Longman AS & A-Level Course in

CHEMISTRY

5th Edition
(Revised edition)

Based on
NEW SYLLABUS

JGR Briggs

Revised by:
F.B.S Maudarbocus
A.H Vydelingum

Longman

The LONGMAN AS & A - LEVEL COURSE IN CHEMISTRY completely covers the new syllabus for Africa. It covers all topics, including the volumetric calculations that may be required for Practical Examination and new topics such as Application of Chemistry.

The text is written in concise point form for easy study and revision. Chemical names and compounds are limited to those required for A - Level examination. A large number of worked examples, particulary on calculations, are included in the text.

The text is arranged by topics according to the syllabus. Each topic includes an exercise consisting of examination - type questions. Answers are provided at the end of the book.

This new edition has been written to reflect recent changes in the Cambridge - A - Level Chemistry syllabus and includes the following :

- The chemistry of life
- Applications of analytical chemistry
- Design and material

This book can be used as a basic text and/or for self - study and revision purposes.

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PREFACE

This new edition of Longman AS & A-Level Course in Chemistry originally written by J. G. R. Briggs which F. B. S. Maudarbocus and A.H. Vydelingum have amended is expected to meet the exigencies of the new Cambridge Higher Certificate Syllabus for the year 2007 and onwards. The content provides an excellent Course text for all AS and A2 specifications. The authors believe that the materials contribute towards scientific knowledge, environmental, industrial and societal concerns.

The new chapters make sure that the students have the prerequisites to thoroughly understand both the chemistry involved and the technology required.These new chapters develop fundamental concepts from the most elementary of ideas. The symbols, terminology and units are according to the International system of units. Organic Chemicals are named following the I.U.P.A.C System.

F. B. S. Maudarbocus and A.H. Vydelingum hope that this new edition will facilitate learning and help towards the achievement of excellence. Our thanks go to the late J.G.R Briggs who had laid the framework of this A-Level Chemistry text.

Fazila B.S. Maudarbocus
&
Anwar H.Vydelingum

INTRODUCTION

This fifth edition of the Longman AS & A-level Course in Chemistry has been written to take account of the recent changes in the Cambridge 9258 and 9701 A-level syllabi for Chemistry. This revised edition has the same aim as the earlier editions, that is, to provide a comprehensive guide to A-level Chemistry in a concise, easy-to-follow point form. It completely covers the new Cambridge 9258 and 9701 A-level syllabi.

New features of this fifth edition include:

- **Extensive** revision of the text and the addition of a **new topic** ***Applications of Analytical Chemistry, Peptides and Protein*** and ***Design and Materials.***
- **Extensive revision** of questions to reflect the change in content and style of the new examinations;
- **New examples** of Cambridge Examination Questions.

The key features of this book are:

- the text is written in a concise point form;
- the topics are arranged in order of the syllabus;
- the chemical terms used are those required by the syllabus and for the examinations;
- worked examples and illustrations are provided (particularly on calculations);
- exercises are provided at the end of each chapter. They consist of the three types of questions (multiple choice, structured and descriptive) at both AS and A-Level. There are also a number of questions requiring the use of the Data Tables which are available at the end of the book;
- a chapter on volumetric calculations cover also the problems in Practical Examination;
- a glossary of chemical terms;
- data tables similar to those used in the A-level examinations, including tables on electronegativity and electron affinity;
- answers to questions.

CONTENTS

Core Topics **Pages**

CHAPTER

1

ATOMS, MOLECULES, MOLES, AND STOICHIOMETRY

SYLLABUS OBJECTIVES

In this chapter you should be able to:

- define the following terms: relative atomic mass; relative isotopic mass; relative molecular mass; relative formula mass (all based on the ^{12}C scale of masses)
- define the mole in terms of the Avogadro Constant
- interpret mass spectra of elements and molecules in terms of isotopic abundances and molecular fragmentation
- define the terms empirical formula and molecular formula
- calculate the relative atomic mass of an element from the relative abundances of its isotopes, *or* its mass spectrum
- calculate the empirical and molecular formula of a compound from its element composition by mass
- calculate the empirical and molecular formula of a compound (eg hydrocarbons) from combustion data
- do chemical calculations using reacting masses of substances and volumes of gases (including use of the mole)

Relative Mass

The Mole and the Avogadro Constant

Determination of Relative Atomic Mass by Mass Spectrometry

Mass Spectra of Molecules

Empirical Formulae of Compounds

Molecular Formulae

Empirical Formula and Relative Molecular Mass of Gaseous Hydrocarbons

1.1 Relative Mass

- The three fundamental particles of an atom, properties and location in the atom are given in the table below:

Particle	Relative charge	Relative mass	Location in the atoms
Protons	+1	1	In the nucleus
Electron	- 1	$\frac{1}{1840}$	In orbits around the nucleus
Neutron	Nil	1	In the nucleus

- The relative masses of atoms, molecules and ions are obtained by comparison with the mass of one atom of the carbon-12 isotope, ^{12}C.

Relative Mass Scale

- **The relative mass of a particle** $= 12 \times \dfrac{\textbf{mass of the particle}}{\textbf{mass of one atom of } ^{12}\textbf{C}}$

Relative Isotopic Mass

- **The relative isotopic mass of an isotope**

$$= 12 \times \frac{\textbf{mass of one atom of the isotope}}{\textbf{mass of one atom of } ^{12}\textbf{C}}$$

- The relative isotopic mass of an isotope is *almost* the same as its nucleon number. For example, the relative isotopic mass of $^{21}Ne = 20.994 \approx 21$.

  The nucleon number of an isotope can be used as the *approximate* relative isotopic mass for calculations.

Relative Atomic Mass, A_r

- Most elements consist of a mixture of isotopes. The *average* relative isotopic mass of the atoms must be used for calculations.
- **The relative atomic mass of an element,**

$$A_r = 12 \times \frac{\textbf{average mass of one atom of the element}}{\textbf{mass of one atom of } ^{12}\textbf{C}}$$

- If an element consists of two isotopes, *Y* and *Z*, the relative atomic mass of the element,

$$A_r = \frac{\left[\begin{array}{c}\text{no. of atoms of Y x}\\ \text{relative isotopic mass of Y}\end{array}\right] + \left[\begin{array}{c}\text{no. of atoms of Z x}\\ \text{relative isotopic mass of Z}\end{array}\right]}{\text{total number of atoms of Y and Z}}$$

Question The element rhenium consists of two isotopes ^{185}Re and ^{187}Re, in the atomic ratio of 2:3. Calculate the relative atomic mass of rhenium to three significant figures.

Answer Using the mass numbers as the relative isotopic masses,

$$\text{relative atomic mass, } A_r = \frac{(2 \text{ x } 185) + (3 \text{ x } 187)}{2 + 3} = 186.2 = 186 \text{ (three significant figures)}$$

- The abundance of an isotope is the percentage of the isotope found in the naturally occurring element.

  For example, the abundance of ^{35}Cl = 75.53%. This means that 75.53% of chlorine atoms are ^{35}Cl.

- The relative atomic mass can be calculated from the abundances of the isotopes. If an element consists of two isotopes, **Y** and **Z**, the relative atomic mass of the element,

$$A_r = \frac{\left[\begin{array}{c}\text{abundance of Y x}\\ \text{relative isotopic mass of Y}\end{array}\right] + \left[\begin{array}{c}\text{abundance of Z x}\\ \text{relative isotopic mass of Z}\end{array}\right]}{100}$$

Question Natural chlorine has the following isotopes:

isotope	*relative isotopic mass*	*percentage abundance*
^{35}Cl	34.97	75.53
^{37}Cl	36.97	24.47

Calculate the relative atomic mass of chlorine.

Answer

$$\text{Relative atomic mass, } A_r = \frac{(75.53 \text{ x } 34.97) + (24.47 \text{ x } 36.97)}{100} = 35.5$$

- Man-made elements such as americium (Z = 95) and technetium (Z = 43) do not have relative atomic masses. These elements are not found in the Earth. The isotopes present in samples depend on the method by which they are made.

Relative Molecular Mass, M_r

- **The relative molecular mass of a molecular substance,**

$$M_r = 12 \times \frac{\textbf{average mass of one molecule of the substance}}{\textbf{mass of one atom of } ^{12}\textbf{C}}$$

- The relative molecular mass = sum of the relative atomic masses of all the atoms shown in the molecular formula

  For example, the relative molecular mass of H_2O $= 1.008 + 1.008 + 15.999 = 18.015 = 18.02$ (four significant figures).

Relative Formula Mass

- **The relative formula mass of a substance**

$$= 12 \times \frac{\textbf{average mass of all the atoms in the formula}}{\textbf{mass of one atom of } ^{12}\textbf{C}}$$

- The relative formula mass = sum of the relative atomic masses of all the atoms shown in the formula

  For example, the relative formula mass of $CuSO_4.5H_2O$ $= 63.55 + 32.06 + 4(15.999) + 5(1.008 + 1.008 + 15.999)$ $= 249.68 = 249.7$ (four significant figures).

- In the calculation of the relative formula mass of ions, the charge on the ion is ignored.

  For example, the relative formula mass of OH^- $= 15.999 + 1.008 = 17.007 = 17.01$ (four significant figures).

1.2 The Mole and the Avogadro Constant

The Mole

- **One mole of a substance is that amount of the substance that contains the same number of particles as the number of atoms in exactly 12 grams of the isotope ^{12}C.**

- The mass of one mole of atoms of an element = relative atomic mass of the element in grams = A_r grams

  This is known as the **molar mass** of the element.

  For example, the relative atomic mass of nitrogen = 14. Hence the molar mass of nitrogen atoms is 14 g.

- The number of moles of atoms in a sample of an element

$$= \frac{\text{mass in grams of the element}}{\text{molar mass of the element}}$$

Question

(a) How many moles of atoms are contained in 2.8 g of iron?
[Fe = 56]

(b) What is the mass of 0.4 mole of oxygen atoms?
[0 = 16]

Answer

(a) Number of moles = $\frac{2.8}{56}$ = 0.05 mole

(b) Mass in grams = no. of moles x molar mass
= 0.4 x 16 = 6.4 g

- The mass of one mole of molecules of a substance = relative molecular mass of the substance in grams = M_r grams
  This is known as the **molar mass** of the substance.
  For example, the relative molecular mass of ammonia, NH_3 = 17. Hence one mole of ammonia molecules has a mass of 17 g.
- The number of moles of molecules in a sample

$$= \frac{\text{mass in grams of the sample}}{\text{molar mass of the substance}}$$

Question

In 36 g of water,

(a) how many moles of molecules are present?

(b) how many moles of hydrogen atoms are present?

[H = 1; O = 16]

Answer

The relative molecular mass of H_2O = 18.

(a) Number of moles of H_2O molecules = $\frac{\text{mass in grams}}{\text{molar mass of } H_2O} = \frac{36}{18}$ = 2 moles

(b) Each molecule of H_2O contains two hydrogen atoms.
Number of moles of hydrogen atoms = 2 x no. of moles of H_2O molecules
= 2 x 2 = 4 moles

The Avogadro Constant

- The number of particles in one mole of any substance is a constant known as the **Avogadro constant (*L*)**.
- The Avogadro constant, $L = 6.02 \times 10^{23}\ \text{mol}^{-1}$.
- The number of particles in a sample = no. of moles x Avogadro constant

Question

How many oxygen atoms are there in 4.00 g of oxygen?
[O = 16.0; $L = 6.02 \times 10^{23}\ \text{mol}^{-1}$]

Answer

Number of moles of oxygen atoms $= \frac{\text{mass in grams}}{\text{molar mass}} = \frac{}{16.0}$

Number of oxygen atoms = no. of moles x Avogadro constant

$$= \frac{4.00}{16.0} \times 6.02 \times 10^{23} = 1.5 \times 10^{23}$$

- The Avogadro constant can be found from an electrolysis experiment (see Chapter 7).

Moles of Gases

- Equal volumes of gases, measured under the same conditions of temperature and pressure, contain equal number of moles (and therefore equal number of molecules). This is known as **Avogadro's law**.

  For example, the number of moles and molecules in 10 cm^3 of O_2 = the number of moles and molecules in 10 cm^3 of CH_4.

Question

The equation for the complete combustion of ethene is:

$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$$

What volume of oxygen is required to completely burn 50 cm^3 of ethene?

Answer

The equation shows that 3 moles of O_2 react with 1 mole of C_2H_4.

Volume of O_2 used = 3 x volume of C_2H_4

= 3 x 50 cm^3 = 150 cm^3

- At s.t.p., one mole of gas molecules occupies a volume of 22.4 dm^3. This volume is known as the **molar volume of gases** **(V_m)**.

  S.t.p. means 'standard temperature and pressure' – which is approximately 101 kPa and 273 K (0°C) (see *Molar Volume of Gases* in Chapter 5).

Question

Calculate the volume of 24 x 10^{23} molecules of gas at s.t.p.

[1 mole of gas occupies 22.4 dm^3 at s.t.p.; Avogadro constant = 6.02 x 10^{23} mol^{-1}]

Answer

Number of moles of gas $= \frac{24 \times 10^{23}}{6.02 \times 10^{23}} = 4$ moles

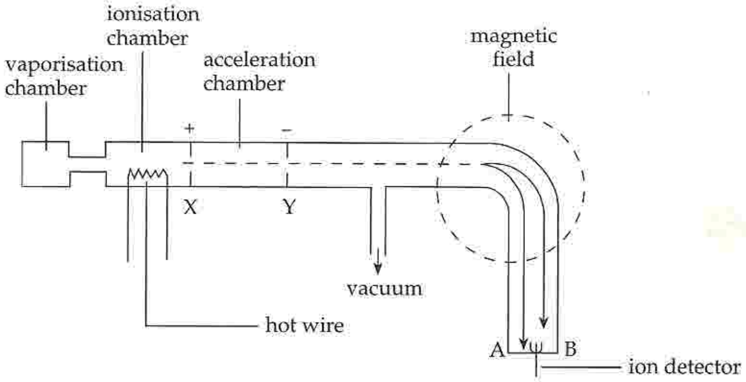
Volume of gas = no. of moles x molar volume

= 4 x 22.4 = 89.6 dm^3

1.3 Determination of Relative Atomic Mass by Mass Spectrometry

The Mass Spectrometer

- The relative mass of atoms is determined by a **mass spectrometer**. Fig 1.1 shows a simplified diagram of a mass spectrometer.



▶ Fig 1.1

- A sample of the element is placed in the vaporisation chamber, where it is vaporised into gaseous atoms.
- The gaseous atoms are then ionised by a hot wire in the ionisation chamber to become gaseous positive ions.
- In the acceleration chamber, the positive ions are accelerated by an electric field towards plate Y. This electric field is produced by a high voltage between plates X and Y.
- The positive ions are then deflected by the magnetic field. Ions with small masses are deflected the most and appear near A in the diagram. Ions with large masses are deflected the least and appear near B in the diagram.
- The ion detector determines
  (a) where, on AB, the ions appear, and
  (b) how many ions appear.
  This data is fed into a computer which then prints a **mass spectrum** of the element (Fig 1.2). The relative mass of the ion (= the relative isotopic mass of the atom) can then be calculated.
- In practice, the ion detector is kept in a fixed position. The magnetic field is varied so that ions of different masses arrive at the detector at different times.
- A pump maintains a vacuum inside the mass spectrometer as any air molecules inside would block the movement of the ions.

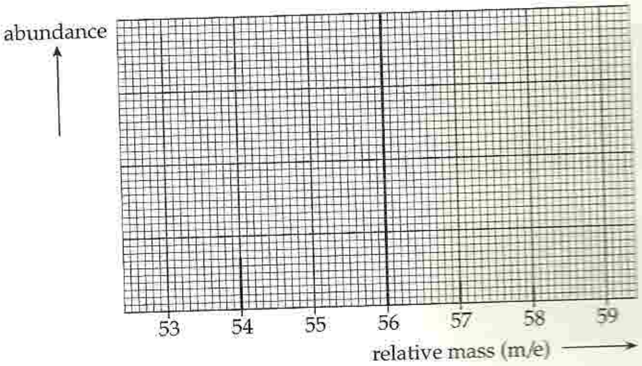
The Atomic Mass Spectrum

- The following information can be obtained from the mass spectrum of an element:
  (a) the isotopes which are present in the element;
  (b) the relative isotopic mass of each isotope;
  (c) the abundance of each isotope.
  With this information, the relative atomic mass of an element can be calculated.

- An example of a mass spectrum of an element is shown in Fig 1.2, for the element iron.

(a) The mass spectrum of iron shows that natural iron consists of four isotopes: ^{54}Fe, ^{56}Fe, ^{57}Fe and ^{58}Fe.
The height of each line is proportional to the abundance of each isotope. In this example, ^{56}Fe is the most abundant of the four isotopes.

(b) In practice, the computer will also print out the exact relative isotopic mass and abundance for each isotope (Table 1.1).



▲ Fig 1.2 Mass spectrum of iron

▶ Table 1.1

isotope	relative isotopic mass	percentage abundance
^{54}Fe	53.9396	5.82
^{56}Fe	55.9349	91.66
^{57}Fe	56.9354	2.19
^{58}Fe	57.9333	0.33

(c) The information in Table 1.1 can then be used to calculate the relative atomic mass of iron:

$$A_r \text{ of iron} = \frac{\begin{array}{c}(\text{rel. isotopic mass of } ^{54}\text{Fe x abundance}) + (\text{rel. isotopic mass of } ^{56}\text{Fe x abundance}) \\ + (\text{rel. isotopic mass of } ^{57}\text{Fe x abundance}) + (\text{rel. isotopic mass of } ^{58}\text{Fe x abundance})\end{array}}{100}$$

$$= \frac{(53.94 \times 5.82) + (55.94 \times 91.7) + (56.94 \times 2.19) + (57.93 \times 0.33)}{100} = 55.8$$

Question

Fig 1.3 shows the mass spectrum for the element rubidium, symbol Rb.

(a) What isotopes are present in rubidium?

(b) What is the percentage abundance of each of the isotopes?

(c) Calculate the relative atomic mass of rubidium.

Answer

(a) The isotopes are ^{85}Rb and ^{87}Rb.

(b) The heights of the lines are proportional to the abundance of each isotope.

isotope	*height of line*
^{85}Rb	18 units
^{87}Rb	7 units
Total:	25 units

Percentage abundance of ^{85}Rb = $\frac{18}{25}$ x 100% = 72%

Percentage abundance of ^{87}Rb = $\frac{7}{25}$ x 100% = 28%

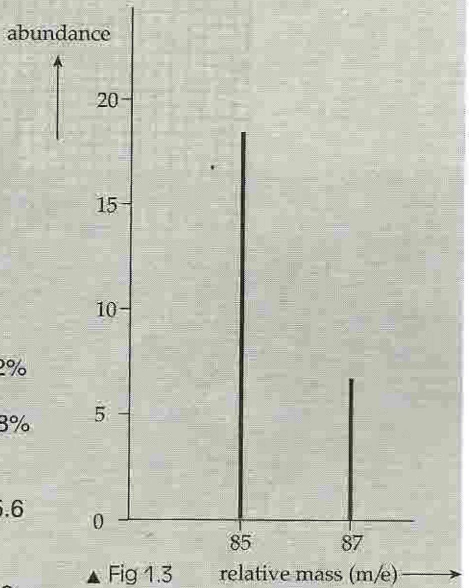
(c) *Either:*

Relative atomic mass = $\frac{(85 \times 72) + (87 \times 28)}{100}$ = 85.6

Or:

Relative atomic mass = $\frac{(85 \times 18) + (87 \times 7)}{25}$ = 85.6

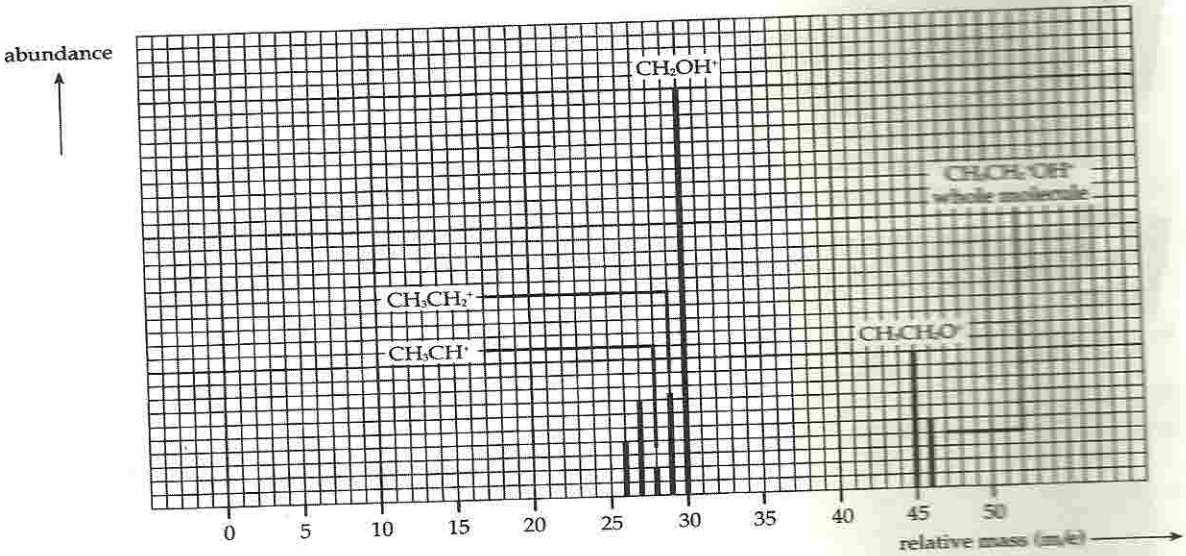
Note: As the relative isotopic mass mass number, the mass number has been used in the calculation above.



▲ Fig 1.3

1.4 Mass Spectra of Molecules

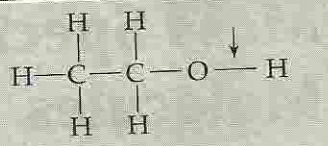
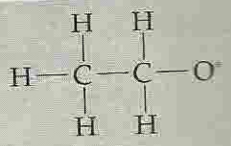
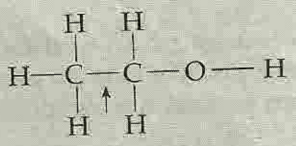
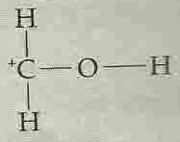
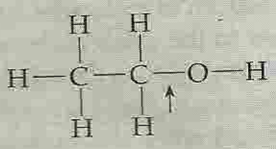
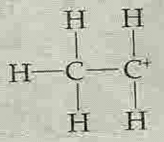
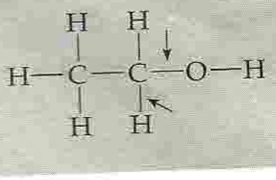
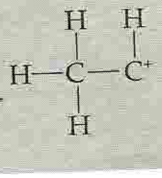
- When molecules of a substance are analysed in a mass spectrometer, positive ions are produced (like from atoms). The positive ions produce a mass spectrum.
- The mass spectrum of molecules contains two types of lines:
  - (a) a line due to the *whole* molecule. This line gives the *largest* relative mass which is the relative molecular mass.
  - (b) other lines due to *fragments* of the molecule. These fragments are produced when the molecules break up inside the mass spectrometer.
- The mass spectrum of ethanol is shown in Fig 1.4.



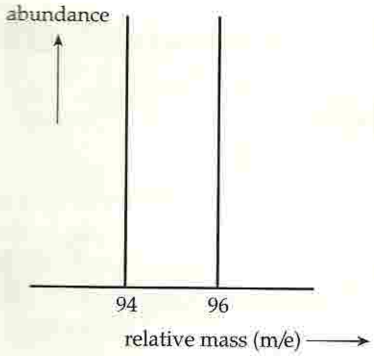
▲ Fig 1.4

(a) The line with the largest mass (mass = 46) is due to the whole molecule. Hence the relative molecular mass of ethanol = 46. Note that this line has a very small abundance as most molecules break up into fragments inside the mass spectrometer.

(b) The other lines in the mass spectrum are due to fragments of ethanol molecules, produced when the ethanol molecules break up in the ionisation chamber. Fragments are formed when one or more of the covalent bonds break – as shown in Table 1.2.

bond broken shown by arrow	fragment produced in mass spectrum	relative mass
 $H-C-C-O-H$	 $H-C-C-O^+$	45
 $H-C-C-O-H$	 $^+C-O-H$	31
 $H-C-C-O-H$	 $H-C-C^+$	29
 $H-C-C-O-H$	 $H-C-C^+$	28

▸ Table 1.2 Fragments produced from ethanol molecules



▲ Fig 1.5 Mass spectrum of CH_3Br

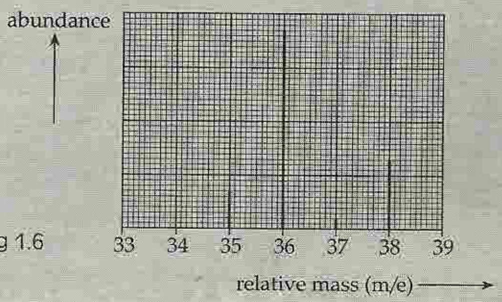
- If one of the elements in the molecule consists of two or more isotopes, then more than one line is produced by the whole molecule.

  An example is the mass spectrum of bromomethane, CH_3Br (Fig 1.5). Carbon is almost all ^{12}C and hydrogen is almost all ^{1}H. But bromine consists of roughly equal amounts of ^{79}Br and ^{81}Br. Hence the mass spectrum of bromomethane contains two lines due to CH_3Br^+:

ion in mass spectrum	*relative mass*
$^{12}C^{1}H_3{}^{79}Br^+$	94
$^{12}C^{1}H_3{}^{81}Br^+$	96

Question

The mass spectrum of hydrogen chloride is shown in Fig 1.6. Explain the mass spectrum.



