyes, nose and throat producing sulfurous acid and causing irritation and tissue damage. This gas can also be harmful to the biotic environment.

16. a. Multiply each equation by a suitable factor (ie equalise the common reagent). ∴ As SO_3 is the common reagent multiply the coefficients of equation ② by two to ensure the moles of SO_3 used in equation ② equals the moles of SO_3 produced in equation ①. Add the two equations and simplify the result.

① $2SO_2 + O_2 \rightarrow 2SO_3$ .... ***x 1*** *gives* .... $2SO_2 + O_2 \rightarrow 2SO_3$

② $SO_3 + H_2O \rightarrow H_2SO_4$ .... ***x 2*** *gives* .... $2SO_3 + 2H_2O \rightarrow 2H_2SO_4$

Combining both equations: ... $2SO_2 + O_2 + 2SO_3 + 2H_2O \rightarrow 2SO_3 + 2H_2SO_4$

When simplified: .... $\mathbf{2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4}$

b. $n(CuFeS_2) = \frac{m}{M} = \frac{1.00 \times 10^6}{183.54} = 5.45 \times 10^3$ mol (3SF)

and $n(SO_2) = \frac{4}{2} \times n(CuFeS_2) = 1.09 \times 10^4$ mol

$PV = nRT$ *ie* $\mathbf{V(SO_2)} = \frac{nRT}{P} = \frac{1.09 \times 10^4 \times 8.3145 \times (27.0 + 273.15)}{101} = \mathbf{2.69 \times 10^5\ L}$ (3SF)

Remember: R has the value 8.3145 when pressure is in kPa, temperature in K and volume in L.

c. $n(H_2SO_4) = \frac{2}{2} \times n(SO_2) = 1.09 \times 10^4$ mol (3SF)

and $\mathbf{m(H_2SO_4)} = n \times M = 1.09 \times 10^4 \times 98.086 = \mathbf{1.07 \times 10^6\ g}$ *or* **1.07 tonne** (3SF)

d. % yield $H_2SO_4 = \frac{\text{actual yield} \times 100}{\text{theoretical yield}}$

thus **actual yield** $= \frac{\%\text{yield } H_2SO_4 \times \text{theoretical yield}}{100} = \frac{93 \times 1.07 \times 10^6}{100} = \mathbf{9.94 \times 10^5\ g\ H_2SO_4}$ (3SF)

Set 14 Limiting reagent calculations

1. stoichiometric ratio $= \frac{n(K_2CO_3)}{n[FeCl_3]} = \frac{3}{2} = 1.5$ *and* actual ratio #1 $= \frac{n(K_2CO_3)}{n[FeCl_3]} = \frac{1.80}{1.30} = 1.38$

actual ratio #2 $= \frac{n(K_2CO_3)}{n[FeCl_3]} = \frac{2.00}{1.30} = 1.54$ *and* actual ratio #3 $= \frac{n(K_2CO_3)}{n[FeCl_3]} = \frac{2.20}{1.30} = 1.69$

Experiment #1: The actual ratio (1.38) is less than the required stoichiometric ratio (1.5)∴ **K_2CO_3 is the LR**. Thus K_2CO_3 determines the quantity of $Fe_2(CO_3)_3(s)$ produced in experiment #1.
Experiment #2 and #3: The actual ratios (1.54 and 1.69) are greater than the required stoichiometric ratio (1.5)∴ **$FeCl_3$ is the LR** in both of these experiments. Thus $FeCl_3$ determines the quantity of $Fe_2(CO_3)_3(s)$ produced in experiment #2 and #3.

Experiment #1 n[$Fe_2(CO_3)_3$produced] = $\frac{1}{3} \times n(K_2CO_3) = \frac{1 \times 1.80}{3} =$ **0.600 mol** (3SF)

Experiment #2 and #3 n[$Fe_2(CO_3)_3$produced] = $\frac{1}{2} \times n(FeCl_3) = \frac{1 \times 1.30}{2} =$ **0.650 mol** (3SF)

2. n[HCl in each experiment] $= cV = 2.50 \times 50.0 \times 10^{-3} = 0.125$ mol

Experiment #1 $n[Zn] = \frac{m}{M} = \frac{3.12}{65.38} = 0.0477$ mol   Experiment #2 $n[Zn] = \frac{m}{M} = \frac{3.85}{65.38} = 0.0589$ mol

Experiment #3 $n[Zn] = \frac{m}{M} = \frac{4.21}{65.38} = 0.0644$ mol   Experiment #3 $n[Zn] = \frac{m}{M} = \frac{4.57}{65.38} = 0.0699$ mol

Continued next page.

For each experiment the stoichiometric ratio is the same ie $\text{stoichiometric ratio} = \frac{n(Zn)}{n[HCl]} = \frac{1}{2} = 0.5$

$$\text{actual ratio \#1} = \frac{n(Zn)}{n[HCl]} = \frac{0.0477}{0.125} = 0.382 \quad \textit{and} \quad \text{actual ratio \#2} = \frac{n(Zn)}{n[HCl]} = \frac{0.0589}{0.125} = 0.471$$

$$\text{actual ratio \#3} = \frac{n(Zn)}{n[HCl]} = \frac{0.0644}{0.125} = 0.515 \quad \textit{and} \quad \text{actual ratio \#4} = \frac{n(Zn)}{n[HCl]} = \frac{0.0699}{0.125} = 0.559$$

Experiment #1 and #2: The actual ratios (0.382 and 0.471) are both less than the required stoichiometric ratio (0.5) ∴ Zn is the LR (g) produced for experiment #1 and #2. As there is more Zn used in experiment #2 then more hydrogen is produced in experiment #2 than #1.
Experiment #3 and #4: The actual ratios (0.515 and 0.599) are both greater than the required stoichiometric ratio (0.5) ∴ **HCl is the LR** in both of these experiments. As the same amount of HCl is present in both experiment #3 and #4 then the amount of hydrogen produced in both of these experiments will be the same despite the greater amount of Zn in experiment #4.

3. **a.** $n[H_3C_6H_5O_7] = \frac{m}{M} = \frac{2.15}{192.124} = 0.0112 \text{ mol}$ *and* $n[NaHCO_3] = \frac{m}{M} = \frac{2.65}{84.008} = 0.0315 \text{ mol}$

$$\text{stoichiometric ratio} = \frac{n(H_3C_6H_5O_7)}{n[NaHCO_3]} = \frac{1}{3} = 0.333 \quad \textit{and} \quad \text{actual ratio} = \frac{n(H_3C_6H_5O_7)}{n[NaHCO_3]} = \frac{0.0112}{0.0315} = 0.355$$

The actual ratio (0.355) is greater than the required stoichiometric ratio (0.333) ∴ **$NaHCO_3$ is the LR**. Thus $NaHCO_3$ determines the quantity of $CO_2(g)$.

b. $n(CO_2) = \frac{3}{3} \times n(NaHCO_3) = \frac{3 \times 0.0315}{3} = 0.0315 \text{ mol}$

As the gas is measured at STP then:

$\mathbf{n(CO_2)} = \frac{V_{(STP)}}{22.71}$ *ie* $V_{(STP)} = n \times 22.71 = 0.0315 \times 22.71 =$ **0.716 L** of CO_2 gas at STP (3SF)

c. For non STP conditions use P V = n R T thus:

$\mathbf{V(CO_2)} = \frac{n\,R\,T}{P} = \frac{0.0315 \times 8.3145 \times 310.15}{106} =$ **0.767 L** (3SF)

Remember: R has the value 8.3145 when pressure is in kPa, temperature in K and volume in L.

d. Given the normal empty volume of the stomach is around 50 mL, this amount of gas will cause a pressure build up and probably result in a **burp** or **two**!

4. $n(CaCO_3) = \frac{m}{M} = \frac{5.55}{100.09} = 0.0555 \text{ mol}$ *and* $n(HNO_3) = c\,V = 3.95 \times 21.0 \times 10^{-3} = 0.0830 \text{ mol}$

$$\text{actual mole ratio} = \frac{n(HNO_3)}{n(CaCO_3)} = \frac{0.0830}{0.0555} = 1.50 \quad \textit{and} \quad \text{stoichiometric ratio} = \frac{n(HNO_3)}{n(CaCO_3)} = \frac{2}{1} = 2$$

The actual ratio (1.50) is less than the required stoichiometric ratio (2) ∴ **HNO_3 is the LR.** Thus HNO_3 determines the quantity of other reagents involved in the reaction.

$n[CaCO_3 \text{ used}] = \frac{1}{2} \times n(HNO_3) = 0.0415 \text{ mol}$ (3SF)

$n(CaCO_3$ remaining) $= n(CaCO_3 \text{ added}) - n(CaCO_3 \text{ used}) = 0.0555 - 0.0415$
= **0.0140 mol** (4DP as addition/subtraction rules apply, ie 3SF)

5. a. $n[Al(NO_3)_3] = c\,V = 1.55 \times 55.0 \times 10^{-3} = 0.0853$ mol (3SF)

and $n(Na_2CO_3) = c\,V = 1.00 \times 135 \times 10^{-3} = 0.135$ mol (3SF)

actual mole ratio = $\dfrac{n(Al(NO_3)_3)}{n[Na_2CO_3]} = \dfrac{0.0853}{0.135} = 0.631$ stoichiometric ratio = $\dfrac{n(Al(NO_3)_3)}{n[Na_2CO_3]} = \dfrac{2}{3} = 0.666$

The actual ratio (0.631) is less than the required stoichiometric ratio (0.666) ∴ **$Al(NO_3)_3$ is the LR.** Thus $Al(NO_3)_3$ determines the quantity of other reagents involved in the reaction.

$n[Al_2(CO_3)_3 \text{ formed}] = \dfrac{1}{2} \times n[Al(NO_3)_3] = 0.0426$ mol (3SF)

also **$m[Al_2(CO_3)_3$ formed]** = n M = 0.0426 x 233.99 = **9.97 g** (3SF)

b. As $Al(NO_3)_3$ is the limiting reagent then all of the Al^{3+} is precipitated along with the $Al_2(CO_3)_3$ thus:
$c(Al^{3+})$ = 0 mol L^{-1}.

$n[Na_2CO_3 \text{ used}] = \dfrac{3}{2} \times n[Al(NO_3)_3] = 0.128$ mol (3SF)

also $n(CO_3^{2-} \text{ used}) = n[Na_2CO_3 \text{ used}] = 0.128$ mol (3SF)

$n[CO_3^{2-} \text{ remaining}] = n[CO_3^{2-} \text{ added}] - n[CO_3^{2-} \text{ used}] = 0.135 - 0.128$
= 0.007 (3DP as addition/subtraction rules apply, ie only 1SF remains)

Note: $n(CO_3^{2-}$ added) = $n(Na_2CO_3$ added)

$V[\text{mixture}] = V[Al(NO_3)_3 \text{ solution}] + V[Na_2CO_3 \text{ solution}] = 0.0550 + 0.135$
= 0.190 L (3DP as addition/subtraction rules apply, ie 3SF)

$c(CO_3^-$ $\dfrac{n}{V} = \dfrac{0.007}{0.190} =$ **0.04 mol L^{-1}** (1SF)

6. a. % (O_2 in air) = $\dfrac{V(O_2) \times 100}{V(air)}$ ∴ $V(O_2) = \dfrac{\%(O_2) \times V(air)}{100} = \dfrac{20.9 \times 1.24 \times 10^7}{100} = 2.59 \times 10^6$ L

P V = n R T *ie* **$n(O_2)$** = $\dfrac{P\,V}{R\,T} = \dfrac{235 \times 2.59 \times 10^6}{8.3145 \times (365 + 273.15)} =$ **1.15×10^5 mol** (3SF)

b. $n(S) = \dfrac{m}{M} = \dfrac{1.69 \times 10^6}{32.07} = 5.27 \times 10^4$ mol

Actual mole ratio = $\dfrac{n(O_2)}{n(S)} = \dfrac{1.15 \times 10^5}{5.27 \times 10^4} = 2.18$ *and* stoichiometric ratio = $\dfrac{n(O_2)}{n(S)} = \dfrac{3}{2} = 1.5$

The actual ratio (2.18) is greater than the required stoichiometric ratio (1.5) ∴ **S is the LR.** Thus S determines the quantity of other reagents involved in the reaction.

c. **$n(H_2SO_4$ produced)** = $\dfrac{2}{2} \times n(S) =$ **5.27×10^4 mol** (3SF) ie **theoretical yield is 5.27×10^4 mol of sulfuric acid per hour** (3SF)

7. a. % (Fe_2O_3 in ore) = $\dfrac{m[Fe_2O_3]}{m[ore]} \times 100$

thus $m(Fe_2O_3) = \dfrac{m[ore] \times \%\, Fe_2O_3}{100} = \dfrac{245 \times 10^6 \times \mathbf{97}}{100} = 2.4 \times 10^8$ g **(2SF)**

Remember, convert tonnes to grams thus 1.00 tonne = 1.00×10^6 g.

% (C in coke) = $\dfrac{m[C]}{m[coke]} \times 100$ *thus* $m(C) = \dfrac{m[coke] \times \%\, C}{100} = \dfrac{63.5 \times 10^6 \times 98}{100} = 6.2 \times 10^7$ g (2SF)

$n(Fe_2O_3) = \dfrac{m}{M} = \dfrac{2.4 \times 10^8}{159.7} = 1.5 \times 10^6$ mol (2SF) *and* $n(C) = \dfrac{m}{M} = \dfrac{6.2 \times 10^7}{12.01} = 5.2 \times 10^6$ mol (2SF)

Determine the overall equation for the conversion of Fe_2O_3 to Fe. CO is the linking reagent. Multiplying the coefficients of equation ① by 3 and equation ② by 2 ensures the moles of CO used in equation ② is equal to the moles of CO produced in equation ①.

① $2C + O_2 \rightarrow 2CO$.......................... *x 3 gives*..........$6C + 3O_2 \rightarrow 6CO$

② $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$..... *x 2 gives*.....$2Fe_2O_3 + 6CO \rightarrow 4Fe + 6CO_2$

Combining both equations:......... $6C + 3O_2 + 2Fe_2O_3 + 6CO \rightarrow 6CO + 4Fe + 6CO_2$

When simplified:...................................$6C + 3O_2 + 2Fe_2O_3 \rightarrow 4Fe + 6CO_2$

Actual mole ratio = $\frac{n(Fe_2O_3)}{n[C]} = \frac{1.5 \times 10^6}{5.18 \times 10^6} = 0.29$ *and* stoichiometric ratio = $\frac{n(Fe_2O_3)}{n[C]} = \frac{2}{6} = 0.333$

The actual ratio (0.29) is less than the stoichiometric ratio (0.333) ∴ **Fe_2O_3 is the limiting reagent.**

b. n[Fe formed] = $\frac{4}{2} \times n[Fe_2O_3] = 3.0 \times 10^6$ mol (2SF)

also **m[Fe formed]** = n M = $3.0 \times 10^6 \times 55.85$ = **1.7×10^8 g (170 tonnes)** (2SF)

c. n[C used] = $\frac{6}{2} \times n(Fe_2O_3) = 4.5 \times 10^6$ mol (2SF) *also* m[C used] = n M = $4.5 \times 10^6 \times 12.01 = 5.4 \times 10^7$ g

m[C remaining] = m[C added] - m[C used]
= $6.2 \times 10^7 - 5.4 \times 10^7$ = **0.9×10^7 g** (1DP as addition/subtraction rules apply, ie only 1SF remains)

d. The yield (efficiency) of industrial processes is rarely 100%. In this example the complete conversion of the Fe_2O_3 to Fe may not have occurred despite Fe_2O_3 being a limiting reagent. Also it may not have been possible to recover all of the Fe produced in the blast furnace. Some may remained mixed with the slag.

8. a. V(air) = rate of air flow x time of flow = 2.25 x **72** x 60 = 9.7×10^3 L (**2SF**)
Note: The air flow rate is in L per **minute** so time must also be in **minutes, ie** 72 x 60.

% (CO_2 in air) = $\frac{V(CO_2) \times 100}{V(air)}$ ∴ **$V(CO_2)$** = $\frac{\%(CO_2) \times V(air)}{100} = \frac{0.038 \times 9.7 \times 10^3}{100}$ = **3.7 L** (2SF)

b. P V = n R T *ie* **$n(CO_2)$** = $\frac{P\,V}{R\,T} = \frac{102 \times 3.7}{8.3145 \times (26 + 273.15)}$ = **0.15 mol** (2SF)

c. n(NaOH) = c V = 1.25 x 0.75 = 0.94 mol

Actual mole ratio = $\frac{n(NaOH)}{n[CO_2]} = \frac{0.94}{0.15} = 6.2$ *and* stoichiometric ratio = $\frac{n(NaOH)}{n[CO_2]} = \frac{2}{1} = 2.0$

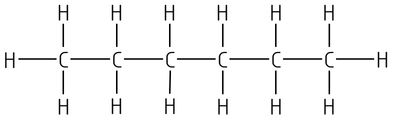
The actual ratio (6.2) is greater than the required stoichiometric ratio (2.0) ∴ **CO_2 is the LR.**

d. For Laura's experiment to work all of the CO_2 gas present in the air sample bubbled through the solution must be absorbed. This way the correct amount of CO_2 present can be determined and hence its concentration in air can be correctly found.

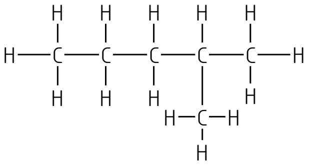
Set 15 Organic chemistry: Alkanes and alkenes

1. a./b. carbon/hydrogen **c.** C_nH_{2n+2} **d.** single **e.** three **f./g./h.** zero/one/two

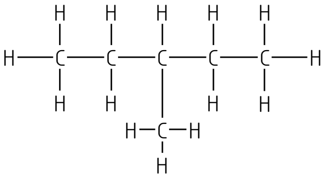
2. structure 1 (hexane)



structure 2 (2-methylpentane)



structure 3 (3-methylpentane)



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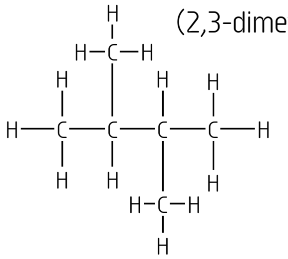
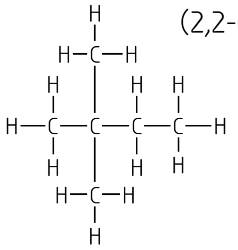
2. *continued*

structure 4
(2,3-dimethylbutane)



structure 5
(2,2-dimethylbutane)



Note: Structure names are not required as part of the answer for this question.

2. a. Structural isomers are compounds having the same molecular formula but a different structural formula. This happens when molecules contain the same number and type of atoms but the sequence in which the atoms are bonded is different. All of the different structures shown above have the same molecular formula of C_6H_{14} thus they are the five structural isomers of C_6H_{14}.

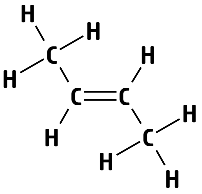
b. Chain isomers and position isomers are two types of structural isomer. Chain isomers are structurally different as they vary in the length of their main carbon chain. For example, structure 1 (above) and structure 2 (above) are chain isomers of C_6H_{14} as their main chains have different lengths, six carbon atoms and five carbon atoms respectively. Similarly structure 1 and structure 3 are also chain isomers however, structure 2 and structure 3 are not chain isomers. The latter pair; structure 2 and structure 3; are instead position isomers as they have the same chain length (five carbon atoms) but their methyl group is located in a different position on the chain, ie on carbon two and three respectively.

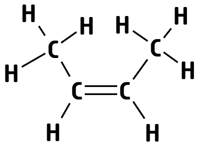
3. For hydrocarbon molecules with the same number of carbon atoms the two general formulas show an alkene molecule will have two less hydrogen atoms than an alkane molecule. The two less hydrogen atoms is a result of the extra bond between a pair of carbon atoms within the alkene, ie the double bond. The two double bonded carbon atoms need fewer hydrogen atoms, one less each (ie two less hydrogen atoms in total) to satisfy their remaining bonding capacity than a pair of single bonded carbon atoms.

For this reason, alkenes are said to be unsaturated as there is the potential to add in two more hydrogen atoms by breaking the double bond between a pair of carbon atoms. This would then result in an alkane which is said to be saturated as there is no further possibility of adding in more hydrogen atoms.

4. *Cis-trans* isomers have the same molecular formula and structural formula, ie same sequence of bonding between their atoms, but a different spatial arrangement. In but-2-ene the different geometries result from the inability of the double bonded carbon atoms to rotate along the axis of their double bond. As a result the two methyl groups become locked on one side or the other of the double bond.

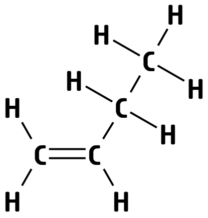
trans-but-2-ene

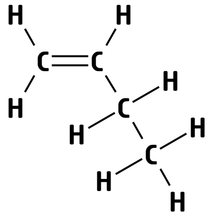




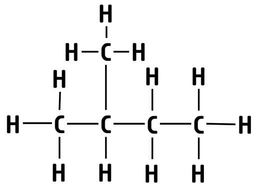
cis-but-2-ene

5. The isomer but-1-ene does not have *cis-trans* isomers. Although it is possible to draw **apparent** *cis-trans* isomers these are actually the same compound. This is evident as when one of the structures is rotated through 180° it can be superimposed over the other structure, this is not possible for actual *cis-trans* isomers. The reason but-1-ene does not have *cis-trans* isomerism is a result of one of the double bonded carbon atoms having two identical attached groups, ie the terminal carbon atom (carbon number 1) has two attached hydrogen atoms.

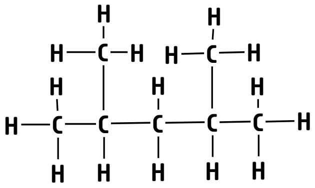




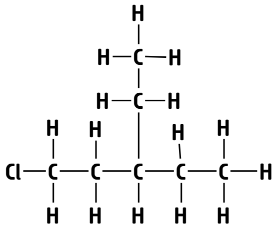
6. a.