▶ Fig 1.6

Answer

Hydrogen consists almost entirely of ^{1}H. Chlorine consists of the isotopes ^{35}Cl and ^{37}Cl. Hence hydrogen chloride consists of two molecules: $^{1}H^{35}Cl$ relative mass = 36
$^{1}H^{37}Cl$ relative mass = 38

These two molecules produce the lines of mass 36 and 38 in the mass spectrum. The molecules also break up in the mass spectrometer to produce Cl^+ fragments:
$^{35}Cl^+$ relative mass = 35
$^{37}Cl^+$ relative mass = 37

These two ions produce the lines of mass 35 and 37 in the mass spectrum.

line in mass spectrum relative mass	*formula of ion that produces line*
35	$^{35}Cl^+$
36	$^{1}H^{35}Cl^+$
37	$^{37}Cl^+$
38	$^{1}H^{37}Cl^+$

The ratio of the abundances of the lines at 35 and 37 is the same as the ratio of the abundances of ^{35}Cl and ^{37}Cl isotopes.

1.5 Empirical Formulae of Compounds

- The **empirical formula** of a compound shows the ratio of the atoms of each element in the compound. An example is the empirical formula of ethanoic acid which is CH_2O. This formula shows that ethanoic acid consists of the elements carbon, hydrogen and oxygen and that the atoms are in the ratio *one carbon atom : two hydrogen atoms : one oxygen atom.*
- The empirical formula of a compound can be found from the masses of the elements that combine together. The number of moles of atoms of each element that combine together can then be calculated from relative atomic masses. The ratio of the moles of each element gives the empirical formula.
- The empirical formula can also be found from the percentage composition of a compound.

Question

A sample of a compound has the composition: sodium 9.20 g; sulphur 12.8 g; oxygen 9.60 g.
Find the empirical formula.
[O = 16.0; Na = 23.0; S = 32.0]

Answer

		sodium (Na)	sulphur (S)	oxygen (O)
Step 1	Write down the mass of each element	9.20 g	12.8 g	9.60 g
Step 2	Write down the relative atomic mass of each element	23.0	32.0	16.0
Step 3	Divide each mass by its relative atomic mass to obtain the number of moles	$\frac{9.20}{23.0} = 0.40$	$\frac{12.8}{32.0} = 0.40$	$\frac{9.60}{16.0} = 0.60$
Step 4	Divide each number by the smallest (in this case it is 0.40)	$\frac{0.40}{0.40} = 1$	$\frac{0.40}{0.40} = 1$	$\frac{0.60}{0.40} = 1.5$
Step 5	Multiply each number by a convenient integer to obtain whole numbers (in this case multiply by 2)	$1 \times 2 = 2$	$1 \times 2 = 2$	$1.5 \times 2 = 3$

Note that this final step is not always necessary. The formula of the compound is $Na_2S_2O_3$.

Question An organic compound has the following percentage composition by mass: 38.7% carbon; 51.6% oxygen; 9.7% hydrogen
Find the empirical formula.
[H = 1.0; C = 12.0; O = 16.0]

Answer

		carbon (C)	oxygen (O)	hydrogen (H)
Step 1	Write down the mass of each element	38.7 g	51.6 g	9.7 g
Step 2	Write down the relative atomic mass of each element	12.0	16.0	1.0
Step 3	Divide each mass by its relative atomic mass to obtain the number of moles	$\frac{38.7}{12.0} = 3.23$	$\frac{51.6}{16.0} = 3.23$	$\frac{9.7}{1.0} = 9.7$
Step 4	Divide each number by the smallest (in this case it is 3.23)	$\frac{3.23}{3.23} = 1.0$	$\frac{3.23}{3.23} = 1.0$	$\frac{9.7}{3.23} = 3.0$

The formula of the compound is $C_1O_1H_3$ or COH_3.

1.6 Molecular Formulae

- Many substances consist of **molecules**. A molecule consists of a small number of atoms joined together by covalent bonds. The **molecular formula** shows all the atoms of each element contained in one molecule. For example, the molecular formula of butane is C_4H_{10}. This means one molecule of butane contains four carbon atoms and ten hydrogen atoms. Note that the empirical formula of butane, which only shows the ratio of the atom, is C_2H_5.

  Examples of molecular formulae include H_2O (water), H_2 (hydrogen gas), CO_2 (carbon dioxide gas) and $C_2H_4O_2$ (ethanoic acid).
- The molecular formula is a simple multiple of the empirical formula,

  molecular formula = (empirical formula)$_n$

  where $n = 1, 2, 3$ etc.
- The molecular formula can be calculated from the empirical formula and from the relative molecular mass.

Question Glucose has empirical formula CH_2O and relative molecular mass 180. Find the molecular formula of glucose.
[H = 1.0; C = 12.0; O = 16.0]

Answer

Relative mass of the empirical formula, $CH_2O = 12 + 2(1) + 16 = 30$
Relative molecular mass = n x relative mass of the empirical formula

$$\therefore (CH_2O)n = 180$$
$$30n = 180$$
$$n = \frac{180}{30} = 6$$

$$\therefore \text{molecular formula of glucose} = (CH_2O)_6 = C_6H_{12}O_6$$

1.7 Empirical Formula and Relative Molecular Mass of Gaseous Hydrocarbons

- Hydrocarbons burn in oxygen according to the equation

$$C_xH_y(g) + (x + \frac{y}{4})O_2(g) \rightarrow xCO_2(g) + \frac{y}{2}H_2O(l)$$

- Under room conditions or at s.t.p., the water product is a liquid. Hence the volume of water is negligible compared with the volumes of the C_xH_y, O_2 and CO_2 gases in the equation.
- Equal volumes of gases, under the same conditions of temperature and pressure, contain equal numbers of molecules. Hence, if 1 cm^3 of C_xH_y is completely burnt in oxygen,

  volume of oxygen used = $(x + \frac{y}{4})$ cm^3
  volume of CO_2 produced = x cm^3
  volume of water produced (as liquid) 0 cm^3

Question

10 cm^3 of a gaseous hydrocarbon required 20 cm^3 of oxygen gas for complete combustion.
10 cm^3 of carbon dioxide was produced in the combustion. All gases were measured under the same conditions. Calculate the molecular formula of the hydrocarbon and hence its relative molecular mass.

Answer

$$\begin{array}{lllll} C_xH_y & + & (x+\frac{y}{4})O_2 & \rightarrow & xCO_2 + \frac{y}{2}H_2O \\ 10\ cm^3 & & 20\ cm^3 & & 10\ cm^3 \end{array}$$

As the volumes of C_xH_y and CO_2 are the same, $x = 1$.
If 1 cm^3 of C_xH_y had been burnt, 2 cm^3 of oxygen would have been used,

ie $(x + \frac{y}{4}) = 2$

As $x = 1$, $y = 4$.
Hence the formula of the hydrocarbon = C_1H_4 or CH_4.
The relative molecular mass of the hydrocarbon = 16.

- Carbon dioxide gas can be absorbed completely by soda lime. Hence when the gaseous products of combustion are passed over soda lime, the decrease in volume of gas = volume of carbon dioxide.

Question

20 cm^3 of a gaseous hydrocarbon was mixed with 150 cm^3 of oxygen. The mixture was sparked so that the hydrocarbon was completely burnt. The gaseous products had a total volume of 130 cm^3. When this product was passed over soda lime, the volume of the product decreased to 90 cm^3. All gases were measured at s.t.p.. Deduce the molecular formula of the hydrocarbon.

Answer

Volume of carbon dioxide produced = 130 − 90 = 40 cm^3
Volume of unused oxygen remaining after combustion = 90 cm^3
Hence the volume of oxygen used in the combustion = 150 − 90 = 60 cm^3.

$$\begin{array}{lllll} C_xH_y & + & (x+\frac{y}{4})O_2 & \rightarrow & x\,CO_2 + \frac{y}{2}H_2O \\ 20\ cm^3 & & 60\ cm^3 & & 40\ cm^3 \\ 1\ cm^3 & & \frac{60}{20} = 3\ cm^3 & & \frac{40}{20} = 2\ cm^3 \end{array}$$

Hence, $x = 2$.

$(x + \frac{y}{4}) = 3$

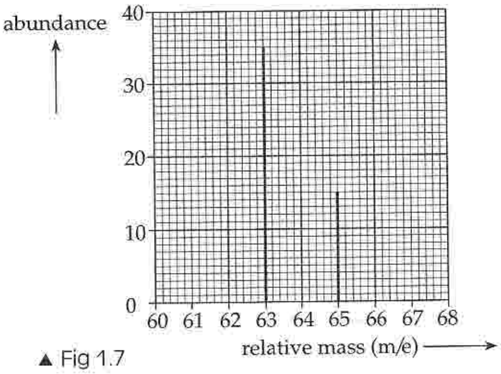
As $x = 2$, $y = 4$. Therefore the formula of the hydrocarbon = C_2H_4.

EXERCISE 1

Multiple Choice Questions

Section I

1



▲ Fig 1.7

The atomic mass spectrum of an element is shown in Fig 1.7. What is the relative atomic mass of the element?

A 64.0 **C** 63.6
B 63.8 **D** 63.4

2 A sample of plutonium from a nuclear reactor was found to have the following composition:

isotope	*percentage abundance*
^{239}Pu	50
^{240}Pu	30
^{241}Pu	15
^{242}Pu	5

What is the relative atomic mass of the plutonium sample?

A 239.25 **C** 239.75
B 239.50 **D** 240.50

3 The relative molecular mass of ^{12}CO is 27.9994. What is the relative molecular mass of $^{12}CO_2$?

A 43.9982 **C** 43.9994
B 43.9988 **D** 44.0000

4 The Avogadro constant, $L = 6.0\ \ 10^{23}$ mol^{-1}. What is the mass of one molecule of water? [relative molecular mass = 18]

A $\frac{6.0 \times 10^{23}}{18}$ g **C** $\frac{6.0}{18} \times 10^{-23}$ g

B $\frac{18}{6.0 \times 10^{23}}$ g **D** $\frac{1}{6.0 \times 18 \times 10^{23}}$ g

5 Which one of the following is the relative atomic mass of an element?

A $\dfrac{\text{average mass of one atom of the element}}{\text{mass of one atom of } ^{1}\text{H}}$

B $\dfrac{\text{average mass of one atom of the element}}{\frac{1}{12} \times \text{average mass of one atom of carbon}}$

C $\dfrac{\text{average mass of one atom of the element}}{\text{mass of one atom of } ^{12}\text{C}}$

D $\dfrac{\text{average mass of one atom of the element}}{\frac{1}{12} \times \text{mass of one atom of } ^{12}\text{C}}$

6 How many atoms are present in 8.8 g of carbon dioxide? [C = 12; O = 16; Avogadro constant = 6.0×10^{23} mol^{-1}]

A 1.2×10^{23} **C** 3.6×10^{23}
B 2.4×10^{23} **D** 52.8×10^{23}

7 How many *hydrogen atoms* are present in 15 g of ethane, C_2H_6? [H = 1, C = 12; Avogadro constant = 6.0×10^{23} mol^{-1}]

A $15 \times 6.0 \times 10^{23}$
B $15 \times 6 \times 6.0 \times 10^{23}$
C $\frac{15}{30} \times 8 \times 6.0 \times 10^{23}$
D $\frac{15}{30} \times 6 \times 6.0 \times 10^{23}$

8 Which one of the following contains the largest number of *atoms*? [H = 1; C = 12; F = 19; Br = 80]

A 8 g of methane
B 15 g of hydrogen fluoride
C 15.6 g of benzene
D 21.8 g of bromoethane

9 Which one of the following contains the largest number of molecules? All the samples are at s.t.p. [H = 1; C = 12; Br = 80; 1 mol of gas has a volume of 22.4 dm^3 at s.t.p.]

A 1 dm^3 of carbon dioxide, CO_2
B 1 g of methane, CH_4
C 1 dm^3 of hydrogen, H_2
D 1 g of bromine, Br_2

10 20 cm³ of a gaseous alkane required 100 cm³ of oxygen for complete combustion (both volumes measured at the same temperature and pressure). What is the formula of the alkane?

A C_2H_6 C C_4H_{10}
B C_3H_8 D C_5H_{12}

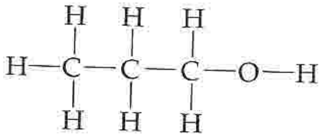
11 10 cm³ of propene, C_3H_6, was completely burnt in oxygen. What are the volumes of oxygen gas used and carbon dioxide produced (measured under the same conditions of temperature and pressure)?

	volume of oxygen	*volume of carbon dioxide*
A	30 cm³	30 cm³
B	45 cm³	30 cm³
C	45 cm³	60 cm³
D	90 cm³	60 cm³

12 The relative molecular mass of methane, CH_4, is 16.043. What is the relative molecular mass of ethane, C_2H_6? [C = 12.011]

A 30.022 C 30.070
B 30.064 D 30.086

*13



$$H-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-O-H$$

The structure of a molecule of propan–l–ol is shown above. Which line is least likely to be found in the mass spectrum of propan–l–ol?

	relative mass of line
A	17
B	21
C	29
D	59

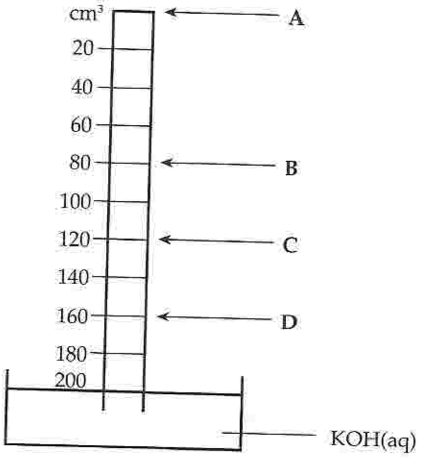
*14 Which of the following relative mass (m/e) values corresponds to the mass spectrum of chlorine gas?

A 35 36 37
B 35 35.5 37
C 35 37 70 74
D 35 37 70 72 74

15 A tube is filled with 40 cm³ of methane and 160 cm³ of oxygen at room temperature. The open end of the tube is placed in a beaker of KOH(aq) as shown in Fig 1.8. The gas mixture was sparked to make the following reaction take place:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

What is the final level of liquid in the tube after it has cooled back to room temperature?



▶ Fig 1.8

Section II

Summary of directions

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

16 Which of the following contain the same number of atoms as 6.0 g of water, H_2O?
[H = 1; He = 4; O = 16; 1 mol of gas occupies 22.4 dm³ at s.t.p.]
1 16.0 g of oxygen, O_2
2 22.4 dm³ of hydrogen, H_2, at s.t.p.
3 6.0 g of helium, He

17 A sample of ethanol contains 3×10^{23} carbon atoms. The sample contains
1 0.25 mol of oxygen atoms.
2 1.5 mol of hydrogen atoms.
3 0.5 mol of ethanol molecules.
[Avogadro constant = 6.0×10^{23} mol⁻¹]

18 Which of the following could not appear in the mass spectrum of methane, CH_4?
1 CH_5^+ 2 CH_2^{2+} 3 CH_3^+

Structured Questions

*1 (a) Define *relative atomic mass, A_r*.
(b) The element silver is used in the photographic industry and consists of the two naturally occurring isotopes given in the table below.

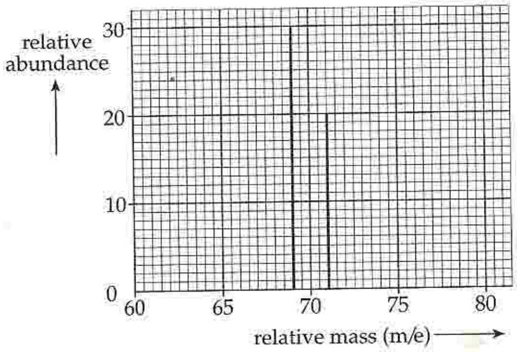
isotope	number of protons	number of neutrons	percentage abundance
^{107}Ag			51.4
^{109}Ag			48.6

(i) Complete the table, using the *Data Tables* at the end of this book to help you.

(ii) Use the data in the table to write an expression for the relative atomic mass of silver.

*2 The element gallium (symbol Ga) is used in light emitting diodes.

(a) The atomic mass spectrum of natural gallium is shown in Fig 1.9.



▲ Fig 1.9

(i) Write in symbol form the isotopes present in natural gallium.

(ii) Use the information in the mass spectrum to calculate a value for the relative atomic mass, A_r, of gallium.

(b) Gallium forms the oxide, Ga_2O_3. This oxide reacts with gallium, under suitable conditions, to produce another oxide containing 89.7% gallium.

(i) Calculate the empirical formula of the second oxide.

(ii) Construct a balanced equation for the formation of this oxide from Ga_2O_3.

3 Water consists of the isotopes ^1H, ^2H and ^{16}O.

(a) Write down the formulae of all the different H_2O molecules in water.

(b) Which one of these molecules has the largest mass?

(c) A sample of water was analysed in a mass spectrometer. Write the formulae of the ions that produce the following eight peaks in the mass spectrum.

relative mass	1	2	3	4	17	18	19	20
formula of ion								

4 A mixture of $^2H_2$ and $^{81}Br_2$ was analysed in a mass spectrometer. The mass spectrum was found to contain the following lines:

line	relative mass
I	2
II	4
III	81
IV	83
V	162

(a) Give the formulae of the particles that produce the lines I to V.

(b) Explain how the particles of line IV are produced.

5 Ethanol has molecular formula C_2H_5OH. A sample of ethanol has a mass of 2.3 g.

(a) (i) How many moles of ethanol molecules are present in the sample?

(ii) How many molecules are present in the sample?

(iii) How many hydrogen atoms are present in the sample?

(b) The sample was completely burnt in oxygen.

(i) Write down a balanced equation for the combustion.

(ii) How many moles of water molecules were produced in the combustion?

(iii) What mass of carbon dioxide was produced in the combustion?

(iv) How many oxygen molecules were used up in the combustion?

[H = 1; C = 12; O = 16; Avogadro constant = 6.0×10^{23} mol^{-1}]

6 20 cm^3 of a gaseous hydrocarbon was mixed with 100 cm^3 of oxygen and the mixture sparked so that the hydrocarbon was completely burnt. The volume of gas remaining at the end of the combustion was 70 cm^3. After passing over soda lime, this volume was reduced to 10 cm^3. All gases were measured at 25°C and at the same pressure.

(a) What volume of oxygen gas remained unburnt at the end?
(b) What volume of oxygen gas was used in the combustion?
(c) What volume of carbon dioxide was produced in the combustion?
(d) Deduce the formula of the hydrocarbon.
(e) What is the relative molecular mass of the hydrocarbon?
[H = 1; C = 12]

7 (a) What do you understand by the following terms:-
(i) relative atomic mass
(ii) relative isotopic mass
(iii) the nucleon number

(b) Explain how the mass spectrograph of an element can be used to determine the relative atomic mass of an element. Hence suggest why the relative atomic mass of some elements are not always integers.

(c) The carbon tetrachloride molecule, CCl_4, contains atoms of carbon and chlorine. Carbon exists mainly in two isotopic form, ^{12}C and ^{13}C in the abundance ratio 9:1 and chlorine exists in two isotopic form ^{35}Cl and ^{37}Cl in the abundance ratio 3:1
(i) Determine all the peaks that will appear in the mass spectrograph of carbon tetrachloride.
(ii) Calculate the relative intensities of the lines due to CCl_4^+ ion.

(d) A sample of ethanol is suspected to be contaminated with propanone. Describe how the mass spectrograph can be used to check for the purity of the ethanol.

Descriptive Questions

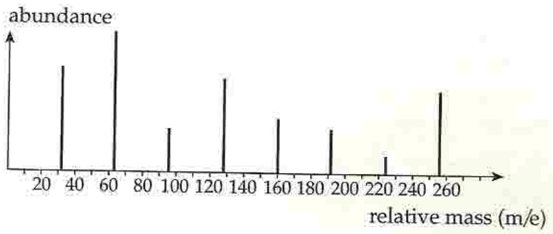
1 (a) Define *relative isotopic mass.*

(b) The mass spectrum of boron consists of two peaks. One peak is at relative mass (m/e) 10 and the other peak at relative mass 11. The two peaks have relative abundances of 1 : 4. Show how this data can be used to determine the relative atomic mass of boron.

(c) Boron forms a molecular hydride containing 15.6% hydrogen and with a relative molecular mass of 102. Use this data and the relative atomic mass of boron from the *Data Tables* at the end of this book to calculate the empirical and molecular formulae of the hydride.

*2 (a) The mass spectrum of chloromethane, CH_3Cl, has two major peaks with relative masses of 50 and 52. Explain this fact.

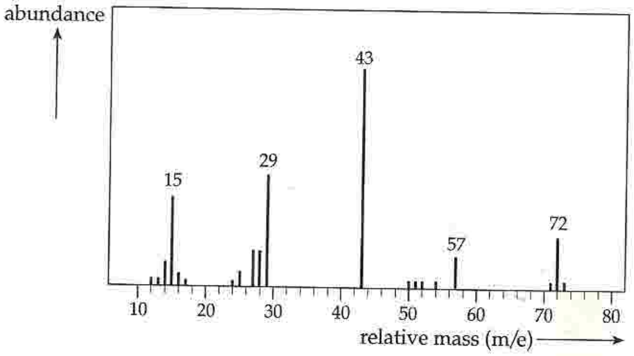
(b) The mass spectrum of sulphur vapour is shown in Fig 1.10. Explain the mass spectrum as fully as you can.



▲ Fig 1.10

3 (a) Define the terms
(i) *empirical formula;*
(ii) *molecular formula.*

(b) Compound Z has composition by mass: 66.7% carbon; 22.2% oxygen and 11.1% hydrogen. The mass spectrum of Z is shown in Fig 1.11.



▲ Fig 1.11

Calculate the empirical formula of Z. Using the mass spectrum to determine the molecular formula of Z, suggest a possible structural formula for Z and suggest the formulae of the numbered peaks in the mass spectrum.

*4 (a) (i) What do you understand by the term isomers?

(ii) Write the structural formulas for all isomers which may be represented by the molecular formula C_2H_6O and describe how you are going to identify each of the isomers using mass spectroscopy.

(b) What are the peaks that may be expected to be obtained when the mass spectrograph of ethanal is determined.

(c) A compound, X, contains 54.6% of carbon, 9.1% of hydrogen and 36.3% of oxygen. Some peaks were observed in the mass spectrograph of X at the m/e values shown below :-

m/e	Ions
1	
15	
29	
43	
46	
59	
88	

(i) Complete the table above by writing the ions responsible for each peak.

(ii) Deduce the possible identity of X.

(iii) What further information is required to confirm the identity of X?

*5 (a) Magnesium exists in three isotopic forms. The specific masses and relative abundancies of two of the three isotopes of magnesium are tabulated below:

Specific masses	Relative abundancies,%
25.0	10.1
26.0	11.2

Use the Data Booklet to determine for the third isotope of magnesium:-

(i) its relative abundancy

(ii) its relative isotopic mass.

(b) The two main isotopes of copper are ^{63}Cu nd ^{65}Cu. The relative atomic mass of copper is 63.4.

(i) Which of these two isotopes is the more abundant?

(ii) Calculate the relative abundances of the two isotopes.

(iii) What is the ratio of the number of ^{63}Cu atoms to ^{65}Cu atoms that is expected to be found in a natural sample of copper.

CHAPTER

2

ATOMIC STRUCTURES

- Atomic Particles
- Structure of the Atom
- Structure of Ions
- Isotopes
- Electronic Configuration
- Formula of Ions
- Ionisation Energy
- Shapes of Orbitals

SYLLABUS OBJECTIVES

In this chapter you should be able to:

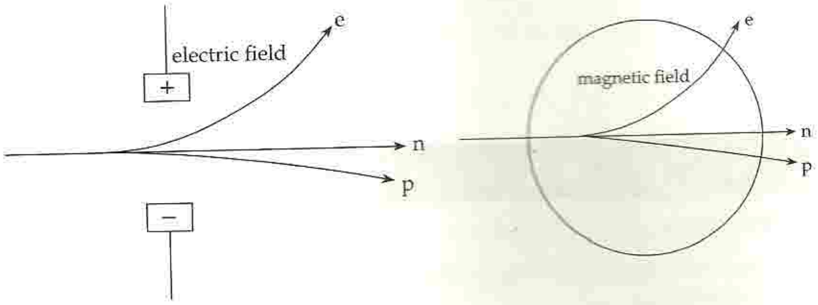
- describe the relative masses and electric charges of protons, neutrons and electrons
- predict how protons, neutrons and electrons move in electric and magnetic fields
- describe the distribution of mass and electric charge within an atom
- deduce the number of protons, neutrons and electrons in atoms and ions
- work out the number of protons and neutrons in atoms from nucleon and proton numbers
- distinguish between isotopes from the number of neutrons in their atoms
- describe the number and relative energy of the *s*, *p* and *d* orbitals of the 1st, 2nd and 3rd main quantum levels and of the 4*s* and 4*p* main quantum level of the 4th shell
- describe the shapes of *s* and *p* orbitals
- state the electronic configurations of atoms, and their ions, of all elements up to proton number 36 (krypton)
- explain the factors that influence ionisation energies
- predict the electronic configuration of elements from successive ionisation energies
- use successive ionisation energies to find the position of elements in the Periodic Table (eg the Group it is in)

2.1 Atomic Particles

- Atoms are made of **protons, neutrons and electrons**.
- The charges of protons, neutrons and electrons and their relative masses have already been given in section 1.1
- Protons are positively charged and are attracted to negative electrodes. Electrons are negatively charged and are attracted to positive electrodes. Neutrons are neutral and are not attracted to charged electrodes.