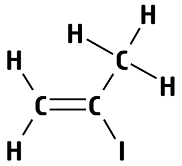
b.



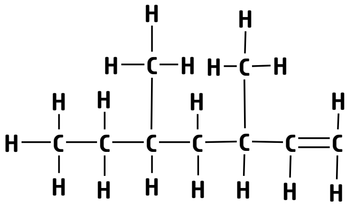
c.



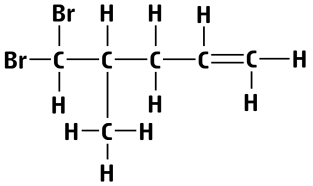
d.



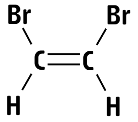
e.



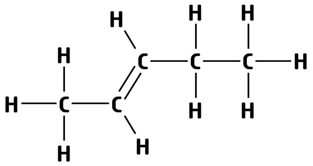
f.



g.



h.



7. **a.** 2-methylpentane
b. 3-methylhexane
c. 1-chloro-2,3-dimethylbutane
d. 2-chloropropene
e. pent-2-ene
f. 5-bromopent-2-ene
g. *trans*-1-bromopropene
h. *cis*-but-2-ene
i. propene

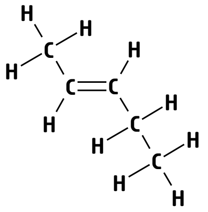
8. **a.** These are the same substance. Both are 2-methylpentane.
b. These structural isomers of formula C_4H_{10} are chain isomers. One is methylpropane and the other is butane.
c. These are the same substance. Both are 2,3-dimethylpentane.
d. These are the same substance. Both are 1,2-dichloroethane. These are **not** *cis-trans* isomers.
e. These are *cis-trans* isomers. They are *cis*-1,2-dichloroethene and *trans*-1,2-dichloroethene.
f. These structural isomers are position isomers. They are 1,2-dibromoethane and 1,1-dibromoethane.
g. These are *cis-trans* isomers. They are *trans*-1-chloropropene and *cis*-1-chloropropene.
h. One is a *cis-trans* isomer and the other is a structural isomer. They are *cis*-1-chlorobut-1-ene and 2-chlorobut-1-ene.

9. **a.** isomers include: pentane, methylbutane and dimethylpropane
b. isomers include: 3-fluoropropene, 2-fluoropropene, *cis*-1-fluoropropene and *trans*-1-fluoropropene
c. isomers include: but-1-ene, *cis*-but-2-ene, *trans*-but-2-ene and methylpropene
Note: Cyclic isomers have not been included.

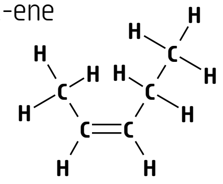
10. **a.** methylbutane
b. 4-methylpent-1-ene
c. butane
d. methylbutane
e. *cis*-1,2-dibromoethene or *trans*-1,2-dibromoethene
f. *cis*-but-2-ene or *trans*-but-2-ene

11. Geometric isomers are not possible for **c**, **d** and **f**. *Cis* and *trans* structures are possible for **a**, **b** and **e**.

a. *trans*-pent-2-ene



cis-pent-2-ene



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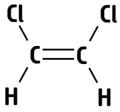
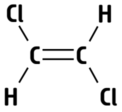
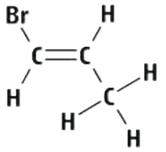
11. b. *cis*-1,2-dichloroethene



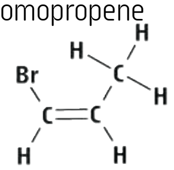
trans-1,2-dichloroethene



e. *trans*-1-bromopropene



cis-1-bromopropene



12. The boiling point of molecular compounds like hydrocarbons depends on the nature and strength of their intermolecular forces. In particular the boiling points will increase with increasing strength of intermolecular forces. In hydrocarbons the only type of intermolecular force of attraction are dispersion forces. These forces increase in strength as the number of electrons per molecule increases. In hydrocarbon molecules the number of electrons per molecule increases steadily with the number of carbon atoms in the molecule. Thus as the number of carbon atoms per molecule increases so does the total number of electrons and the hence the dispersion forces become stronger. This leads to the observed increase in boiling points seen for hydrocarbon molecules with progressively more carbon atoms per molecule.

13. Dispersion forces are the only intermolecular forces present in hydrocarbons. As these forces are very weak for molecules with few electrons, then the smaller molar mass hydrocarbons (ie those having only a few carbon atoms per molecule) have very weak dispersion forces and hence have very low boiling points. In particular, hydrocarbons like methane (1C), ethane (2C) and propane (3C) have the least electrons per molecule and hence they have the weakest dispersion forces. This causes their boiling points to be well below room temperature and so they are all gases at room temperature.

14. Ranking: 2,2-dimethylbutane (lowest boiling point) 3-methylpentane hexane (highest boiling point).

Explanation: Hydrocarbon molecules attract one another by dispersion forces. The stronger these are the higher the boiling point. Dispersion forces increase with the number of electrons per molecule however, this is the same for each of the isomers. Dispersion forces also increase with increasing molecular surface area. This means linear molecules will have greater dispersion forces than more spherical or branched molecules of the same size. Hence the straight chain isomer (hexane) will have the strongest dispersion forces and the highest boiling point. The most spherical isomer (2,2-dimethylbutane) has the weakest dispersion forces and the lowest boiling point.

[The actual boiling points for all of the isomers of C_6H_{14} are: 2,2-dimethylbutane (49.7 °C), 2,3-dimethylbutane (58.0 °C), 2-methylpentane (60.3 °C), 3-methylpentane (63.3 °C) and hexane (68.7 °C).]

15. The solubility of molecular substances depends upon the nature of the intermolecular forces present within the substances. Substances whose molecules attract by similar types of intermolecular forces will be soluble in one another. Petroleum is a mixture of hydrocarbons and hydrocarbon molecules attract most strongly by dispersion forces. Sea water is essentially water, $H_2O(l)$ with various other dissolved substances. The major intermolecular forces acting in water are hydrogen bonding and dipole-dipole forces. Water molecules can interact by dispersion forces but in water this is much weaker than its ability to attract by hydrogen bonding. Consequently water molecules will not be attracted to the hydrocarbon molecules in petroleum as water molecules attract most strongly by hydrogen bonding and hydrocarbon molecules attract most strongly by dispersion forces. Thus oil and water will not mix.

16. a. Both tetrachloroethene and ethene attract by dispersion forces only. The strength of dispersion forces increases with molecular size, specifically with the number of molecular electrons. As tetrachloroethene, C_2Cl_4 molecules are much larger than ethene, C_2H_4 molecules (80 molecular electrons compared to 16) then the dispersion forces and consequently the boiling point of tetrachloroethene is much greater than for ethene.

b. The solubility of molecular substances depends upon the nature of the intermolecular forces present within the substances. Substances whose molecules attract by similar types of intermolecular forces will be soluble in one another. As tetrachloroethene molecules attract by dispersion forces then it will be able to dissolve other substances that also attract strongly by dispersion forces. This includes substances that are non-polar and cannot attract by dipole-dipole forces or by hydrogen bonding.

17. a. $CH_2{=}CH_2(g) + Br_2(g) \rightarrow CH_2BrCH_2Br(l)$

b. $CH_2{=}CHCH_3(g) + Cl_2(g) \rightarrow CH_2ClCHClCH_3(l)$

c. $CH_3CH{=}CHCH_3(g) + H_2(g) \rightarrow CH_3CH_2CH_2CH_3(g)$

d. $CH_2{=}CH_2(g) + H_2O(g) \rightarrow CH_3CH_2OH(g)$

18. a. Yes. Propene rapidly decolourises bromine water. Propane will eventually have the same result but the reaction and colour change is much slower.

b. Yes. Hexene rapidly decolourises bromine water. Benzene will eventually have the same result but the reaction and colour change is much slower.

c. No. Both pentane and butane will eventually decolourise bromine water. Both will react slowly so no significant difference can be detected.

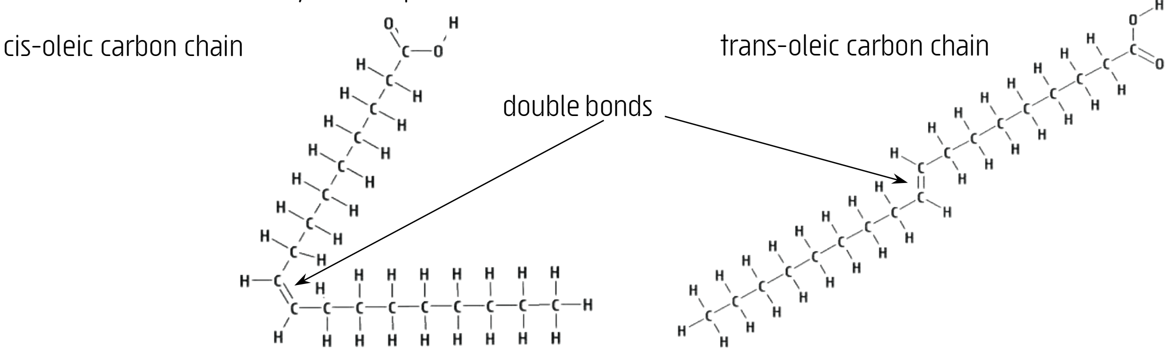
d. Yes. 2-methylhex-1-ene will rapidly decolourises bromine water. 2-methylhexane will eventually have the same result but the reaction is much slower.

19. a. Petroleum oils are hydrocarbons, ie they contain the elements hydrogen and carbon only. This edible oil is not a hydrocarbon as it contains the element oxygen as well as hydrogen and carbon.

b. The highlighted carbon chains contain various double bonds. Some of these double bonds will be lost as they become saturated with hydrogen during the addition reaction (hydrogenation).

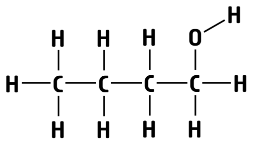
c. Platinum acts as a catalyst speeding up the hydrogenation reaction. Using fine particles of Pt catalyst increases its surface area further maximising rate.

d. The reaction described here does not involve the hydrogenation of a double bond. Instead this undesirable side reaction causes some double bonds to change configuration from the *cis* form to the *trans* form. *Cis* isomers typically have a V shape. This happens as the carbon atoms of the double bond are unable to freely rotate, locking the structure into either the linear *trans* configuration or the V shape *cis* configuration. This is shown here for the oleic acid chain of the fatty acid in question.



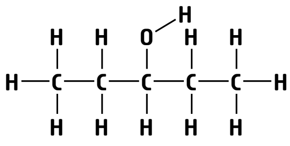
Set 16 Organic chemistry: Functional groups

1. **a.**



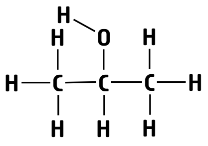
butan-1-ol is a primary alcohol

b.



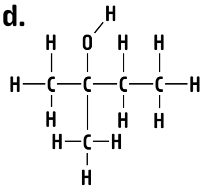
pentan-3-ol is a secondary alcohol

c.



propan-2-ol is a secondary alcohol

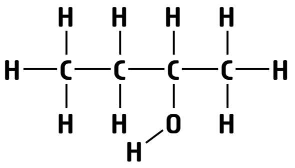
d.



2-methylbutan-2-ol is a tertiary alcohol

2. **a.** butan-2-ol **b.** methylpropan-2-ol

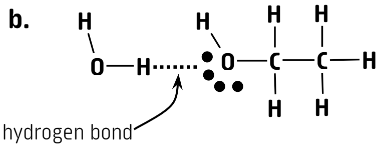
3. The structure representing butan-3-ol is incorrectly named. It is actually **butan-2-ol**. When numbering the carbon chain, start numbering from the chain end that gives the lowest number to the principal functional group, (see 11.2) in this case the alcohol group has a lower number (2) by numbering from the right.



4. Intermolecular forces present in ethanol include; hydrogen bonding, dipole-dipole forces and dispersion forces. Ethane molecules by comparison only interact by dispersion forces. The presence of hydrogen bonding in ethanol explains its higher boiling point. It can also be seen that the dispersion forces are very slightly stronger in ethanol as it has a greater molecular size (more molecular electrons) and dispersion forces increase with molecular mass/size/number of electrons. This aspect however, is of very minor importance in explaining the large difference in their boiling points.

5. **a.** Ethanol molecules are polar and can hydrogen bond (each ethanol molecule contains one -OH group). Hence ethanol molecules attract other molecules most strongly by hydrogen bonding or dipole-dipole forces. Water molecules are also polar and can attract by hydrogen bonding or dipole-dipole forces. Thus water and ethanol will be very soluble in one another as water molecules and ethanol molecules will be able to mix and attract one another by similar intermolecular forces. This is why water and ethanol readily form a homogeneous mixture (solution) instead of forming separate layers.

b.

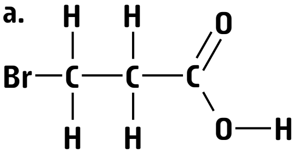


Alternatively a lone pair from H_2O may hydrogen bond to the H of the –OH functional group.

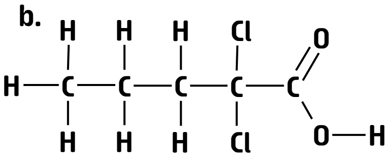
6. **a.** propanal **b.** pentan-3-one **c.** butanone **d.** ethanal

7. The difference in boiling points of these molecular compounds is related to the overall strength of their respective intermolecular forces. The greater the strength and extent of intermolecular forces, the higher the boiling point. All three substances have similar molecular size/number of molecular electrons so the strength of dispersion forces is similar for all three. Both propan-1-ol and propanal are polar and so can also interact by dipole-dipole forces. For this reason both of these substances have a higher boiling point than butane. As propan-1-ol is also able to interact by hydrogen bonding, its boiling point will be the highest of the three substances.

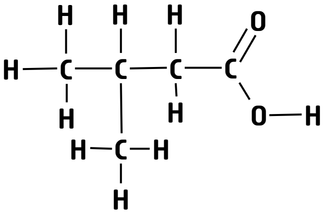
8. **a.**



b.



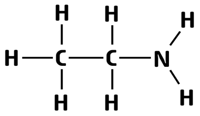
c.



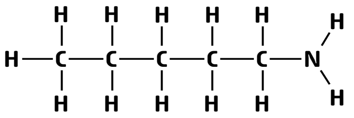
9. Short chain carboxylic acids, like ethanoic acid, are polar and attract most strongly by hydrogen bonding (each ethanoic acid molecule has one -OH group). Water molecules are also polar and attract most strongly by hydrogen bonding. Thus water is a good solvent for ethanoic acid and other short chain carboxylic acids, as water molecules and these carboxylic acid molecules will be able to mix and attract one another strongly by hydrogen bonding.

Long chain carboxylic acids like palmitic acid are also polar and can hydrogen bond (each acid molecule contains one -OH group). However, these larger carboxylic acid molecules are attracted most strongly to one another by dispersion forces. For this reason water is a poor solvent for long chain carboxylic acids (fatty acids) as water molecules attract most strongly by hydrogen bonding or dipole-dipole forces while fatty acid molecules attract most strongly by dispersion forces. Thus fatty acid molecules and water molecules will not attract strongly and hence they do not mix.

10. ethanamine



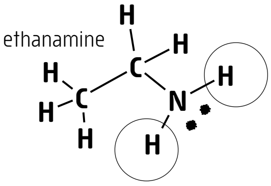
pentan-1-amine

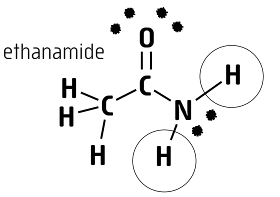


The short chain amine, ethanamine is polar and can hydrogen bond (each molecule contains one -NH_2 group). Hence its molecules can attract water molecules by hydrogen bonding or dipole-dipole forces. Thus water is a good solvent for ethanamine.

The long chain amine, pentan-1-amine is much less polar and although its molecules can attract by hydrogen bonding (each molecule contains one -NH_2 group) dispersion forces are more significant due to its much larger molecular size. Thus water is a poor solvent for pentan-1-amine and it is most probably insoluble in water.

11. a/b.

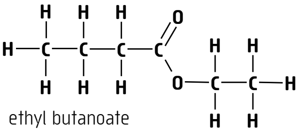




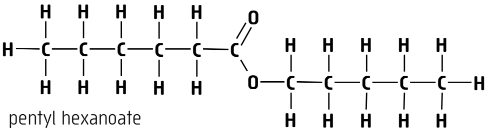
c. In ethanamine, the N atom of the -NH_2 functional group draws electrons away from the H atom causing it to develop a positive dipole moment, δ^+. However in the compound ethanamide it is the combined effect of both the highly electronegative oxygen atom and nitrogen atom that together contribute to electrons being more strongly attracted away from the hydrogen atoms of the amino group. This results in a larger dipole moment, δ^+ forming on the hydrogen atoms of the amino group in ethanamide molecules than in ethanamine molecules.

d. The effect of hydrogen bonding is stronger in ethanamide than in ethanamine for two reasons. Firstly the individual hydrogen bonds are stronger in ethanamide than in ethanamine. This happens as the N-H dipole moment in ethanamide is much greater than that in ethanamine. (As outlined above.) Furthermore, the extent of hydrogen bonding in ethanamide is greater than in ethanamine. In both cases these molecules have two possible hydrogen bonding hydrogen atoms, ie those of the NH_2 group. However, in ethanamine there is only one lone pair of electrons per molecule available for hydrogen bonding (the N atom's lone pair) whereas in ethanamide there are three lone pairs available (two on the O atom and one on the N atom). The greater availability of lone pairs in ethanamide means the hydrogen bonding will be more extensive than in ethanamine. Thus the stronger and more extensive hydrogen bonding in ethanamide results in it having the higher boiling point.

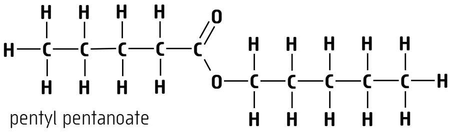
12.



ethyl butanoate



pentyl hexanoate



pentyl pentanoate

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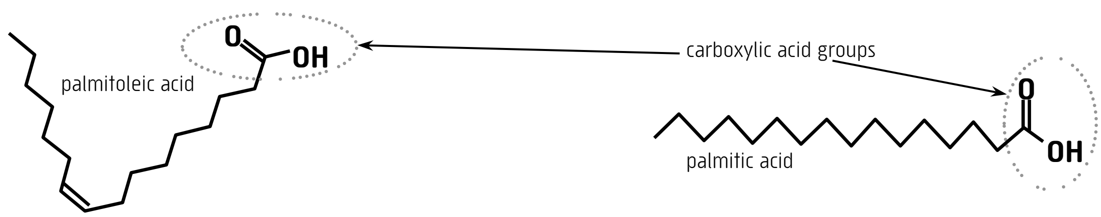
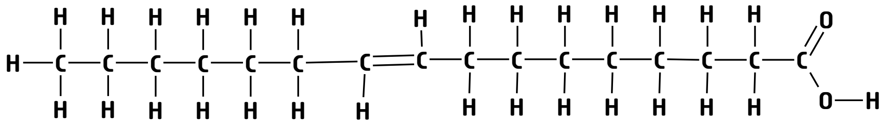
13. a.



b. Monounsaturated fatty acids have one carbon to carbon double bond (C = C) per molecule. The wire frame structure shows the presence of one C to C double bond in the palmitoleic acid.

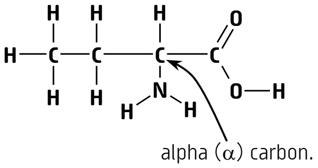
c. Palmitic acid contains a single carboxylic acid group (-COOH) and thus is a carboxylic acid. As it has a relatively long carbon chain, it is referred to as a fatty acid. The structure does not contain carbon to carbon double bonds, ie **is not** unsaturated, so it is said to be saturated.

d. The two structures differ by a double bond only, hence their molecular formulas differ by 2H atoms only. Thus palmitoleic acid is $C_{16}H_{30}O_2$. The fully drawn structure below confirms the molecular formula is $C_{16}H_{30}O_2$.



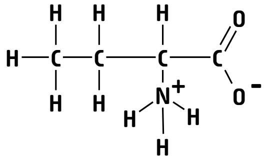
e. The two structures differ by a double bond only. Thus during the biosynthesis, palmitic acid has lost two hydrogen atoms, ie become unsaturated hence part of the enzyme name is desaturase, ie to make unsaturated. The double bond has been introduced on the 9th carbon of the fatty acid, when numbering in the usual way from the carboxylic acid group being number 1. Hence the delta 9 in the enzyme name delta-9 desaturase.

14. a.



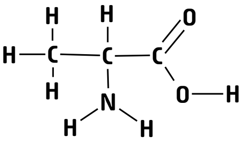
b. In amino acids the α-carbon is the carbon atom next along from the carboxylic acid group,-COOH, ie carbon number 2 in the chain of carbons. Note, carbon number 1 is the terminal carbon of the -COOH functional group.

c. Zwitterions are dipolar ions with an overall neutral charge. The weakly acidic –COOH group and the weakly basic $–NH_2$ group in the α-amino acid structure change to form an anionic $-COO^-$ group and a cationic $-NH_3^+$ group.

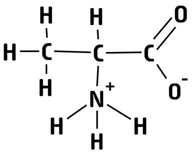


15. Structure A is an α-amino acid. Alpha amino acids have an amino group $-NH_2$ on the first carbon following the carboxylic acid functional group (-COOH), ie on carbon number 2 or the α-carbon. Structure B is not an α-amino acid as there is no amino group on carbon number 2.

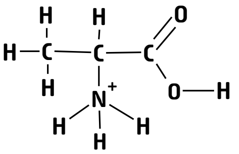
16.