  The deflection of the three types of atomic particles in an electric field is shown in Fig 2.1.

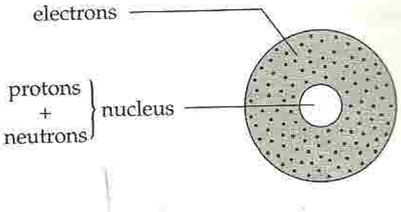
  Moving protons and electrons are deflected by a magnetic field. Neutrons are not deflected by a magnetic field. The deflection of the three types of atomic particles in a magnetic field is also shown in Fig 2.1.



▶ Fig 2.1 Deflection of atomic particles in electric and magnetic fields

2.2 Structure of the Atom

- The protons and neutrons are found in the nucleus of the atom while the electrons surround the nucleus (Fig 2.2).
- As protons and neutrons have much larger mass than electrons, almost all the mass of an atom is concentrated in the nucleus.
- The sum of the protons in an atom is called the **proton number** (Z).



▲ Fig 2.2 Structure of an atom

- The sum of the protons and the neutrons in an atom is called the **nucleon number**.
- The relative mass of an atom is *almost* the same as its nucleon number. The nucleon number is sometimes used as the approximate relative mass in calculations (see Chapter 1).
- The symbol for an atom:

nucleon number
charge on atom or ion
Element Symbol
proton number

For example, the symbol for the most common atom of carbon is $^{12}_{6}C$. The composition of this atom is:

6 protons (equals the proton number)
12 – 6 = 6 neutrons (nucleon number – proton number)
6 electrons (same as the number of protons)

2.3 Structure of Ions

- In a neutral atom, number of electrons = number of protons.
- In a negative ion, the number of electrons is *greater than* the number of protons. A negative ion is obtained by adding electrons to a neutral atom.

  For example, the most common ion of oxygen is $^{16}_{8}O^{2-}$. The composition of this ion is:

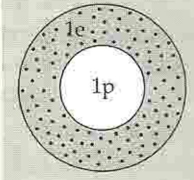
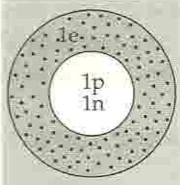
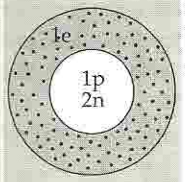
  8 protons
  16 – 8 = 8 neutrons
  neutral O atom has 8 electrons, so the O^{2-} ions has 8 + 2 = 10 electrons
- In a positive ion, the number of electrons is *less than* the number of protons. A positive ion is obtained by removing electrons from a neutral atom.

  For example, the most common sodium ion is $^{23}_{11}Na^{+}$. The composition of this sodium ion is:

  11 protons
  23 – 11 = 12 neutrons
  neutral Na atom has 11 electrons, so Na^{+} ion has 11 – 1 = 10 electrons
- The mass of an ion is virtually the same as the mass of a neutral atom, because electrons have very small masses compared with protons and neutrons.

2.4 Isotopes

- Atoms of the same element with the same proton number *different numbers of neutrons* are called **isotopes**.
- The three isotopes of hydrogen are shown in Table 2.2.

structure of neutral atom			
proton number	1	1	1
number of neutrons	0	1	2
nucleon number (number of protons + neutrons)	1	2	3
relative isotopic mass (mass of atom compared with $\frac{1}{12}$ of the mass of an atom of ${}^{12}C$)	1.007825	2.014102	3.016049
atom in symbol form	${}^{1}_{1}H$	${}^{2}_{1}H$	${}^{3}_{1}H$

▶ Table 2.2

- Isotopes of the same element can be recognised from their identical element symbol or proton number. For example, ${}^{12}_{6}C$ and ${}^{14}_{6}C$ are isotopes of carbon. The same C symbol and proton number 6 means that they are atoms of the same element. The different nucleon numbers, 12 and 14, show that they are isotopes.
- Isotopes of an element have the *same*:
  - (a) proton number;
  - (b) number of electrons in a neutral atom;
  - (c) electronic configuration;
  - (d) chemical properties.
- Isotopes of an element have *different*:
  - (a) numbers of neutrons in an atom;
  - (b) nucleon numbers;
  - (c) relative isotopic mass;
  - (d) physical properties (eg melting point, density), though these differences are very small.

Question

A sample of carbon consists of the isotopes ${}^{12}C$ and ${}^{13}C$. A sample of oxygen consists of the isotopes ${}^{16}O$ and ${}^{17}O$. Write the formulae of all the different CO_2 molecules that can be formed from these samples.
Which molecule has the largest mass?

Answer

There are six different molecules:

$^{12}C^{16}O_2$, $^{12}C^{16}O^{17}O$, $^{12}C^{17}O_2$, $^{13}C^{16}O_2$, $^{13}C^{16}O^{17}O$ and $^{13}C^{17}O_2$

The molecule with the largest mass is $^{13}C^{17}O_2$. It has a relative mass of approximately 13 + 2(17) = 47.

2.5 Electronic Configurations

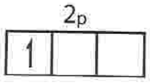
- Electrons are arranged around the nucleus of an atom, in **energy levels**. The energy levels are numbered 1, 2, 3 etc, starting from the nucleus. These numbers are known as **principal quantum numbers n,** where n = 1,2,3 ...etc).
- Each main quantum level consists of a number of **sublevels**, labelled *s, p, d,* or *f*. The number of sublevels in each shell equals the quantum number. Hence, the n = 1 has *one* sublevels, n = 2 has *two* sublevels, etc.

Main quantum level, ***n***	number of sublevels in the mainlevel	identity of sublevels
1	1	1*s*
2	2	2*s* and 2*p*
3	3	3*s*, 3*p* and 3*d*

- Each sublevel contains a number of **orbitals**, in which the electrons are placed. The number of orbitals in each sublevel depends on the type of sublevel.

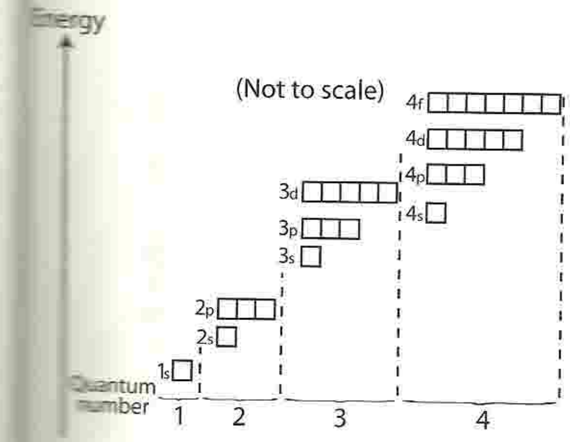
type of sublevel	*number of orbitals*
s	1
p	3
d	5
f	7

- Each orbital can be represented by a square box. Hence the three 2*p* orbitals are represented as shown below.



An electron is represented by an arrow, ↑ or ↓. Thus one electron is shown in the set of 2*p* orbitals drawn above.

- The relative energies of the orbitals of atoms up to approximately atomic number 20, are shown in Fig 2.3.



▲ Fig 2.3 Energy levels of atoms

Figure 2.3 shows that the sublevels of the second quantum level (2*s* and 2*p*) are both higher in energy than the single sublevel (1*s*) of the first quantum level. All three sublevels of the third quantum level (3*s*, 3*p* and 3*d*) have higher energy than the sublevel of the second quantum level. However, the 4*s* sublevel of the fourth quantum level has overlapped the 3*d* sublevel. This is important in the ***Electronic Configuration of Atoms*** see later): electrons fill the lower energy 4*s* before the 3*d* (see the electronic configurations of potassium and calcium in Table 2.3).

Electronic Configuration of Atoms

- The arrangement of electrons in atoms is known as the **electronic configuration**.

- Electrons are arranged in orbitals according to a set of rules:
  - (a) Each orbital can hold a maximum of two electrons.
  - (b) Electrons always go into an empty orbital with the lowest energy.
  - (c) In a sublevel, electrons stay as far apart as possible. Hence two electrons will go into two different orbitals of the same energy, rather than into the same orbital.
  - (d) Electrons have spin. An electron can spin in two different directions – shown as $\upharpoonleft$ or $\downharpoonright$.
    - (i) Two electrons in the same orbital (ie same 'box') have *opposite* spins.

      ie $\boxed{\upharpoonleft\downharpoonright}$ and not $\boxed{\upharpoonleft\upharpoonleft}$

    - (ii) Single electrons in the same sublevel have the same spin.

      ie $\boxed{\upharpoonleft}\boxed{\upharpoonleft}\boxed{}$ and not $\boxed{\upharpoonleft}\boxed{\downharpoonright}\boxed{}$

- The electronic configuration of the hydrogen atom (Z = 1) is

  $$\overset{1s}{\boxed{\upharpoonleft}}$$

  It can also be written simply as $1s^1$.

- The electronic configuration of the helium atom (Z = 2) is

  $$\overset{1s}{\boxed{\upharpoonleft\downharpoonright}}$$

  (Remember that electrons in the same orbital must have opposite spins.) It can also be written simply as $1s^2$.

- The lithium atom (Z = 3) has three electrons. Two electrons go into the 1*s* orbital. The 1*s* orbital is now full; so the third electron goes into the 2*s* orbital (the next orbital with lowest energy). The electronic configuration is

  $$\overset{1s}{\boxed{\upharpoonleft\downharpoonright}} \quad \overset{2s}{\boxed{\upharpoonleft}}$$

  It can also be written simply as $1s^2\,2s^1$.

- Beryllium (Z = 4) has the electronic configuration

$$\overset{1s}{\boxed{\uparrow\downarrow}} \quad \overset{2s}{\boxed{\uparrow\downarrow}}$$

This can be written simply as $1s^2\,2s^2$.

- Boron (Z = 5) has five electrons. The first four electrons fill the 1*s* and 2*s* orbitals. So the fifth electron goes into the 2*p* orbital. The electronic configuration is

$$\overset{1s}{\boxed{\uparrow\downarrow}} \quad \overset{2s}{\boxed{\uparrow\downarrow}} \quad \overset{2p}{\boxed{\uparrow}\boxed{}\boxed{}}$$

or simply $1s^2\,2s^2\,2p^1$

- Carbon (Z = 6) has six electrons. Two electrons must be in the 2*p* orbitals. The correct electronic configuration is

$$\overset{1s}{\boxed{\uparrow\downarrow}} \quad \overset{2s}{\boxed{\uparrow\downarrow}} \quad \overset{2p}{\boxed{\uparrow}\boxed{\uparrow}\boxed{}}$$

or simply $1s^2\,2s^2\,2p^2$

The following electronic configurations for carbon are *wrong*:

Reason for error:

$$\overset{1s}{\boxed{\uparrow\downarrow}} \quad \overset{2s}{\boxed{\uparrow\downarrow}} \quad \overset{2p}{\boxed{\uparrow\downarrow}\boxed{}\boxed{}}$$

– the 2*p* electrons should be in *different* orbitals

$$\boxed{\uparrow\downarrow} \quad \boxed{\uparrow\downarrow} \quad \boxed{\uparrow}\boxed{\downarrow}\boxed{}$$

– the single electrons in the same sublevel should have the same spin

$$\boxed{\uparrow\downarrow} \quad \boxed{\uparrow} \quad \boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}$$

– the 2*s* orbital has space for one more electron so it should contain 2 electrons (electrons go into the orbital with lowest level energy, where there is space)

- The electronic configurations of the first 38 elements (Z = 1 to 38) are shown in Table 2.3. These are known as the **ground state** electronic configurations of the elements.

element	atomic number	electronic configuration	simplified electronic configuration
hydrogen	1	$\overset{1s}{\boxed{\uparrow}}$	$1s^1$
helium	2	$\boxed{\uparrow\downarrow}$	$1s^2$
lithium	3	$\boxed{\uparrow\downarrow} \quad \overset{2s}{\boxed{\uparrow}}$	$1s^2 2s^1$

▲ Table 2.3 Electronic configuration of isolated atoms in the ground state

(continued)

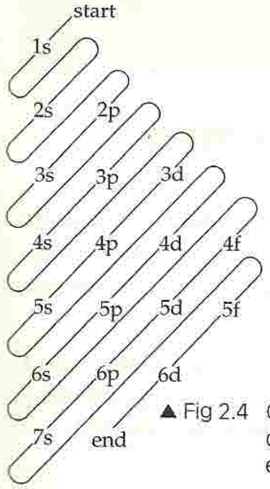
element	atomic number	electronic configuration	simplified electronic configuration
beryllium	4	1s [⇅] 2s [⇅]	$1s^22s^2$
boron	5	[⇅] [⇅] 2p [↑][ ][ ]	$1s^22s^22p^1$
carbon	6	[⇅] [⇅] [↑][↑][ ]	$1s^22s^22p^2$
nitrogen	7	[⇅] [⇅] [↑][↑][↑]	$1s^22s^22p^3$
oxygen	8	[⇅] [⇅] [⇅][↑][↑]	$1s^22s^22p^4$
fluorine	9	[⇅] [⇅] [⇅][⇅][↑]	$1s^22s^22p^5$
neon	10	[⇅] [⇅] [⇅][⇅][⇅]	$1s^22s^22p^6$
sodium	11	[⇅] [⇅] [⇅][⇅][⇅] 3s [↑]	$1s^22s^22p^63s^1$
magnesium	12	[⇅] [⇅] [⇅][⇅][⇅] [⇅]	$1s^22s^22p^63s^2$
aluminium	13	[⇅] [⇅] [⇅][⇅][⇅] [⇅] 3p [↑][ ][ ]	$1s^22s^22p^63s^23p^1$
silicon	14	[⇅] [⇅] [⇅][⇅][⇅] [⇅] [↑][↑][ ]	$1s^22s^22p^63s^23p^2$
phosphorus	15	[⇅] [⇅] [⇅][⇅][⇅] [⇅] [↑][↑][↑]	$1s^22s^22p^63s^23p^3$
sulfur	16	[⇅] [⇅] [⇅][⇅][⇅] [⇅] [⇅][↑][↑]	$1s^22s^22p^63s^23p^4$
chlorine	17	[⇅] [⇅] [⇅][⇅][⇅] [⇅] [⇅][⇅][↑]	$1s^22s^22p^63s^23p^5$
argon	18	[⇅] [⇅] [⇅][⇅][⇅] [⇅] [⇅][⇅][⇅]	$1s^22s^22p^63s^23p^6$
potassium	19	[⇅] [⇅] [⇅][⇅][⇅] [⇅] [⇅][⇅][⇅] 4s [↑]	$1s^22s^22p^63s^23p^64s^1$
calcium	20	[Ar] 4s [⇅]	$1s^22s^22p^63s^23p^64s^2$
scandium	21	[Ar] [⇅] 3d [↑][ ][ ][ ][ ]	$1s^22s^22p^63s^23p^64s^23d^1$
titanium	22	[Ar] [⇅] [↑][↑][ ][ ][ ]	$1s^22s^22p^63s^23p^64s^23d^2$
vanadium	23	[Ar] [⇅] [↑][↑][↑][ ][ ]	$1s^22s^22p^63s^23p^64s^23d^3$
chromium	24	[Ar] [↑] [↑][↑][↑][↑][↑]	$1s^22s^22p^63s^23p^64s^13d^5$
manganese	25	[Ar] [⇅] [↑][↑][↑][↑][↑]	$1s^22s^22p^63s^23p^64s^23d^5$
iron	26	[Ar] [⇅] [⇅][↑][↑][↑][↑]	$1s^22s^22p^63s^23p^64s^23d^6$

(continued)

element	atomic number	electronic configuration	simplified electronic configuration
cobalt	27	[Ar] [⇅] [⇅ ⇅ ↑ ↑ ↑]	$1s^22s^22p^63s^23p^64s^23d^7$
nickel	28	[Ar] [⇅] [⇅ ⇅ ⇅ ⇅ ⇅]	$1s^22s^22p^63s^23p^64s^23d^8$
copper	29	[Ar] [↑] [⇅ ⇅ ⇅ ⇅ ⇅]	$1s^22s^22p^63s^23p^64s^13d^{10}$
zinc	30	[Ar] [⇅] [⇅ ⇅ ⇅ ⇅ ⇅]	$1s^22s^22p^63s^23p^64s^23d^{10}$
gallium	31	[Ar] [⇅] [⇅ ⇅ ⇅ ⇅ ⇅] 4p [↑ ☐ ☐]	$1s^22s^22p^63s^23p^64s^23d^{10}4p^1$
germanium	32	[Ar] [⇅] [⇅ ⇅ ⇅ ⇅ ⇅] [↑ ↑ ☐]	$1s^22s^22p^63s^23p^64s^23d^{10}4p^2$
arsenic	33	[Ar] [⇅] [⇅ ⇅ ⇅ ⇅ ⇅] [↑ ↑ ↑]	$1s^22s^22p^63s^23p^64s^23d^{10}4p^3$
selenium	34	[Ar] [⇅] [⇅ ⇅ ⇅ ⇅ ⇅] [⇅ ↑ ↑]	$1s^22s^22p^63s^23p^64s^23d^{10}4p^4$
bromine	35	[Ar] [⇅] [⇅ ⇅ ⇅ ⇅ ⇅] [⇅ ⇅ ↑]	$1s^22s^22p^63s^23p^64s^23d^{10}4p^5$
krypton	36	[Ar] [⇅] [⇅ ⇅ ⇅ ⇅ ⇅] [⇅ ⇅ ⇅]	$1s^22s^22p^63s^23p^64s^23d^{10}4p^6$
rubidium	37	[Ar] [⇅] [⇅ ⇅ ⇅ ⇅ ⇅] [⇅ ⇅ ⇅] 5s [↑]	$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^1$
strontium	38	[Ar] [⇅] [⇅ ⇅ ⇅ ⇅ ⇅] [⇅ ⇅ ⇅] [⇅]	$1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^2$

Note: The symbol [Ar] in the table represents the electronic configuration of argon. Thus the electronic configuration of scandium is

1s	2s	2p	3s	3p	4s	3d
[⇅]	[⇅]	[⇅ ⇅ ⇅]	⇅	[⇅ ⇅ ⇅]	⇅	[↑ ☐ ☐ ☐ ☐]

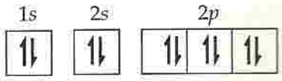


▲ Fig 2.4 Order of filling orbitals with electrons

- The diagram in Fig 2.4 is a useful way to remember the order of filling orbitals with electrons.
- Two elements have unexpected electronic configurations:
  (a) The electronic configuration of chromium is … $4s^1\ 3d^5$ and not $4s^2\ 3d^4$ as expected. This is because the first arrangement has less interelectronic repulsion, since the $3d$ sublevel is single occupied.
  (b) The electronic configuration of copper is … $4s^1\ 3d^{10}$ and not $4s^2\ 3d^9$ because a completely filled $3d$ sublevel is more stable.

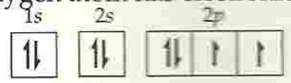
Electronic Configuration of Ions

- The same rules apply in the addition of extra electrons to form negative ions. Hence the electronic configuration of the fluoride ion, F^- is



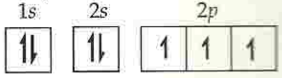
or simply $1s^2\,2s^2\,2p^6$

- To obtain the electronic configuration of positive ions, electrons are removed in the reverse order (ie the last electron is removed first). For example, the oxygen atom has electronic configuration



Thus the oxygen ion, O^+, is obtained by removing one electron from the oxygen atom. The electron removed is the last one (from the 2*p* subshell):

O^+ ion:

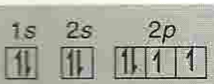


or simply $1s^2\,2s^2\,2p^3$

Question What are the electronic configurations of (a) the O^{6+} ion, and (b) the P^{3-} ion?

Answer

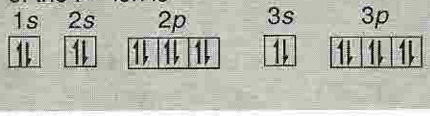
(a) The electronic configuration of the oxygen atom is



To obtain O^{6+}, six electrons are removed. Hence the last six electrons are removed – the four electrons from the 2*p*, and the two electrons from the 2*s*. The electronic configuration of O^{6+} is

(b) The electronic configuration of the phosphorus atom is

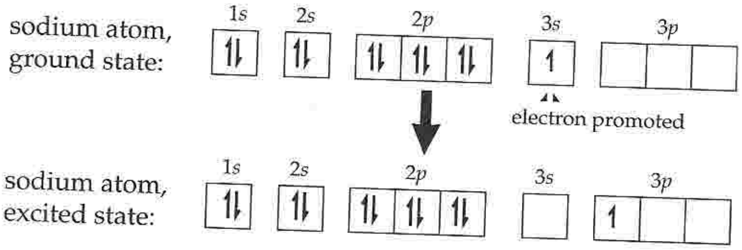
To obtain P^{3-}, three more electrons must be added. Hence the electronic configuration of the P^{3-} ion is



Electronic Configurations of Excited Atoms and Ions

- When the electrons of an atom or ion are in orbitals of lowest energy, the atoms or ions are said to be in their **ground state**. All the electronic structures described earlier in this chapter are ground state structures.
- When one or more electrons of an atom or ion absorb energy and move from their ground state orbitals into higher energy orbitals, the electrons are said to be **promoted** and the atoms **excited**.

- An example of an excited sodium atom is shown below:



2.6 Formula of Ions

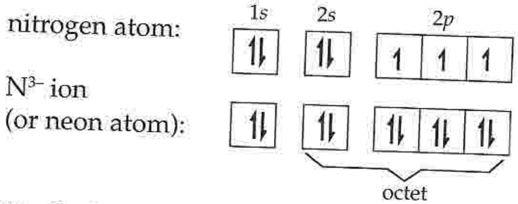
The Octet Rule

- The electron arrangements of noble gases are relatively stable. Atoms of noble gases do not lose or gain electrons to form ions in compounds.

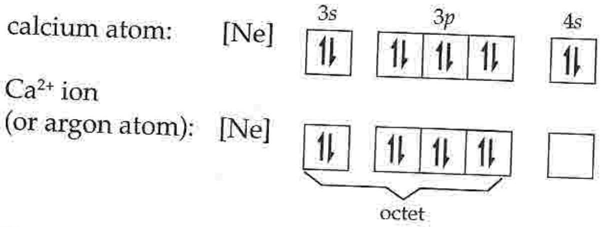
  Atoms of noble gases (except helium) have eight electrons in their outer orbital (a stable 'octet').

- According to the **octet rule**, atoms form ions by losing or gaining electrons to attain the electron arrangement of a noble gas (ie eight electrons in their outer orbitals).

  For example, nitrogen gains three electrons to attain the electron arrangement of neon (the nearest noble gas):



Similarly, calcium loses two electrons to obtain the electron arrangement of argon:

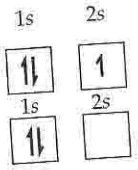


- The octet rule successfully predicts the formulae of ions formed by elements in Groups I – VII in the Periodic Table. The rule does not apply well to transition metals.
- The octet rule does not predict if a particular element will actually form ions, it only gives the formula *if* an ion is formed.

- A few atoms can also lose or gain electrons to attain the electronic structure of helium, with a *total of 2 electrons*. An example is lithium, which loses one electron to form the Li^+ ion:

lithium atom:

lithium ion, Li^+:



Question Predict the formula of the ion formed by (a) fluorine, (b) aluminium and (c) beryllium in ionic compounds. Explain your answer.
[Atomic numbers: fluorine = 9; aluminium = 13; beryllium = 4]

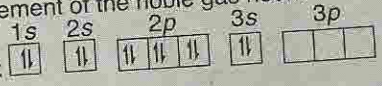
Answer

(a) Fluorine has electronic configuration:

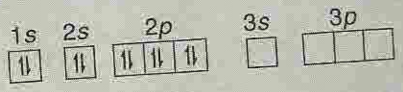
Fluorine will form the ion F^- in ionic compounds. The F^- ion has the electron arrangement:

This is the same as the electron arrangement of the noble gas neon.

(b) Aluminium has electronic configuration:

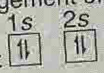


Aluminium will form the ion Al^{3+} in ionic compounds. The Al^{3+} ion has the electron arrangement:

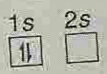


This is the same as the electron arrangement of the noble gas neon.

(c) Beryllium has electronic configuration:



Beryllium will form the ion Be^{2+} in ionic compounds. The Be^{2+} ion has the electronic configuration:

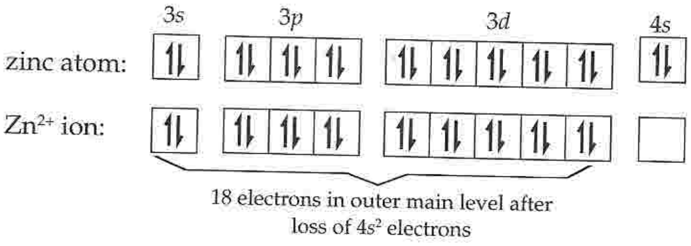


This is the same as the electron arrangement of the noble gas helium.

The 18-Electron Rule

- Eighteen electrons in the outer orbital is also a stable electron arrangement. This applies to elements with *d* orbitals in the outer level.

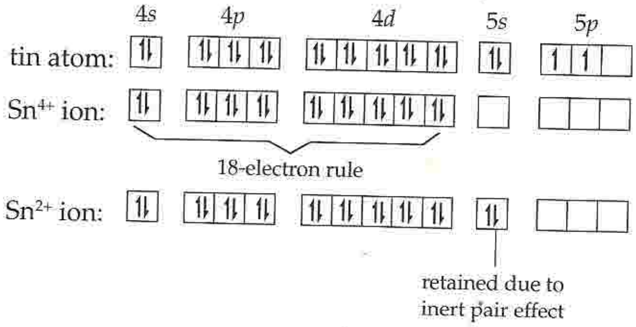
For example, zinc:



The Inert Pair Effect

- For atoms with *large* proton numbers, a pair of electrons in the outer *s* orbital is stable. These electrons are not easily lost to form ions. This is known as the **inert pair effect**.

  For example, tin forms a 4+ ion by losing *all* its outer electrons, and forms a 2+ ion by losing the outer 5*p* electrons only:



- The inert pair effect becomes stronger towards the bottom of the Periodic Table. Hence in Group IV, the effect is not observed in carbon and silicon.

  The effect is responsible for some Sn^{2+} ionic compounds of tin (though most compounds of tin contain Sn^{4+} are covalent). The effect is much stronger in lead, such that many ionic lead compounds contain Pb^{2+} ions (Pb^{4+} ions are rare).

2.7 Ionisation Energy

- **This is the energy required to remove one mole of electrons from one mole of gaseous atoms so as to form one mole of gaseous unipositive ions.**

  For example, the ionisation energy of an oxygen atom is the energy required to produce the reaction:

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

  The electron is removed from the outer sublevel of the oxygen atom (ie a 2*p* electron).

- Some examples of ionisation energy are the enthalpy changes of the following reactions:

element	*ionisation equation*	*ionisation energy*
oxygen	$O(g) \rightarrow O^+(g) + e^-$	$\Delta H = +1310\ \text{kJ mol}^{-1}$
nitrogen	$N(g) \rightarrow N^+(g) + e^-$	$\Delta H = +1400\ \text{kJ mol}^{-1}$
iron	$Fe(g) \rightarrow Fe^+(g) + e^-$	$\Delta H = +760\ \text{kJ mol}^{-1}$

- Ionisation energies depend on:
  (a) the size of the atom;
  (b) the nuclear charge.

  The electron lost in ionisation is always removed from the outer sublevel, on the outside of the atom. The bigger the atom is, the further this electron is from the nucleus. Hence the weaker the attractive force of the nucleus, the lesser the energy required to remove the electron.

  The bigger the nuclear charge, the bigger the attractive force of the nucleus on the electrons. Hence the larger the energy required to remove an electron to produce ionisation.

  See also *Ionisation Energy* in Chapter 11.

- When more than one electron is removed from an atom, the energy required to remove the *first* electron is called the **first ionisation energy**.

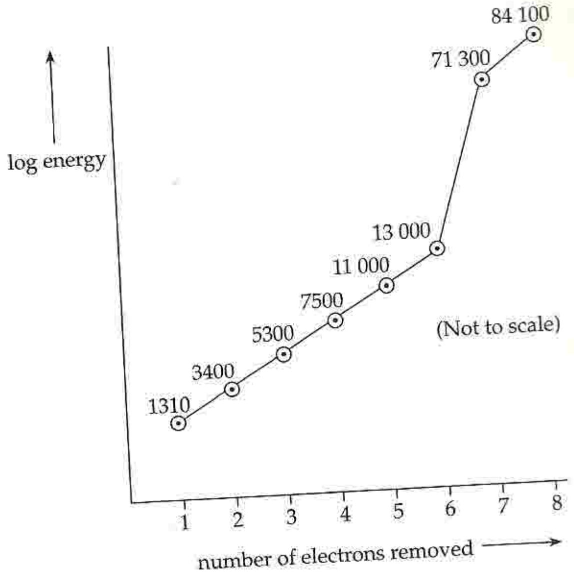
  The energy required to remove the second electron is called the **second ionisation energy**.

  For example, the second ionisation energy of oxygen is the enthalpy change of the following reaction:

  $$O^+(g) \rightarrow O^{2+}(g) + e^-;\ \Delta H = +3400\ \text{kJ mol}^{-1}$$

  The second ionisation energy is larger than the first ionisation energy because more energy is required to pull an electron away from a *positive ion* (compared with a neutral atom).

- Fig 2.5 shows the successive ionisation energies for the removal of each electron from an oxygen atom.



▶ Fig 2.5 Successive ionisation energies for oxygen, in kJ mol^{-1}

The ionisation energies increase from one electron to the next because the charge on the positive ion remaining increases, hence increasing the attractive force on the remaining electrons.

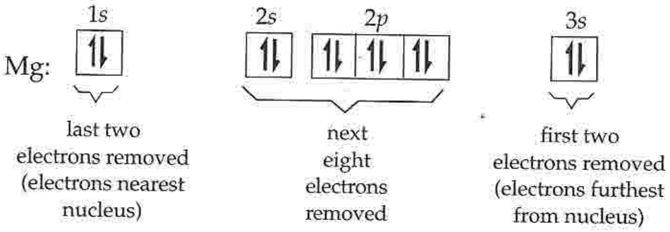
In Fig 2.5, there is a big increase in the energy required to remove the seventh electron. The first six electrons are removed from the second main quantum (ie $2s^2\,2p^4$). The seventh electron is removed from the inner *main quantum level, n=1* (1*s*). The electrons in the first energy level are closer to the nucleus and hence much more strongly held.

- Ionisation energies can be used to find out about the electronic configuration of atoms.

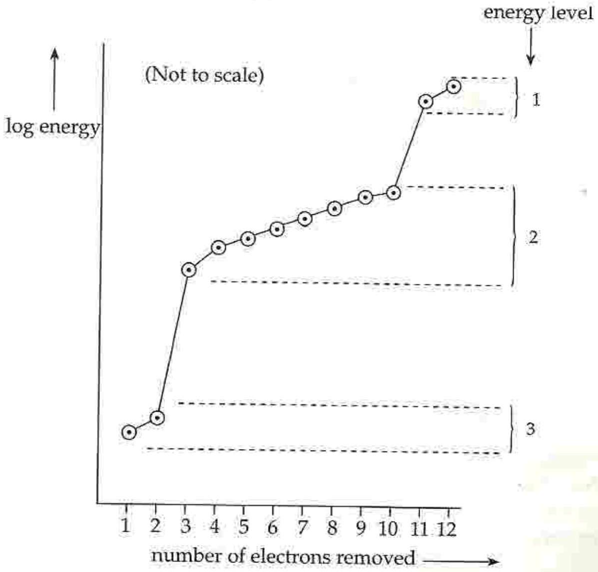
  For example, magnesium has twelve electrons in the arrangement $1s^2\ 2s^2\ 2p^6\ 3s^2$. During ionisation, electrons are removed in order of their energies. The electrons with the highest energies are removed first (ie those electrons in the outer shell). Hence in this case, the two 3*s* electrons are removed first.

  The next eight electrons of magnesium are removed from an *inner* main quantum level n=2 which is nearer the nucleus. Hence there is a large increase in the energy required to remove the third to tenth electrons.

  Finally, the last two electrons are in another *inner* main level n=1. Hence there is another big increase in the energy required to remove these last two electrons.



A graph of log ionisation energy against number of electrons removed is shown in Fig 2.6. The two big increases in the graph, for the removal of the third and the eleventh electrons are due to the change in main energy level.



▶ Fig 2.6 Successive ionisation energies for magnesium, in kJ mol^{-1}

Question

(The first eight successive ionisation energies for an element are as follows (in kJ mol^{-1})

790 1600 3200 4400 16 100 19 800 23 800 23 800

(a) How many electrons are there in the outer shell of the element?

(b) Which group in the Periodic Table does the element belong?

(c) Write down the outer electronic configuration of the element.

Answer

(a) There is a big increase in the ionisation energy when the fifth electron is removed. The increase is much larger (about 12 000) than the increase for the first four electrons:

ionisation energy: 790 1600 3200 4400 16 100

increase: 810 1600 1200 11 700

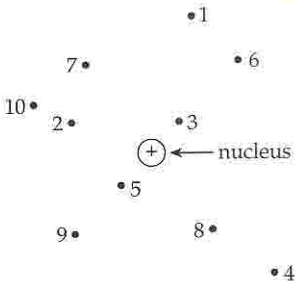
Hence the first four electrons must be in the outer shell. The fifth electron must be in an inner shell.

(b) Group IV – as all elements in Group IV have four outer electrons.

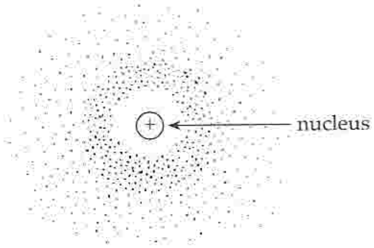
(c) The outer electronic configuration is $\overset{s}{\boxed{\uparrow\downarrow}}\ \overset{p}{\boxed{\uparrow}\boxed{\uparrow}\boxed{}}$

2.8 Shapes of Orbitals

- Electrons in atoms do not occupy fixed positions. In practice, electrons may be considered to move almost anywhere. If the positions of the hydrogen atom electron were plotted at one-second intervals, a result similar to that shown in Fig 2.7 would be obtained.



▶ Fig 2.7 Position of electron in hydrogen atom at every second for ten seconds

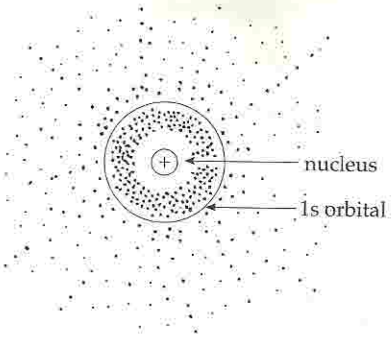


▲ Fig 2.8 Position of electron in hydrogen atom at every second over a long period of time

- It is not possible to predict exactly where an electron is at a particular time. However, if the position of the hydrogen electron is plotted every second over a very long period of time, a result similar to that shown in Fig 2.8 would be obtained.

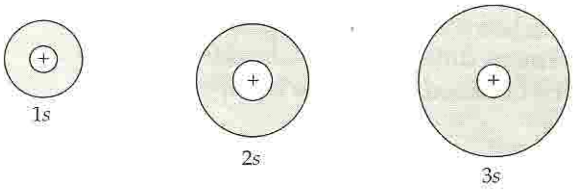
  We can then draw a sphere around the hydrogen atom, and say that the hydrogen atom electron spends 90% of its time inside this sphere (Fig 2.9). The sphere, in a simple way, is the 1s orbital for the electron in the hydrogen atom.

  An orbital is the space around the nucleus where there is the highest probability of finding an electron with a particular energy.



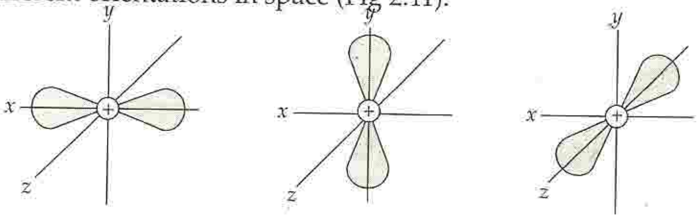
▶ Fig 2.9 1*s* orbital for hydrogen

- All *s* orbitals are spheres. They only differ in size. The 3*s* orbital is bigger than the 2*s*, which is bigger than the 1*s* (Fig 2.10).



▶ Fig 2.10 1*s* orbitals

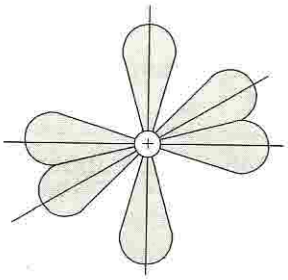
- The shape of *p* orbitals is different from the shape of *s* orbitals. The three *p* orbitals of a main level have the same shape, but have different orientations in space (Fig 2.11).



▶ Fig 2.11 The three 2*p* orbitals

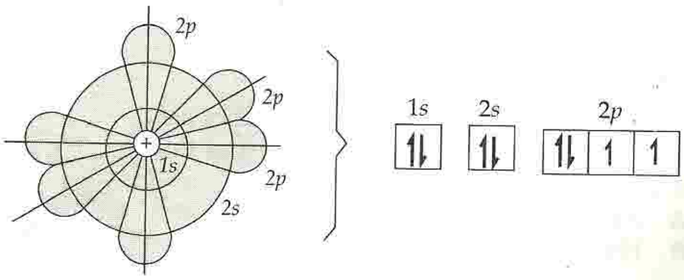
The three 2*p* orbitals are shown together in Fig 2.12.

The 3*p* orbitals have the same shape as the 2*p* orbitals, but are larger.



▲ Fig 2.12 The three 2*p* orbitals together

- In reality, all the orbitals are present in atoms. However, in practice, we only consider the orbitals containing electrons or orbitals which are involved in chemical bonds. For example, the orbitals of the first and second main energy levels in oxygen are shown together in Fig 2.13.



▶ Fig 2.13 The electrons in the orbitals of an oxygen atom

EXERCISE 2

Multiple Choice Questions

Section I

1 What is the composition of the ion $^{18}O^{2+}$?

	proton	*electron*	*neutron*
A	8	6	10
B	8	10	10
C	8	8	12
D	10	8	10

2 Oxygen consists of the isotopes ^{16}O, ^{17}O and ^{18}O. Carbon consists of the isotopes ^{12}C and ^{13}C. How many different carbon dioxide molecules can be obtained from these isotopes?

A 5 **C** 10
B 6 **D** 12

3 Which one of the following pairs of atoms or ions contains the *same* number of neutrons?

A ^{14}C and ^{12}C **C** $^{23}Na^+$ and $^{24}Mg^{2+}$
B $^{19}F^-$ and ^{20}Ne **D** ^{32}S and ^{27}Al

*4 What is the electronic configuration, in the ground state, of the atom which is *isoelectronic* (has the same number of electrons) with the HCl molecule?

A $1s^2, 2s^2, 2p^6, 3s^2$
B $1s^2, 2s^2, 2p^6, 3s^2, 3p^2$
C $1s^2, 2s^2, 2p^6, 3s^2, 3p^4$
D $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$

5 Which one of the following represents the electron arrangement of the C^+ ion in the ground state?

	1*s*	2*s*	2*p*
A	☐	☐	1 | 1 | 1
B	☐	☐	1 | 1 | 1
C	☐	☐	1 | 1 | ☐
D	☐	☐	1 | ☐ | ☐

6 Which one of the following particles does *not* contain the same number of electrons as the fluoride ion, F^-?

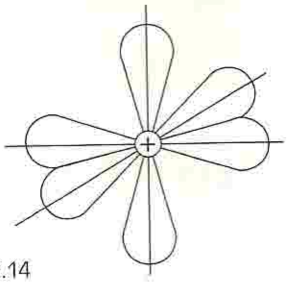
A Ne **C** Li^+
B H_2O **D** Al^{3+}

7 The electronic configurations of the elements potassium, gallium (an element in Group III), bromine and element X are given below. Which one could be the electronic configuration of element X?

A $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^5$
B $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^1$
C $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^3$
D $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$

8 Fig 2.14 shows

A one *p* orbital.
B three *p* orbitals.
C six *p* orbitals.
D two *p* orbitals and two *s* orbitals.



▶ Fig 2.14

For Questions 9 and 10, refer to the electronic configurations below.

A $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$
B $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$
C $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$
D $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6$

9 Which electronic configuration applies to an element in Group IV?

10 Which electronic configuration applies to a noble gas?

11 The first seven successive ionisation energies (in kJ mol^{-1}) for four elements are given below. Which one could be that of a Group VII element?

A 580, 1800, 2700, 11 600, 14 800, 18 400, 23 300
B 1010, 1900, 2900, 5000, 6300, 21 300, 25 400
C 1140, 2100, 3500, 4800, 5800, 8500, 9900
D 1000, 2300, 3400, 4600, 7000, 8500, 27 100

12 Which equation represents the *first* ionisation energy of bromine?

A $Br(l) \rightarrow Br^+(g) + e^-$

B $Br(g) \rightarrow Br^+(g) + e^-$

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

D $\frac{1}{2}Br_2(g) \rightarrow Br^+(g) + e^-$

13 Which equation represents the *second* ionisation energy of iron?

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

B $Fe(s) \rightarrow Fe^{2+}(g) + 2e^-$

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

D $Fe^+(s) \rightarrow Fe^{2+}(g) + e^-$

14 Which one of the following particles has more protons than neutrons *and* more electrons than protons?
$[H = {}^1H; D = {}^2H; T = {}^3H; O = {}^{16}O]$

A OH^- **C** OD^-

B T^+ **D** D_3O^+

15 Which particle has the largest mass?

A ${}^1H_2$ **C** ${}^4He$

B ${}^2H^-$ **D** ${}^4He^{2+}$

16 Germanium has the electronic configuration [Ar] $3d^{10}$ $4s^2$ $4p^2$, where [Ar] represents the configuration of argon.

In which order are the electrons lost in forming the Ge^{4+} ion?

	1st	2nd	3rd	4th
A	4*p*	4*p*	4*s*	4*s*
B	4*p*	4*p*	3*d*	3*d*
C	4*s*	4*s*	4*p*	4*p*
D	3*d*	4*s*	4*p*	3*d*

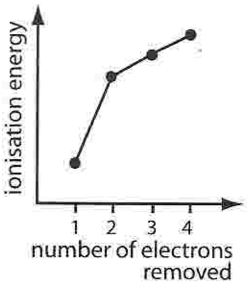
17 The first nine successive ionisation energies for an element are (kJ mol^{-1}):
1000, 2300, 3400, 4600, 7000, 8500, 27 100, 31 700, 36 600
In which group of the Periodic Table will the element be placed?

A Group I **C** Group IV

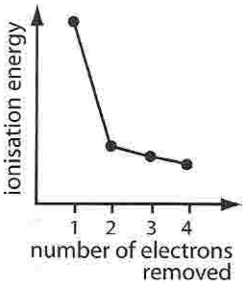
B Group II **D** Group VI

18 Which graph correctly shows the first four successive ionisation energies of aluminium?

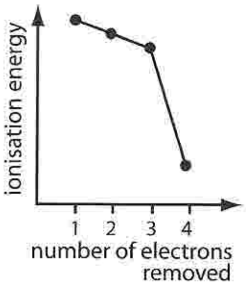
A



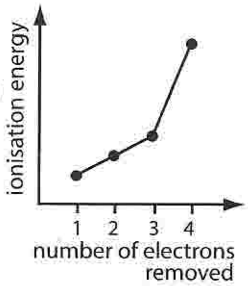
C



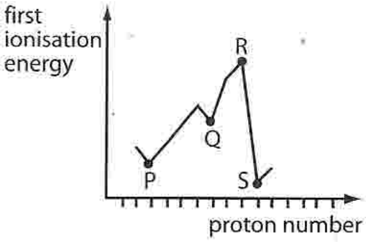
B



D



19 Which one of the elements marked on the graph is an alkali metal?



A Element P **C** Element R

B Element Q **D** Element S

Section II

Summary of directions

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

*20 Atoms which have the same electronic configuration are said to be isoelectronic. Which of the following are isoelectronic with the O^{2-} ion?

1 Fe^{2-} **2** N^{3-} **3** Al^{3+}

21 Which particles would, on losing an electron, have a half-filled set of *p* orbitals?

1 N^+ **2** N^- **3** P^-

22 Which statements are true about neutrons and protons?

1 Both particles have greater mass than an electron.

2 Both particles are deflected by a magnetic field.

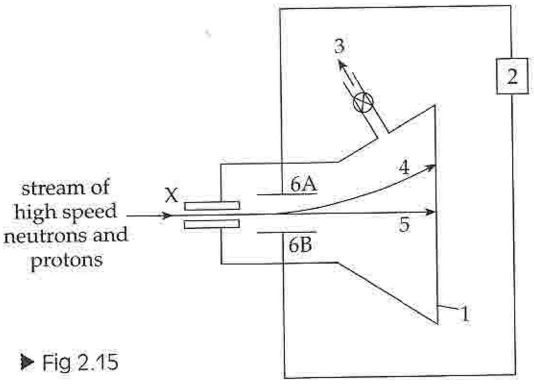
3 All atoms contain equal numbers of both particles.

Structured Questions

1 Fig 2.15 is a sketch of a simple apparatus to investigate the effect of an electric field on a stream of neutrons and protons produced from an experiment.

(a) Label the numbered parts of the diagram, 1–6.

(b) Draw on the diagram a line to show how you would expect a stream of high speed electrons to move if introduced into the apparatus through *X*.

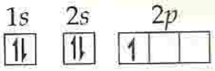


▶ Fig 2.15

2 Bromine has proton number 35; oxygen has proton number 8. Complete the following table.

Particle	Number of protons	Number of electrons	Number of neutrons
^{79}Br atom			
$^{81}Br^+$ ion			
$^{16}O^{2-}$ ion			
$^{16}O_2$ molecule			
$^{16}O_2^+$ ion			

*3 (a) The electronic configuration of a boron atom is shown below:



Draw similar diagrams for the electronic configurations of

(i) a carbon atom;

(ii) a boron ion, B^{2+};

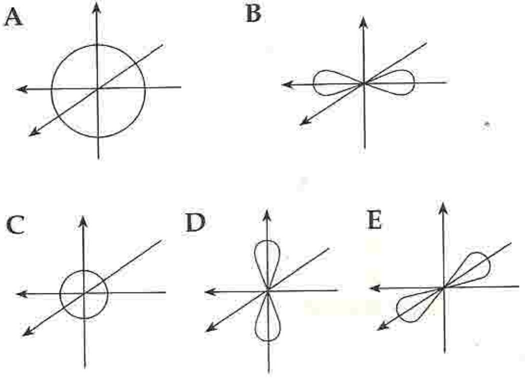
(iii) a carbon ion, C^{4-}.

(b) Predict the likely formula of the ion formed by the following elements in ionic compounds. In each case, give a reason.

(i) Hydrogen;

(ii) phosphorus [proton number = 15].

4 The orbitals of the first two principal energy levels (shells) of atoms are shown in Fig 2.16. The diagrams are to the same scale, but are not necessarily placed in any order.



▲ Fig 2.16

(a) Which orbitals will be empty of electrons in an atom of beryllium?

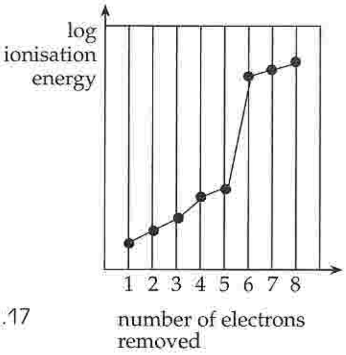
(b) In an atom of element **X**, orbitals **A** and **C** are full of electrons, **B** and **D** are half-full and **E** is empty.

(i) What is the proton number of element **X**?

(ii) What is the likely relative atomic mass of element **X**?

(c) In a carbon ion, orbitals **A** and **C** are full of electrons. The other orbitals are empty. What is the charge on the carbon ion?
[Proton numbers: beryllium = 4; carbon = 6]

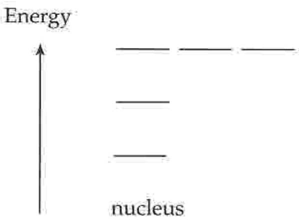
*5 Fig 2.17 shows the energy required to remove eight electrons, one at a time, from an atom of element **Q**.



▶ Fig 2.17

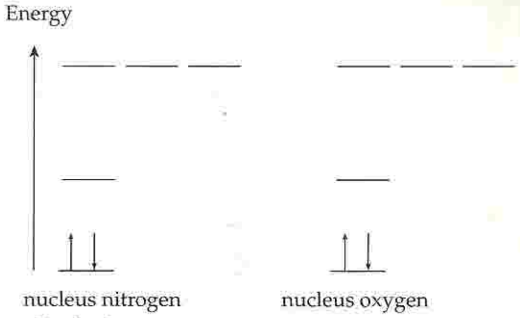
(a) (i) To which group in the Periodic Table does element **Q** belong?
(ii) What is the electron arrangement in the *outer* shell of **Q**?
(iii) Why can *not* **Q** be nitrogen?
(b) Explain why the ionisation energies *increase* as the electrons are removed.
(c) Why is the energy difference between the removal of the 5th and 6th electrons much larger than the energy difference between the removal of the 4th and 5th electrons?
(d) Name *one* element that could be the element **Q** and write its full electronic configuration.

*6 (a) Fig 2.18 shows an energy level diagram for the orbitals occupied by electrons, in atoms of the period lithium to neon.



▶ Fig 2.18

(i) Label the energy levels to show the type of orbitals at each energy level.
(ii) Sketch the shapes of all these orbitals.
(b) The energy level diagrams for nitrogen and oxygen are shown in Fig 2.19.



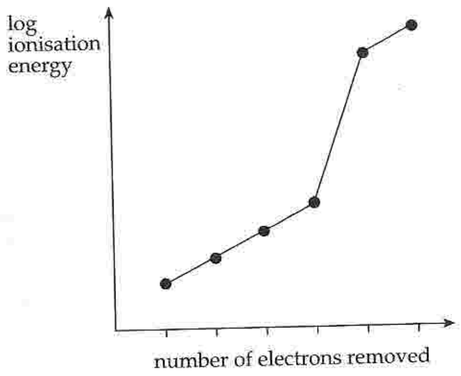
▲ Fig 2.19

(i) Add arrows for electrons to complete the electronic configurations on Fig 2.19.
(ii) Explain why the ionisation energy for nitrogen is higher than that of oxygen.
(iii) Write the formulae of the simple ions formed by nitrogen and oxygen in ionic compounds.
(iv) Why do nitrogen and oxygen form *negative* ions in compounds, but not positive ions?

7 (a) (i) Define the term 'first ionisation energy'.
(ii) State and explain the factors that determine the magnitude of the first ionisation energy of an element.
(iii) Plot the graph for the variation of the first ionisation energy of the elements from sodium to calcium in the Periodic Table and comment on the shape of the graph.
(b) Chlorine exists in two isotopic forms namely chlorine-35(^{35}Cl) and chlorine-37(^{37}Cl).
(i) Will the magnitude of the first ionisation energy of the two isotopes of chlorine be the same? Explain your reasoning.
(ii) Will the two isotopes of chlorine have the same chemical properties? Why?
(iii) Will the two isotopes of chlorine have the same physical properties explain why?