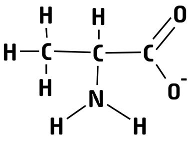
general structure of alanine



zwitterion form



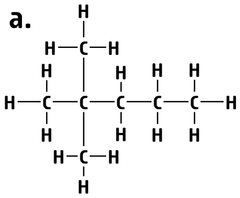
cationic form (acidic solution)



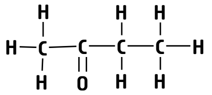
anionic form (basic solution)

17.
- **a.** carboxylic acid
- **b.** ester
- **c.** aldehyde
- **d** amide
- **e.** alkene (double bond)
- **f.** ketone
- **g.** alcohol
- **h.** amine
- **i.** ester

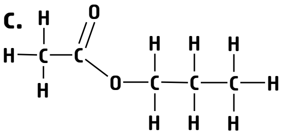
18. **a.**



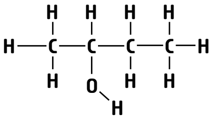
b.



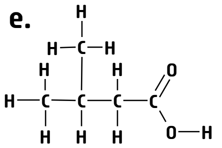
c.



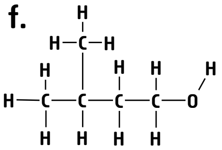
d.



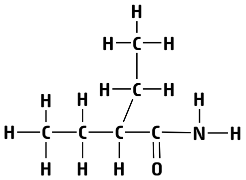
e.



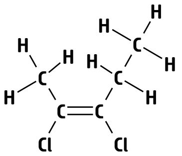
f.



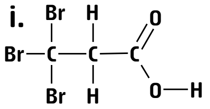
g.



h.



i.



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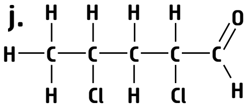

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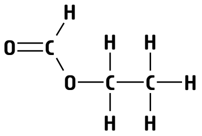

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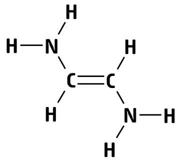

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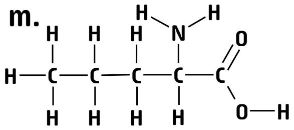

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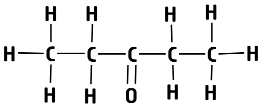

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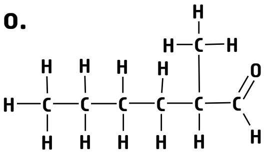

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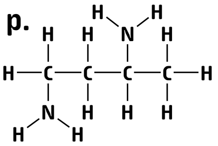

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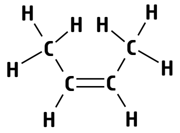

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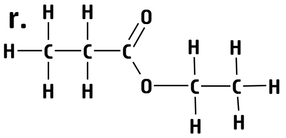
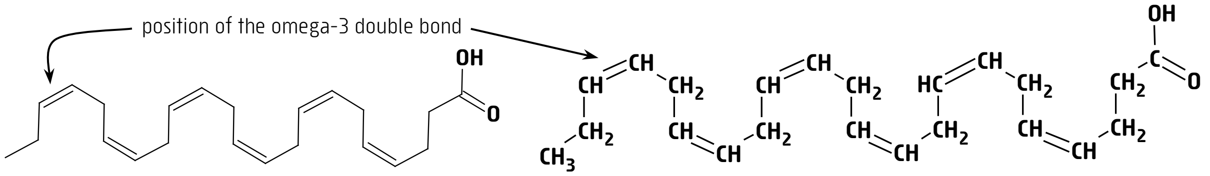


19. **a.** propan-2-ol
b. methyl ethanoate
c. ethanal
d 5,5-dibromopentanoic acid
e. butanone
f. ethanamine
g. 3-methylbutan-2-ol
h. ethanoic acid
i. methylpropanamide
j. ethyl propanoate
k. pentan-2-one
l. propan-2-ol
m. propanal

20. **a.** ethanoic acid and methyl methanoate
b. methylpropan-2-ol
c. methyl ethanoate and ethyl methanoate
d. propanal and propanone

21.



Both of these structures represent docosahexaenoic acid. Notice the *cis* configuration for each of the six C to C double bonds. Unsaturated molecules like this contain at least one C to C double bond.
Polyunsaturated compounds contain two or more double bonds. Hence docosahexaenoic acid is polyunsaturated. Omega-3 fatty acids have a double bond between the 3rd and 4th carbon atoms from the end of the carbon chain furthest from the carboxylic acid group. Also docosahexaenoic acid is a fatty acid as it is a **long chain** carboxylic acid.

22. 1° alcohols of $C_5H_{12}O$; pentan-1-ol, 2-methylbutan-1-ol, 3-methylbutan-1-ol, 2,2-dimethylpropan-1-ol.
2° alcohols of $C_5H_{12}O$ include; pentan-2-ol, pentan-3-ol, 3-methylbutan-2-ol.
3° alcohols of $C_5H_{12}O$ include; 2-methylbutan-2-ol only.

23. a. A volatile solvent is one that will evaporate easily at low temperatures. Having the active varnish ingredients dissolved in a solvent makes it easier to apply an even thin coat of the active varnish components to the surface being varnished. Once applied it is important for the solvent to quickly evaporate, so that the active varnish components will dry and cure (go solid). If the solvent does not evaporate then the varnish remains liquid and will 'run'.

A perfume contains strongly fragrant oils dissolved in a solvent. Having the fragrant oils dissolved in a solvent makes it easier to apply a thin layer of the perfume oils to the skin. Once applied to the body the solvent needs to evaporate otherwise the skin will remain 'wet'. Once the solvent evaporates the active fragrant oils are left thinly spread over the skin surface.

b. For a molecular substance to be volatile it must readily evaporate. This means the intermolecular forces within the substance need to be weak, as evaporation involves molecules being separated from one another as they convert from the liquid phase to the gas phase. Both pentanoic acid and propyl ethanoate molecules can attract by dispersion forces and dipole-dipole forces. The dispersion forces are of equal strength in both compounds as their molecules are of the same size, ie same number of electrons and similar shape. However, pentanoic acid is capable of hydrogen bonding (each molecule contains one -OH functional group) so the overall strength of intermolecular forces is considerably greater in pentanoic acid than in propyl ethanoate. As pentanoic acid molecules are more strongly attracted to one another they are less likely to evaporate, ie less likely to be volatile.

Set 17 Organic chemistry: Redox reactions

1. a. $2CH_3OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 4H_2O(g)$

b. $CH_3OH(l) + O_2(g) \rightarrow CO(g) + 2H_2O(g)$

c. $2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(g)$

d. $2CH_3CHOHCH_3(l) + 9O_2(g) \rightarrow 6CO_2(g) + 8H_2O(g)$

e. $CH_3COOH(l) + 2O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$

2. a. The oxidation numbers of the various elements in the reaction are:

$$2\underset{\mathbf{2-}}{\underset{\uparrow}{C}}\underset{\mathbf{1+}}{\underset{\uparrow}{H_3}}\underset{\mathbf{2-}}{\underset{\uparrow}{O}}\underset{\mathbf{1+}}{\underset{\uparrow}{H}}(l) \quad + \quad 3\underset{\mathbf{0}}{\underset{\uparrow}{O_2}}(g) \quad \rightarrow \quad 2\underset{\mathbf{4+}}{\underset{\uparrow}{C}}\underset{\mathbf{2-}}{\underset{\uparrow}{O_2}}(g) \quad + \quad 4\underset{\mathbf{1+}}{\underset{\uparrow}{H_2}}\underset{\mathbf{2-}}{\underset{\uparrow}{O}}(g)$$

The oxidation number of carbon increases from 2- to 4+ showing it has been oxidised. Also, the oxidation number of oxygen decreases from 0 to 2- showing it has been reduced. Hence this is a redox reaction, ie it involves both oxidation and reduction.

b. The oxidation numbers of carbon in this reaction change from 2- (CH_3OH) to 2+ (CO). The increasing oxidation number corresponds to oxidation hence methanol has been oxidised. However as carbon monoxide can potentially be further oxidised to form CO_2 and the oxidation number of carbon increased to its maximum of 4+ then the reaction represents incomplete oxidation.

3. a. CH_3CH_2COOH

b. $CH_3CH_2CH_2COOH$

c. NR

d. CH_3CH_2CHO

e. $HOOCCH_2COOH$

f. CH_3COCH_3

g. NR

h. NR

i. $HOOCCH_2COCH_2CH_3$

4. a. Potassium dichromate is the oxidising agent. When it oxidises ethanol it changes colour from orange to green. Sulfuric acid is required as potassium dichromate only works efficiently as an oxidising agent in an acidic medium, ie H^+ ions are needed for the reduction of $Cr_2O_7^{2-}$.

b. As alcoholic breath enters the tube, any ethanol that may be present reacts with crystals of acidified potassium dichromate. This changes their colour from orange to green. Depending upon the amount of alcohol in the person's breath, this colour change extends further along the tube of crystals. The extent of the colour change is read from the scale and is an indication of the concentration of ethanol in their breath.

c. The amount of ethanol entering the tube depends upon the concentration of ethanol in the person's breath and the volume of breath. Thus for consistent results, there must be a fixed volume of breath, so that the amount of colour change (measured from the scale) can be related to the concentration of ethanol in the exhaled air.

d. Water is the single most abundant component of blood. As ethanol and water both interact strongly by the same types of intermolecular forces, hydrogen bonding, they will be very soluble in one another. Thus once consumed, ethanol is easily transported around the body in blood.

Although the intermolecular forces in ethanol are quite strong, it has a lower boiling point than water and thus also evaporates more easily than water. In the lungs, gases like oxygen, carbon dioxide, and water vapour are readily exchanged between exhaled and inhaled air and a person's blood. As ethanol is more volatile than water then it too is present in the exhaled breath of a person who has consumed alcoholic beverages.

5. a. $CH_3CH_2OH(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + 4H^+(aq) + 4e^-$
b. $CH_3CH_2CH_2CH_2OH(aq) \rightarrow CH_3CH_2CH_2CHO(aq) + 2H^+(aq) + 2e^-$
c. $CH_3CHOHCH_3(aq) \rightarrow CH_3COCH_3(aq) + 2H^+(aq) + 2e^-$
d. $CH_3CH_2CHO(aq) + H_2O(l) \rightarrow CH_3CH_2COOH(aq) + 2H^+(aq) + 2e^-$

6. a. The vinegary taste is due to ethanoic acid resulting from the oxidation of ethanol by bacteria and air.

b. Oxygen is the oxidising agent responsible for oxidising ethanol (CH_3CH_2OH) to ethanoic acid (CH_3COOH).

c. Air is the source of oxygen that spoils wine (oxidises ethanol) so excluding air from entering the wine cask as it empties ensures it remains fresh.

7. a. propan-1-ol
b. propan-2-ol
c. butan-1-ol (partial oxidation)
d. butan-2-ol
e. butane-1,4-diol
f. butane-1,3-diol

8. a. $5CH_3CH_2CHO(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 5CH_3CH_2COOH(aq) + 2Mn^{2+}(aq) + 3H_2O(l)$
The purple mixture would become colourless (or very pale pink).

b. $5CH_3CH_2CHOHCH_3(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 5CH_3CH_2COCH_3(aq) + 2Mn^{2+}(aq) + 8H_2O(l)$
The purple mixture would become colourless (or very pale pink).

c. $3CH_3OH(aq) + 2Cr_2O_7^{2-}(aq) + 16H^+(aq) \rightarrow 3HCOOH(aq) + 4Cr^{3+}(aq) + 11H_2O(l)$
The orange mixture becomes green in colour.

d. $3CH_3CH(CH_3)CHOHCH_3(aq) + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow 3CH_3CH(CH_3)COCH_3(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$
The orange mixture turns green.

e. $3HCHO(aq) + Cr_2O_7^{2-}(aq) + 8H^+(aq) \rightarrow 3HCOOH(aq) + 2Cr^{3+}(aq) + 4H_2O(l)$ The orange mixture turns green.

f/g. NR

h. $5CH_3CH_2CH_2OH(aq) + 4MnO_4^-(aq) + 12H^+(aq) \rightarrow 5CH_3CH_2COOH(aq) + 4Mn^{2+}(aq) + 11H_2O(l)$
The purple mixture goes colourless (or very pale pink).

i. NR

9. a. i. methylpropan-2-ol ii. methylpropan-1-ol *and* butan-1-ol iii. butan-2-ol

b. propanone

c. i. Add acidified potassium permanganate solution. Ethanol turns the purple solution colourless. The solution remains purple with ethanoic acid.
ii. Add acidified potassium permanganate solution. Propanal turns the purple solution colourless. The solution remains purple with propanone.
iii. Add acidified potassium permanganate solution. 3-methylhexan-2-ol turns the purple solution colourless. The solution remains purple with 3-methylhexan-3-ol. Alternatively substitute acidified potassium dichromate solution. In each case the colour changes are orange to green.

Set 18 Carboxylic acids, esterification and soaps

1. a. Lactic acid is a carboxylic acid as it contains the carboxyl functional group, -COOH. In milk, the –COOH group of lactic acid acts as a proton donor causing a rise in the $H_3O^+(aq)$ [ie $H^+(aq)$] concentration. This makes the milk acidic and hence sour tasting.

b. Lactic acid is a weak acid and so it raises the concentration of $H^+(aq)$ (equation below) thus lowering pH.
$CH_3CH(OH)COOH(aq) \rightleftharpoons CH_3CH(OH)COO^-(aq) + H^+(aq)$

2. **a.** Methanoic acid: $HCOOH(aq) + H_2O(l) \rightleftharpoons HCOO^-(aq) + H_3O^+(aq)$

Propanoic acid: $CH_3CH_2COOH(aq) + H_2O(l) \rightleftharpoons CH_3CH_2COO^-(aq) + H_3O^+(aq)$

b. The K_a value for methanoic acid is fairly small indicating it is a fairly weak acid.

c. Methanoic acid is the stronger acid of the two. This is evident as the K_a value for methanoic acid is larger than the K_a value for propanoic acid. The larger K_a value means the equilibrium position for the reaction forming hydrogen ions is further to the right, ie a higher $H_3O^+(aq)$ concentration.

3. **a.** $HCOOH(aq) + NaOH(aq) \rightarrow HCOONa(aq) + H_2O(l)$

Observation: Clear colourless solutions remain clear and colourless. The solution may heat up.

b. $2CH_3COOH(aq) + Mg(s) \rightarrow (CH_3COO)_2Mg(aq) + H_2(g)$

Observation: Slow fizzing occurs as a colourless gas is evolved and the silvery metal strip dissolves. The solution will heat but remains clear and colourless.

c. $2CH_3CH_2COOH(aq) + CaCO_3(s) \rightarrow (CH_3CH_2COO)_2Ca(aq) + H_2O(l) + CO_2(g)$

Observation: Slow fizzing occurs as a colourless gas is evolved and a white solid dissolves. The solution will heat up but remains clear and colourless.

d. $CH_3COOH(aq) + NaHCO_3(aq) \rightarrow CH_3COONa(aq) + H_2O(l) + CO_2(g)$

Observation: Fizzing occurs as a colourless gas is evolved. Solution remains clear and colourless.

4. **a.** This test will be successful. Fizzing and a colourless gas are seen when $NaHCO_3(aq)$ is added to propanoic acid, CH_3CH_2COOH. No change is observed with propanol, $CH_3CH_2CH_2OH$.

b. This test will be unsuccessful. No change is observed with propanal, CH_3CH_2CHO or with propane, $CH_3CH_2CH_3$

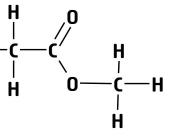
c. This test will be successful. Fizzing and a colourless gas are seen when $NaHCO_3(aq)$ is added to methanoic acid, $HCOOH$. No change is observed with methyl ethanoate, CH_3COOCH_3.

5. **a.** Sulfuric acid acts as a catalyst. It increases the reaction rate for the formation of the ester.

b. As well as an ester, water will also be formed.

c. The organic reagents are both volatile and flammable. Without the refluxing apparatus most of the organic reagent will be lost from the reaction flask as they easily evaporate when heated. Using a condenser prevents the loss of volatile organic reagents during heating by condensing their vapours and returning the liquid to the reaction flask. An electric heating mantle is an added safety precaution against igniting any flammable organic vapours that may form.

6. **a.**



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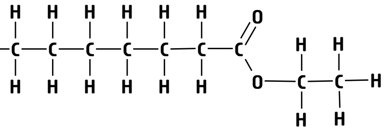

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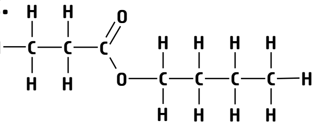

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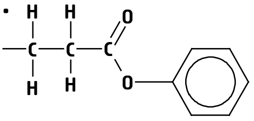


7. **a.** $CH_3OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOCH_3(l) + H_2O(l)$ methyl ethanoate

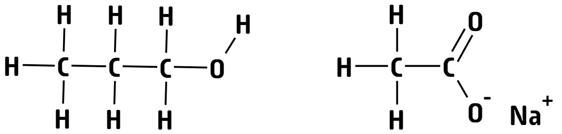
b. $CH_3CH_2OH(l) + CH_3CH_2COOH(l) \rightleftharpoons CH_3CH_2COOCH_2CH_3(l) + H_2O(l)$ ethyl propanoate

c. $CH_3CH_2CH_2OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOCH_2CH_2CH_3(l) + H_2O(l)$ propyl ethanoate

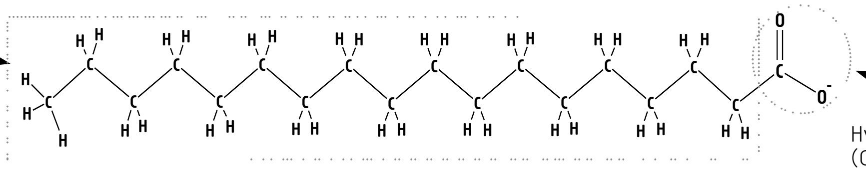
8. **a.** The ester is both volatile and flammable. There is a danger of ester vapours igniting and causing a fire. They should avoid using a naked flame to heat their reaction mixture and ensure there are no other people in the laboratory using a naked flame. Heating should be with an electric mantle or a water bath on an electric hot plate. To avoid producing excessive amounts of organic vapour, a refluxing apparatus can be used.

b. Sodium hydroxide is a strong base and can cause skin burns if accidently touched. If particles of the solid accidently enter the eye then severe eye damage may result. Xinyi and Kirsten must use safety glasses for eye protection and avoid skin contact with the solid sodium hydroxide.

c. The products formed are propanol and sodium ethanoate.
Note: The carboxylic acid, ethanoic acid would form except the solution is strongly basic and so ethanoic acid is present as the salt sodium ethanoate.



9. a. Yes, soap solutions would be electrically conducting. As soap is essentially a soluble ionic compound, it dissociates in water producing sodium ions and stearate ions. The dissociation of soap shows how this happens: $NaC_{17}H_{35}COO(s) \rightarrow Na^{+}(aq) + C_{17}H_{35}COO^{-}(aq)$.

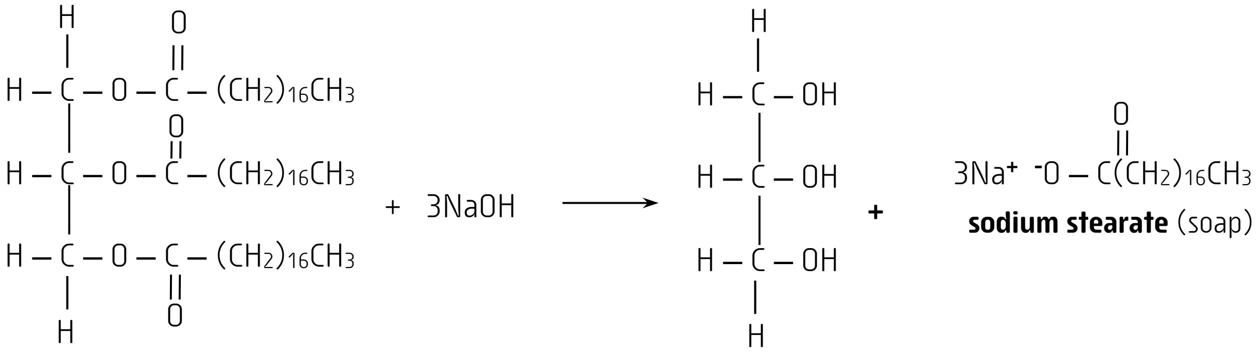
b. 

Hydrophobic end. (Boxed.) This is the water repelling part of the soap structure.

Hydrophilic end. (Circled.) Hydrophilic means water attracting.

c. The long carbon chain section of the soap ion is largely non-polar and hence can only interact by dispersion forces. Water molecules are very polar and mainly interact by hydrogen bonding or dipole-dipole forces. For this reason the hydrocarbon (tail section) of the soap ion can not interact with water as they attract by different types of intermolecular forces. This is why the tail or non-polar end of the soap ion is hydrophobic.

The negatively charged end of the soap ion is the hydrophilic end. This part of the soap ion is strongly attracted to the positive end of a water molecule's dipole. The attraction between an ion and the dipole of a water molecule is known as an ion-dipole force. These forces explain why the charged end of a soap ion are hydrophilic and water attracting.

d. 

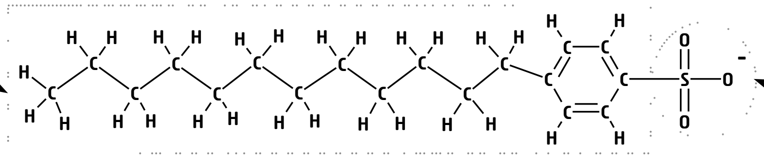
tristearin

glycerol (or propane-1,2,3-triol)

sodium stearate (soap)

e. Hard water is water containing dissolved calcium or magnesium salts. The presence of $Ca^{2+}(aq)$ and $Mg^{2+}(aq)$ causes the precipitation of stearate ions as insoluble calcium or magnesium stearate. Precipitation of soap ions: $2C_{17}H_{35}COO^{-}(aq) + Ca^{2+}(aq) \rightarrow Ca(C_{17}H_{35}COO)_2(s)$. When this happens the soap is not able to function as normal as it is no longer in solution.

10. a. Soap is manufactured from the raw materials, sodium hydroxide or potassium hydroxide and the natural biological products fats or oils, eg olive oil, palm oil or animal fat like tallow. As fats and oils are natural products so the resulting soap may be considered a natural product. Detergents however are manufactured from sulfuric acid and various refined and modified petroleum products. Neither of these substances is considered a natural product and hence detergents are synthetic.

b. 

Hydrophobic end. (Boxed.)

Hydrophilic end. (Circled.)

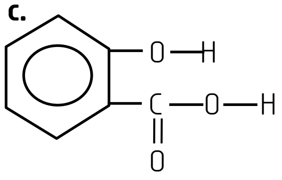
c. Both soaps and detergents have hydrophobic (water repelling) and hydrophilic (water attracting) sections in their respective anions. It is the interaction of these hydrophobic and hydrophilic sections with water and non-polar grease and dirt that allows both soaps and detergents to have a similar cleaning action. Both are able to stabilise ("dissolve") non-polar substances in water by micelle formation. These are minute suspended ("dissolved") spherical globules that contain the non-polar grease or dirt. In this process the hydrophobic parts of the soap or detergent anions are attracted (by dispersion forces) to the non-polar dirt or grease to form the inside of the micelle. The outside of the micelle consists of the hydrophilic parts of the soap or detergent ion. The micelle surface (outside) is stabilised as it is strongly attracted by ion-dipole forces to the surrounding polar water molecules.

d. Detergents are not affected by hard water as the calcium and magnesium salts of detergent anions are soluble in water. This means detergents can work equally well in soft water [ie water that does not contain free $Ca^{2+}(aq)$ or $Mg^{2+}(aq)$] or hard water [ie water that does contain free $Ca^{2+}(aq)$ or $Mg^{2+}(aq)$].

11. **a.** Reflux together ethanoic acid, octan-1-ol and a few drops of sulfuric acid.

b. For pentyl butanoate, reflux together butanoic acid, pentan-1-ol and a few drops of sulfuric acid. For pentyl ethanoate, use ethanoic acid, pentan-1-ol and a few drops of sulfuric acid.

c.



and CH_3COOH

Set 19 Empirical formula

1. **a.** HO **b.** $C_3H_7N_2O$ **c.** CH_2O **d.** C_3H_8.

2. Since the sample contains C and H only and has a total mass of 10.00 g, then:
m(hydrogen) = 10.00 - m(carbon) = 10.00 – 7.490 = 2.510 g

elements	**C**	**H**
mass of each	7.490 g	2.510 g
moles in sample	$\frac{7.490}{12.01}$	$\frac{2.510}{1.008}$
	0.6236	2.4901
÷ by smallest	$\frac{0.6236}{0.6236}$	$\frac{2.4901}{0.6236}$
ratio	1.000	3.993
simplest whole ratio	1	4

∴ the **empirical formula** is **CH_4**

Where partial working has been evaluated this is shown (for your convenience) with the correct number of significant figures. However, the complete number is carried forward into later parts of the calculation. It is essential that you carry full numerical figures until completion of a calculation. This is especially important in an empirical formula calculation. Only round your final answer.

3. Since the compound contains C, H and O only and the sample has a total mass of 3.4330 g then:

m(O) = 3.4330 - [m(C) + m(H)]
= 3.4330 - (2.1300 + 0.3575)
= 0.9455 g

elements	**C**	**H**	**O**
mass of each	2.130 g	0.3575 g	0.9455 g
÷ each by M	$\frac{2.130}{12.01}$	$\frac{0.3575}{1.008}$	$\frac{0.9455}{16.00}$
moles	0.1774	0.3547	0.05909
÷ by smallest, ie by 0.05909 mol	$\frac{0.1774}{0.05909}$	$\frac{0.3547}{0.05909}$	$\frac{0.05909}{0.05909}$
ratio	3.001	6.002	1.000

∴ the **empirical formula** is **C_3H_6O**

4. Since the sum of the percentage of Fe + O is 100, then for the iron oxide with 77.7% Fe:
%O = 100.0 - %Fe = 100.0 – 77.7 = 22.3%

elements	**Fe**	**O**
% of each	77.7%	22.3%
mass in 100 g	77.7 g	22.3 g
moles in 100 g	$\frac{77.7}{55.85}$	$\frac{22.3}{16.00}$
	1.3912	1.3937
÷ by smallest	$\frac{1.3912}{1.3912}$	$\frac{1.3937}{1.3912}$
ratio	1.000	1.002
simplest whole ratio	1	1

Since the sum of the percentage of Fe + O is 100, then for the iron oxide with 72.4% Fe:
%O = 100.0- %Fe = 100.0 – 72.4 = 27.6%

Fe	**O**	
72.4%	27.6%	
72.4 g	27.6 g	
$\frac{72.4}{55.85}$	$\frac{27.6}{16.00}$	
1.2963	1.725	
$\frac{1.2963}{1.2963}$	$\frac{1.725}{1.2963}$	
1.000	1.331	multiply each by 3
3	4	

∴ the **empirical formula** is: **FeO** and **Fe_3O_4**

5. Since the sum of the three percentages is 100, then:
% Oxygen = 100 - (%K + %Cr) = 100 - (40.27 + 26.78) = 32.95%

elements	**K**	**Cr**	**O**	
% of each	40.27%	26.78%	32.95%	
mass in 100 g	40.27	26.78	32.95	
moles in 100 g	$\frac{40.27}{39.10}$	$\frac{26.78}{52.00}$	$\frac{32.95}{16.00}$	
	1.030	0.5150	2.059	
÷ by smallest	$\frac{1.030}{0.5150}$	$\frac{0.5150}{0.5150}$	$\frac{2.059}{0.5150}$	
ratio	2.000	1.000	3.999	∴the **empirical formula** is **K_2CrO_4**

6. As all of the carbon from the hydrocarbon is converted to CO_2 then:
n(CO_2 from combustion) = n(C in the original 3.550 g of hydrocarbon).

$$n(CO_2) = \frac{m}{M} = \frac{11.14}{44.01} = 0.2531 \text{ mol}$$

also n(C) = n(CO_2) = 0.2531 mol *and* m(C) = n x M = 0.2531 x 12.01 = 3.040 g

Since the hydrocarbon contains the elements C and H only then:
m(H) = m(compound) - m(C in compound) *thus* m(H) = m(compound) - m(C) = 3.550 - 3.040 = 0.5100 g

and $$n(H) = \frac{m}{M(H)} = \frac{0.5100}{1.008} = 0.5060 \text{ mol}$$

elements in the hydrocarbon	**C**	**H**	
moles of each (found previously)	0.2531	0.5060	divide by 0.2531
ratio	1.000	1.999	

∴ the **empirical formula** of the hydrocarbon is **CH_2**

7. $n(H_2O) = \frac{m}{M} = \frac{8.198}{18.016} = 0.4550$ mol *and* $n(H) = 2 \times n(H_2O) = 2 \times 0.4550 = 0.9101$ mol

m(H) = n x M = 0.9101 x 1.008 = 0.9174 g *and* m(C) = 5.249 - m(H) = 5.249 - 0.9174 = 4.332 g

C	H	As the sample contains the elements C and H only.
4.332 g	0.9174 g	
$\frac{4.332}{12.01}$	$\frac{0.9174}{1.008}$	Find the moles of each element, ie divide the mass of each element by its molar mass.
0.3607	0.9101	Divide all molar amounts by the smallest molar value, ie 0.3607.
1.000	2.523	Multiplying by 2 produces a whole number ratio. (See border note p142.)
2.000	5.047	

∴ the **empirical formula** is **C_2H_5**

8. $n(CO_2) = \frac{m}{M} = \frac{7.974}{44.01} = 0.1812$ mol *and* $n(C) = n(CO_2) = 0.1812$ mol

$m(C) = n \times M = 0.1812 \times 12.01 = 2.176$ g This gives the mass of carbon in the 3.996 g sample.

$n(H_2O) = \frac{m}{M} = \frac{3.264}{18.016} = 0.1812$ mol *and* $n(H) = 2 \times n(H_2O) = 2 \times 0.1812 = 0.3623$ mol

$m(H) = n \times M = 0.3623 \times 1.008 = 0.3652$ g This gives the mass of hydrogen in the 3.996 g sample.

As the 3.996 g sample contains C, H and O only then: $m(O) = 3.996 - [m(C) + m(H)]$
$= 3.996 - (2.176 + 0.3652) = 1.455$ g

C	H	O	
2.176 g	0.3652 g	1.455 g	
$\frac{2.176}{12.01}$	$\frac{0.3652}{1.008}$	$\frac{1.455}{16.00}$	Find the moles of each element, ie divide the mass of each element by its molar mass.
0.1812	0.3623	0.09092	Divide all by the smallest molar value, ie 0.09092.
1.993	3.985	1.000	

∴ the **empirical formula** is **C_2H_4O**

9. a. $\mathbf{M_{ef}}(C_3H_4O_3) = 3 \times 12.01 + 4 \times 1.008 + 3 \times 16.00 = 88.06$ g moL^{-1}

ratio $(M/M_{ef}) = \frac{M}{M_{ef}} = \frac{176}{88.062} = \mathbf{2.00}$ ∴ the molecular formula is twice the empirical formula, ie the **molecular formula** of **ascorbic acid** is **$C_6H_8O_6$**.

b. $\mathbf{M_{ef}}(CH_2) = 12.01 + 2 \times 1.008 = 14.026$g mol^{-1}

ratio $(M/M_{ef}) = \frac{M}{M_{ef}} = \frac{84.16}{14.026} = \mathbf{6.000}$ ∴ the molecular formula is six times the empirical formula, ie the **molecular formula** of **cyclohexane** is **C_6H_{12}.**

c. $\mathbf{M_{ef}}(CH) = 12.01 + 1.008 = 13.018$ g mol^{-1}

ratio $(M/M_{ef}) = \frac{M}{M_{ef}} = \frac{78.1}{13.018} = \mathbf{6.00}$ ∴ the molecular formula is six times the empirical formula, ie the **molecular formula** of **benzene** is **C_6H_6.**

10. As the gas is measured at STP, then: $n = \frac{V_{STP}}{22.71} = \frac{1.217}{22.71} = 0.05359$ mol

and $M(\text{molecular}) = \frac{m}{n} = \frac{3.121}{0.05359} = 58.23$ g mol^{-}

also $\mathbf{M_{ef}}(C_2H_5) = 2 \times 12.01 + 5 \times 1.008 = 29.06$ g mol^{-}

ratio $(M/M_{ef}) = \frac{M}{M_{ef}} = \frac{58.23}{29.06} = 2.004$ ie The molecular formula is twice the empirical formula.

∴ the **molecular formula** is **C_4H_{10}**

11. a. $PV = nRT$ *ie* $n = \dfrac{PV}{RT} = \dfrac{80.2 \times 2.25}{8.3145 \times 408.15} = 0.0532\ \text{mol}$

Use the correct value for R (8.3145), use temperature in kelvin, volume in litres and pressure in kPa.

$n = \dfrac{m}{M}$ *ie* $M = \dfrac{m}{n} = \dfrac{6.182}{0.0532} = 116\ \text{g mol}^{-}$

Find the empirical formula mass from the given empirical formula C_3H_6O.

$M_{ef}(C_3H_6O) = 3 \times 12.01 + 6 \times 1.008 + 16.00 = 58.08\ \text{g mol}^{-}$

ratio $(M/M_{ef}) = \dfrac{M}{M_{ef}} = \dfrac{116}{58.08} = 2.00$ ie The molecular formula, M is twice the empirical formula, M_{ef}.

∴ the **molecular formula** is $\mathbf{C_6H_{12}O_2}$

b. ethyl butanoate

12.a. $n(CO_2) = \dfrac{m}{M} = \dfrac{12.16}{44.01} = 0.2763\ \text{mol}$

and $n(C) = n(CO_2) = 0.2763\ \text{mol}$ Since there is one mole of C in every mole of CO_2.

∴ $m(C) = n \times M = 0.2763 \times 12.01 = 3.318\ \text{g}$ This gives the mass of carbon in the 7.882 g sample.

$n(H_2O) = \dfrac{m}{M} = \dfrac{4.563}{18.016} = 0.2533\ \text{mol}$ *and* $n(H) = 2 \times n(H_2O) = 2 \times 0.2533 = 0.5065\ \text{mol}$

$m(H) = n \times M = 0.5065 \times 1.008 = 0.5106\ \text{g}$ This gives the mass of hydrogen in the 7.882 g sample.

As the 7.882 g sample contains C, H and O only then:

$m(O) = 7.882 - [m(C) + m(H)] = 7.882 - (3.318 + 0.5106) = 4.053\ \text{g}$

C	**H**	**O**	
3.318g	0.5106 g	4.053 g	Mass of each element in the 7.882 g sample.
$\dfrac{3.318}{12.01}$	$\dfrac{0.5106}{1.008}$	$\dfrac{4.053}{16.00}$	Find the moles of each element, ie divide the mass of each element by its molar mass.
0.2763	0.5065	0.2533	Divide all by the smallest molar value, ie 0.2533.
1.091	2.00	1.000	Multiplying by 11 produces a whole number ratio. (See border note p142.)
12.00	22.00	11.00	

∴ the **empirical formula** is $\mathbf{C_{12}H_{22}O_{11}}$

b $PV = nRT$ *ie* $n = \dfrac{PV}{RT} = \dfrac{101.9 \times 0.3242}{8.3145 \times 438.15} = 9.068 \times 10^{-3}\ \text{mol}$

Use the correct value for R (8.3145), use temperature in kelvin, volume in litres and pressure in kPa.

also $M = \dfrac{m}{n} = \dfrac{3.115}{9.068 \times 10^{-3}} = 343.5\ \text{g mol}^{-}$

and $\mathbf{M_{ef}}(C_{12}H_{22}O_{11}) = 12 \times 12.01 + 22 \times 1.008 + 11 \times 16.00 = 342.30\ \text{g mol}^{-}$

ratio $(M/M_{ef}) = \dfrac{M}{M_{ef}} = \dfrac{343.5}{342.30} = 1.003$ ie The molecular formula is the same as the empirical formula.

∴ the **molecular formula** is $\mathbf{C_{12}H_{22}O_{11}}$

13.a. $n(CO_2) = \dfrac{m}{M} = \dfrac{3.219}{44.01} = 0.07314\ \text{mol}$

also $n(C) = n(CO_2) = 0.07314\ \text{mol}$ Since there is one mole of C in every mole of CO_2.

∴ $m(C) = n \times M = 0.07314 \times 12.01 = 0.8784\ \text{g}$

$n(H_2O) = \dfrac{m}{M} = \dfrac{1.537}{18.016} = 0.08531\ \text{mol}$

and $n(H) = 2 \times n(H_2O) = 2 \times 0.08531 = 0.1706\ \text{mol}$ As there are two moles of H in every mole of H_2O.

so $m(H) = n \times M = 0.1706 \times 1.008 = 0.1720\ \text{g}$

As the combustion of alanine released 300.3 mL (0.3003 L) of nitrogen at 102.1 kPa and 302.5 K then:

$$n(N_2) = \frac{PV}{RT} = \frac{102.1 \text{ x } 0.3003}{8.3145 \text{ x } 302.5} = 0.01219 \text{ mol}$$

$m(N) = m(N_2) = n\,M = 0.01219 \text{ x } 28.02 = 0.3416 \text{ g}$

$m(O) = 2.170 - [m(C) + m(H) + m(N)]$

$= 2.170 - (0.8784 + 0.1720 + 0.3416)$

$= 0.7780 \text{ g}$

As the sample has a mass of 2.170 g and contains the elements C, H, N and O only.

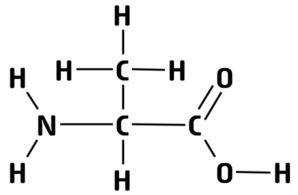
C	**H**	**N**	**O**	
0.8784 g	0.1720 g	0.3416 g	0.7780 g	
$\frac{0.8784}{12.01}$	$\frac{0.1720}{1.008}$	$\frac{0.3416}{14.01}$	$\frac{0.7780}{16.00}$	Find the moles of each element, ie divide the mass of each element by its molar mass.
0.07314	0.1706	0.02438	0.04862	Divide all by the smallest molar value, ie 0.02438.
3.000	6.998	1.000	1.994	

∴ the **empirical formula** is **$C_3H_7NO_2$**

b. $M_{ef}(C_3H_7NO_2) = 3 \text{ x } 12.01 + 7 \text{ x } 1.008 + 14.01 + 2 \text{ x } 16.00 = 89.10 \text{ g mol}^{-}$

$$\text{ratio } (M/M_{ef}) = \frac{M}{M_{ef}} = \frac{88.7}{89.10} = 0.996$$

∴ the **molecular formula** is **$C_3H_7NO_2$** and the **structural formula** is:



14.a. $n(CO_2) = \frac{m}{M} = \frac{10.60}{44.01} = 0.2409 \text{ mol}$

and $n(C) = n(CO_2) = 0.2409 \text{ mol}$ Since there is one mole of C in every mole of CO_2.

so $m(C) = n \text{ x } M = 0.2409 \text{ x } 12.01 = 2.893 \text{ g}$

$n(H_2O) = \frac{m}{M} = \frac{2.136}{18.016} = 0.1186 \text{ mol}$

Also as there are two moles of H in every mole of H_2O then: $n(H) = 2 \text{ x } n(H_2O) = 2 \text{ x } 0.1186 = 0.2371 \text{ mol}$

$m(H) = n \text{ x } M = 0.2371 \text{ x } 1.008 = 0.2390 \text{ g}$

Also as the sample contains C, H and O only then:

$m(O) = 10.79 - [m(C) + m(H)] = 10.79 - (2.893 + 0.2390) = 7.658 \text{ g}$

C	**H**	**O**	
2.893 g	0.2390 g	7.658 g	
$\frac{2.893}{12.01}$	$\frac{0.2390}{1.008}$	$\frac{7.658}{16.00}$	Find the moles of each element, ie divide the mass of each element by its molar mass.
0.2409	0.2371	0.4786	Divide all by the smallest molar value, ie 0.2371.
1.016	1.000	2.019	

∴ the **empirical formula** is **CHO_2**

b. $n(NaOH) = c\,V = 0.2021 \text{ x } 16.25 \text{ x } 10^{-3} = 3.284 \text{ x } 10^{-3} \text{ mol}$

The compound contains two carboxylic acid groups per molecule ∴ it is a diprotic acid thus its formula can be represented as H_2X and the reaction with NaOH as: $2NaOH + H_2X \rightarrow Na_2X + 2H_2O$

hence $n(\text{acid in 20 mL}) = \frac{1}{2} \text{ x } n(NaOH) = \frac{1 \text{ x } 3.284 \text{ x } 10^{-3}}{2} = 1.642 \text{ x } 10^{-3} \text{ mol}$

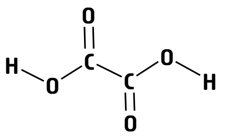
and $n(\text{acid in 250 mL}) = \frac{250}{20} \text{ x } 1.642 \text{ x } 10^{-3} = 2.053 \text{ x } 10^{-2} \text{ mol}$

ie $M(\text{acid}) = \frac{m}{n} = \frac{1.851}{2.053 \text{ x } 10^{-2}} = 90.18 \text{ g mol}^{-}$ *also* $M_{ef}(CHO_2) = 12.01 + 1.008 + 2 \text{ x } 16.00 = 45.02 \text{ g mol}^{-}$

$$\text{ratio } (M/M_{ef}) = \frac{M}{M_{ef}} = \frac{90.18}{45.02} = 2.003$$

∴ the **molecular formula** is **$C_2H_2O_4$**

c. The **structural formula** is:



15.a. $n(CaCO_3) = \frac{m}{M} = \frac{31.34}{100.09} = 0.3131$ mol

As there is one mole of carbon in each mole of $CaCO_3$ then: $n(C) = n(CaCO_3) = 0.3131$ mol

also $m(C) = n \times M = 0.3131 \times 12.01 = 3.761$ g

As the sample contains C and H only then: $m(H) = 4.406 - m(C) = 4.406 - 3.761 = 0.6455$ g

C	**H**	
3.761 g	0.6455	
$\frac{3.761}{12.01}$	$\frac{0.6455}{1.008}$	
0.3131	0.6403	Divide all by the smallest molar value, ie 0.3131.
1.000	2.045	

∴ the **empirical formula** is **CH_2**

b. $n = \frac{PV}{RT} = \frac{129.5 \times 1.754}{8.3145 \times 349.15} = 0.07824$ mol *and* $M(\text{molecular}) = \frac{m}{n} = \frac{4.485}{0.7824} = 57.32$ g mol^{-}

$\mathbf{M_{ef}}(CH_2) = 12.01 + 2 \times 1.008$
$= 14.03$ g mol^{-}

ratio $(M/M_{ef}) = \frac{M}{M_{ef}} = \frac{57.32}{14.03} = 4.086$

∴the **molecular formula** is **C_4H_8**

c. The fast reaction with bromine suggests the presence of a double bond. Four possible IUPAC names are: **but-1-ene, *cis*-but-2-ene**, ***trans*-but-2-ene** and **methylpropene**.

16. This analysis involves two separate samples, a 7.335 g sample and a 4.719 g sample. In situations like this it is convenient to determine the percentage composition of the individual elements within each sample. The percentage composition of the compound can then be used to find the empirical formula.

$n(CO_2) = \frac{m}{M} = \frac{15.36}{44.01} = 0.3490$ mol

As there is one mole of C in every mole of CO_2 then: $n(C) = n(CO_2) = 0.3490$ mol

and $m(C) = n \times M = 0.3490 \times 12.01 = 4.192$ g

also $\%(C) = \frac{m(C)}{m(\text{aspartame})} \times 100 = \frac{4.192 \times 100}{7.335} = 57.15\ \%C$

$n(H_2O) = \frac{m}{M} = \frac{4.041}{18.016} = 0.2243$ mol

Also as there are two moles of H in every mole of H_2O then: $n(H) = 2 \times n(H_2O) = 2 \times 0.2243 = 0.4486$ mol

and $m(H) = n \times M = 0.4486 \times 1.008 = 0.4522$ g

also $\%(H) = \frac{m(H)}{m(\text{aspartame})} \times 100 = \frac{0.4552 \times 100}{7.335} = 6.165\ \%H$

Use titration data to find the amount of NH_3 and thus % N present in the 4.719 g aspartame sample.