Descriptive Questions

1 (a) Define the terms
(i) proton number; and
(ii) nucleon number.
(b) Fig 2.20 shows the successive ionisation energies of an element, for the removal of all the electrons from an atom. Explain the graph and write down the full electronic configuration of the element.



▲ Fig 2.20

(c) Sketch the shapes of all the orbitals of the first two principal energy levels (shells) of an atom. Label the orbitals.

2 Manganese [proton number = 25] is used in the manufacture of mild steel.

(a) Naturally occuring manganese consists entirely of the isotope ^{55}Mn.

Suggest the symbol for another isotope of manganese. Describe how this isotope is *similar* to and *different* from ^{55}Mn in its atomic particles.

(b) What differences (if any) would you expect in the chemical properties of two different isotopes of manganese? Explain your answer.

(c) Write the full electronic configuration of
- (i) an atom of ^{55}Mn in an excited state;
- (ii) the ion $^{55}\text{Mn}^{4+}$ in the ground state.

3 (a) (i) Name the three subatomic particles that are present in an atom.

(ii) Tabulate the relative charges , the relative masses and the location of the three main subatomic particles in an atom.

(b) (i) What is an orbital?

(ii) Draw the shape of the 's' and 'p' orbitals.

(c) (i) Write down the electronic structure of sulphur and use the Data Booklet to plot a graph of successive ionisation energies against number of electrons removed.

(ii) Does the graph indicate the existence of subshells and shells in an atom? How?

4. (a) Write the electronic structure in terms of s , p and d electrons of atoms of
- (i) magnesium
- (ii) fluorine
- (iii) nickel
- (iv) chromium
- (v) copper

(b) Explain the following:
- (i) The first ionisation energy of oxygen is less than that of nitrogen.
- (ii) The first ionisation energy of sodium is less than that of neon.
- (iii) The first ionisation energy of chlorine is less than that of fluorine.

(c) When charged particles are passed through an electric field they are deflected.
- (i) State the factor that determines the direction in which the charge particles will be deflected.
- (ii) State the factors that determine the magnitude by which the charge particle will be deflected.

(d) When a beam of hydrogen ions, $^{1}\text{H}^{+}$, is passed through a certain electric field, it is deflected by 20^0 from its original trajectory.

Calculate the angles of deflection of
- (i) sodium ion, $^{23}\text{Na}^{+}$
- (ii) nitride ion, $^{14}\text{N}^{3-}$

when a beam of these ions is passed through the same electric field.

CHAPTER

3

VOLUMETRIC CALCULATIONS

SYLLABUS OBJECTIVES

In this chapter you should be able to:

- do chemical calculations using volumes and concentrations of solutions (particularly using moles)
- do volumetric calculations (in the practical examination) on titrations of:
  - acids and alkalis
  - potassium manganate(VII) with iron(II) and ethanedioate
  - iodine and thiosulphate
  - other reagents

3.1 Important Relationships

This chapter is concerned with the volumetric calculations that are required for the theory examinations and for the practical examinations. Some knowledge of titrations from O-level is assumed.

1 $$\text{volume of solution in dm}^3 = \frac{\text{volume of solution in cm}^3}{1000}$$

2 $$\text{number of moles of solute in a solution} = \text{volume of solution in dm}^3 \times \text{concentration in mol dm}^{-3}$$

3 $$\text{concentration of a solution in mol dm}^{-3} = \frac{\text{no. of moles of solute in the solution}}{\text{volume of the solution in dm}^3}$$

4 $$\text{concentration of solution in mol dm}^{-3} = \frac{\text{concentration of solution in g dm}^{-3}}{\text{molar mass of solute}}$$

5 $$\text{concentration of solution in g dm}^{-3} = \text{concentration in mol dm}^{-3} \times \text{molar mass}$$

Note: The molar mass may be taken to be the same as the relative molecular mass, M_r.

3.2 Calculations of Ions in a Solution

- The steps in calculating the number of moles of ions in an aqueous solution of an ionic compound are:
  - (a) calculate the number of moles of ionic compound in the given volume of solution;
  - (b) find the number of moles of ions in 1 mole of the ionic compound;
  - (c) multiply the two numbers together to give the number of moles of the particular ion.

Question How many moles of sodium ions, Na^+, are present in 250 cm^3 of 0.4 mol dm^{-3} Na_2SO_4?

Answer

Number of moles of Na_2SO_4 in the solution = volume in dm^3 x concentration in mol dm^{-3}

$$= \frac{250}{1000} \times 0.4$$

$$= 0.1 \text{ mole}$$

1 mole of Na_2SO_4 contains 2 moles of Na^+.
Therefore number of moles of Na^+ in the solution = 0.1 x 2
= 0.2 mole

Question

What is the total number of moles of ions in 500 cm^3 of 0.5 mol dm^{-3} $(NH_4)_2Cu(SO_4)_2(aq)$?

Answer

Number of moles of $(NH_4)_2Cu(SO_4)_2$ in the solution = volume in dm^3 x concentration in mol dm^{-3}

$$= \frac{500}{1000} \times 0.5$$

$$= 0.25 \text{ mole}$$

1 mole of $(NH_4)_2Cu(SO_4)_2$ contains 2 moles of NH_4^+, 1 mole of Cu^{2+} and 2 moles of SO_4^{2-}. The total number of moles = 2 + 1 + 2 = 5 moles.
Therefore the total number of moles of ions in the solution = 5 x 0.25 = 1.25 moles

Note: In these calculations, it is assumed that the ionic compound is fully ionised in solution.

3.3 Titrations

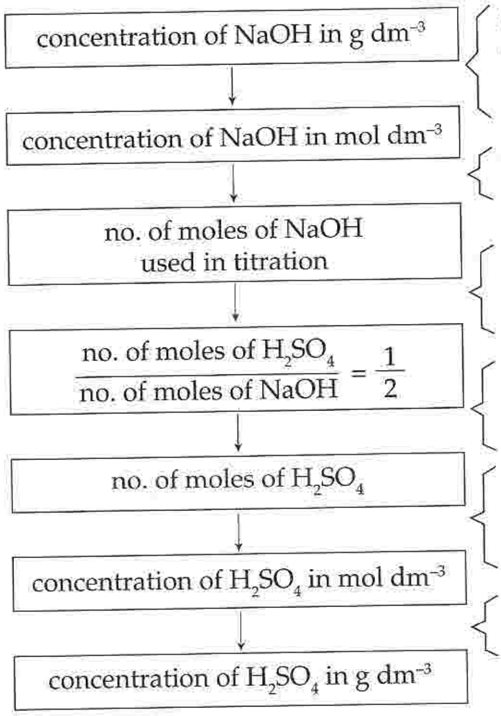
- The basic purpose of a titration is to find the volume of a solution required to react with a known volume of another solution.

  For example, in an acid-base titration, the aim of a titration may be to find the volume of alkali (from a burette) required to neutralise 25.0 cm^3 of an acid (from a pipette).

3.4 Acid-Base Titrations

- The calculations for a titration between H_2SO_4 and NaOH is outlined in the following scheme. The procedure assumes that the concentrations of the NaOH is known in g dm^{-3}, and that the aim is to find the concentration of the H_2SO_4 in g dm^{-3}. The equation for the reaction is

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$$



Step	Notes
step 1	always work in moles concentration of NaOH in mol dm^{-3} $= \frac{\text{concentration in g dm}^{-3}}{M_r}$
step 2	no. of moles of NaOH = volume in dm^3 x concentration
step 3	from the equation, determine the ratio of the no. of moles of NaOH to the no. of moles of H_2SO_4
step 4	no. of moles of H_2SO_4 $= \frac{1}{2}$ x no. of moles of NaOH
step 5	concentration of H_2SO_4 in mol dm^{-3} $= \frac{\text{no. of moles of } H_2SO_4}{\text{volume of solution in dm}^3}$
step 6	concentration of H_2SO_4 in g dm^{-3} = concentration in mol dm^{-3} x M_r

Question

Solution M1 contains 4.00 g of NaOH per dm^3. Solution M2 contains H_2SO_4. In an experiment, 25.0 cm^3 of solution M2 reacted with 18.0 cm^3 of solution M1. Calculate

(a) the concentration of M2 in moles per dm^3;
(b) the concentration of M2 in grams of H_2SO_4 per dm^3 and
(c) the number of grams of SO_4^{2-} ion in 1 dm^3 of solution M2.
[H = 1.00; O = 16.0; Na = 23.0; S = 32.0]

Answer

(a) Concentration of NaOH $= \frac{4.00}{40}$ mol dm^{-3}

Number of moles of NaOH used in the reaction = concentration x volume in dm^3

$$= \frac{4.00}{40} \times \frac{18.0}{1000} \text{ mole}$$

Equation for the reaction is $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

From the equation, $\frac{\text{no. of moles of } H_2SO_4}{\text{no. of moles of NaOH}} = \frac{1}{2}$

ie Number of moles of H_2SO_4 $= \frac{1}{2}$ x no. of moles of NaOH

$$= \frac{1}{2} \times \frac{4.00}{40} \times \frac{18.0}{1000} \text{ mole}$$

Answer

Hence concentration of $H_2SO_4 = \dfrac{\text{no. of moles of } H_2SO_4}{\text{volume of solution M2}}$

$$= \frac{\frac{1}{2} \times \frac{4.00}{40} \times \frac{18.0}{1000}}{\frac{25}{1000}} = 0.036 \text{ mol dm}^{-3}$$

(b) Concentration of H_2SO_4 in g dm^{-3} = concentration in mol dm^{-3} x relative molecular mass

= 0.036 x 98 = 3.53 g dm^{-3}

(c) Mass of SO_4^{2-} in 1 dm^3 of M2 = concentration in mol dm^{-3} x relative mass of SO_4^{2-}

= 0.036 x 96 = 3.46 g dm^{-3}

Question

Calculate the volume of 0.2 mol dm^{-3} HNO_3 required to dissolve 4.0 g of copper(II) oxide, CuO.
[O = 16.0; Cu = 64.0]

Answer

Number of moles of CuO = $\dfrac{\text{mass of CuO in grams}}{\text{relative molecular mass of CuO}} = \dfrac{4.0}{80} = 0.05$ mole

Equation for the reaction is $CuO + 2HNO_3 \rightarrow Cu(NO_3)_2 + H_2O$

From the equation, $\dfrac{\text{no. of moles of } HNO_3}{\text{no. of moles of CuO}} = \dfrac{2}{1}$

ie Number of moles of HNO_3 = 2 x no. of moles of CuO
= 2 x 0.05 mole

Volume of $HNO_3 = \dfrac{\text{no. of moles}}{\text{concentration in mol dm}^{-3}} = \dfrac{2 \times 0.05}{0.2} = 0.5 \text{ dm}^3 = 500 \text{ cm}^3$

EXERCISE 3A

1 In an experiment, 20.0 cm^3 of 0.2 mol dm^{-3} NaOH reacted with 32.0 cm^3 of H_2SO_4 solution. Calculate the concentration of the H_2SO_4 in
(a) mol dm^{-3}, and
(b) g dm^{-3}.
[H = 1.00; O = 16.0; S = 32.0]

2 Calculate the volume of 0.12 mol dm^{-3} KOH required to react with 25.0 cm^3 of H_3PO_4, containing 4.90 g of H_3PO_4 per dm^3 solution according to the equation:

$$2KOH + H_3PO_4 \rightarrow K_2HPO_4 + 2H_2O$$

[H = 1.00; O = 16.0; P = 31.0]

3 Solution FA2 contains NaOH. Solution FA3 contains 20.8 g of HOOC—CH_2—COOH per dm^3.
In an experiment, 20.0 cm^3 of solution FA2 required 40.0 cm^3 of FA3 for neutralisation, using phenolphthalein indicator. Calculate
(a) the concentration of NaOH in mol dm^{-3};
(b) the number of grams of hydroxide ion, OH^-, per dm^3 of FA3.
[H = 1.00; C = 12.0; O = 16.0]

*4 Calculate the volume of 0.4 mol dm^{-3} HCl required to react with 5.00 g of calcium carbonate.

*5 500 cm^3 of nitric acid reacted completely with 3.94 g of barium carbonate, $BaCO_3$. Calculate the concentration of the nitric acid in
(a) mol dm^{-3}, and
(b) g dm^{-3}.

*6 2.00 g of sulphur trioxide was dissolved in water. The solution produced required 200 cm^3 of sodium hydroxide solution for neutralisation. Calculate the concentration of the sodium hydroxide in mol dm^{-3}.

*7 Sulphur dichloride dioxide, SO_2Cl_2, is hydrolysed by water to sulphuric acid and hydrochloric acid. A sample of SO_2Cl_2 dissolved in water required 80.0 cm^3 of 0.200 mol dm^{-3} NaOH for neutralisation.
(a) Write the equation for the reaction of SO_2Cl_2 with water.
(b) Calculate the mass of SO_2Cl_2 in the sample.

*8 Ethanoyl choride, CH_3COCl, reacts with water to produce hydrochloric acid and ethanoic acid. 1.57 g of ethanoyl chloride was added to excess water and was titrated with 0.12 mol dm^{-3} sodium hydroxide.
(a) Construct a balanced equation for the reaction of ethanoyl chloride with water.
(b) Calculate the volume of sodium hydroxide solution required for complete reaction.

*9. Brass is an alloy of zinc and copper. 1.00g of brass was placed in 12.5cm^3 of 1.0moldm^{-3} solution of sulphuric acid .The mixture was warmed until effervescence stopped. When the mixture was titrated with 0.1moldm^{-3} sodium hydroxide 25.00cm^3 of alkali was required to neutralize the unreacted acid. Calculate the percentage of zinc in brass.

Relative Molecular Mass of Acids and Bases

Question

Solution M8 contains 20.1 g of the acid HZO_4 per dm^3 of solution.
Solution M9 contains 1.7 g of hydroxide ion, OH^-, per dm^3 of solution. In a titration, 20.0 cm^3 of M8 required 40.0 cm^3 of M9 for reaction.
Calculate
(a) the concentration of M8 in mol dm^{-3};
(b) the relative molecular mass of HZO_4; and
(c) the relative atomic mass of element Z.
[H = 1.00; O = 16.0]

Answer

a) Concentration of M9 = $\frac{1.7}{17}$ mol of OH^- per dm^3 = 0.1 mol dm^{-3}

Number of moles of OH^- used in the titration = volume in dm^3 x concentration in mol dm^{-3}

$$= \frac{40.0}{1000} \times 0.1 \text{ mole}$$

HZO_4 must be monobasic as it only has one hydrogen atom.
Hence in the reaction, 1 mole of HZO_4 must react with 1 mole of OH^-.
The number of moles of HZO_4 used in the reaction = no. of moles of OH^-

$$= \frac{40.0}{1000} \times 0.1 \text{ mole}$$

$$\text{The concentration of M8} = \frac{\text{no. of moles of } HZO_4}{\text{volume of M8 in } dm^3}$$

$$= \frac{\frac{40.0}{1000} \times 0.1}{\frac{20.0}{1000}} = 0.2 \text{ mol } dm^{-3}$$

(b) From (a), 0.2 mole of HZO_4 has a mass of 20.1 g

Hence 1 mole of HZO_4 has a mass of $\frac{20.1}{0.2}$ = 100.5 g

ie the relative molecular mass of HZO_4 = 100.5

(c) The relative atomic mass of Z = 100.5 – (1 + 64) = 35.5.

Question

Hydrated sodium carbonate has the formula $Na_2CO_3.xH_2O$.
Solution FB3 contains 14.3 g of $Na_2CO_3.xH_2O$ per dm^3.
Solution FB4 contains 0.12 mol dm^{-3} HCl.
In an experiment, 20.0 cm^3 of FB3 was found to react with 16.7 cm^3 of FB4. Deduce the value of *x* in the formula of the hydrated sodium carbonate.
The equation for the reaction is $Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$
[H = 1.00; C = 12.0; O = 16.0; Na = 23.0]

Answer

Number of moles of HCl used in the titration = $\frac{16.7}{1000} \times 0.12$ mole

From the equation, $\frac{\text{no. of moles of } Na_2CO_3}{\text{no. of moles of HCl}} = \frac{1}{2}$

ie Number of moles of Na_2CO_3 = $\frac{1}{2}$ x no. of moles of HCl

$$= \frac{1}{2} \times \frac{16.7}{1000} \times 0.12 \text{ mole}$$

$$\text{Hence concentration of } Na_2CO_3 = \frac{\text{no. of moles of } Na_2CO_3}{\text{volume of FB3 in } dm^3}$$

$$= \frac{\frac{1}{2} \times \frac{16.7}{1000} \times 0.12}{\frac{20.0}{1000}} = 0.05 \text{ mol } dm^{-3}$$

0.05 mole of $Na_2CO_3.xH_2O$ has a mass of 14.3 g.

Answer

Hence 1 mole of $Na_2CO_3.xH_2O$ has a mass of $\frac{14.3}{0.05} = 286$ g.

ie the relative molecular mass of $Na_2CO_3.xH_2O = 286$.

$(46 + 12 + 48) + x(18) = 286$

Hence $x = 10$

EXERCISE 3B

*1 A solution of a monobasic acid contains 19.2 g of HXO_4 per dm^3. 25.0 cm^3 of the acid solution reacted with 20.8 cm^3 of an alkali containing 4.80 g of NaOH per dm^3. Calculate

(a) the concentration of HXO_4 in mol dm^{-3};

(b) the relative atomic mass of element **X**.

*2 A solution of an acid contains 7.30 g of $HOOC{-}(CH_2)_n{-}COOH$ per dm^3 of solution. 20.0 cm^3 of this acid solution was titrated with NaOH, using phenolphthalein indicator. In the titration, 25.0 cm^3 of the alkali was used. The sodium hydroxide contained 1.36 g of hydroxide ion per dm^3. Calculate

(a) the relative molecular mass of the acid;

(b) the value of n in the formula.

*3 A solution of an acid contains 25.2 g of $(COOH)_2.xH_2O$ per dm^3. 50.0 cm^3 of this solution required 40.0 cm^3 of 0.500 mol dm^{-3} KOH for titration with phenolphthalein indicator. Calculate the value of x.

4 Solution FA7 contains 12.6 g of $Ba(OH)_2.xH_2O$ per dm^3. Solution FA8 contains 0.12 g of hydrogen ion, H^+, per dm^3. In a titration, 25.0 cm^3 of FA7 required 16.7 cm^3 of FA8 for complete reaction. Calculate

(a) the concentration of FA7 in mol dm^{-3};

(b) the value of x in $Ba(OH)_2.xH_2O$.

[H = 1.00; O = 16.0; Ba = 137]

*5 Solution M3 contains 3.14 g of the alkali $\mathbf{M}(OH)_3$ per dm^3.

Solution M4 contains 0.125 mol dm^{-3} HCl.

In a titration, 20.0 cm^3 of M3 required 16.0 cm^3 of M4 for complete reaction. The equation for the reaction was

$$\mathbf{M}(OH)_3 + 2HCl \rightarrow \mathbf{M}(OH)Cl_2 + 2H_2O.$$

Calculate the relative molecular mass of $\mathbf{M}(OH)_3$ and hence the relative atomic mass of element **M**.

*6 Solution FB4 contains 6.72 g of the metal hydroxide **M**OH per dm^3. Solution FB5 contains 20.6 g of the monobasic acid $C_6H_3N_3O_7$ per dm^3. In a titration, 25.0 cm^3 of FB4 was found to react with 33.3 cm^3 of FB5 using phenolphthalein indicator. In a separate experiment, a purple colour was obtained when aqueous iron(III) chloride was added to FB5.

(a) Calculate the number of moles of **M**OH in 1 dm^3 of solution.

(b) Calculate the mass of $\mathbf{M}^+$ in 1 dm^3 of FB4.

(c) Deduce a structural formula for the monobasic acid.

(d) Is the monobasic acid weak or strong? Give a reason.

Determination of Acid-base Equations

Question

Solution M4 contains 0.12 mol dm^{-3} Na_2CO_3.
Solution M5 contains 0.20 mol dm^{-3} HCl.
In a titration, 20.0 cm^3 of solution M4 was found to react with 12.0 cm^3 of solution M5.
Calculate the number of moles of HCl that react with one mole of Na_2CO_3.
Hence deduce the equation for the reaction.

Answer

Number of moles of Na_2CO_3 used in the titration $= \frac{20.0}{1000} \times 0.12$ mole

Number of moles of HCl used in the titration $= \frac{12.0}{1000} \times 0.20$ mole

Thus $\frac{20.0}{1000} \times 0.12$ mole of Na_2CO_3 reacts with $\frac{12.0}{1000} \times 0.20$ mole of HCl.

Hence 1 mole of Na_2CO_3 reacts with $\dfrac{\frac{12.0}{1000} \times 0.20}{\frac{20.0}{1000} \times 0.12}$ mole of HCl

$= 1.0$ mole of HCl

Therefore the equation for the reaction is: $HCl + Na_2CO_3 \rightarrow NaHCO_3 + NaCl$.

Note: The ratio of HCl to Na_2CO_3 in the equation must be the same as the ratio obtained from the titration.

EXERCISE 3C

*1 A solution contained 16.8 g of NaH_2PO_4 per dm^3. 25.0 cm^3 of this solution reacted with 17.5 cm^3 of sodium hydroxide containing 6.80 g of hydroxide ion per dm^3.

(a) Calculate the number of moles of NaH_2PO_4 and OH^- used in the titration.
(b) Hence deduce the equation for the reaction.

*2 Solution FA1 contains 6.200 g of the acid H_3MO_3 per dm^3. Solution FA2 contains 1.700 g of hydroxide ion, OH^- per dm^3. In a titration, 25.0 cm^3 of FA1 reacted exactly with 50.0 cm^3 of FA2. From these results, deduce the possible relative atomic masses of element **M**.

(a) Find the number of moles of OH^- used in the titration.
(b) Write down all the possible equations for the reaction (there are three of them).
(c) For each equation in turn, work out the concentration of H_3MO_3. Then calculate the relative formula mass of H_3MO_3 and hence the relative atomic mass of **M**.
(d) Look up the *Data Tables* and decide which of your calculated relative atomic masses is/are reasonable. Allow for a small error in the titration.

*3 A salt has the formula NaH_2XO_4. A solution of the salt contains 12.00 g of NaH_2XO_4 per dm^3. In an experiment, 25.0 cm^3 of the solution of NaH_3XO_4 was found to react with 20.8 cm^3 of 0.120 mol dm^{-3} NaOH. Write down the possible equations for the reaction in the titration and hence deduce the possible relative atomic masses of element **X**.

Question

Solid FA 2 is a mixture of sodium carbonate, Na_2CO_3, and sodium chloride, NaCl. 5.00 g of FA2 was dissolved in 250 cm^3 of solution in a volumetric flask. 25.00 cm^3 of this solution was titrated with 0.120 mol dm^{-3} hydrochloride acid using a suitable indicator. 34.80 cm^3 of acid solution was needed for the titration. The equation for the reaction is

$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$$

Calculate

(a) the number of moles of sodium carbonate in the 25.00 cm^3 solution titrated;

(b) the number of moles of sodium carbonate in the 250.0 cm^3 solution in the volumetric flask;

(c) the mass of sodium carbonate in the 1.00 g sample of FA2 and;

(d) the percentage by mass of sodium chloride in FA2.

Answer

(a) No. of moles of HCl used in the titration $= \frac{34.80}{1000} \times 0.120$

$= 0.004176$ mol

$= 0.00418$ mol

No. of moles of Na_2CO_3 = no. of moles of HCl = 0.00418 mol

(b) No. of moles of Na_2CO_3 in 250 cm^3 solution = 10 x 0.00418 = 0.0418 mol

(c) Mass of Na_2CO_3 in the 1.00 g sample = no. of moles X M_r

$= 0.04176 \times 106 = 4.43$ g

(d) Mass of sodium chloride in the sample = 5.00 – 4.43 = 0.57 g

Percentage of sodium chloride $= \frac{\text{mass of NaCl}}{\text{mass of sample}} \times 100$

$= \frac{0.57}{5.00} \times 100 = 11.4$ %

Note: Sodium chloride is inert. Only the sodium carbonate reacts with the hydrochloric acid.

EXERCISE 3D

*1 Solid FA3 is a mixture of sodium carbonate Na_2CO_3, and sodium chloride, NaCl. 2.00 g of FB3 was dissolved in 250 cm^3 of solution in a volumetric flask. 25.00 cm^3 of this solution was titrated with 21.40 cm^3 of hydrochloric acid using a suitable indicator. The equation for the reaction is

$$Na_2CO_3 + 2HCl \rightarrow H_2O + CO_2 + 2NaCl$$

Calculate

(a) the number of moles of sodium carbonate in the 25.00 cm^3 solution titrade;

(b) the number of moles of sodium carbonate in the 250.0 cm^3 solution in the volumetric flask;

(c) the mass of sodium carbonate in the 2.00 g sample of FA3 and

(d) the percentage by mass of sodium chloride in FA3.

*2 1.00 g of impure calcium carbonate was added to 50 cm^3 of 0.500 mol dm^{-3} HCl. The acid was in excess, therefore all the $CaCO_3$ reacted. The acid remaining was titrated with 35.00 cm^3 of 0.200 mol dm^{-3} NaOH.

(a) Write an equation for the reaction between HCl and NaOH.

(b) Calculate

  (i) the volume of 0.500 mol dm^{-3} HCl that reacted with 35.0 cm^3 of 0.200 mol dm^{-3} NaOH and

  (ii) the volume of 0.500 mol dm^{-3} HCl that reacted with the $CaCO_3$.

(c) Write an equation for the reaction of HCl and $CaCO_3$.