$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$

$n(NaOH) = c\,V = 0.1249 \times 28.18 \times 10^{-3} = 3.520 \times 10^{-3}$ mol
and $n(\text{HCl remaining in 100 mL}) = n(NaOH) = 3.520 \times 10^{-3}$ mol

$n(\text{HCl originally in the 100 mL solution}) = c\,V = 0.3559 \times 0.1000 = 3.559 \times 10^{-2}$ mol HCl

$n(NH_3 \text{ reacting with HCl}) = n(\text{HCl originally present in 100 mL}) - n(\text{HCl remaining in 100 mL})$
$= 3.559 \times 10^{-2} - 3.520 \times 10^{-3} = 3.207 \times 10^{-2}$ mol NH_3

$n(N) = n(NH_3) = 3.207 \times 10^{-2}$ mol *and* $m(N) = n\,M = 3.207 \times 10^{-2} \times 14.01 = 0.4493$ g

$\%(N) = \frac{m(N)}{m(\text{aspartame})} \times 100 = \frac{0.4493 \times 100}{4.719} = 9.521\ \%N$ Note the second sample size is 4.719 g

Determine the %O in the compound by subtraction.

$\%(O) = 100.0 - [\%C + \%H + \%N] = 100.0 - (57.15 + 6.165 + 9.521) = 27.17\ \%\ O$

Determine the empirical formula from the percentage composition of the compound.

C	**H**	**O**	**N**	
57.15 %	6.165 %	27.17 %	9.521 %	The % by mass of each element in aspartame.
57.15 g	6.165 g	27.17 g	9.521 g	The mass of each element in 100.0 g of aspartame.
$\frac{57.15}{12.01}$	$\frac{6.165}{1.008}$	$\frac{27.17}{16.00}$	$\frac{9.521}{14.01}$	Find the moles of each element, ie divide the mass of each element by its molar mass.
4.758	6.116	1.698	0.6796	Divide all by the smallest molar value, ie 0.6796.
7.001	8.999	2.499	1.000	Multiply all values by 2 for a whole number ratio.
14.00	18.00	4.997	2.000	

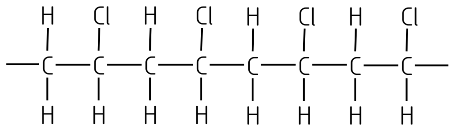
∴ the **empirical formula** is $C_{14}H_{18}N_2O_5$

Set 20 Polymers, proteins and polypeptides

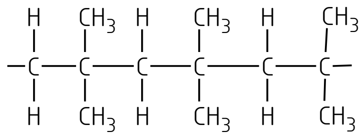
1. **a.** molar mass
b. polymers
c. proteins
d. biological
e. monomers
f. moulded
g. fibres
h. fabric
i. thermoplastics
j. thermosetting
k. straight
l. side chains
m. elastic

2. **a.** The letter n represents a very large and variable whole number. Typically of the order of several thousand. It shows the formula of the polymer is not fixed but variable and shows the polymer molecule must be very large.

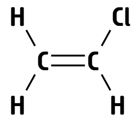
b.



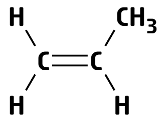
c.



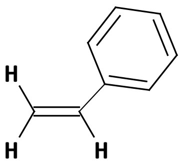
3. **a.** **i**



ii.

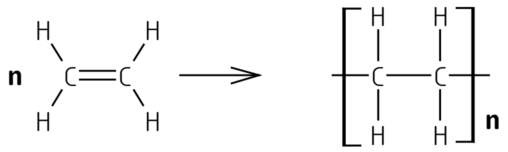


iii.

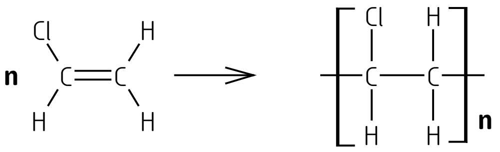


b. During addition polymerisation the double bond of the monomer opens. This allows both carbon atoms of the double bond to form a new covalent bond. In this way monomer molecules to join end to end forming a polymer structure.

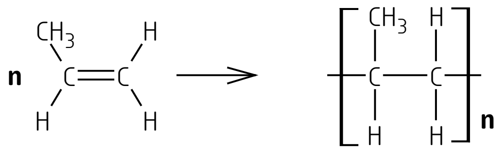
4. **a.**



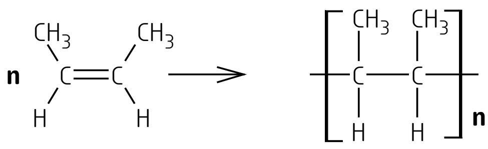
d.



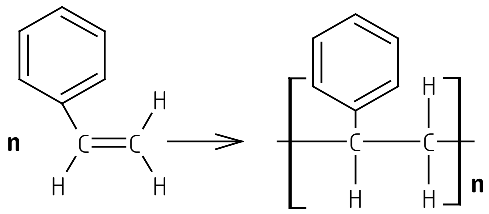
b.



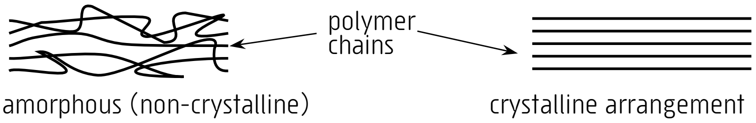
e.



c.



5. a. Crystallinity in a polymer describes the extent to which individual polymer chains are regularly aligned in the solid. The greater the degree of regular alignment the more crystalline the polymer. Disordered and tangled chains describe an amorphous polymer.



b. The molecules of LDPE have long chains with multiple short side chains. The side chains typically consisting of around one to four carbon atoms each. The polymer chains of HDPE have very few or no side chains. As a consequence LDPE molecules pack less efficiently than HDPE molecules and so LDPE has a more amorphous and less crystalline structure than HDPE. For this reason LDPE molecules interact less efficiently by dispersion forces than HDPE molecules. This causes the melting point of LDPE to be lower than for HDPE. Also, as a result of the less efficient packing of molecular chains in LDPE it has a lower density than HDPE. Furthermore, the weaker intermolecular forces in LDPE mean it is softer and more flexible than HDPE.

c. LDPE has a low melting point (105 °C-115 °C), is soft, very flexible and insulating. Used for packaging film, tubing, bottles, electrical cable insulation and toys.

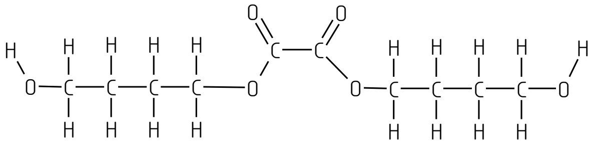
HDPE has a higher melting point (120 °C-135 °C), is tougher and more rigid. Used for water pipes, toys, buckets and crates.

UHMWPE is the strongest and toughest of the polyethenes. It is used as a bearing material in hip and knee replacement joints. UHMWPE fibres are used to make fabric for bullet proof vest panels.

6. Polytetrafluoroethene (PTFE or Teflon®) is chemically very stable, non-stick, low friction, water and oil repellent, has a high melting point (for a polymer) and a high electrical resistance. Uses include: Inert non-stick coatings on cooking equipment, coatings on bearings and low friction surfaces, cable insulation and for internal reactor coatings where corrosive conditions would damage other materials.

7. a. The missing product is water, H_2O.

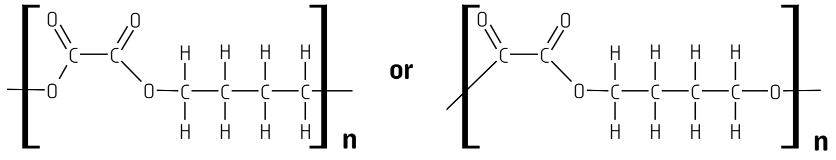
b.



c. The ester group links the monomer units.

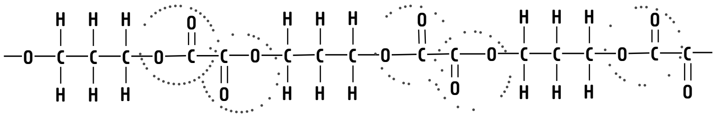
d. n units of butane-1,4-diol are required and 2n units of water would be formed

e.



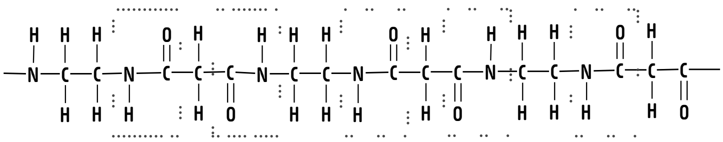
8. a. Monomer units join end to end by eliminating a small molecule like water (H_2O).

b. i



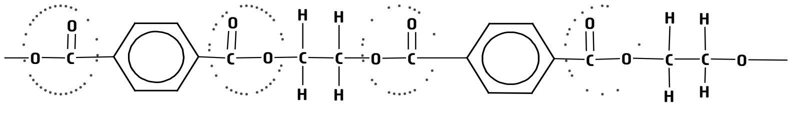
Polyester section showing various ester linkages (circled).

ii



Polyamide section showing amide linkages (boxed).

iii



Polyester section showing ester linkages (circled).

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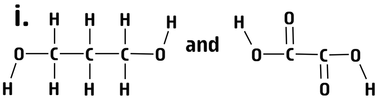
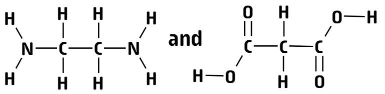
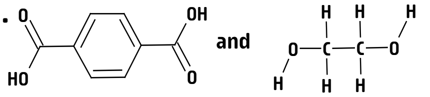
c. i.



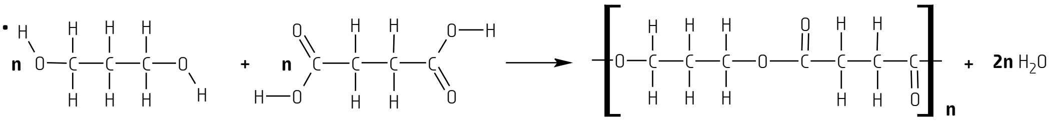
ii.



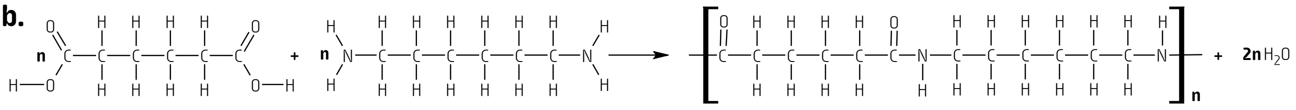
iii.



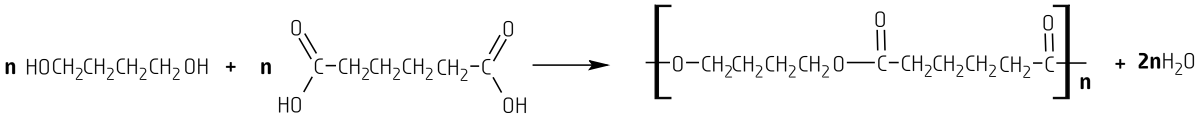
9. a.



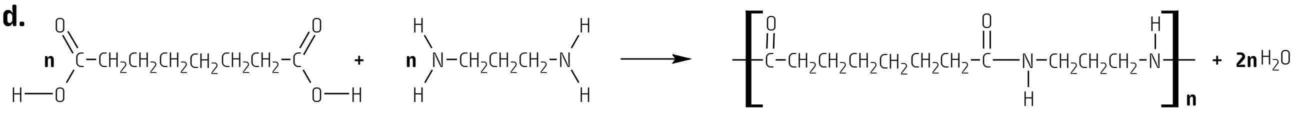
b.



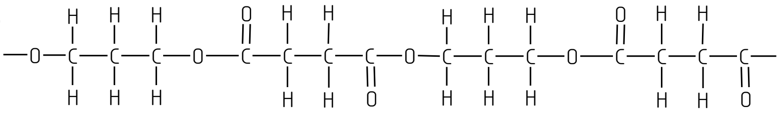
c.



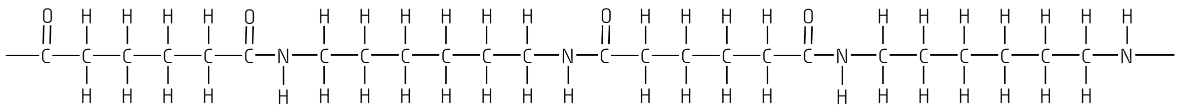
d.



10. a.

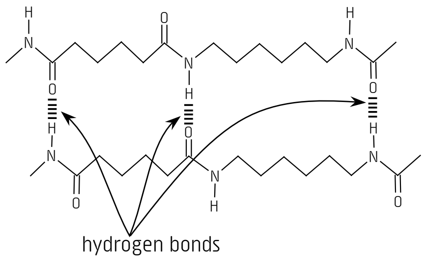


b.



11. The molecular structure of nylon 6,6 is such that its polymer chains contain amide groups –CONH- at regular intervals along the chain. The simplified diagram at right shows how hydrogen bonds will occur between the H atom of an – NH group and a lone pair of electrons on an O atom from an adjacent molecule.

The process of cold drawing nylon fibres enhances the formation of hydrogen bonds within the fibres. As the fibres are stretched the polyamide molecules untangle and become aligned. Due to the attractive forces of hydrogen bonding they will naturally align in such a way that maximises the amount of hydrogen bonding between adjacent polymer chains.



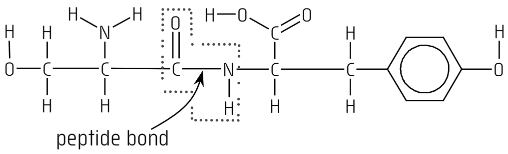
In this simplified wire diagram it is understood a carbon atom is located at each junction. Hydrogen atoms occupy any free spaces.

12. The polyester, polyethylene terephthalate (PET) is particularly stiff and strong, though the extent of these properties does depend upon the degree of crystallinity produced during manufacture. It is impervious to gases and does not absorb water. For this reason it is an ideal polymer for manufacturing food grade jars and bottles for soft drink, water, juices, oils and so on. It is also used for producing a very strong film, called Mylar. A major use is for fibre production that is used on its own (called Dacron® or Terylene®) or blended with other fibres for making into fabric for clothing, soft furnishings, reinforcing fibres in tyres and for carpet making.

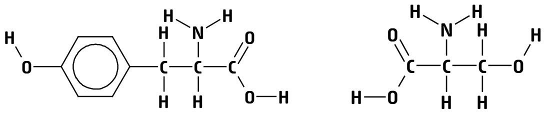
The polymer nylon is one of many polyamides. These polymers have high strength, good wear and abrasion resistance, durability, low coefficient of friction and good chemical resistance. Nylon is used to produce fibres which are particularly strong with good durability and wear resistance. These are used to make fabric for clothing and underwear, stockings, fishing line, rope, carpet, reinforcing fibres in tyres and fabric for parachute, seat belt and tent manufacture. Nylon can also be moulded into solid products including; hoses, zip fasteners, skate wheels, gears, cams and bearings.

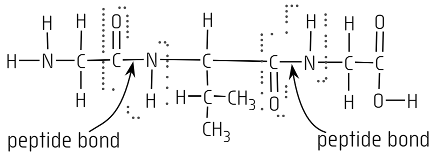
13. Amino acids contain both the amino functional group (— NH_2) and the carboxylic acid functional group (— COOH). In α-amino acids the amino group is attached to the carbon atom next to the — COOH functional group (carbon number 2). α-amino acids molecules are able to link together to form large chains known as polypeptides. They do this in a form of condensation polymerisation reaction where one H_2O molecule is eliminated for every linkage formed. When the number of α-amino acid molecules in a peptide chain is large (usually greater than 50, though there is no specific number) then it is known as a protein. Proteins are essential chemical substances found in living systems. Their function may be structural such as in collagen and keratin for skin and hair or they may act as enzymes, be involved in transport of chemical substances, movement or as hormones that control various biological processes.

14. a.

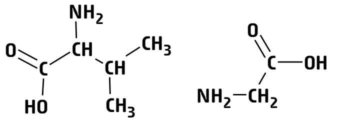


b. The two amino acids forming the dipeptide.


(tyrosine) (serine)



b. The amino acids forming the tripeptide.

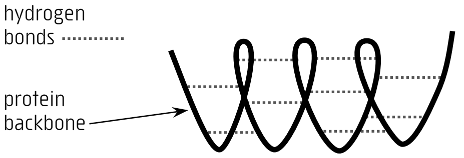

(one valine molecule) (two glycine molecules)

c. Amino acid molecules join together by the elimination of one H_2O molecule for every linkage formed. This is similar to condensation polymerisation.

15. When two α-amino acid molecules join they do so by a condensation reaction. In the process one α-amino acid molecule loses an H atom from the $-NH_2$ functional group while the other molecule loses an –OH group from its carboxylic acid functional group, -COOH. This produces a water molecule and allows the remainder of each amino acid molecule, called a residue (ie what is left after the H and OH have been lost to form water) to join together. Thus it is a series of residues, not entire α-amino acid molecules, that remain in the polypeptide or protein chain.

16. The specific sequence of individual α-amino acid residues that forms a protein or polypeptide is its primary structure. The sequence is always listed from the N-terminus end of the protein, ie the end with the NH_2 functional group. The primary structure of the dipeptide and tripeptide from question 14 are respectively: **ser-tyr** and **gly-val-gly**.

17. The α-helix is a coiled section of protein chain. Only the protein backbone is involved in forming the α-helix. The α-helix shape is maintained by hydrogen bonds between a lone pair of electrons on a carbonyl group (C=O) and the polar hydrogen of an amide group (N-H) that is situated four amino acid residues further along the main protein backbone.



18. Both the β-pleated sheet and the α-helix are examples of protein secondary structure. These structures are held in place by hydrogen bonding directly from the main protein backbone (not hydrogen bonds from the side chains). A β-pleated sheet occurs where two or more sections of a protein chain align side by side instead of the spiral arrangement that occurs in an α-helix. β-pleated sheets may form if a protein chain folds back along itself or if two or more separate protein chains align alongside one another. In either case the protein chains are held in the β-pleated sheet formation by hydrogen bonds. The overall effect is to produce a corrugated sheet structure called a β-pleated sheet.

19. A protein's tertiary structure is its overall 3D shape. It's the shape that forms as a result of the main chain folding and bonding back on itself. The tertiary structure involves the entire protein molecule and is a unique, though, irregular arrangement, not like the regular arrangement in the β-pleated sheet or α-helix. Tertiary structure is created and held in place by various bonds that form between some of the residue side chains (R). These bonds include disulfide bridges, hydrogen bonding, dipole-dipole forces, dispersion forces and ionic bonds.

The overall 3D shape or conformation of a protein is vital to its function. It is the protein conformation (and its primary structure) that determines how it will interact with other molecules and hence determines its function.

20. a. Bond type and associated structure: ② is an ionic bond creating tertiary structure, ③ is a disulfide bridge contributing to the tertiary structure, ⑤ shows several hydrogen bonds responsible for creating secondary structures, ie an α-helix and a β-pleated sheet, ⑧ represents dispersion forces that contribute to the tertiary structure, ⑨ represents covalent bonds within the main protein chain or backbone, these contribute to the primary structure.

b. This is the terminal $-NH_2$ group of the first α-amino acid in the chain. This NH_2 group is not joined to another α-amino acid. The group is shown in zwitterion form, ie as a $-NH_3^+$.

c. Position ④ represents the end of the main protein chain. There should be a free carboxylic acid group, –COOH here. As the other end of the chain is shown in zwitterion form then so should the carboxylic acid be shown as a negatively charged carboxylate ion, ie $-COO^-$.

d. The shaded areas ⑥ and ⑦represent secondary structures within the protein. ⑥ is a β-pleated sheet while ⑦ shows an α-helix.

e. Hydrogen bonds can contribute to tertiary structure but are not shown in this diagram in this context.

21. a. As outlined in the background to the question, sugar undergoes an **acid catalysed** hydrolysis reaction. The lemon juice provides the acid required to catalyse the reaction thus increasing its reaction rate. Heating the mixture further increases the sugar hydrolysis reaction rate.

b. Invertase is a protein. Also as it is an enzyme (biological catalyst) for this reaction it increases the reaction rate by lowering activation energy.

c. **i** The low yield at 8 °C is most probably due to the low average collision energy of particles involved in the reaction. Thus few collisions have an energy greater than or equal to the activation energy for the reaction. (Only collisions with an energy $\geq E_{act}$ can proceed to form products, this applies to all reactions, even catalysed ones.) As a result the reaction rate is slow and the yield after 12 minutes is low.

ii The low yield at 90 °C is for a different reason. Collision energy will be high but the enzyme has possibly been deactivated by the higher temperature. Typically enzymes are denatured by high temperature. For example, the enzyme's overall three dimensional structure, its conformational shape, may change due to breaking of bonds that determine its secondary or tertiary structure. As an enzyme's shape affects its function, then at the higher temperature the enzyme may no longer be able to catalyse the hydrolysis reaction. As a result the reaction rate is now slow and the yield after 12 minutes is low.

d. The optimum pH range is the pH where a given enzyme is most effective in catalysing a given reaction. This pH range varies for different enzymes. Also as an enzyme's overall three dimensional structure (conformation) is affected by pH then a changing pH will affect its ability to function as a catalyst. pH values outside the optimum range mean a greater percentage of the enzyme will have an altered shape and thus be unable to catalyse the hydrolysis reaction.

Set 21 Industrial synthesis

1. **a.** synthesised
b. chemical reaction
c. sequence
d. several
e. rate
f. equilibrium
g. reaction rate
h. yield
i. cost
j. compromise
k. green
l. toxic
m. renewable
n. energy
o. natural
p. atom
q. twelve

2. ethanol synthesis by **fermentation**

$$\% \text{ atom economy} = \frac{m[CH_2CH_2OH] \times 100}{m[C_6H_{12}O_6]]} = \frac{2 \times 46.068 \times 100}{180.156} = 51.142\%$$

ethanol synthesis by **addition**

$$\% \text{ atom economy} = \frac{m[CH_2CH_2OH] \times 100}{m[CH_2CH_2] + m[H_2O]} = \frac{46.068 \times 100}{28.052 + 18.016} = 100.00\%$$

Although fermentation is regarded as a greener approach to the production of ethanol (for other reasons) its atom economy is a low 51.14%. This is due to the formation of the waste product $CO_2(g)$. The synthesis of ethanol by the addition of water to ethene has a 100% atom economy. All of the reagent mass is incorporated into the desired product, ethanol.

3. Catalysts increase reaction rate without being depleted by the reaction. The faster rate means products are formed quicker thus reducing cost. Less energy is needed with a catalyst present as the reactions proceed with a lower activation energy so lower temperatures can be used to achieve a satisfactory rate.

Enzymes are complex protein structures that occur naturally in living systems. Here they catalyse various metabolic processes needed to carry out life functions. Enzymes can be particularly advantageous as industrial catalysts. When suitable enzymes can be found or engineered they tend to be very specific in the reactions they catalyse. In this way unwanted side reactions are minimised and hence there is less waste of reagent. This also simplifies the process of separation of the desired product from the final reaction mixture as there are fewer or no undesirable products present. Enzymes are also less likely to be toxic when compared with the typical transition metal compounds or strong acids that are often used to catalyse industrial synthesis reactions.

4. A biofuel is one derived from biomass such as agricultural crops or animal products. Two examples of biofuels are biodiesel; which is manufactured from various animal fats or plant oils; and bioethanol which is typically manufactured from crops that either contain sugar or can be processed to produce sugar. These are said to be renewable fuels as the crops from which they originate can be regrown and thus replenished and so the supply of fuel is not constrained by a limited resource.

These fuels do produce carbon dioxide when they are burnt and in the case of ethanol carbon dioxide is also formed during its production by fermentation. However the amount of carbon dioxide released by the combustion (and fermentation) of a biofuel is balanced by the amount of carbon dioxide removed from the atmosphere by plants through photosynthesis during the production of the original biomass. In this way it can be argued that the combustion of a biofuel does not contribute to raising the concentration of atmospheric CO_2. It **must be noted** however, that the production of biofuels may involve the use of fossil fuels in crop production, fuel manufacture or transportation. CO_2 produced this way does contribute to elevated atmospheric CO_2 levels.

5. a. Hydrolysis: $C_{12}H_{22}O_{11}(aq) + H_2O(l) \rightarrow 2C_6H_{12}O_6(aq)$

Fermentation: $C_6H_{12}O_6(aq) \rightarrow 2C_2H_5OH(aq) + 2CO_2(g)$

b. Catalysts in the form of enzymes (invertase and zymase) are used to increase the rate of these reactions.

c. High temperatures typically cannot be used when enzymes are involved. Most enzymes operate best at moderate temperatures and they do not tolerate high temperatures. When heated to higher temperatures enzymes will become chemically altered, ie they become denatured. Once altered like this the enzymes are rendered inactive so no longer catalyse the reaction they were intended to speed up.

d. Aerobic respiration of sugars results in the formation of water and carbon dioxide:

$C_6H_{12}O_6(aq) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$.

This is an undesirable reaction as it leads to the release of all of the available energy present in the sugar (ie the complete oxidation of sugar to CO_2 and H_2O) and the loss of the potential biofuel ethanol. Aerobic respiration is prevented by excluding air, ie using a sealed container, for the fermentation reaction.

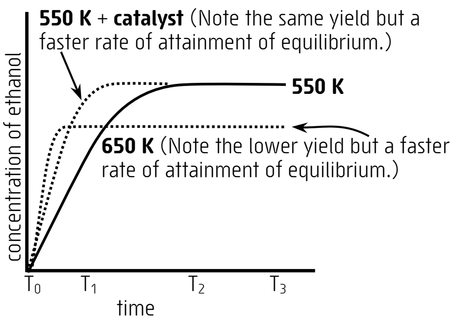
e. Yeast, which contain the enzymes needed to speed up the fermentation process, are poisoned by alcohol. Once the alcohol concentration in the fermentation mixture reaches 14% the yeast will die and thus the fermentation ceases. Hence fermentation alone can not produce an alcohol concentration above 14%.

6. These crops contain either sugar or starch and can be processed to produce ethanol by fermentation. Ideally the crops are available locally as biomass transportation would increase production costs and energy loss. Preferably the chosen biomass should be able to be produced cheaply (this is dependant upon local conditions) or be a waste product of a local industry. Hence the choice of biomass depends on the region.

7. a. The forward reaction is proceeding at a fast rate and as yet the reverse reaction rate is insignificant. Hence the concentration of ethanol rises rapidly.

b. Between T_2 and T_3 there is no net change in the concentration of ethanol. This can happen in a reversible reaction like this one if the reaction occurs in a closed system and the reaction has reached equilibrium. At this point the rate of the forward and reverse reactions is equal. Hence over time the concentration of $CH_3CH_2OH(g)$ remains constant.

c.



8. a. Both the forward and reverse reactions involve collisions between particles in the gas phase. Increasing the total pressure on the system (by compressing it) increases the concentration of all particles in the gaseous phase. The increased particle concentration results in an increased rate of collision involving the reacting particles in both the forward and reverse reaction. Hence both the forward and reverse reaction rates increase. (Actually, the forward reaction rate increases by a greater factor as it involves more moles of gas than the reverse reaction.) The increased rates of reaction mean the system reaches equilibrium faster.

b. Notice water is present in the equilibrium constant expression. This is a consequence of it being in the gaseous phase and hence having a **variable** concentration. In aqueous solutions liquid water essentially has a **fixed** concentration and so is excluded from the equilibrium constant expression.

$$K_c = \frac{[CH_3CH_2OH]}{[CH_2CH_2][H_2O]}$$

c. If the pressure on the system is increased (by reducing volume) then the concentration of all the gaseous substances (reactants and products) will increase by the same factor, eg all doubled, tripled etc. This will cause the denominator in Q_c to increase by a greater factor than the numerator (as both $[CH_2CH_2]$ and $[H_2O]$ have increased). Thus increasing the pressure reduces the value of the reaction quotient, Q_c. For the system to return to equilibrium, ie where $Q_c = K_c$, then the concentration of $[CH_3CH_2OH]$ must increase while the concentration of both $[CH_2CH_2]$ and $[H_2O]$ must decrease. Thus the yield must increase at a higher pressure.

d. The addition of water to ethene to produce ethanol is an exothermic process and as such high ethanol yield is favoured by low temperature. However as with all reactions the speed of this reaction reduces with a lower temperature. The moderate temperature used is 300 °C as this promotes a reasonable reaction rate while still maintaining a satisfactory yield. (Although the yield is only around 5% it is still possible to achieve around 95% yield by recycling any unreacted gases.)

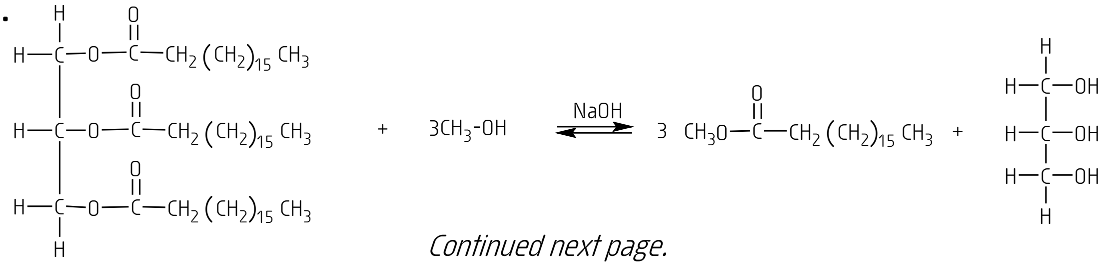
e. In the reaction chamber, the speed of reaction is further increased by passing the reacting gases over a catalyst bed consisting of $H_3PO_4(l)$ (the catalyst) coated onto solid silica particles.

9.

	Ethanol by **fermentation**	Ethanol by **addition**
Energy use	Is conducted at room pressure and ambient temperature (≈37 °C) so less energy is needed to heat reagents or create high pressures.	Considerable energy is needed to heat reagents (≈300 °C) and raise pressure (60-70 atm) in order to achieve a satisfactory reaction rate and yield.
Renewable feedstock	Uses renewable biomass and biomass waste products.	Uses ethene which is a non renewable fossil fuel based product.
Production or use of toxic substances	Neither sugar nor yeast are toxic reagents. While the product CO_2 occurs naturally in the environment. High concentrations of CO_2 are asphyxiating in confined spaces.	Ethene is a highly flammable hazardous gas. It is an asphyxiant (due to oxygen exclusion). The acid catalyst, pure phosphoric acid, is a corrosive and hazardous substance.
Inherent safety due to production method.	Fermentation occurs in enclosed vats at ambient temperature and pressure and may be considered to pose few safety risks.	Involves the use of high temperatures and pressures as well as the flammable gas ethene and the corrosive acid catalyst H_3PO_4. These reagents and conditions pose inherent safety risks.
Atom economy	Fermentation has a low atom economy as a considerable amount of the reactant mass ends up as a waste, ie CO_2.	Has a 100% atom economy as all of the reactant atoms are incorporated into ethanol, ie there is no other product.

10. **a.** 3 **b.** 5 **c.** 3 **d.** 1 **e.** 4 **f.** 5 **g.** 6 **h.** 2

11. a.



Continued next page.

a. *Continued.* The transesterification reaction (previous page) is carried out in a sealed reaction vessel at a moderate temperature of around 60 °C using a strong base catalyst like NaOH or KOH (other bases can also be used). The alcohol is present in a large excess, eg at around twice the required stoichiometric ratio.

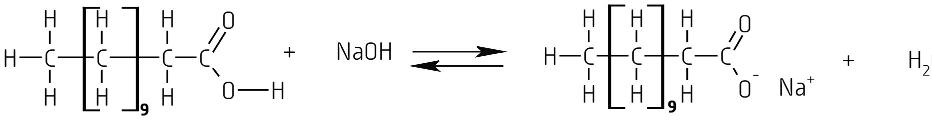
b. The transesterification reaction is an equilibrium process. Using a high concentration of ethanol (or methanol) in the reaction mixture favours the conversion of the triglyceride into the products, biodiesel and glycerol. Excess methanol can be separated from the final reaction mixture and recycled.

c. The reaction products, biodiesel and glycerol, are essentially insoluble in one another hence once the reaction is complete they form two separate layers. Biodiesel is separated from the top layer while the denser glycerol forms a bottom layer. Most of the excess methanol (or other alcohol), the base catalyst and any soap that may have formed remain in the glycerol layer with smaller amounts in the biodiesel. Biodiesel is then washed with warm water to remove any residual methanol, catalyst, glycerol or soap it may contain. The impurities are very soluble in water while water is insoluble in diesel. The water along with the various impurities will settle as a bottom layer and pure diesel is removed from the top layer. The diesel may need further treatment to completely dry it.

d. Once refined of its impurities (ie catalyst, soap and excess alcohol) glycerol becomes a valuable co-product of the transesterification process.

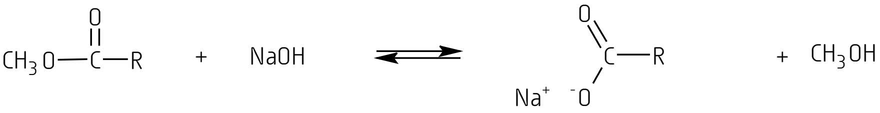
12. a. If the fats or oils contain FFAs then upon addition of the catalyst, eg NaOH, soap is formed. Soap formation is undesirable as it causes glycerol and biodiesel to form an emulsion. Emulsion formation greatly complicates the purification of biodiesel as well as its initial separation from glycerol. This unwanted side reaction also reduces yield by wasting a reactant.

b.



This equation shows how the FFA, lauric acid is converted into soap upon the addition of sodium hydroxide (in the presence of water). (See also 12(a).)

c.



(Note: This reaction does depend upon some water being present in the reaction mixture as NaOH must be in a dissolved, ie aqueous form.)

13. Lipases are naturally occurring enzymes found in the cellular material of almost all living things. In biodiesel production they catalyse the transesterification of fats and oils into biodiesel. Their use offers several potential advantages in terms of green principles of chemical synthesis compared to traditional base catalysts. These include:

- They operate at milder temperatures and milder pH (ie no potentially hazardous strong bases are required)
- They tolerate feedstock high in FFAs thus there is no need for pre-treatment of FFAs.
- Lipase can simultaneously catalyse the transesterification of TGs into biodiesel as well as the esterification of FFAs into biodiesel. This simplifies the use of oils naturally high in FFAs.
- Do not cause side reactions, such as soap formation, that waste reagents and complicate diesel separation.
- Simplifies product purification and reduces the environmental problem of basic waste water disposal.
- Involves significantly less energy as lower temperatures are involved and the products (biodiesel and glycerol) need less or no refining.

14. While the rate of formation of ammonia in the Haber process increases with increasing temperature, the equilibrium yield of ammonia decreases with increasing temperature. A compromise temperature of 350-550 °C is used as this promotes a reasonable rate without seriously compromising yield. The rate of this reaction also increases with increasing pressure as does the equilibrium yield. For this reason a high pressure of 15-35 MPa is used in the process. *Continued next page.*

Although even higher pressure would further improve both rate and yield, the cost of maintaining extremely high pressures would make the process uneconomic. A catalyst of iron-iron oxide fused with MgO, Al_2O_3 and SiO_2 is used to further increase the rate of the process. It has no effect on yield. Finally the overall yield of the process is further improved by extracting ammonia from the reaction mixture and recycling the un-reacted $N_2(g)$ and $H_2(g)$.

15. a. (i) ammonia yield at equilibrium is 84% (ii) ammonia yield at equilibrium is 21%

b. Explanation in terms of K_c: K_c is constant for all conditions except for temperature. For exothermic reactions, as in the Haber process, K_c decreases with increasing temperature. Thus at the higher temperature (600 °C) the equilibrium constant, K_c for the Haber process has a lower value. The lower K_c means reactants are favoured (more than at 300°C), ie the reactant concentrations increase while those of the products decrease. Thus at 600 °C there is a lower equilibrium yield of products.

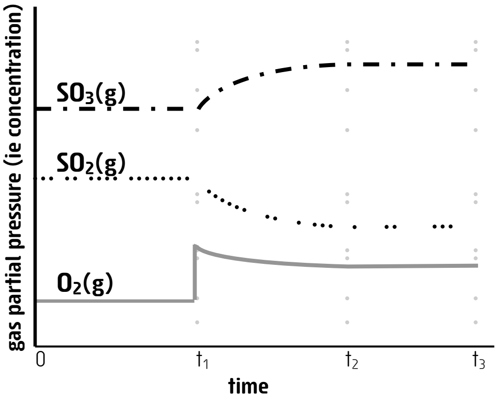
Explanation in terms of forward and reverse reaction rates: At the higher temperature (600 °C) both the forward and reverse reactions are proceeding at a faster rate. However the rate increase is greater for the **endothermic** reaction (ie the reverse reaction, the formation of reactants) than for the **exothermic** reaction (ie forward reaction, formation of products). Consequently for equilibrium to be achieved at 600 °C, ie the rate of the forward reaction equals the rate of the reverse reaction, the concentration of the products must be lower than at it would be at 300 °C.

c. At these conditions the equilibrium yield of ammonia is 24%. The overall yield of the process can be increased to around 100% by extracting ammonia from the equilibrium reaction mixture and recycling any un-reacted $N_2(g)$ and $H_2(g)$ back into the reaction chamber.

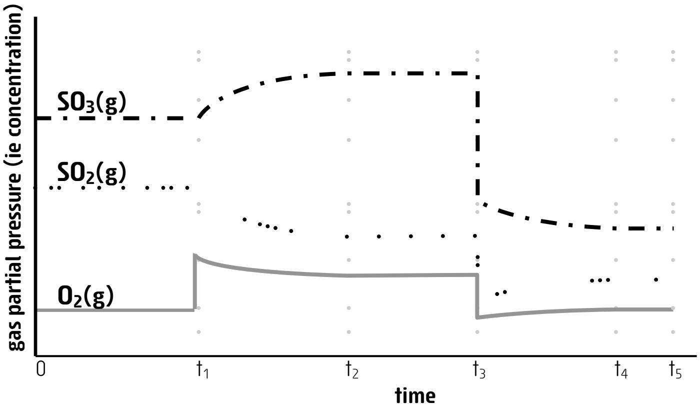
16. Sulfur combustion readily goes to completion: .... $2S(l) + 2O_2(g) \rightarrow 2SO_2(g)$..................... ①
Conversion of sulfur dioxide to sulfur trioxide
② is an equilibrium process: .... $2SO_2(g) + O_2(g) \rightleftharpoons (g)$....................... ②
Producing oleum readily goes to completion: .... $2H_2SO_4(l) + 2SO_3(g) \rightarrow 2H_2S_2O_7(l)$........... ③
Formation of sulfuric acid readily goes to completion:.... $2H_2O(l) + 2H_2S_2O_7(l) \rightarrow 4H_2SO_4(l)$ .... ④
Overall: .... $\underline{2S(l) + 3O_2(g) + 2H_2O(l) \rightarrow 2H_2SO_4(l)}$..... ⑤

Note: When adding a pair of equations it is important to equalise the coefficients of the linking reagent in each pair of reactions. Thus in reactions ① and ② the coefficient of the linking reagent (SO_2) must be equalised before adding these. To do this all of the coefficients in equation ① have been multiplied by two so that the coefficient of the linking reagent **2**$SO_2(g)$ in reaction ① now matches its coefficient in reaction ②. In a similar way the coefficients in equation ③ have been multiplied by two so that the coefficient of the reagent **2**$SO_3(g)$ in reaction ③ now matches its coefficient in reaction ②. Similarly the coefficients in equation ④ have been doubled. Adding these four equations and simplifying the result (ie adding together common reagents and cancelling down reactants if they also appear as products) gives the overall equation for the Contact process.

17. a.



b.



c. A high equilibrium yield of $SO_3(g)$ is favoured by low temperature and high pressure. Low temperature is a problem as it reduces the rate of attainment of equilibrium and could make the process uneconomic. A high pressure would be especially useful as high pressure favours both a high rate of attainment of equilibrium and a high yield of $SO_3(g)$ so using a high pressure would help to make the process more economic. High pressure systems can be expensive to operate and maintain so this consideration would have a bearing on the actual pressure chosen.

d. In practice a temperature of around 450 °C is used. This is a compromise between using a very low temperature; which would give a high equilibrium yield but a low rate; and a very high temperature that would give an extremely low yield but a high rate.

A pressure in the range 1-2 atmospheres (ie ≈100-200 kPa) is usually used. This is an economic compromise as although higher pressures give a greater yield and a greater rate such high pressure systems are expensive to maintain. Satisfactory yield and rate can be achieved using a pressure slightly higher than normal atmospheric pressure (1-2 atmospheres). A high yield is obtained by extracting the product gas SO_3 from the reacting system and recycling the unreacted gases. Doing this several times gives an ultimate yield of SO_3 close to 100%.

A catalyst of V_2O_5 is also used. The reacting gases are cycled through beds of granular catalyst to further increase the rate of reaction. The catalyst has no effect on yield.

18. a. $\text{c(ethanol in g L}^{-1}) = \dfrac{\text{m(ethanol in g)}}{\text{V(solution in L)}}$ *thus* **m(ethanol)** = c x V = 38 x 0.375 = 14.25 = **14 g ethanol** (2SF)

b. $\mathbf{C_6H_{12}O_6}$(aq) $\mathbf{2C_2H_5OH}$(aq) (g)

$n(C_2H_5OH) = \dfrac{m}{M} = \dfrac{14}{46.068} = 0.31\text{ mol}$ (2SF)

Note: Although only two significant figures are shown above (ie 14 g) for the quoted mass of ethanol, the full calculated value, ie 14.25 g is carried into later parts of the calculation.

$n(C_6H_{12}O_6) = \dfrac{1}{2} \text{ x } n(C_2H_5OH) = \dfrac{0.31}{2} = 0.15\text{ mol of } C_6H_{12}O_6$ (2SF)

$\mathbf{m(C_6H_{12}O_6)}$ = n x M = 0.15 x 180.156 = **28 g** (2SF)

c. $n(CO_2) = \dfrac{2}{2} \text{ x } n(C_2H_5OH) = \dfrac{2 \text{ x } 0.31}{2} = 0.31\text{ mol}$ (2SF)

and for STP conditions $\mathbf{V(CO_2)}$ = n x 22.71 = 0.31 x 22.71 = **7.0 L at STP** (2SF)

19. a. $n(H_2O) = \dfrac{m}{M} = \dfrac{1.255 \text{ x } 10^6}{18.016} = 6.966 \text{ x } 10^4\text{ mol}$ *and* $n(C_2H_4) = \dfrac{m}{M} = \dfrac{2.541 \text{ x } 10^6}{28.052} = 9.058 \text{ x } 10^4\text{ mol}$

$\text{actual ratio} = \dfrac{n(H_2O)}{n[C_2H_4]} = \dfrac{6.966 \text{ x } 10^4}{9.058 \text{ x } 10^4} = 0.7690$ *and* $\text{stoichiometric ratio} = \dfrac{n(H_2O)}{n[C_2H_4]} = \dfrac{1}{1} = 1.00$

The actual ratio (0.7690) is less than the required stoichiometric ratio (1.00) ∴ $\mathbf{H_2O}$ **is the LR**.

b. As H_2O is the LR, it determines the maximum quantity of CH_3CH_2OH that can be produced.