(d) Calculate

  (i) the number of moles of $CaCO_3$ that reacted with the HCl;

  (ii) the mass in grams of $CaCO_3$ in the 0.500 g sample and

  (iii) the percentage purity of the calcium carbonate.

[C = 12.0; O = 16.0; Ca = 40.0]

Note: You may assume that only the $CaCO_3$, not the impurity, reacts with the acid.

3.5 Redox Titrations

- Redox titrations are similar to acid-base titrations. The reaction is between an oxidising agent and a reducing agent.
- Usually the equation for the reaction is obtained by adding together two half-equations — one for the oxidising agent and another for the reducing agent. The common oxidising and reducing agents in titrations are listed below.

oxidising agents

manganate(VII)
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

dichromate(VII)
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

iodine
$I_2 + 2e^- \rightarrow 2I^-$

hydrogen peroxide
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$

reducing agents

iron(II)
$Fe^{2+} \rightarrow Fe^{3+} + e^-$

ethanedioate
$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$

thiosulphate(VI)
$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$

iodide
$2I^- \rightarrow I_2 + 2e^-$

hydrogen peroxide
$H_2O_2 \rightarrow 2H^+ + O_2 + 2e^-$

Note:

(1) Hydrogen peroxide, H_2O_2, can either be an oxidising agent *or* a reducing agent, depending on the particular reaction.

(2) Ethanedioate is usually titrated with potassium manganate(VII). The reaction mixture is heated to about 60°C as it is too slow at room temperature.

Question

25.0 cm^3 of a solution of 0.100 mol dm^{-3} solution of $Fe^{2+}(aq)$ reacted with 26.80 cm^3 of potassium manganate(VII) solution, $KMnO_4(aq)$, acidified with excess sulphuric acid.
Calculate
(a) the concentration of the $KMnO_4$ in mol dm^{-3} and
(b) the mass of manganese in 1 dm^3 of the $KMnO_4$ solution.

Answer

(a) Number of moles of Fe^{2+} used in the titration = volume in dm^3 x concentration

$$= \frac{25.0}{1000} \times 0.100 \text{ mole}$$

Equations for the reaction:

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$
$$Fe^{2+} \longrightarrow Fe^{3+} + e^-$$

Multiplying the second equation by 5 (so that the electrons cancel) and adding both equations:

$$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

From the equation, $\dfrac{\text{no. of moles of } MnO_4}{\text{no. of moles of } Fe^{2+}} = \dfrac{1}{5}$

ie number of moles of $MnO_4^- = \dfrac{1}{5} \times$ no. of moles of $Fe^{2+} = \dfrac{1}{5} \times \dfrac{25.0}{1000} \times 0.100$

Hence the concentration of $MnO_4^- = \dfrac{\text{no. of moles of } MnO_4^-}{\text{volume of solution in dm}^3}$

$$= \frac{\frac{1}{5} \times \frac{25.0}{1000} \times 0.10}{\frac{28.8}{1000}} = 0.0187 \text{ mol dm}^{-3}$$

(b) 1 mole of MnO_4^- contains 1 mole of Mn.
Hence 1 dm^3 contains 0.0187 mole of MnO_4^- and 0.0187 mole of Mn.
ie the mass of manganese = 0.0187 x 54.9 g = 1.02 g

Question

A 20.0 cm^3 sample of hot acidified ethanedioic solution required 32.50 cm^3 of 0.0400 mol dm^{-3} potassium manganate(VII) solution for reaction.
Calculate
(a) the concentration of the ethanedioic acid in mol dm^{-3} and
(b) the volume of CO_2 gas, measured at 100 kPa pressure and 300 K temperature, produced in the reaction.
[R = 8.31 J K^{-1} mol^{-1}]

Answer

(a) Number of moles of $(COO)_2^{2-}$ used in the reaction $= \frac{32.50}{1000} \times 0.0400$ mol

$= 0.00130$ mol

Equations for reaction:

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$
$$(COO)_2^{2-} \longrightarrow 2CO_2 + 2e^-$$

Multiplying the first equation by 2 and the second equation by 5 (so that the electrons cancel) and adding both equations:

$$2MnO_4^- + 16H^+ + 5(COO)_2^{2-} \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

From the equation, $\frac{\text{no. of moles of } (COO)_2^{2-}}{\text{no. of moles of } MnO_4^-} = \frac{5}{2}$

So, the no. of moles of $(COO)_2^{2-} = \frac{5}{2} \times$ no. of moles of MnO_4^-

$= \frac{5}{2} \times 0.00130$ mol

Concentration of acid $= \frac{\text{no. of moles of } (COO)_2^{2-}}{\text{volume in dm}^3} = \frac{\frac{5}{2} \times 0.00130}{\frac{20.0}{1000}}$

$= 0.163$ mol dm^{-3}

(b) From the equation, no. of moles of CO_2 produced $= \frac{10}{2} \times$ no. of moles of MnO_4^-

$= 5 \times 0.00130$

$= 0.00650$ mol

Applying the Ideal Gas Equation: $V = \frac{nRT}{P} = \frac{0.00650 \times 8.31 \times 300}{100\,000}$

$= 0.000162$ m^3 [or 162 cm^3]

EXERCISE 3E

*1 25.0 cm^3 of hydrogen peroxide solution reacted with 20.0 cm^3 of 0.025 mol dm^{-3} MnO_4^- in a titration, in the presence of excess acid.

$$2MnO_4^- + 16H^+ + 5H_2O_2 \rightarrow 2Mn^{2+} + 5O_2 + 8H_2O$$

Calculate the concentration of the hydrogen peroxide in (a) mol dm^{-3}, and (b) g dm^{-3}.

2 What volume of 0.45 mol dm^{-3} iron(II) sulphate is required to react with 50.0 cm^3 of 0.02 mol dm^{-3} $KMnO_4$, acidified with excess dilute sulphuric acid?

*3 Fe^{2+} reacts with acidified dichromate(VI) according to the equations:

$Fe^{2+} \rightarrow Fe^{3+} + e^-$

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

25.0 cm^3 of iron(II) sulphate solution, acidified with excess dilute sulphuric acid, reacted with 40.0 cm^3 of 0.25 mol dm^{-3} potassium dichromate(VI) solution in a titration. Calculate

(a) the concentration in grams per dm^3 of the Fe^{2+} in iron(II) sulphate;

(b) the number of moles of Cr^{3+} ions produced in the titration.

4 Calculate the volume of oxygen gas produced when 25.0 cm^3 of 0.200 mol dm^{-3} hydrogen peroxide, H_2O_2, is titrated with potassium manganate(VII) solution in the presence of excess sulphuric acid.
(Refer to question 1 for the equation)
[1 mole of gas occupies 24 000 cm^3 under experimental conditions]

*5 Chlorate(V) ions, ClO_3^-, act as an oxidising agent according to the half-equation:

$ClO_3^- + \ldots H^+ + \ldots e^- \rightarrow Cl^- + \ldots H_2O$

(a) Complete the half-equation.

Chlorate(V) ions are reduced by Fe^{2+} ions.

(b) Write a balanced equation for the reaction between Fe^{2+} and ClO_3^-.

In an experiment, 25.0 cm^3 of a solution of $KClO_3$ was titrated with a solution of iron(II) sulphate containing 6.72 g of Fe^{2+} per dm^3. In the titration, 20.0 cm^3 of iron(II) sulphate was used for the reaction.

(c) (i) What other substance is required for the titration?

(ii) Calculate the concentration of the $KClO_3$ in mol dm^{-3}.

(iii) Calculate the mass in grams of potassium in 1 dm^3 of the $KClO_3$ solution.

6 Solution FA2 contains 10.0 g of iron cations, Fe^{2+} and Fe^{3+}, dissolved in 500 cm^3 of solution. Solution FA6 contains 0.015 mole of $KMnO_4$ per dm^3. In an experiment, 10.0 cm^3 of solution FA2 was pipetted into a titration flask. Excess dilute sulphuric acid was added and the mixture titrated with FA6. 26.65 cm^3 of FA6 was required to reach an end-point.

(a) Calculate the mass of Fe^{2+} in

(i) 10 cm^3 of FA2, and hence in

(ii) 500 cm^3 of FA2.

(b) Calculate the percentage of Fe^{3+} ions in FA2.

7 A solution of iodine contained 50.8 g of iodine per dm^3. 20.0 cm^3 of this iodine solution was reacted with 44.8 cm^3 of sodium thiosulphate solution. Calculate the mass of $Na_2S_2O_3.5H_2O$ in one dm^3 of solution.

Question

A solution of an oxidising agent contains 5.80 g of XO_4^{2-} per dm^3 of solution.
25.0 cm^3 of this solution, acidified with dilute sulphuric acid, required 37.5 cm^3 of 0.1 mol dm^{-3} $Fe^{2+}(aq)$ for reaction.
The equation for the reaction is: $XO_4^{2-} + 8H^+ + 3Fe^{2+} \rightarrow X^{3+} + 3Fe^{3+} + 4H_2O$

Calculate the relative atomic mass of element X.
[O = 16.0]

Answer

Number of moles of Fe^{2+} used in the titration $= 0.1 \times \frac{37.5}{1000}$ mole

From the equation, $\frac{\text{no. of moles of } XO_4^{2-}}{\text{no. of moles of } Fe^{2+}} = \frac{1}{3}$

ie number of moles of XO_4^{2-} used in the titration $= \frac{1}{3} \times$ no. of moles of Fe^{2+}

$= \frac{1}{3} \times 0.1 \times \frac{37.5}{1000}$ mole

Answer

Hence the number of moles of XO_4^{2-} in 1 dm^3 (ie the concentration in mol dm^{-3})

$$= \frac{\frac{1}{3} \times 0.1 \times \frac{37.5}{1000}}{\frac{25}{1000}}$$

$$= \frac{\frac{1}{3} \times 0.1 \times 37.5}{25}$$

$\frac{\frac{1}{3} \times 0.1 \times 37.5}{25}$ mole of XO_4^{2-} has a mass of 5.80 g.

Hence 1 mole of XO_4^{2-} has a mass of $\frac{5.80 \times 25.0}{\frac{1}{3} \times 37.5 \times 0.1} = 116$ g

ie the relative formula mass of $XO_4^{2-} = 116$

Hence the relative atomic mass of $X = 116 - 4(16) = 52$.

EXERCISE 3F

*1 Solution FA2 contains 6.20 g of the ethanedioate, $\mathbf{M_2C_2O_4}$, per dm^3.
Solution FA3 contains 1.19 g of MnO_4^- per dm^3.
10.0 cm^3 of FA2 was pipetted into a titration flask. 25.0 cm^3 of ordinary dilute sulphuric acid was added. The mixture was then titrated with FA3 in the burette and the end-point was reached when 20.0 cm^3 of FA3 had been added.

(a) (i) How do you know when the end-point was reached?

(ii) What other condition is required for the titration to be successful?

(b) Calculate the relative formula mass of $\mathbf{M_2C_2O_4}$ and the relative mass of **M**, an ion with a charge of +1.

(c) **M** contains five atoms. What is **M**?

*2 A solution contains 28.6 g of the metal ethanedioate, $\mathbf{MC_2O_4}$, per dm^3 of solution. 25.0 cm^3 of this solution of $\mathbf{MC_2O_4}$ was placed in a titration flask together with excess dilute sulphuric acid. The titration flask solution reacted with 20.0 cm^3 of 0.1 mol dm^{-3} $KMnO_4$.

(a) Write a balanced ionic equation for the reaction between $KMnO_4$ and $\mathbf{MC_2O_4}$.

(b) Calculate the number of moles of $\mathbf{MC_2O_4}$ in 1 dm^3 of solution.

(c) Calculate the relative atomic mass of metal **M**.

*3 Solution FA1 contains 3.71 g of metal chromate, $\mathbf{MCrO_4}$, per dm^3 of solution.
Solution FA2 contains 0.100 mole of Fe^{2+} per dm^3 of solution.
In an experiment, 25.0 cm^3 of FA1 was placed in a titration flask and excess dilute sulphuric acid added. This solution reacted with 20.0 cm^3 of FA2. The equation for the reaction is

$$CrO_4^{2-} + 8H^+ + 3Fe^{2+} \rightarrow Cr^{3+} + 4H_2O + 3Fe^{3+}$$

Calculate

(a) the concentration of $\mathbf{MCrO_4}$ in FA1, in mol dm^{-3} and

(b) the relative atomic mass of element **M**.

[O = 16.0; Cr = 52.0]

3.6 Titrations with Iodine

- A common redox titration is the addition of an oxidising agent to excess potassium iodide solution. The iodide ions are oxidised to iodine. The iodine is then titrated with sodium thiosulphate, using starch as indicator. The equation for the reaction between iodine and thiosulphate is

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

Question

25.0 cm^3 of aqueous potassium iodate(V) reacted with excess acidified potassium iodide solution according to the equation $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$.

The iodine produced in the reaction required 18.0 cm^3 of sodium thiosulphate solution for reaction. The sodium thiosulphate solution contains 24.8 g of $Na_2S_2O_3.5H_2O$ per dm^3 of solution. Calculate the concentration of the potassium iodate(V), KIO_3, solution. [H = 1.00; O = 16.0; Na = 23.0; S = 32.0; K = 39.0; I = 127]

Answer

M_r of $Na_2S_2O_3.5H_2O = 248$

Concentration of $S_2O_3^{2-} = \frac{24.8}{248} = 0.100 \text{ mol dm}^{-3}$

Number of moles of $S_2O_3^{2-}$ used when $S_2O_3^{2-}$ reacts with $I_2 = \frac{18.0}{1000} \times 0.100$ mole

The equation for the reaction between $S_2O_3^{2-}$ and I_2 is $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

From this equation, $\frac{\text{no. of moles of } I_2}{\text{no. of moles of } S_2O_3^{2-}} = \frac{1}{2}$

ie number of moles of $I_2 = \frac{1}{2} \times$ no. of moles of $S_2O_3^{2-} = \frac{1}{2} \times \frac{18.0}{1000} \times 0.100$ mole

From the first equation, $\frac{\text{no. of moles of } IO_3^- \text{used}}{\text{no. of moles of } I_2 \text{ produced}} = \frac{1}{3}$

ie number of moles of $IO_3^- = \frac{1}{3} \times$ no. of moles of $I_2 = \frac{1}{3} \times \frac{1}{2} \times \frac{18.0}{1000} \times 0.100$ mole

$$\text{Therefore concentration of } IO_3^- = \frac{\text{no. of moles}}{\text{volume in dm}^3} = \frac{\frac{1}{3} \times \frac{1}{2} \times \frac{18.0}{1000} \times 0.100}{\frac{25.0}{1000}}$$

$$= 0.012 \text{ mol dm}^{-3}$$

Hence concentration of KIO_3 in g dm^{-3} = 0.012 x 214 g dm^{-3} = 2.57 g dm^{-3}

EXERCISE 3G

*1 Potassium iodate(V), KIO_3, reacts with excess acidified potassium iodide solution according to the equation

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

In an experiment, 20.0 cm³ of KIO_3 solution was added to excess acidified potassium iodide. The iodine produced was then titrated with 22.45 cm³ of sodium thiosulphate. The reaction is

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

The concentration of the thiosulphate was 29.8 g of $Na_2S_2O_3.5H_2O$ per dm³. Calculate the concentration of the potassium iodate(V) in g dm^{-3}.

*2 A solution of a metal chromate(VI) contains 15.60 g of **M**CrO_4 per dm³. 10.0 cm³ of the chromate(VI) solution was added to excess acidified potassium iodide. The chromate(VI) ions reacted with the iodide ions according to the equation

$$CrO_4^{2-} + 8H^+ + 3I^- \rightarrow \frac{3}{2}I_2 + 4H_2O + Cr^{3+}$$

The iodine produced was titrated with thiosulphate solution. 30.0 cm³ of thiosulphate solution containing 11.2 g of $S_2O_3^{2-}$ per dm³ was used in the titration. Calculate the relative atomic mass of metal **M**.

*3 A solution of a metal iodate(VII) contained 5.53 g of **M**IO_4 per dm³. 25.0 cm³ was added to excess acidified potassium iodide. The iodate(VII) ions reacted with the iodide according to the equation

$$IO_4^- + 7I^- + 8H^+ \rightarrow 4I_2 + 4H_2O$$

The iodine produced required 33.3 cm³ of 0.120 mol dm^{-3} $S_2O_3^{2-}$ for reaction. Calculate the relative atomic mass of element **M**. Suggest the identity of **M**.

*4 Copper ions react with potassium iodide solution according to the equation

$$2Cu^{2+}(aq) + 4I^-(aq) \rightarrow 2CuI(s) + I_2(aq)$$

25.0 cm³ of a solution of copper(II) sulphate was added to excess potassium iodide solution. The iodine produced was titrated with 21.0 cm³ of 0.05 mol dm^{-3} $Na_2S_2O_3$ sodium thiosulphate solution.

(a) Write an ionic equation for the reaction between I_2 and $Na_2S_2O_3$.

(b) Calculate the concentration of the copper sulphate solution in grams per dm³ of copper.

*5 Iodate(V) ions react with iodide ions according to the equation

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

Solution FC3 contains 3.50 g of IO_3^- per dm³.
Solution FC4 contains KI.
Solution FC5 contains dilute hydrochloric acid of unknown concentration.
Solution FC6 contains 24.8 g of $Na_2S_2O_3.5H_2O$ per dm³ of solution. The following experiment was carried out to find the concentration of the hydrochloric acid.

10.0 cm³ of FC5 was pipetted into a titration flask. Approximately 25.0 cm³ of FC3 was then added (in excess), followed by an excess of FC4. The iodine produced was then titrated with FC6; 27.0 cm³ of FC6 being required to reach an end-point. Calculate

(a) the number of moles of I_2 produced in the titration;

(b) the number of moles of H^+ in 1 dm³ of FC5 and

(c) the mass of hydrogen chloride in 1 dm³ of FC5.

6 Iodate(V) ions react with acidified iodide ions according to the equation

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

In an experiment, 40.0 cm³ of hydrochloric acid was added to *excess* potassium iodide solution and *excess* potassium iodate(V) solution. The iodine produced required 12.0 cm³ of 0.05 mol dm^{-3} $S_2O_3^{2-}$ for reaction. Calculate the concentration of the hydrochloric acid in

(a) mol dm^{-3}, and

(b) grams of H^+ per dm³.

3.7 Determination of Redox Equations

Question

Hydroxylamine, NH_2OH, can be oxidised to nitrogen according to the following half-equation:

$$2NH_2OH \rightarrow N_2 + 2H_2O + 2H^+ + 2e^-$$

(a) Hydroxylamine can also be oxidised to nitrogen oxide, N_2O. Write a half-equation for this oxidation.
In an experiment, 160 cm^3 of 0.05 mol dm^{-3} $NH_2OH(aq)$ was reacted with 40 cm^3 of 0.40 mol dm^{-3} $Fe^{3+}(aq)$. In the reaction, the Fe^{3+} was reduced to Fe^{2+}.

(b) Calculate
  (i) the number of moles of NH_2OH used in the reaction;
  (ii) the number of moles of Fe^{3+} used in the reaction;
  (iii) the number of moles of Fe^{3+} that reacted with 1 mole of NH_2OH.

(c) Hence deduce whether the NH_2OH is oxidised to N_2 or N_2O by the Fe^{3+}. Write a balanced ionic equation for the reaction.

Answer

(a) $2NH_2OH \rightarrow N_2O + H_2O + 4H^+ + 4e^-$

(b) (i) $\frac{160}{1000} \times 0.05 = 0.008$ mole of NH_2OH

(ii) $\frac{40}{1000} \times 0.40 = 0.016$ mole of Fe^{3+}

(iii) 0.008 mole of NH_2OH reacted with 0.016 mole of Fe^{3+}.

Hence 1 mole of NH_2OH reacts with $\frac{0.016}{0.008} = 2$ moles of Fe^{3+}.

(c) $Fe^{3+} + e^- \rightarrow Fe^{2+}$

2 Fe^{3+} accept 2 electrons. So 1 NH_2OH must produce 2 electrons in the reaction.
When NH_2OH is oxidised to N_2, 1 NH_2OH produces 1 electron (see first equation). However this is not the correct equation.
When NH_2OH is oxidised to N_2O, 1 NH_2OH produces 2 electrons (see equation in (a) above). Hence this is the correct equation. NH_2OH is oxidised to N_2O by Fe^{3+}.
The equation for the reaction is:

$$2NH_2OH + 4Fe^{3+} \rightarrow N_2O + H_2O + 4H^+ + 4Fe^{2+}$$

EXERCISE 3H

1 Tin(II) ions can be oxidised to tin(IV) ions by iodate(V), in the presence of HCl as shown.

$$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$$

The half-equation for the reduction of the iodate(V) in the reaction is believed to be one of the following:

$IO_3^- + 6H^+ + 3Cl^- + 2e^- \rightarrow ICl_3 + 3H_2O$ ...... (i)

$IO_3^- + 6H^+ + Cl^- + 4e^- \rightarrow ICl + 3H_2O$ ...... (ii)

$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$ ...... (iii)

$IO_3^- + 6H^+ + 6e^- \rightarrow I^- + 3H_2O$ ...... (iv)

In an experiment, 25.0 cm^3 of 0.025 mol dm^{-3} IO_3^-(aq) was found to react with 31.2 cm^3 of 0.04 mol dm^{-3} Sn^{2+} in the presence of excess hydrochloric acid. Calculate

(a) the number of moles of Sn^{2+} used in the reaction;

(b) the number of moles of IO_3^- used in the reaction;

(c) the number of moles of Sn^{2+} that reacted with 1 mole of IO_3^-.

(d) Hence which half-equation for the reduction of IO_3^- is correct?

*2 Nitric(V) acid can be reduced to a number of different products. Some half-equations for this reduction are

$NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$ ...... (i)

$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O$ ...... (ii)

$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$ ...... (iii)

$NO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}N_2 + 3H_2O$ ...... (iv)

(a) Give the formula of a nitrogen compound in which the nitrogen atom has an oxidation number *different* from any of the ions and molecules shown above.

In an experiment 25.0 cm^3 of 0.40 moles per dm^3 nitric(V) acid, in the presence of excess dilute sulphuric acid, was found to react with 150.0 cm^3 of a solution of iron(II) sulphate containing 11.2 g of Fe^{2+} per dm^3. Calculate

(b) the number of moles of NO_3^- used in the reaction;

(c) the number of moles of Fe^{2+} used in the reaction;

(d) the number of moles of Fe^{2+} that reacted with one mole of NO_3^-.

(e) Hence which half-equation is likely to be correct for the reduction of nitric(V) acid?

(f) What would you expect to *observe* in the mixture of products when this reaction is carried out? Give a brief explanation.

3 Nitrate(III) ions, NO_2^-, may be reduced under different conditions to nitrogen oxide, NO; dinitrogen oxide, N_2O; or nitrogen, N_2.

(a) The half-equation for the reduction of NO_2^- to N_2O is

$$2NO_2^- + 6H^+ + 4e^- \rightarrow N_2O + 3H_2O$$

Write similar half-equations for the reduction of NO_2^- to NO and to N_2.

(b) In an experiment, 40.0 cm^3 of 0.05 mol dm^{-3} NO_2^- was found to react with 60.0 cm^3 of 0.1 mol dm^{-3} Ti^{2+}. In the reaction the Ti^{2+} was oxidised to Ti^{3+}. Calculate the number of moles of

(i) NO_2^- used in the reaction;

(ii) Ti^{2+} used in the reaction;

(iii) Ti^{2+} that reacted with 1 mole of NO_2^-.

(c) From (b) deduce whether NO_2^- was reduced to NO, N_2O or N_2. Hence write a balanced equation for the reaction between NO_2^- and Ti^{2+}.

Question

A solution of $Ti^{2+}(aq)$ is oxidised to a higher oxidation state by a solution of $Fe^{3+}(aq)$. In the reaction, the $Fe^{3+}(aq)$ is reduced to $Fe^{2+}(aq)$.
In an experiment, 40.0 cm^3 of 0.02 mol dm^{-3} $Ti^{2+}(aq)$ was found to react with 32.0 cm^3 of 0.05 mol dm^{-3} $Fe^{3+}(aq)$.

(a) Calculate
   - (i) the number of moles of Ti^{2+} used in the experiment;
   - (ii) the number of moles of Fe^{3+} used in the experiment and
   - (iii) the number of moles of Fe^{3+} that reacted with one mole of Ti^{2+}.

(b) Hence deduce the higher oxidation state of titanium and write a balanced ionic equation for the reaction.

Answer

a) (i) Number of moles of $Ti^{2+} = \frac{40.0}{1000} \times 0.02 = 0.8 \times 10^{-3}$ mole

(ii) Number of moles of $Fe^{3+} = \frac{32.0}{1000} \times 0.05 = 1.6 \times 10^{-3}$ mole

(iii) 0.8×10^{-3} moles of Ti^{2+} react with 1.6×10^{-3} moles of Fe^{3+}.

Hence 1 mole of Ti^{2+} reacts with $\frac{1.6 \times 10^{-3}}{0.8 \times 10^{-3}} = 2$ moles of Fe^{3+}.

(b) $Fe^{3+} + e^- \rightarrow Fe^{2+}$
2 Fe^{3+} react with 1 Ti^{2+}. 2 Fe^{3+} accept 2 electrons (according to the equation above).
Therefore 1 Ti^{2+} must produce 2 electrons: $Ti^{2+} \rightarrow Ti^{4+} + 2e^-$
Hence the higher oxidation state of titanium is Ti^{4+}.
The equation for the reaction is $2Fe^{3+}(aq) + Ti^{2+}(aq) \rightarrow 2Fe^{2+}(aq) + Ti^{4+}(aq)$

EXERCISE 3I

1 Vanadium(II) ions can be oxidised quantitatively by acidified manganate(VII) ions, to a higher oxidation state. Two half-equations for the reaction can be written:

$$V^{2+} \rightarrow V^{z+} + (z-2)e^-$$
$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

In an experiment, 25.0 cm^3 of 0.02 mol dm^{-3} V^{2+} was found to react with 15.0 cm^3 of 0.02 mol dm^{-3} MnO_4^-, acidified with sulphuric acid.

(a) Calculate
   - (i) the number of moles of V^{2+} used in the titration;
   - (ii) the number of moles of MnO_4^- used in the titration and
   - (iii) the number of moles of V^{2+} that reacted with one mole of MnO_4^-.

(b) Hence deduce the number of electrons given up by one V^{2+} ion when it is oxidized.

(c) What is the new oxidation number of vanadium after oxidation (ie what is z)?

2 Chromium(II) ions can be titrated with $[CuCl_4]^{2-}$ ions, according to the half-equations:

$$Cr^{2+} \rightarrow Cr^{3+} + e^-$$
$$[CuCl_4]^{2-} + \dots e^- \rightarrow \dots + \dots$$

The second half-equation is incomplete.
In an experiment, 20.0 cm^3 of 0.04 mol dm^{-3} Cr^{2+} was found to react with 40.0 cm^3 of 0.01 mol dm^{-3} $[CuCl_4]^{2-}$.
Calculate

(a) the number of number of moles of Cr^{2+} and $[CuCl_4]^{2-}$ used in the reaction;

(b) the number of moles of $[CuCl_4]^{2-}$ that react with one mole of Cr^{2+}.

(c) Hence deduce the number of electrons accepted by one $[CuCl_4]^{2-}$ ion.

(d) (i) What is the oxidation number of copper in $[CuCl_4]^{2-}$?

(ii) Assuming that the copper gains the electrons, what is the new oxidation number of the copper atom after the reaction?

(iii) Hence write a complete half-equation for the reaction of $[CuCl_4]^{2-}$.

3 A solution of uranium ions, $UO_2^{2+}(aq)$ is yellow. The $UO_2^{2+}(aq)$ are reduced by zinc powder and acid to green $U^{z+}(aq)$ ions.

(a) What is the oxidation number of the uranium in UO_2^{2+}? (Assume that the oxygen atoms are not in peroxide bonds.) The $U^{z+}(aq)$ can be oxidised quantitatively to UO_2^{2+} by acidified $MnO_4^-(aq)$. It was found experimentally that 20.0 cm^3 of 0.1 mol dm^{-3} $U^{z+}(aq)$ reacted with 16.0 cm^3 of 0.05 mol dm^{-3} $MnO_4^-(aq)$.

(b) (i) Calculate the number of moles of $U^{z+}(aq)$ used in the titration.

(ii) Calculate the number of moles of $MnO_4^-(aq)$ used in the titration.

(iii) Hence calculate the number of moles of $U^{z+}(aq)$ that react with 1 mole of acidified $MnO_4^-(aq)$.

(iv) Deduce the number of electrons transferred per mole of U^{z+} in the reaction.

(v) Hence deduce the value of z on U^{z+}.

(c) Write an ion-electron half-equation for the reduction of UO_2^{2+} to U^{z+}.

(d) From the information above *only*, what part of the Periodic Table should uranium be placed in? Give *two* reasons for your answer.

*4 Solution FB11 contains 0.0684 mol dm^{-3} of an ion, X^{5+}, dissolved in dilute sulphuric acid. Solution FB12 contains 1.88 g dm^{-3} of manganate(VII) ion, MnO_4^-. The X^{5+} ion is reduced to X^{n+} by the action of acidified sodium sulphite. The X^{n+} can be oxidised back to X^{5+} by manganate(VII). In an experiment, 25.0 cm^3 of FB11 was reacted with excess sodium sulphite. Any sulphite remaining was then destroyed by boiling the mixture. The X^{n+} product required 21.6 cm^3 of FB12 for reaction.

(a) Calculate the concentration of FB12 in mol dm^{-3}.

(b) Calculate

(i) the number of moles of X^{n+} used in the reaction;

(ii) the number of moles of MnO_4^- used in the reaction and

(iii) the number of moles of X^{n+} that reacted with 1 mole of MnO_4^-.

(c) Hence deduce the value of *n* in X^{n+} and write a balanced ionic equation for the reaction of X^{n+} with MnO_4^-.

*5 Nitrogen exhibits a range of oxidation numbers in its compounds.

(a) Complete the table below which refers to possible reduction products of nitric acid.

formula of products	**oxidation number of nitrogen**
NO_2	
N_2O	
NH_2OH	
NH_4^+	

(b) (i) Copper can reduce nitric acid to NO_2. Write a balanced equation for this reaction.

(ii) Aluminium can reduce nitric acid to NH_4^+.
Write a balanced equation for this reaction.

(iii) Suggest a reason why the reduction products of nitric acid are different for each of these two metals.

(c) The compound NH_2OH is oxidised by $Fe^{3+}(aq)$, which is itself reduced to $Fe^{2+}(aq)$. In the experiment, 25.0 cm^3 of 0.100 mol dm^{-3} NH_2OH required 25.0 cm^3 of 0.200 mol dm^{-3} Fe^{3+} for complete reaction.

(i) How many moles of Fe^{3+} react with one mol of NH_2OH?

(ii) What change in oxidation number does the nitrogen in NH_2OH undergo?

(iii) Which formula from the table in (a) corresponds to the nitrogen-containing product of this reaction?

(iv) Construct an equation for the reaction of NH_2OH with Fe^{2+}.

CHAPTER

4

CHEMICAL BONDS

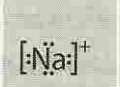
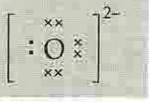
- Dot and Cross Diagrams
- Electrovalent Bonds
- Covalent Bonds
- Pi and Sigma Bonds
- Electronegativity and Type of Bond
- Number of Normal Covalent Bonds Formed by Elements
- Hybridisation
- Shapes of Simple Covalent Molecules
- Shapes of Molecules with Multiple Bonds
- Polar Molecules
- Van Der Waals Forces
- Hydrogen Bonds
- Co-ordinate Bonds
- Metallic Bonds

SYLLABUS OBJECTIVES

- Dot and Cross Diagrams
- Electrovalent Bonds
- Covalent Bonds
- Pi and Sigma Bonds
- Electronegativity and Type of Bond
- Number of Normal Covalent Bonds Formed By Elements
- Shapes of Simple Covalent Molecules
- Shapes of Molecules with Multiple Bonds
- Polar Molecules
- Van Der Waals Forces
- Hydrogen Bonds
- Co-ordinate Bonds
- Metallic Bonds

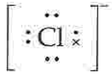
4.1 Dot and Cross Diagrams

- The electrons in the outer orbital of an atom or ion can be represented simply by 'dots' or 'crosses'. Some examples of 'dot and cross' diagrams are shown below.

particle	sodium atom	sodium ion Na^+	oxygen atom	oxide ion, O^{2-}
outer electrons	$3s^1$	$3s^0$	$2s^2\,2p^4$	$2s^2\,2p^6$
'dot and cross' diagram	Na·			

- 'Dots' and 'crosses' are often used to show where electrons come from. For example, a chloride ion can be produced by adding one electron to a chlorine atom. A 'dot and cross' diagram for the chloride ion is shown below. The 'dots' indicate the original electrons of the chlorine and the 'cross' represents the extra electron.

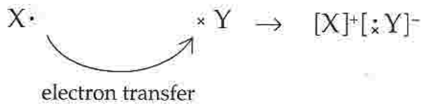
chlorine atom



chloride ion, Cl^-

4.2 Electrovalent Bonds

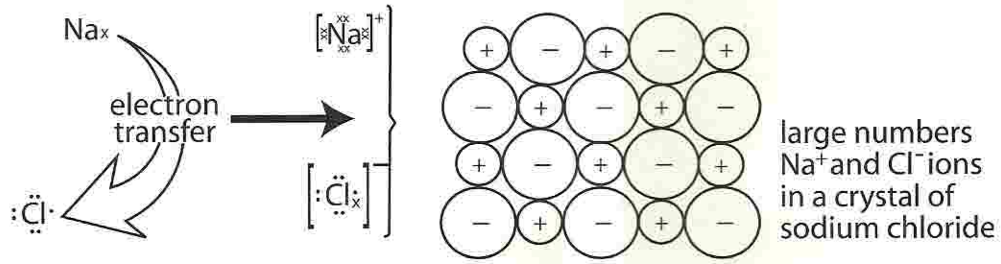
- **Electrovalent bonds** are produced when electrons are transferred from atoms of one element to atoms of another element, producing positive and negative ions. A simple 'dot and cross' diagram for forming an electrovalent bond is:



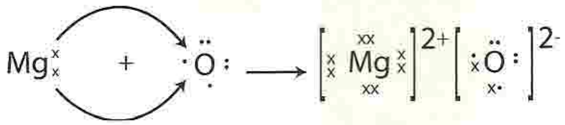
- The positive and negative ions are held together by electrovalent bonds. The bond is the electrostatic force of attraction between the positive and negative ions.

- Sodium chloride is an example of a substance with electrovalent bonds (Fig 4.1).

▶ Fig 4.1



- Magnesium oxide is ionic, containing Mg^{2+} and O^{2-} ions, and therefore contains electrovalent bonds. The ions are formed by transferring two electrons from each magnesium atom to an oxygen atom.



- Electrovalent bonds are only formed between metals and non-metals. Electrovalent bonds are *not* formed between two non-metals.

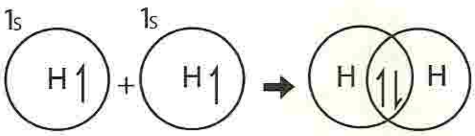
4.3 Covalent Bonds

- A **covalent bond** is formed when two atoms, each with a single electron, come together so that the two electrons are shared between the two atoms.

$$X\cdot \;+\; {}_{\times}Y \;\rightarrow\; X \overset{\times}{\cdot} Y \quad \text{or} \quad X - Y$$

- In the formation of a covalent bond:
  - (a) each atom has an orbital in the outer level containing a single electron;
  - (b) the two orbitals overlap so that an electron pair is produced, which is shared by both atoms.
- The covalent bond in a hydrogen molecule, H_2, is shown in Fig 4.2.

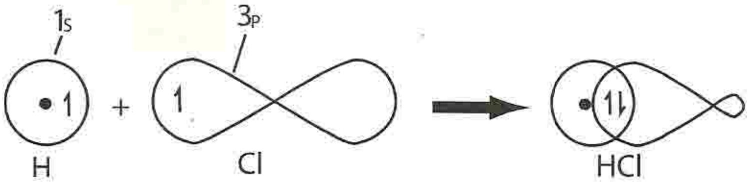
▶ Fig 4.2 Covalent bond in H_2 molecule



This bond can be drawn simply with a 'dot and cross' diagram:

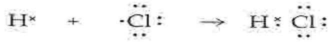
$$H^{\times} + \cdot H \rightarrow H{\times}H$$

- The covalent bond in a hydrogen chloride molecule, HCl, is shown in Fig 4.3.

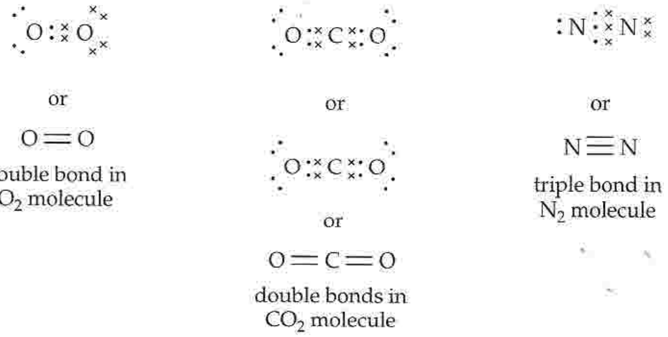


▶ Fig 4.3 Covalent bond in HCl molecule

This bond can be drawn simply with a 'dot and cross' diagram:



- The bond is the force of attraction between the pair of electrons and the two positive nuclei of the atoms.
- Covalent bonds are formed between
  (a) two atoms of non-metallic elements;
  (b) an atom of a non-metallic element and an atom of *some* metals.
- Examples of covalent bonds are the bonds in diamond, silicon dioxide and molecules of I_2, CH_4, H_2O and NH_3.
- In a *double covalent bond*, each atom provides two electrons so that a total of four electrons are shared by the two atoms (Fig 4.4).
- In a *triple covalent bond*, each atom provides three electrons so that a total of six electrons are shared by the two atoms (Fig 4.4).



▶ Fig 4.4 Double and triple covalent bonds

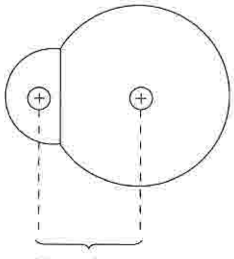
Bond Energy

- The strength of a covalent bond is measured by the **bond energy**. The bond energy is the amount of energy required to break one mole of a covalent bond. The greater the bond energy, the stronger the bond.
- Covalent compounds with small bond energies decompose easily when heated, compared with compounds having large bond energies. An example is the effect of heat on the Group VII hydrides (see Chapter 14). Hydrogen iodide (HI) decomposes when heated to red hot but not hydrogen chloride (HCl). This difference is due to the weaker H—I bond.

covalent bond	H—Cl	H—I
bond energy/kJ mol^{-1}	431	299

▶ Table 4.1

- Very large bond energies can make molecules unreactive. The nitrogen molecule (N_2) is unreactive because of the very large N≡N bond energy of 944 kJ mol^{-1}. A large amount of energy must be supplied to the N_2 molecule to break the triple bond before nitrogen can react with other elements.
- Bond energies can be used to calculate enthalpy changes of reaction (see Chapter 6).


bond length = 0.128 nm

▲ Fig 4.5 Bond length in HCl molecule

Bond Length

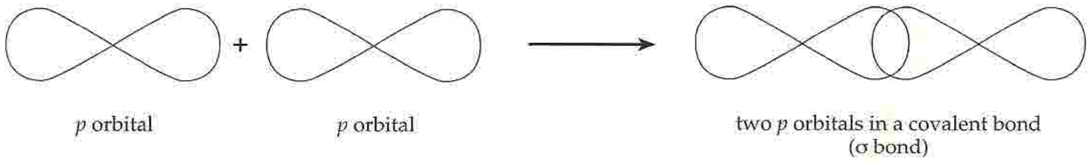
- The covalent **bond length** is the distance between the nuclei of the two atoms in the bond. An example is the H—Cl bond length in hydrogen chloride (Fig 4.5).
- In general, the shorter the bond length, the stronger the covalent bond. This is shown by the example in Table 4.2.

covalent bond	C—Cl	C—Br	C—I
bond length/nm	0.177	0.193	0.214
bond energy/kJ mol^{-1}	338	276	238

▶ Table 4.2 Bond lengths and bond energies

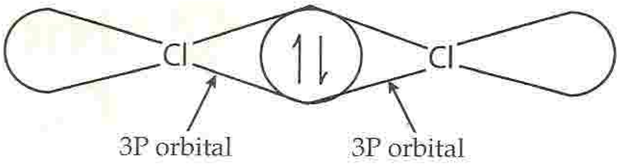
4.4 Pi and Sigma Bonds

- A **sigma bond** (σ bond) is formed when orbitals overlap *head-on* in a covalent bond (Fig 4.6). In a sigma bond, the electron density is concentrated in the orbital overlap volume *between* the two nuclei. A sigma bond can be rotated without breaking the bond.

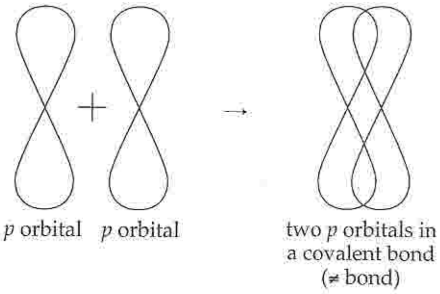


▲ Fig 4.6

An example is the covalent bond in the chlorine molecule, Cl_2. Two 3*p* orbitals from two chlorine atoms overlap to form the covalent bond (Fig 4.7).



▶ Fig 4.7



▲ Fig 4.8

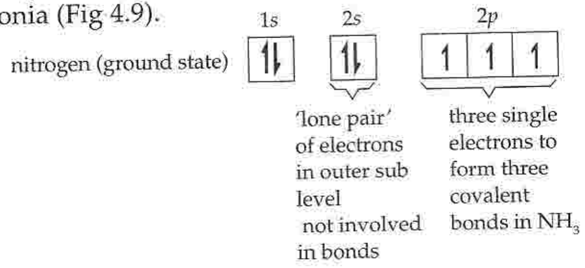
- A **pi bond** (π bond) is formed when orbitals overlap *sideways* in a covalent bond (Fig 4.8). In a pi bond, the electron density is concentrated in the orbital overlap volumes *above and below* the line joining the two nuclei. A pi bond cannot be rotated without breaking the bond.
  An example of a pi bond is the C═C bond in ethene. This bond consists of two parts. One part consists of two *p* orbitals of carbon overlapping in a sigma bond. In the other part of the bond, two *p* orbitals overlap in a pi bond (see Fig 17.5 in Chapter 17).

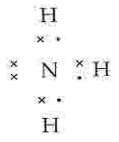
4.5 Electronegativity and Type of Bond

- **Electronegativity** is a measure of the attractive power of atoms for electrons in chemical bonds. It is a number between 0 and 4.0 (see *Data Tables* at the back of this book).
- Metals have small electronegativities thus have a small attraction for electrons.
- Non-metals have big electronegativities thus have a large attraction for electrons.
- When two atoms come together to form a chemical bond, either
  (a) a covalent bond is formed if the *difference* in electronegativity is *small* (usually < 1.5), eg between atoms of two non-metals;
  (b) an electrovalent bond is formed if the *difference* in electronegativity is *large* (usually > 1.5), eg between an atom of a metal and an atom of a non-metal.

4.6 Number of Normal Covalent Bonds Formed By Elements

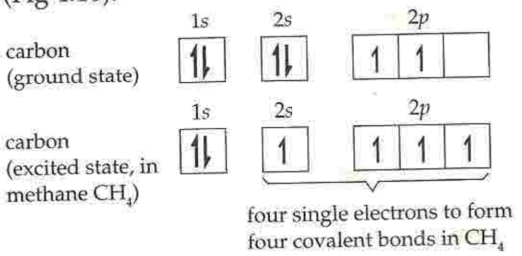
- The minimum number of covalent bonds formed by an element is equal to the number of single electrons in the outer energy level in the ground state electronic configuration, eg nitrogen in ammonia (Fig 4.9).

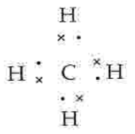




▲ Fig 4.9 'Dot and cross' diagram of ammonia

A pair of electrons in the outer sublevel can be split up. One electron of the pair can be promoted into an empty orbital of another sublevel (though the same main level) eg carbon in methane (Fig 4.10).

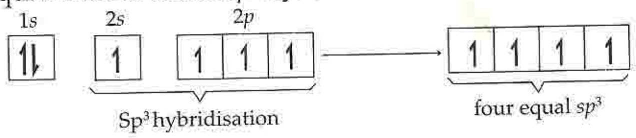


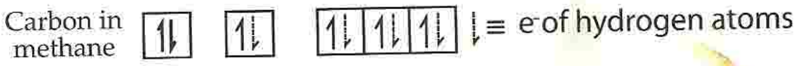


▲ Fig 4.10 'Dot and cross' diagram of methane

- **sp³ hybridisation**

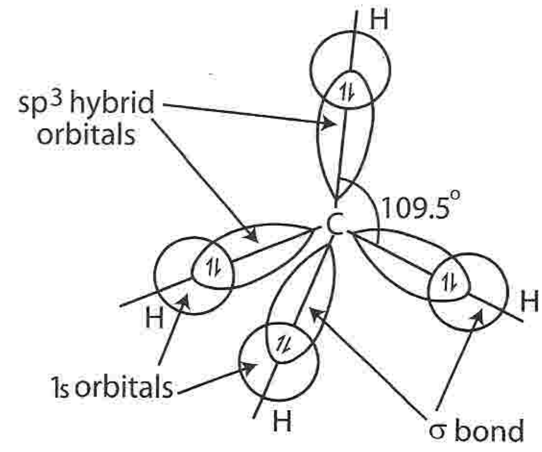
In practice these four orbitals are mixed together to form four equal orbitals called *sp*³ **hybrid orbitals.**





However this does not change the number of single electrons and the number of bonds formed, so hybridisation ('mixing of orbitals') can be ignored when working out 'dot and cross' diagrams.

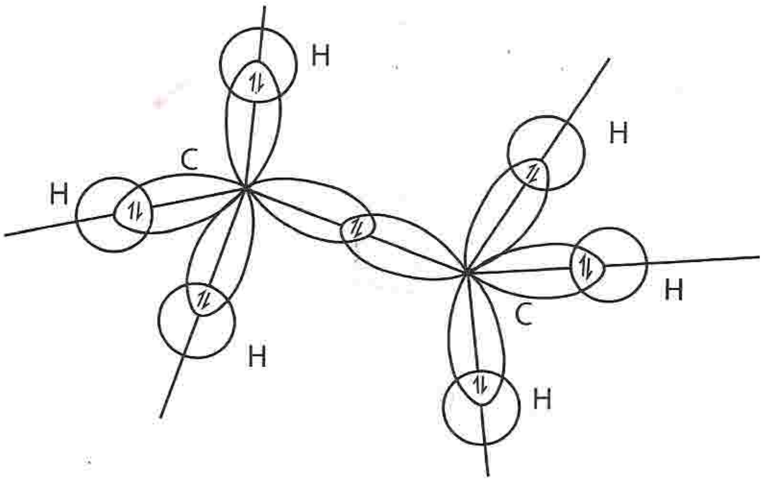
The bonding orbitals in methane are shown in Fig 4.11.



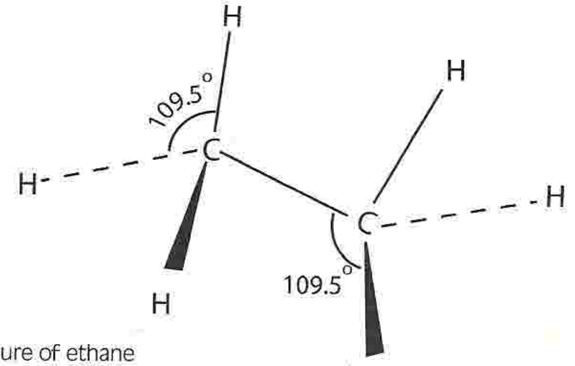
orbital bonding in methane CH_4

The structure of ethane C_2H_6.

During the formation of ethane, each carbon atom undergoes sp^3 hybridisation. Then a C - C sigma bond is formed by sp^3 / sp^3 overlap and six C – H sigma bonds are formed by sp^3 / s overlaps.



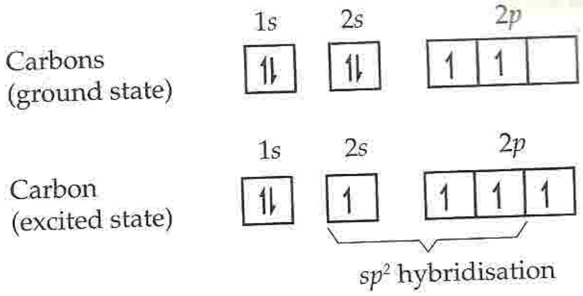
I.e



The structure of ethane

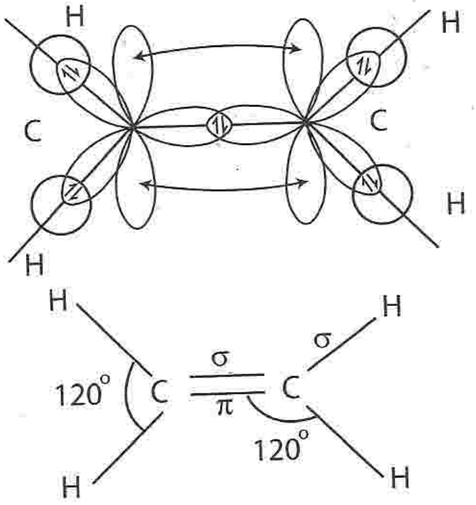
The structure of ethene, C_2H_4

- Sp^2 hybridisation occurs in ethene, C_2H_4. This is the mixing of one s and two p sublevels on the excited carbon atoms before the formation of ethene.



The sp^2 hybrid orbitals lie on the same plane. Each carbon atom has a flat trigonal environment and each bond angle is 120°. One C – C sigma bond is formed by sp^2 / sp^2 overlap and four C – H sigma bonds are form by **sp^2 / s** overlaps.

The remaining unhybridised **2p** orbital on each carbon atom is perpendicular to the plane of the molecule. They overlap sideways above and below the plane of the molecule to form a **Pi** bond.

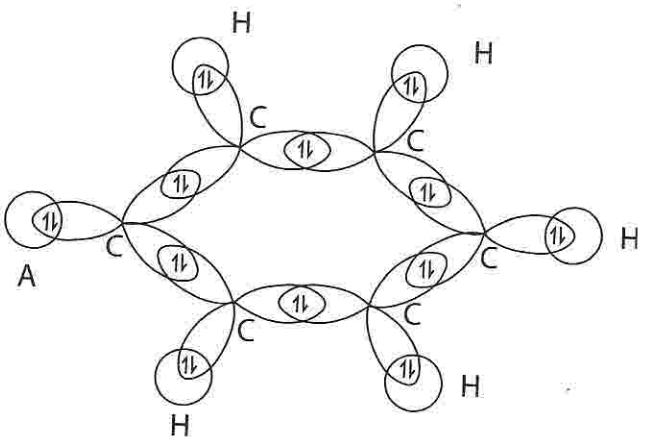


Formation of ethene

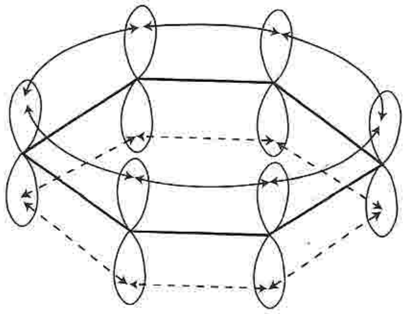
The structure of benzene C_6H_6.