$n(CH_3CH_2OH) = \dfrac{1}{1} \text{ x } n(H_2O) = \dfrac{1 \text{ x } 6.966 \text{ x } 10^4}{1} = 6.966 \text{ x } 10^4\text{ mol of ethanol}$

and $\mathbf{m(C_2H_5OH)}$ = n x M = $6.966 \text{ x } 10^4 \text{ x } 46.068$ = $\mathbf{3.209 \text{ x } 10^6}$ **g ethanol** (4SF)

c. **% yield** $\mathbf{CH_3CH_2OH}$ $= \dfrac{\text{actual yield x 100}}{\text{theoretical yield}} = \dfrac{1.678 \text{ x } 10^5 \text{ x } 100}{3.209 \text{ x } 10^6}$ = **5.229%** (4SF)

d. (i) Some possible causes for the yield being less than 100% include:

- loss of steam or ethene due to unwanted side reactions that unnecessarily consume them
- presence of impurities in the steam or ethene meaning the amount of these added is less than the amount thought
- physical loss of ethanol, eg due to the inability to completely separate ethanol from the reaction mixture.

(ii) Initially, determine the theoretical yield of ethanol from the complete reaction of 2541 kg of ethene.

$n(C_2H_4) = \dfrac{m}{M} = \dfrac{2.541 \text{ x } 10^6}{28.052} = 9.058 \text{ x } 10^4\text{ mol}$ (4SF)

$n(CH_3CH_2OH) = \dfrac{1}{1} \text{ x } n(C_2H_4) = \dfrac{1 \text{ x } 9.058 \text{ x } 10^4}{1} = 9.058 \text{ x } 10^4\text{ mol of ethanol}$

Determine the actual yield of ethanol from the given 96% conversion of 2541 kg of ethene to ethanol.

$$\% \text{ yield } CH_3CH_2OH = \frac{\text{actual yield x 100}}{\text{theoretical yield}}$$

thus $$\text{actual yield} = \frac{\text{\%yield x theoretical yield}}{100} = \frac{96 \times 9.058 \times 10^4}{100} = 8.7 \times 10^4 \text{ mol } CH_3CH_2OH \text{ (2SF)}$$

Determine the theoretical yield of $CH_3COOCH_2CH_3$ from the given 8.7×10^4 mol of ethanol.

$$n(CH_3COOCH_2CH_3) = \frac{1}{1} \times n(CH_3CH_2OH) = \frac{1 \times 8.7 \times 10^4}{1} = 8.7 \times 10^4 \text{ mol of } CH_3COOCH_2CH_3 \text{ (2SF)}$$

thus $m(CH_3COOCH_2CH_3) = n \times M = 8.7 \times 10^4 \times 88.104 = 7.7 \times 10^6$ g ethyl ethanoate (2SF)

Determine the actual yield of ethyl ethanoate for the Fischer reaction yield of 94%.

$$\% \text{ yield } CH_3COOCH_2CH_3 = \frac{\text{actual yield x 100}}{\text{theoretical yield}}$$

thus **actual yield** $= \frac{\text{\%yield x theoretical yield}}{100} = \frac{94 \times 7.7 \times 10^6}{100} = \mathbf{7.2 \times 10^6}$ $\mathbf{COOCH_2CH_3}$ (2SF)

20. a. FFAs are long chain carboxylic acids, use RCOOH as a general formula for the FFAs thus:

RCOOH(l) **OH**(l) $\xrightarrow{\text{cat}}$ (l) **O**(l)

b. Since the oil contains 8.45% FFA then: $m(\text{FFA in the oil}) = \frac{8.45 \times m(\text{oil})}{100} = \frac{8.45 \times 2.55 \times 10^6}{100}$

$= 2.15 \times 10^5$ g of FFA (ie RCOOH) (3SF)

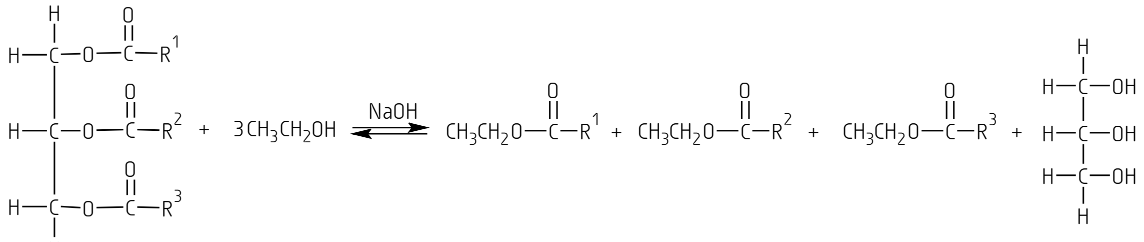
Note: $M(RCOOH) = 200.3 \text{ g mol}^{-1}$ *and* $n(RCOOH) = \frac{m}{M} = \frac{2.15 \times 10^5}{200.3} = 1.08 \times 10^3$ mol of FFA (ie RCOOH) (3SF)

$$n(CH_3OH) = \frac{1}{1} \times n(RCOOH) = \frac{1.08 \times 10^3}{1} = 1.08 \times 10^3 \text{ mol of } CH_3OH \text{ (3SF)}$$

and $\mathbf{m(CH_3OH)} = n \times M = 1.08 \times 10^3 \times 32.042 = \mathbf{3.45 \times 10^4 \text{ g}}$ of methanol (minimum required) (3SF)

c. The product $RCOOCH_3$ is a fatty acid methyl ester which is the biodiesel. So this is significant as it contributes to the total amount of biodiesel formed in the overall process. The other product, H_2O, needs to be removed as its presence along with NaOH (which is added later) will cause an undesirable side reaction where esters and triglycerides in the mixture become converted to soap.

21. a.



Note the use of R^1, R^2 and R^3 to denote the various fatty acid carbon chains in the TG.

b. Note: $M(TG) = 833 \text{ g mol}^{-1}$ (given) *and* $n(TG) = \frac{m}{M} = \frac{4.855 \times 10^6}{833} = 5.83 \times 10^3$ mol of triglyceride (3SF)

The desired mole ratio of C_2H_5OH : TG is given as 6.0 : 1.0.

thus $$n(C_2H_5OH) = \frac{6.0}{1.0} \times n(TG) = \frac{6.0 \times 5.83 \times 10^3}{1.0} = 3.5 \times 10^4 \text{ mol of } C_2H_5OH \text{ (2SF)}$$

and $\mathbf{m(C_2H_5OH)} = n \times M = 3.5 \times 10^4 \times 46.068 = \mathbf{1.6 \times 10^6}$ **g of ethanol** (minimum required) (2SF)

c. The three ethyl esters ($CH_3CH_2OOCR^1$, $CH_3CH_2OOCR^2$ and $CH_3CH_2OOCR^3$) constitute the biodiesel. Use a general formula of $CH_3CH_2OOCR^x$ for the biodiesel. Thus three moles of biodiesel ($CH_3CH_2OOCR^x$) are produced for each mole of TG. The biodiesel molecules ($CH_3CH_2OOCR^x$) have an average molar mass of 293 g mol^{-1}, which is given in the question information.

so $$n(CH_3CH_2OOCR^x) = \frac{3}{1} \times n(TG) = \frac{3 \times 5.83 \times 10^3}{1} = 1.75 \times 10^4 \text{ mol of } CH_3CH_2OOCR^x \text{ (3SF)}$$

thus $m(CH_3CH_2OOCR^x) = n \times M = 1.75 \times 10^4 \times 293 = 5.12 \times 10^6$ g of biodiesel ($CH_3CH_2OOCR^x$) (3SF)

Determine the actual yield of biodiesel given the process has a yield of 97%.

$$\% \text{ yield } CH_3CH_2OOCR^x = \frac{\text{actual yield} \times 100}{\text{theoretical yield}}$$

thus $$\textbf{actual yield} = \frac{\%\text{yield} \times \text{theoretical yield}}{100} = \frac{97 \times 5.12 \times 10^6}{100} = \mathbf{5.0 \times 10^6} \quad \mathbf{CH_2OOCCH_3} \text{ (2SF)}$$

22. a. $\mathbf{S}(l) + \mathbf{O_2}(g) \rightarrow \mathbf{SO_2}(g)$

The following calculations [ie parts (b) and (c)] are for the amounts of reagent involved per minute.

b. $$\% (O_2 \text{ in air}) = \frac{V(O_2) \times 100}{V(\text{air})}$$

$$\therefore \quad V(O_2) = \frac{\%(O_2) \times V(\text{air})}{100} = \frac{20.95 \times 3.57 \times 10^5}{100} = 7.48 \times 10^4 \text{ L of pure oxygen (3SF)}$$

$$PV = nRT \quad \textit{ie} \quad \mathbf{n(O_2)} = \frac{PV}{RT} = \frac{157 \times 7.48 \times 10^4}{8.3145 \times (45 + 273.15)} = \mathbf{4.44 \times 10^3} \quad \text{(3SF)}$$

$$n(S) = \frac{m}{M} = \frac{1.38 \times 10^5}{32.07} = 4.30 \times 10^3 \text{ mol}$$

$$\text{Actual mole ratio} = \frac{n(O_2)}{n(S)} = \frac{4.44 \times 10^3}{4.30 \times 10^3} = 1.03 \text{ (3SF)} \quad \textit{and} \quad \text{stoichiometric ratio} = \frac{n(O_2)}{n(S)} = \frac{1}{1} = 1.0 \text{ exactly}$$

The actual ratio (1.03) is greater than the stoichiometric ratio (1.0) ∴ **sulfur is the limiting reagent.** Thus there is enough air as oxygen is in excess.

c. As there is excess air (O_2) and the limiting reagent is sulfur, then:

$$n(SO_2 \text{ produced per minute}) = \frac{1}{1} \times n(S) = 4.30 \times 10^3 \text{ mol (3SF)}$$

For STP conditions:

$$n(SO_2 \text{ gas}) = \frac{V_{(STP)}}{22.71} \quad \textit{thus} \quad V(SO_2) = n \times 22.71 = 4.30 \times 10^3 \times 22.71 = 9.77 \times 10^4 \text{ L at STP (3SF)}$$

Determine the actual yield of SO_2 given the process has a yield of 99.5%.

$$\textbf{actual yield} = \frac{\%\text{yield} \times \text{theoretical yield}}{100} = \frac{99.5 \times 9.77 \times 10^4}{100} = \mathbf{9.72 \times 10^4} \quad \textbf{per minute at STP} \text{ (3SF)}$$

23. a. $\mathbf{N_2}(g) + \mathbf{3H_2}(g) \rightleftharpoons \mathbf{2NH_3}(g)$

b. Rearrange the molar volume relationship, ie PV = nRT to determine the moles of each gas entering the reaction chamber per minute. Remember when using PV = nRT pressure must be in **kPa**, temperature in **kelvin** and volume in **litres**. Use quantities for 1 minute.

ie $$\mathbf{n(N_2)} = \frac{P\,V}{R\,T} = \frac{3.00 \times 10^4 \times 9.55 \times 10^3}{8.3145 \times 723.15} = \mathbf{4.77 \times 10^4}$$

and $$\mathbf{n(H_2)} = \frac{P\,V}{R\,T} = \frac{3.00 \times 10^4 \times 28.50 \times 10^3}{8.3145 \times 723.15} = \mathbf{1.42 \times 10^5}$$

Actual mole ratio = $\frac{n(H_2)}{n(N_2)} = \frac{1.42 \times 10^5}{4.77 \times 10^4} = 2.98$ (3SF) *and* stoichiometric ratio = $\frac{n(H_2)}{n(N_2)} = \frac{3}{1} = 3.0$ exactly

The actual ratio (2.98) is less than the required stoichiometric ratio (3.0) $\therefore$ **H_2 is the LR.** Thus there is insufficient H_2 for the complete reaction of the available nitrogen.

b. An alternative approach is to determine the limiting reagent by comparing the volumes of each gas. Volume ratios can be used to compare gases instead of mole ratios only when the gases are measured at the same conditions of temperature and pressure. This is because at the same conditions of temperature and pressure equal volumes of different gases contain equal moles of gas, thus their mole ratio and volume ratio will be identical.

Actual mole/volume ratio = $\frac{V(H_2)}{V(N_2)} = \frac{28.50 \times 10^3}{9.55 \times 10^3} = 2.98$ (3SF)

stoichiometric ratio = $\frac{n(H_2)}{n(N_2)} = \frac{3}{1} = 3.0$ exactly

As before the actual ratio (2.98) is less than the required stoichiometric ratio (3.0) $\therefore$ **H_2 is the LR.** Thus there is insufficient H_2 for the complete reaction of the available nitrogen.

c. The graph shows an **NH_3 yield** of **37%** at **30.0 Mpa** and **450.0** ° (It is reasonable to read this scale to 2SF.)

d. $n(NH_3 \text{ produced}) = \frac{2 \times n(H_2)}{3} = \frac{2 \times 1.42 \times 10^5}{3} = 9.48 \times 10^4$ mol (3SF)

Remember H_2 is the limiting reagent. See part (b).

thus $m(NH_3 \text{ per minute}) = n \times M = 9.48 \times 10^4 \times 17.034 = 1.61 \times 10^6$ g (ie 1610 kg) of ammonia per minute (3SF) (This is the **theoretical yield**.)

Determine the **actual yield** of NH_3 given the process has a yield of 37%. (See yield curves.)

Remember: $$\%\text{ yield} = \frac{\text{actual yield} \times 100}{\text{theoretical yield}}$$

thus $$\textbf{actual yield} = \frac{\%\text{yield} \times \text{theoretical yield}}{100} = \frac{37 \times 1.61 \times 10^6}{100} = \mathbf{6.0 \times 10^5}$$ **per minute** (2SF)

e. Inside the reaction chamber the reacting gases reach equilibrium quite quickly. On leaving the chamber the mixture of gases is cooled while still under pressure. Under these conditions ammonia liquefies while nitrogen and hydrogen remain in the gas phase. The unreacted gases are easily separated from the mixture and returned to the reaction chamber where they continue to form ammonia. Recycling the unreacted gases ensures their almost complete conversion to ammonia.

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APPENDICES

Appendix 1: Processing data and significant figures

When processing measurement data from an investigation it is important to be aware of the number of significant figures in the measurements being processed. The following rules are used to count the number of significant figures (SF) in a measurement:

① All **non-zero** digits are significant, eg 7.92 (three SF). (**See zero's note at right**.)

② Zeros **between** two significant digits are significant, eg 60.3 (three SF), 9.0002 (five SF).

③ Zeros **before** the first non-zero digit are not significant, eg 0.35 (two SF), 0.009217 (four SF).

④ Zeros at the **end** of a number and **after** the decimal point are significant, eg 3.500 (four SF), 0.0710 (three SF).

⑤ Zeros at the **end** of a number and **before** the decimal point are not significant unless otherwise indicated, eg 3500 (two SF). If these zeros are significant then scientific notation can be used to show this, eg 3.500 x 10^4 (four SF), 3.50 x 10^4 (three SF) or 3.5 x 10^4 (two SF).

Example 1 How many significant figures are present in each of the following volume measurements?

7.08 x 10^3 mL	three significant figures	see rule ① and ②
7.800 x 10^3 mL	four significant figures	see rule ① and ④
7.0800 x 10^3 mL	five significant figures	see rule ①, ② and ④
0.758 mL	three significant figures	see rule ① and ③
0.0708 mL	three significant figures	see rule ①, ② and ③
780 mL	two significant figures	see rule ① and ⑤

Zeros!

The **non-zero** digits in a measurement are **always** significant but zeros **may** be significant.

Key: significant zero's 0
not significant zero's..........~~0~~

1**00**819.5**0**7	②
~~0~~.181957	③
~~0~~.~~00~~181957	③
181957**.0**	④
181957**.000**	④
181957~~0~~	⑤
181957~~000~~	⑤
181954**.0**	④
181954**000.0**	② and ④

Exact numbers are those which contain no uncertainty. Some examples include the number of protons in an oxygen nucleus is exactly 8, the coefficients of a balanced equation or the subscripts in a formula. Exact numbers **do not** affect the number of significant figures in a calculated result.

Data collected in an investigation often needs to be processed in order to calculate the value of some variable of interest. When this is done, the calculated result **must not** be more precise than the measured data used to calculate it. For a calculation that requires **multiplication** or **division**, the answer is given with only as many significant figures as the measurement with the **least number** of significant figures.

Example 2 Evaluate the following and give the answer to the correct number of significant figures.

a. 1.498 L x 6.8 x 10^{-1} g L^{-1} = 1.01864 g = 1.0 g	This calculation involves multiplication so the answer only has as many SF as the number with the least SF. As 6.8 x 10^{-1} g L^{-1} has the least SF (two) so the answer is **rounded** (see border note*****) to two significant figures even though 1.498 L has four SF.
b. $\frac{1.04 \text{ g x } 7.000}{12.01 \text{ g mol}^{-1}}$ = 0.6061615 = 0.606 mol (3SF)	This calculation involves multiplication and division so the answer only has as many SF as the number with the least SF. As 1.04 g has the least SF (three) so the answer is rounded to three significant figures even though 7.000 and 12.01 both have four SF.

*When **rounding** a number, if the leftmost digit to be deleted is:

- **greater than 5** then increase the final remaining digit by 1.
- **less than 5** then the final remaining digit is unchanged.
- **equal to 5** then increase the final remaining digit by 1.

Eg: The following are rounded to 2 SF.

6.54	becomes	6.5
6.55	becomes	6.6
6.56	becomes	6.6

Sometimes a calculation will require **addition** or **subtraction** of data values. In this case, the answer is quoted with as many **decimal places** as the measurement with the least number of decimal places. When counting decimal places, the measurements must be expressed with the **same powers of ten**. See Example 3.

Example 3 Evaluate the following and quote the answer to the correct number of decimal places (DP).

a. 1.49 x 10^2 g + 6.2 g = 149 g + 6.2 g = 155.2 = 155 g , ie 3 SF)	This calculation involves **addition** so the answer only has as many **decimal places** (DP) as the number with the least DP. (Significant figures are not considered.) To determine the number with the least decimal places, all numbers must be expressed to the same power of ten. Doing this shows 1.49 x 10^2 g has the least decimal places (nil), when written to the same powers of ten as 6.2, ie 1.49 x 10^2 g becomes 149 g so the answer has nil decimal places.
b. 7.5530 x 10^3 L - 6.790 L = 7553.0 L - 6.790 L = 7546.21 L = 7546.2 L , ie 5 SF)	This calculation involves **subtraction** so the answer only has as many DP as the number with the least DP. Using the same powers of ten, the numbers are 7553.0 and 6.790. Thus 7553.0 has the least decimal places (one, when expressed with the same powers of ten) so the answer is rounded to one decimal place.

Important note to students:

The Current SCASA year 12 Examination design brief for use in 2016 refers to the use of significant figures in the following way. 'Numerical answers should be expressed to the **appropriate number of significant figures** and include units where applicable.'

Students would be advised to check the current requirements regarding numeric answers and significant figures closer to the time of their examination.

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Appendix 2: Common ions

Table 1 Name and formula of common positive ions

hydrogen	H^+	magnesium	Mg^{2+}	copper(II)	Cu^{2+}	aluminium	Al^{3+}
lithium	Li^+	calcium	Ca^{2+}	zinc	Zn^{2+}	iron(III)	Fe^{3+}
sodium	Na^+	strontium	Sr^{2+}	lead(II)	Pb^{2+}	chromium(III)	Cr^{3+}
potassium	K^+	barium	Ba^{2+}	mercury(I)	Hg_2^{2+}	gold(III)	Au^{3+}
silver	Ag^+	manganese(II)	Mn^{2+}				
caesium	Cs^+	iron(II)	Fe^{2+}				
rubidium	Rb^+	cobalt(II)	Co^{2+}				
ammonium	NH_4^+	nickel(II)	Ni^{2+}				

Table 2 Name and formula of common negative ions

hydride	H^-	dihydrogenphosphate	$H_2PO_4^-$	sulfide	S^{2-}
fluoride	F^-	ethanoate	CH_3COO^-	carbonate	CO_3^{2-}
chloride	Cl^-	perchlorate	ClO_4^-	sulfate	SO_4^{2-}
bromide	Br^-	chlorate	ClO_3^-	sulfite	SO_3^{2-}
iodide	I^-	chlorite	ClO_2^-	hydrogenphosphate	HPO_4^{2-}
hydroxide	OH^-	hypochlorite	ClO^-	dichromate	$Cr_2O_7^{2-}$
nitrate	NO_3^-	cyanide	CN^-	chromate	CrO_4^{2-}
nitrite	NO_2^-	permanganate	MnO_4^-	oxalate	$C_2O_4^{2-}$
hydrogencarbonate	HCO_3^-				
hydrogensulfate	HSO_4^-	oxide	O^{2-}	phosphate	PO_4^{3-}
hydrogensulfide	HS^-	peroxide	O_2^{2-}	nitride	N^{3-}

Appendix 3: Appearance of common species

Table 3 Colour of selected ions in aqueous solution

Ion	Colour	Ion	Colour	Ion	Colour
Cu^{2+}	blue	Fe^{2+}	pale green	MnO_4^-	purple
$[Cu(NH_3)_4]^{2+}$	deep blue	$FeCl_2^+$	yellow	Cr^{3+}	dark green
$[CuCl_4]^{2-}$	green	Fe^{3+}	pale brown	$Cr_2O_7^{2-}$	orange
Ni^{2+}	green	$[Fe(CN)_6]^{3-}$	red	CrO_4^{2-}	yellow
Co^{2+}	pink	Mn^{2+}	pale pink (may appear colourless)		

Note: The colour of ions in solution will vary due to concentration ligands solvent colourless , Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Ag^+, Au^+, Zn^{2+}, Cd^{2+}, Hg_2^{2+}, Hg^{2+}, Al^{3+}, Sn^{2+}, Sn^{4+}, S^{2-}, F^-, Br^-, I^-, CH_3COO^-, CO_3^{2-}, HCO_3^-, CN^-, $C_2O_4^{2-}$, $HC_2O_4^-$, NO_2^-, NO_3^-, NH_4^+, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, OH^-, SO_3^{2-}, HSO_3^-, SO_4^{2-}, HSO_4^-.

Table 4 Appearance of common elements and their solutions at standard conditions

Substance	Formula	Appearance	Substance	Formula	Appearance
chlorine	$Cl_2(g)$	yellow-green gas	silicon	$Si(s)$	grey solid
chlorine (in) water	$Cl_2(aq)$	pale yellow solution	sodium	$Na(s)$	silvery metallic
bromine	$Br_2(l)$	red liquid	potassium	$K(s)$	silvery metallic
bromine (in) water	$Br_2(aq)$	orange solution	magnesium	$Mg(s)$	silvery metallic
bromine in CH_2Cl_2	$Br_2(CH_2Cl_2)$	red solution	calcium	$Ca(s)$	silvery metallic
iodine	$I_2(s)$	purple solid	iron	$Fe(s)$	silvery metallic
iodine (in) water	$I_2(aq)$	brown solution	copper	$Cu(s)$	salmon pink metallic
iodine in CH_2Cl_2	$I_2(CH_2Cl_2)$	purple solution	zinc	$Zn(s)$	silvery-grey metallic
carbon (graphite)	$C(s)$	black solid	aluminium	$Al(s)$	silvery metallic
nitrogen	$N_2(g)$	colourless gas	silver	$Ag(s)$	silvery metallic
oxygen	$O_2(g)$	colourless gas	gold	$Au(s)$	yellow metallic
sulfur	$S_8(s)$	yellow solid	lead	$Pb(s)$	silvery-grey metallic

Table 5 Appearance of common compounds and their solutions at standard conditions

Substance	Formula	Appearance	Substance	Formula	Appearance
carbon monoxide	$CO(g)$	colourless gas	hydrochloric acid	$HCl(aq)$	colourless solution
carbon dioxide	$CO_2(g)$	colourless gas	hydrogen bromide	$HBr(g)$	colourless gas
sulfur dioxide	$SO_2(g)$	colourless gas	hydrogen iodide	$HI(g)$	colourless gas
sulfur trioxide	$SO_3(g)$	colourless gas	nitrogen monoxide	$NO(g)$	colourless gas*
ammonia	$NH_3(g)$	colourless gas	nitrogen dioxide	$NO_2(g)$	brown gas
hydrogen sulfide	$H_2S(g)$	colourless gas	dinitrogen tetroxide	$N_2O_4(g)$	colourless gas#
hydrogen peroxide	$H_2O_2(l)$	pale blue liquid	nitric acid	$HNO_3(aq)$	colourless solution
hydrogen peroxide	$H_2O_2(aq)$	colourless solution	phosphoric acid	$H_3PO_4(aq)$	colourless solution
hydrogen fluoride	$HF(g)$	colourless gas	sulfuric acid	$H_2SO_4(aq)$	colourless solution
hydrogen chloride	$HCl(g)$	colourless gas	sulfurous acid	$H_2SO_3(aq)$	colourless solution

* Nitrogen monoxide readily forms the brown gas NO_2 on exposure to air.

\# Dinitrogen tetroxide exists in equilibrium with brown NO_2 gas.

Appendix 4: Physical constants and formulas

Physical constants

Standard temperature and pressure (S.T.P.) .... 100.0 kPa and 0.0 °C

Ionisation constant of water (K_w) .... 1.00×10^{-14} at 25 °C

Universal gas constant (R)... 8.3145 J K^{-} -

Number of particles in a mole (Avogadro's constant) .... 6.022×10^{23} mol^{-}

°C (S.T.P) .... 22.71 L

Absolute zero .... 0 K or -273.15 °C

Relating common units

Temperature	0.0 °C = 273.15 K
Pressure	101.3 kPa = 1 atm = 760 mmHg
Concentration	1 mol L^{-1} = 1 M
Volume	1 L = 1×10^3 mL = 1×10^3 cm^3 = 1 dm^3 = 1×10^{-3} m^3

SI prefixes

P	**T**	**G**	**M**	**k**	**d**	**c**	**m**	μ	**n**	**p**	**f**
peta	tera	giga	mega	kilo	deci	centi	milli	micro	nano	pico	femto
10^{15}	10^{12}	10^{9}	10^{6}	10^{3}	10^{-}	-	-	-	-	-	-15

Formulas

$$n(gas) = \frac{V_{STP}}{22.71}$$

where: **n(gas)** = the moles of gas (mol)
V_{STP} = the volume of gas in litres (L) at STP

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

where: **c** = the concentration of solute in moles per litre (mol L^{-1})
n = the amount of solute in moles (mol)
V = the volume of solution (solvent + solute) in litres (L)

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

where: **pH** = minus the logarithmic value of the hydrogen ion concentration
$[H^+]$ = the concentration of hydrogen ions in moles per litre (mol L^{-1})

$$c_{ppm} = \frac{m_s \times 10^6}{m_t}$$

where: **c_{ppm}** = the concentration of solute in parts per million by mass (ppm)
m_s = the mass of solute in grams (g)
m_t = the mass of solution (solvent + solute) in grams (g)

$$m = n \times M \quad \text{also expressed as} \quad n = \frac{m}{M}$$

where: **n** = the amount of substance in moles (mol)
m = the mass of the substance in grams (g)
M = the molar mass of the substance in grams per mole (g mol^{-1})

$$density = \frac{m}{V}$$

where: **density** = the density of the substance in grams per litre (g L^{-1})
m = the mass of a substance in grams (g)
V = the volume of the substance in litres (L)

$$PV = nRT \quad \text{also expressed as} \quad n = \frac{PV}{RT}$$

where: **n** = the amount of gas in moles (mol)
P = the gas pressure in kilopascals (kPa)
V = the volume of gas in litres (L)
R = Universal gas constant, ie 8.3145 J K^{-} -
T = the gas temperature in kelvin units (K)

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Appendix 5: Solubility and precipitate colours

Table 6 Solubility rules for ionic compounds in water

Soluble*¹	**Exceptions**	
	Insoluble*²	**Slightly soluble*³**
All nitrates and ethanoates (acetates)	Nil	Nil
Most chlorides, iodides and bromides	$AgCl$, $AgBr$, AgI, PbI_2.	$PbCl_2$, $PbBr_2$.
Most sulfates	$SrSO_4$, $BaSO_4$, $PbSO_4$.	$CaSO_4$, Ag_2SO_4.

Insoluble*²	**Exceptions**	
	Soluble*¹	**Slightly soluble*³**
Most hydroxides	$NaOH$, KOH, $Ba(OH)_2$. [Note: $AgOH$ and $NH_4OH(s)$	$_2$, $Sr(OH)_2$.
Most carbonates	Na_2CO_3, K_2CO_3, $(NH_4)_2CO_3$.	Nil
Most phosphates	Na_3PO_4, K_3PO_4, $(NH_4)_3PO_4$.	Nil
Most sulfides	Na_2S, K_2S, $(NH_4)_2S$.	Nil

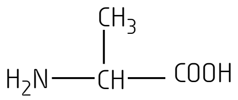
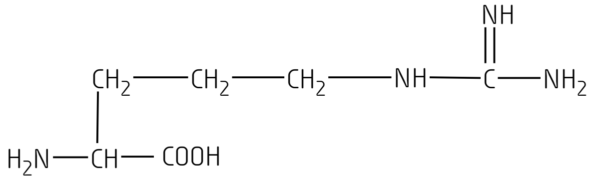
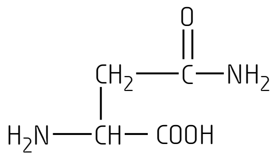
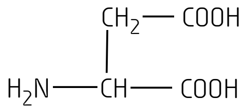
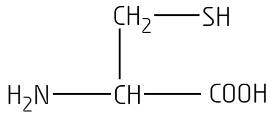
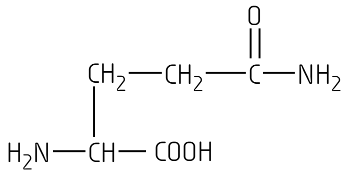
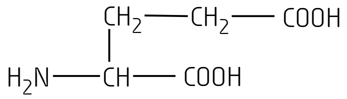
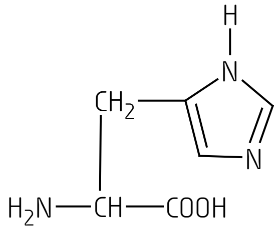
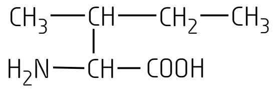
***¹** Soluble means more than 0.1 mole dissolves per litre.
***²** Insoluble means less than 0.01 mole dissolves per litre.
***³** Slightly soluble means between 0.1 and 0.01 moles dissolve per litre.

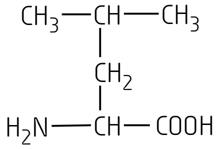
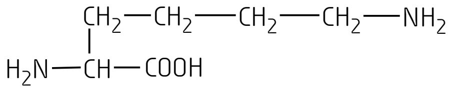
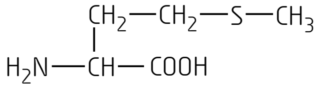
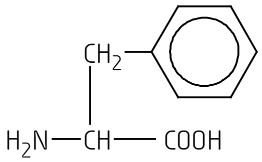
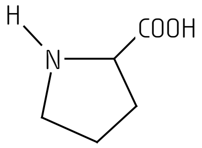
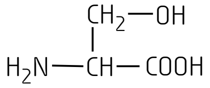
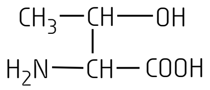
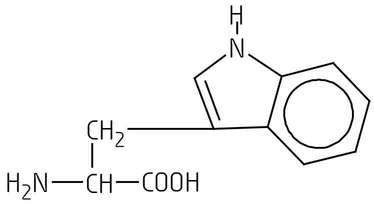
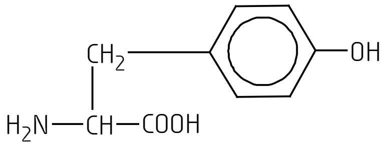
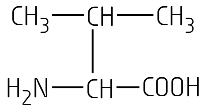
Table 7 Colour and formula of common precipitates

Ions	**Cl^-**	**Br^-**	**I^-**	**SO_4^{2-}**	**OH^-**	**CO_3^{2-}**	**PO_4^{3-}**	**S^{2-}**
Na^+								
K^+								
NH_4^+								
Mg^{2+}					$Mg(OH)_2$ white	$MgCO_3$ white	$Mg_3(PO_4)_2$ white	decomposes
Ca^{2+}				$CaSO_4$ white	$Ca(OH)_2$ white	$CaCO_3$ white	$Ca_3(PO_4)_2$ white	CaS white
Sr^{2+}				$SrSO_4$ white	$Sr(OH)_2$ white	$SrCO_3$ white	$Sr_3(PO_4)_2$ white	SrS grey
Ba^{2+}				$BaSO_4$ white		$BaCO_3$ white	$Ba_3(PO_4)_2$ white	BaS white
Cr^{3+}		$CrBr_3$ grey-green			# $Cr(OH)_3$ blue-gy-green	* $Cr(OH)_3$ blue-gy-green	$CrPO_4$ blue-grey	decomposes
Mn^{2+}					$Mn(OH)_2$ pale pink	$MnCO_3$ pale pink	$Mn_3(PO_4)_2$ white	MnS pink
Fe^{2+}					$Fe(OH)_2$ green	$FeCO_3$ grey/green	$Fe_3(PO_4)_2$ grey-green	FeS black
Fe^{3+}					$Fe(OH)_3$ brown	$Fe_2(CO_3)_3$ brown	$FePO_4$ grey-brown	Fe_2S_3 green-black
Co^{2+}					$Co(OH)_2$ red	$CoCO_3$ red	$Co_3(PO_4)_2$ blue-purple	CoS black
Ni^{2+}					$Ni(OH)_2$ green	$NiCO_3$ green	$Ni_3(PO_4)_2$ green	NiS black
Cu^{2+}					$Cu(OH)_2$ blue	$CuCO_3$ green	$Cu_3(PO_4)_2$ blue	CuS black
Ag^+	$AgCl$ white	$AgBr$ cream	AgI pale yellow	Ag_2SO_4 white	* Ag_2O brown	Ag_2CO_3 yellow	Ag_3PO_4 yellow	Ag_2S black
Zn^{2+}					# $Zn(OH)_2$ white	$ZnCO_3$ white	$Zn_3(PO_4)_2$ white	ZnS grey-white
Cd^{2+}					# $Cd(OH)_2$ white	$CdCO_3$ white	$Cd_3(PO_4)_2$ colourless	CdS yellow
Al^{3+}					# $Al(OH)_3$ white	$Al_2(CO_3)_3$ white	$AlPO_4$ white	decomposes
Sn^{2+}					# $Sn(OH)_2$ white	$SnCO_3$ white	$Sn_3(PO_4)_2$ white	SnS black
Pb^{2+}	$PbCl_2$ white	$PbBr_2$ white	PbI_2 yellow	$PbSO_4$ white	# $Pb(OH)_2$ white	$PbCO_3$ white	$Pb_3(PO_4)_2$ white	PbS grey

\# These compounds are amphoteric and will redissolve in excess OH^-.
* Note: $Ag_2O(s)$ forms instead of $AgOH(s)$, $Cr(OH)_3(s)$ forms instead of $Cr_2(CO_3)_3(s)$.

Appendix 6: α-amino acids

Name	Symbol	Structure
alanine	**Ala**	 $H_2N-\overset{CH_3}{\overset{\vert}{CH}}-COOH$
arginine	**Arg**	 $H_2N-\overset{CH_2-CH_2-CH_2-NH-\overset{NH}{\overset{\Vert}{C}}-NH_2}{\overset{\vert}{CH}}-COOH$
asparagine	**Asn**	 $H_2N-\overset{CH_2-\overset{O}{\overset{\Vert}{C}}-NH_2}{\overset{\vert}{CH}}-COOH$
aspartic acid	**Asp**	 $H_2N-\overset{CH_2-COOH}{\overset{\vert}{CH}}-COOH$
cysteine	**Cys**	 $H_2N-\overset{CH_2-SH}{\overset{\vert}{CH}}-COOH$
glutamine	**Gln**	 $H_2N-\overset{CH_2-CH_2-\overset{O}{\overset{\Vert}{C}}-NH_2}{\overset{\vert}{CH}}-COOH$
glutamic acid	**Glu**	 $H_2N-\overset{CH_2-CH_2-COOH}{\overset{\vert}{CH}}-COOH$
glycine	**Gly**	H_2N-CH_2-COOH
histidine	**His**	
isoleucine	**Ile**	 $H_2N-\overset{CH_3-CH-CH_2-CH_3}{\overset{\vert}{CH}}-COOH$

Name	Symbol	Structure
leucine	**Leu**	 $\begin{array}{c}CH_3-CH-CH_3\\ \vert\\ CH_2\\ \vert\\ H_2N-CH-COOH\end{array}$
lysine	**Lys**	 $\begin{array}{l}\quad CH_2-CH_2-CH_2-CH_2-NH_2\\ \quad\vert\\ H_2N-CH-COOH\end{array}$
methionine	**Met**	 $\begin{array}{l}\quad CH_2-CH_2-S-CH_3\\ \quad\vert\\ H_2N-CH-COOH\end{array}$
phenylalanine	**Phe**	
proline	**Pro**	
serine	**Ser**	 $\begin{array}{l}\quad CH_2-OH\\ \quad\vert\\ H_2N-CH-COOH\end{array}$
threonine	**Thr**	 $\begin{array}{c}CH_3-CH-OH\\ \vert\\ H_2N-CH-COOH\end{array}$
tryptophan	**Trp**	
tyrosine	**Tyr**	
valine	**Val**	 $\begin{array}{c}CH_3-CH-CH_3\\ \vert\\ H_2N-CH-COOH\end{array}$

Appendix 7: Standard Reduction Potentials

Half-reaction	**E° (volts)**
$F_2(g) + 2e^- \rightleftharpoons 2F^-$	
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	+1.76
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$	+1.69
$2HClO(aq) + 2H^+(aq) + 2e^- \rightleftharpoons Cl_2(g) + 2H_2O(l)$	+1.63
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	+1.50
$HClO(aq) + H^+(aq) + 2e^- \rightleftharpoons Cl^- + H_2O(l)$	+1.49
$PbO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Pb^{2+}(aq) + 2H_2O(l)$	+1.46
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.36
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-$	
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	+0.96
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$	+0.70
$I_2(s) + 2e^- \rightleftharpoons 2I^-$	
$Cu^+(aq) + e^- \rightleftharpoons Cu(s)$	+0.52
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-$	
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$S(s) + 2H^+(aq) + 2e^- \rightleftharpoons H_2S(aq)$	+0.17
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0 exactly
$Pb^{2+}(aq) + 2e^- \rightleftharpoons Pb(s)$	-0.13
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	-0.14
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	-0.24
$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$	-0.28
$PbSO_4(s) + 2e^- \rightleftharpoons Pb(s) + SO_4^{2-}(aq)$	-0.36
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	-0.40
$2CO_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2C_2O_4(aq)$	-0.43
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	-0.44
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	-0.74
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	-0.76
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-$	
$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	-1.18
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	-1.68
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	-2.36
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	-2.71
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	-2.87
$Sr^{2+}(aq) + 2e^- \rightleftharpoons Sr(s)$	-2.90
$Ba^{2+}(aq) + 2e^- \rightleftharpoons Ba(s)$	-2.91
$K^+(aq) + e^- \rightleftharpoons K(s)$	-2.94
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	-3.04

Reduction potentials are for standard conditions, ie solution concentrations of 1 mol L^{-} ^{5} kPa and temperatures of 25 °C.
Data has been sourced from G. Aylward & T. Findlay, *SI Chemical Data* (2008, 6th Edition) John Wiley & Sons Australia, LTD.

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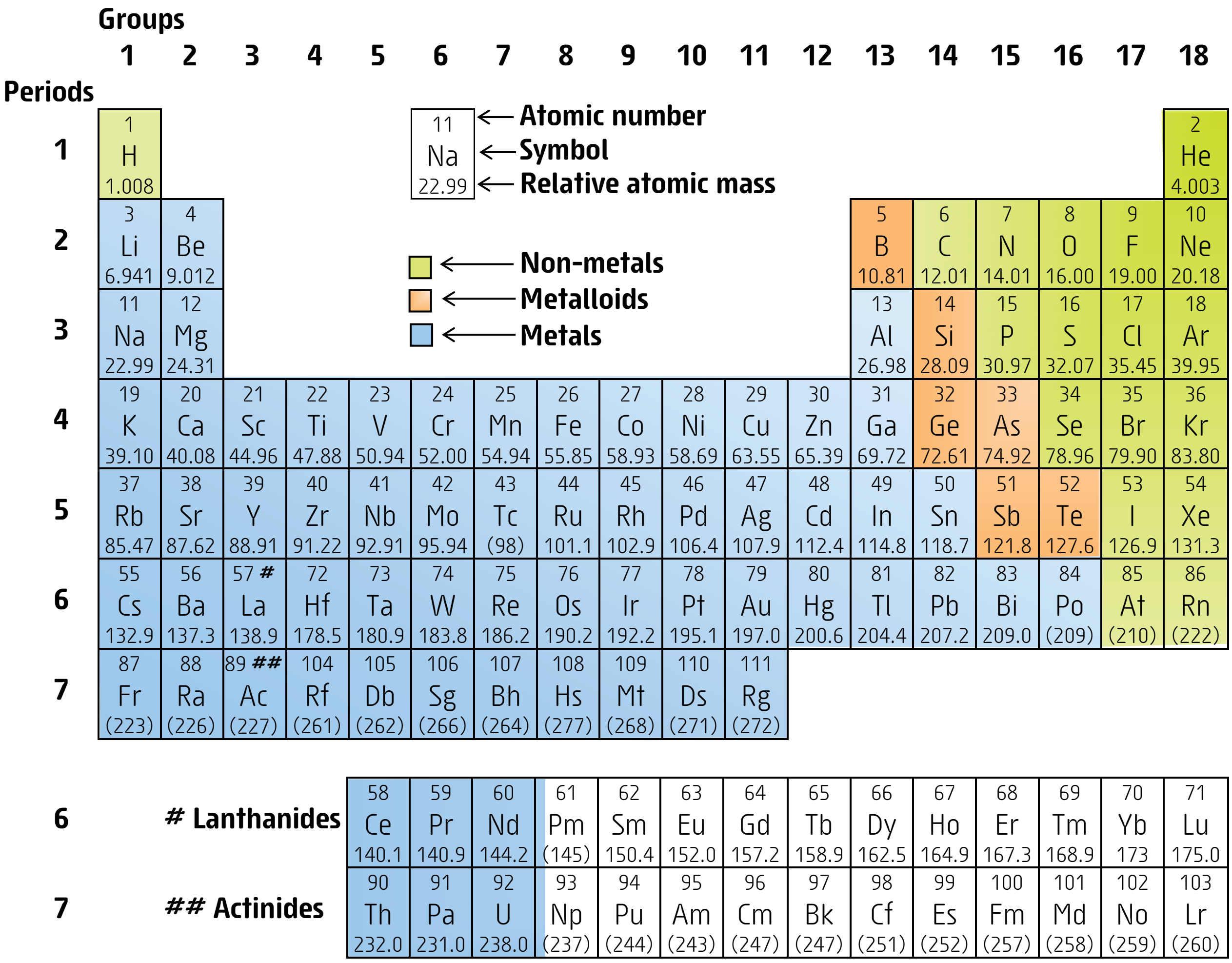
Appendix 6: The periodic table of the elements



11 ← Atomic number
Na ← Symbol
22.99 ← Relative atomic mass

🟩 ← Non-metals
🟧 ← Metalloids
🟦 ← Metals

Periods \ Groups	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.008																	2 He 4.003
2	3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	57 # La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra (226)	89 ## Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (264)	108 Hs (277)	109 Mt (268)	110 Ds (271)	111 Rg (272)							

6	**# Lanthanides**	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.2	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173	71 Lu 175.0
7	**## Actinides**	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)