From x-ray analysis, benzene molecule is planar with the six carbon atoms forming a regular hexagon. This implies that each carbon atom uses **sp^2** hybrid orbitals for bonding. Six **C – C** sigma bonds are formed by **sp2 / sp^2** overlaps. Six **C – H** sigma bonds are formed by sp^2 / s overlaps. The remaining unhybridised **p** orbitals are perpendicular to the plane of the hexagon.

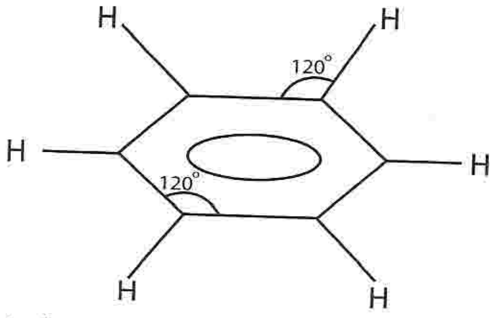
They overlap sideways above and below the ring to form a **Pi** system within which the six electrons are delocalised.



Formation of sigma bond in $C_6 H_6$



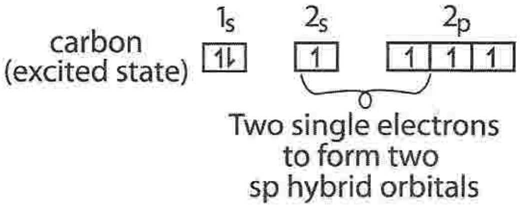
Unhybridised p orbitals overlapping sideways to form a π system



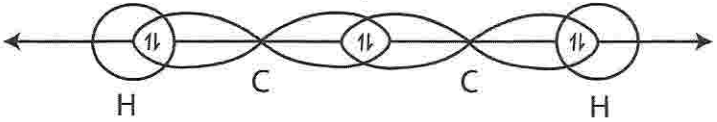
The circle inside the molecule show the π system

The structure of ethyne, $C_2 H_2$.

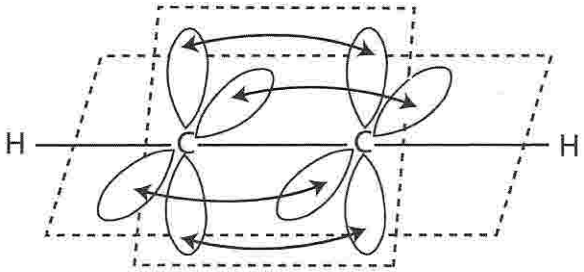
- Sp hybridisation occurs in ethyne, $C_2 H_2$.
  This is the mixing of one **s** and one **p** orbital on each excited carbon atoms to form two **sp** hybrid orbitals.



- The two sp hybrid orbitals lie on a straight line with the angle of 180° between them. Thus, one **C–C** sigma bond is formed by sp/sp overlap. Two **C–H** sigma bonds are formed by **sp / s** overlaps.
  The two pairs of unhybridised **p** orbitals overlap sideways to form two π bonds. Thus, a C≡C is formed with one σ bond and two π bonds.



Formation of σ bonds in $\mathbf{C_2H_2}$



Two pairs of **p** orbitals at right angle to each other forming π bonds

- Elements in the period Na ⟶ Ar can use the 3*d* sublevel. An example is phosphorus, which can form three covalent bonds in the ground state and five covalent bonds in the excited state.

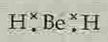
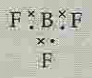
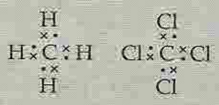
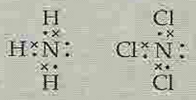
phosphorus (ground state)

$$\overset{3s}{\boxed{\upharpoonleft\downharpoonright}}\quad \underbrace{\overset{3p}{\boxed{\upharpoonleft}\boxed{\upharpoonleft}\boxed{\upharpoonleft}}}_{\text{three single electrons to form three covalent bonds in PCl}_3\text{ and PH}_3}\quad \overset{3d}{\boxed{}\boxed{}\boxed{}\boxed{}\boxed{}}$$

phosphorus (excited state, in PCl_5)

$$\underbrace{\overset{3s}{\boxed{\upharpoonleft}}\quad \overset{3p}{\boxed{\upharpoonleft}\boxed{\upharpoonleft}\boxed{\upharpoonleft}}\quad \boxed{\upharpoonleft}}_{\text{five single electrons to form five covalent bonds in PCl}_5}\overset{3d}{\boxed{}\boxed{}\boxed{}\boxed{}}$$

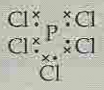
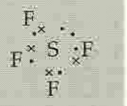
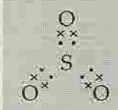
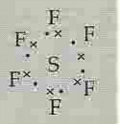
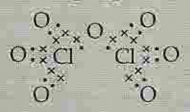
- A summary of the covalent bonds formed by some elements in the period Li ⟶ Ne is shown in Table 4.3.

proton number	element	outer shell electronic configuration			number of covalent bonds	example
4	beryllium	ground state	2*s* $\boxed{\upharpoonleft\downharpoonright}$	2*p* $\boxed{}\boxed{}\boxed{}$		
		excited state	$\boxed{\upharpoonleft}$	$\boxed{\upharpoonleft}\boxed{}\boxed{}$	2	
5	boron	ground state	2*s* $\boxed{\upharpoonleft\downharpoonright}$	2*p* $\boxed{\upharpoonleft}\boxed{}\boxed{}$		
		excited state	$\boxed{\upharpoonleft}$	$\boxed{\upharpoonleft}\boxed{\upharpoonleft}\boxed{}$	3	
6	carbon	ground state	2*s* $\boxed{\upharpoonleft\downharpoonright}$	2*p* $\boxed{\upharpoonleft}\boxed{\upharpoonleft}\boxed{}$		
		excited state	$\boxed{\upharpoonleft}$	$\boxed{\upharpoonleft}\boxed{\upharpoonleft}\boxed{\upharpoonleft}$	4	
7	nitrogen	ground state	2*s* $\boxed{\upharpoonleft\downharpoonright}$	2*p* $\boxed{\upharpoonleft}\boxed{\upharpoonleft}\boxed{\upharpoonleft}$	3	
8	oxygen	ground state	2*s* $\boxed{\upharpoonleft\downharpoonright}$	2*p* $\boxed{\upharpoonleft\downharpoonright}\boxed{\upharpoonleft}\boxed{\upharpoonleft}$	2	
9	fluorine	ground state	2*s* $\boxed{\upharpoonleft\downharpoonright}$	2*p* $\boxed{\upharpoonleft\downharpoonright}\boxed{\upharpoonleft\downharpoonright}\boxed{\upharpoonleft}$	1	
10	neon	ground state	2*s* $\boxed{\upharpoonleft\downharpoonright}$	2*p* $\boxed{\upharpoonleft\downharpoonright}\boxed{\upharpoonleft\downharpoonright}\boxed{\upharpoonleft\downharpoonright}$	0	–

▲ Table 4.3 Covalent bonds of elements in period Li ⟶ Ne

continued

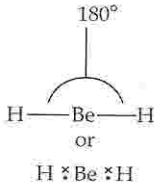
- A summary of the covalent bonds formed by some elements in the period Na ⟶ Ar is shown in Table 4.4.

proton number	element	outer shell electronic configuration		number of covalent bonds	example
13	aluminium	ground state	3s [⇅] 3p [↑][ ][ ]	3	
		excited state	3s [↑] 3p [↑][↑][ ]		
14	silicon	ground state	3s [⇅] 3p [↑][↑][ ]	4	
		excited state	3s [↑] 3p [↑][↑][↑]		
15	phosphorus	ground state	3s [⇅] 3p [↑][↑][↑]	3	
		excited state	3s [↑] 3p [↑][↑][↑] 3d [↑][ ][ ][ ][ ]	5	
16	sulfur	ground state	3s [⇅] 3p [⇅][↑][↑]	2	
		excited states	3s [⇅] 3p [↑][↑][↑] 3d [↑][ ][ ][ ][ ]	4	 
			3s [↑] 3p [↑][↑][↑] 3d [↑][↑][ ][ ][ ]	6	 
17	chlorine	ground state	3s [⇅] 3p [⇅][⇅][↑]	1	
		excited states	3s [⇅] 3p [⇅][↑][↑] 3d [↑][ ][ ][ ][ ]	3	
			3s [⇅] 3p [↑][↑][↑] 3d [↑][↑][ ][ ][ ]	5	
			3s [↑] 3p [↑][↑][↑] 3d [↑][↑][↑][ ][ ]	7	
18	argon	ground state	3s [⇅] 3p [⇅][⇅][⇅]	0	–

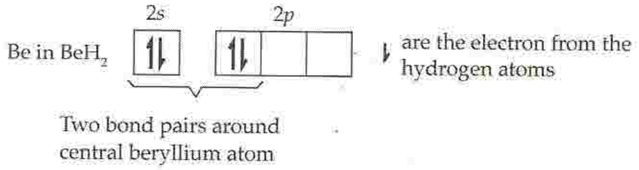
▲ Table 4.4 Covalent bonds of elements in period Na ⟶ Ar

4.7 Shapes of Simple Covalent Molecules

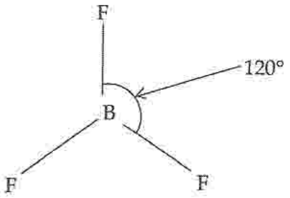
- The electron pairs around an atom are of two types:
  (a) bond pair of electrons (ie the two electrons in a covalent bond);
  (b) lone pair of electrons (ie a pair of electrons in the outer shell which is not involved in a bond).
- These electron pairs around the central atom of a molecule dictate the shape of the molecule.
- The electron pairs repel each other as far apart as possible.
- Force of repulsion between two bond pairs of electrons < Force of repulsion between a lone pair and a bond pair < Force of repulsion between two lone pairs of electrons
- **Two pairs of electrons**
  (a) The electron pairs are arranged at an angle of 180°.
  (b) If the atom is surrounded by *two bond pairs* of electrons, the molecule has a **linear** shape.
  eg – beryllium hydride, BeH_2 (Fig 4.12)



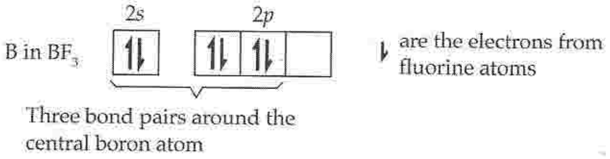
▲ Fig 4.12 Shape of BeH_2 molecule



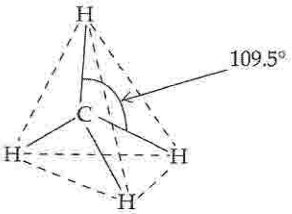
- **Three pairs of electrons**
  (a) The electron pairs are arranged at an angle of 120°.
  (b) If the atom is surrounded by *three bond pairs* of electrons, the molecule has a **trigonal planar** shape.
  eg – boron trifluoride, BF_3 (Fig 4.13)



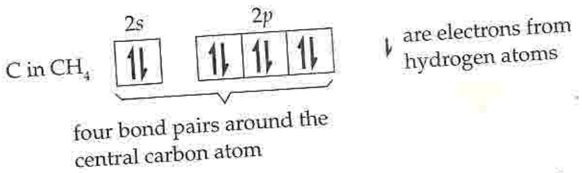
▲ Fig 4.13 Shape of BF_3 molecule



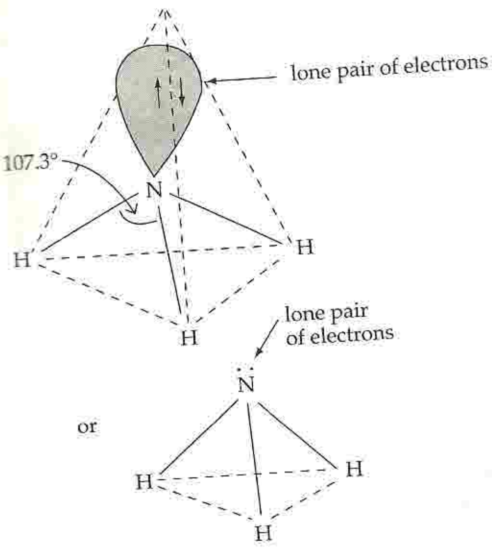
- **Four pairs of electrons**
  (a) The electron pairs are arranged tetrahedrally.
  (b) If the atom is surrounded by *four bond pairs* of electrons, the molecule has a **tetrahedral** shape.
  eg – methane, CH_4 (Fig 4.14)
  The H—C—H bond angle in methane is 109.5°.



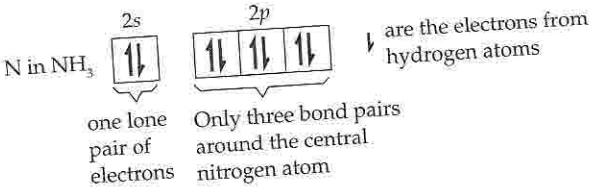
▲ Fig 4.14 Shape of CH_4 molecule



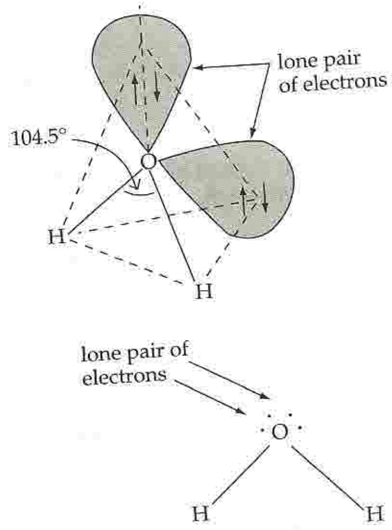
(c) If the atom is surrounded by *three bond pairs* and *one lone pair* of electrons, the molecule has a **pyramidal** shape.
eg ammonia, NH_3 (Fig 4.15)
The H—N—H bond angle in ammonia is 107.3°. This is less than the bond angle in methane because of the greater repulsive force of the lone pair of electrons.



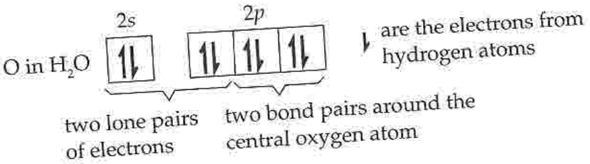
▲ Fig 4.15 Shape of NH_3 molecule



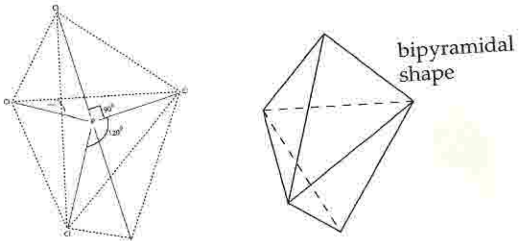
(d) If the atom is surrounded by *two bond pairs* and *two lone pairs* of electrons, the molecule has a **non-linear** shape.
eg water, H_2O (Fig 4.16)
The H—O—H bond angle in water is 104.5°. This is less than the bond angle in ammonia because of the greater repulsive force of the two lone pairs of electrons.



▲ Fig 4.16 Shape of H_2O molecule

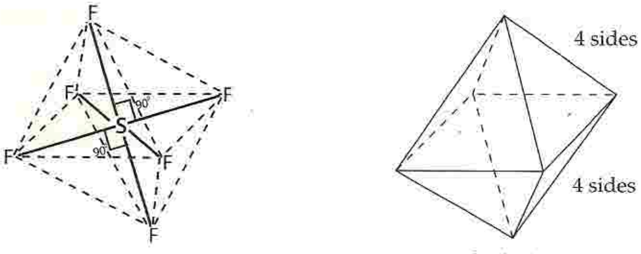


- **Five pairs of electrons**
  (a) If the electron pairs are *all bond pairs*, the molecule has a **bipyramidal** shape.
  eg phosphorus pentachloride, PCl_5 (Fig 4.17)



▶ Fig 4.17 Shape of PCl_5 molecule

- **Six pairs of electrons**
  (a) If the electron pairs are *all bond pairs*, the molecule has an **octahedral** shape.
  eg sulphur hexafluoride, SF_6 (Fig 4.18)



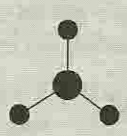
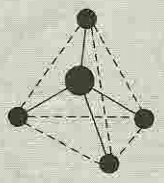
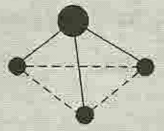
octahedral shape
(a total of eight sides)

▸ Fig 4.18 Shape of SF_6 molecule

(b) If the atom is surrounded by *four bond pairs* and *two lone pairs* of electrons, the molecule has a **square planar** shape.
eg – xenon tetrafluoride, XeF_4 (Fig 4.19)
Many transition metal complex ions is a square planar.

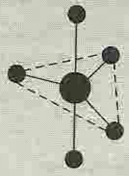
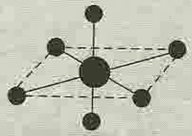
▸ Fig 4.19 Shape of XeF_4 molecule

Summary

total number of electron pairs	number of bond pairs	number of lone pairs	shape of molecule	example
2	2	0	 linear	BeH_2
3	3	0	 trigonal planar	BCl_3
4	4	0	 tetrahedral	CH_4, CCl_4, SiH_4
4	3	1	 pyramidal	NH_3, NCl_3, PCl_3, PH_3

▸ Table 4.5

(continued)

total number of electron pairs	number of bond pairs	number of lone pairs	shape of molecule	example
4	2	2	 non-linear(Bent)	H_2O, H_2S
5	5	0	 trigonal bipyramid	PCl_5
6	6	0	 octahedral	SF_6

▶ Table 4.5

4.8 Shapes of Molecules with Multiple Bonds

- The groups of electrons around the central atom stay as far apart from each other as possible.
- In carbon dioxide, there are two groups of four electrons around the carbon atom. The molecule is linear (Fig 4.20).

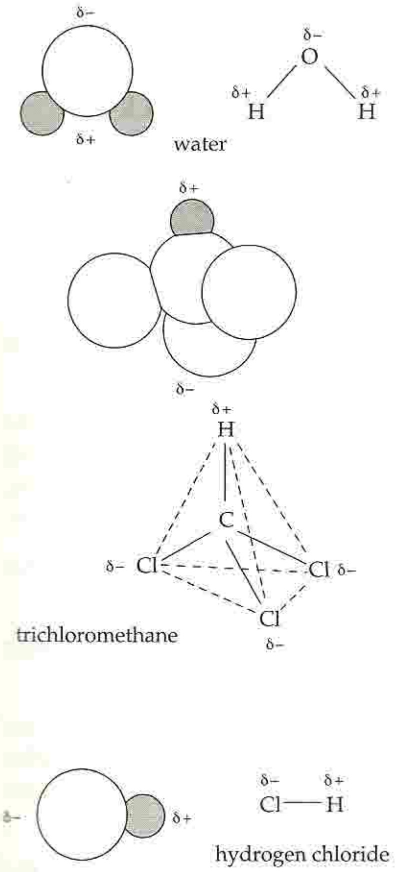
$O=C=O$

▲ Fig 4.20 Shape of CO_2 molecule

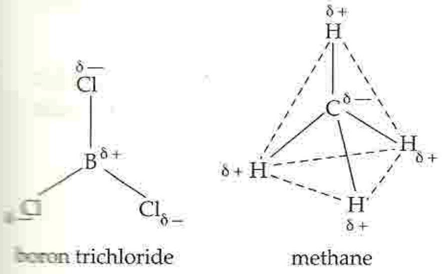
4.9 Polar Molecules

Polar Bonds

- In a covalent bond between two *different* atoms, one atom has a greater attraction for electrons than the other atom.
- The atoms with a greater attractive power for electrons (ie greater electronegativity) pulls the electrons of the covalent bond closer to it. This atom acquires a small negative charge, δ–.



▲ Fig 4.21



▲ Fig 4.22

- The other atom acquires a small positive charge, δ+.
- There is an unequal sharing of electrons. The covalent bond is said to be **polarised**; one end is positive while the other is negative.

$$^{\delta+}X — Y^{\delta-}$$

eg hydrogen chloride molecule $^{\delta+}H—Cl^{\delta-}$

- A covalent bond between two identical atoms (eg two iodine atoms in a molecule of I_2) is not polarised.
- Polarised bonds are chemically more reactive than bonds that are not polarised, as the δ+ and δ− charges can attract reacting molecules, such as H_2O and ions, such as OH^-. This is important in organic chemistry mechanisms.

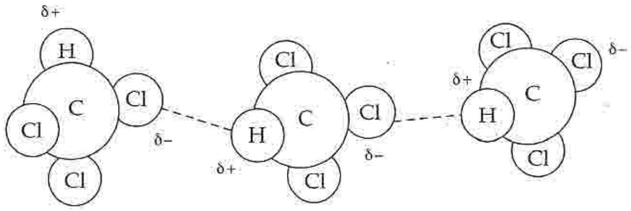
  The chemical unreactivity of hydrocarbon alkanes can be partly explained by the fact that the C—H bonds are almost non-polarised (see Chapter 19).

Polar Molecules

- A molecule which has a small positive charge on one end and a small negative charge on the other end is a polarised molecule. The molecule has a **dipole**.
- A molecule is polarised if
  (a) its bonds are polarised *and*
  (b) it is *not* symmetrical.
- Examples of polarised molecules are water, hydrogen chloride and trichloromethane (Fig 4.21).
- Examples of molecules which are *not* polarised (ie do *not* have a dipole) are chlorine, methane and boron trichloride (Fig 4.22).

Dipole-dipole Bonds

- Polar molecules are held together by dipole-dipole forces in the liquid and solid state. These forces are permanent.
- Examples of dipole-dipole forces are the forces between the molecules in liquid hydrogen chloride and liquid trichloromethane, $CHCl_3$ (Fig 4.23).



► Fig 4.23 Dipole-dipole forces in liquid $CHCl_3$

- Dipole-dipole forces are much weaker than covalent bonds and electrovalent bonds.

4.10 Van Der Waals Forces (Temporary Dipole-Dipole Forces)

- All atoms and molecules experience **Van der Waals** forces (also known as *induced* dipole-dipole forces).
- The induced dipoles are due to the random movement of electrons around atoms. At any point in time, the electron distribution may be slightly displaced towards one side of an atom or molecule, making that side slightly negative and the opposite side positive.
- The induced dipoles attract one another, producing a weak force of attraction.
- Van der Waals forces are very weak. They are only important when all other forces are absent.
- The forces between the molecules in molecular substances, in the solid and liquid states, are usually Van der Waals forces. Examples include solid iodine, liquid bromine and liquid noble gases (see Chapter 5).
- The strength of the Van der Waals forces is proportional to the number of electrons around the atoms and molecules. Therefore the larger the number of electrons, the stronger the forces that hold them together and hence the higher the melting and boiling points of the substance.
- The boiling points of the hydrides of Group IV elements increase down the group as the number of electrons around the molecule become bigger:

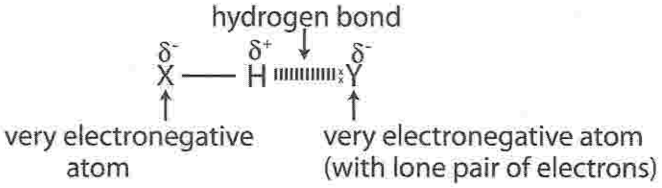
increase in number of electrons around molecules and strength of Van der Waals forces between molecules

Group IV hydride	*boiling point/°C*
CH_4	–162
SiH_4	–112
GeH_4	–90
SnH_4	–52

- The melting and boiling points of the halogen (Group VII) elements increase down the group from F_2 to I_2 as the Van der Waals forces become bigger.

4.11 Hydrogen Bonds

Nature of Hydrogen Bonds



▶ Fig 4.24 Hydrogen bond

- When a hydrogen atom is covalently attached to a very electronegative atom (X in Fig 4.24), the hydrogen atom can form a 'hydrogen bond' with another very electronegative atom (Y in Fig 4.24), which has a lone pair of electrons.

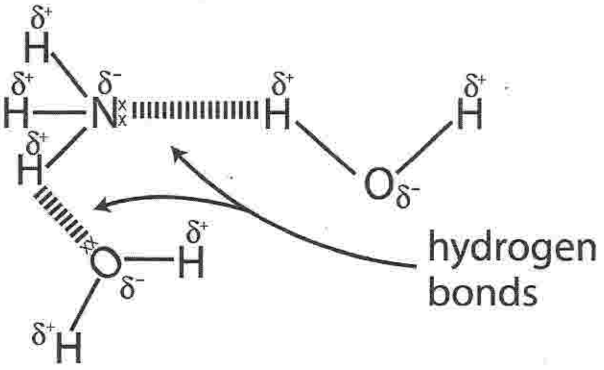
  In the covalent bond between H and X (Fig 4.24), the electrons are drawn towards X. In addition, hydrogen has no inner shell of electrons. Hence the hydrogen nucleus can get very close to the lone pair of electrons of the other electronegative atom (Y in Fig 4.24), without repulsion. Therefore hydrogen bonds are strong.

- Hydrogen bonds are stronger than ordinary dipole-dipole attractions, but weaker than normal covalent and electrovalent bonds.

- The very electronegative atoms (X and Y in Fig 4.24) are usually fluorine, oxygen or nitrogen.

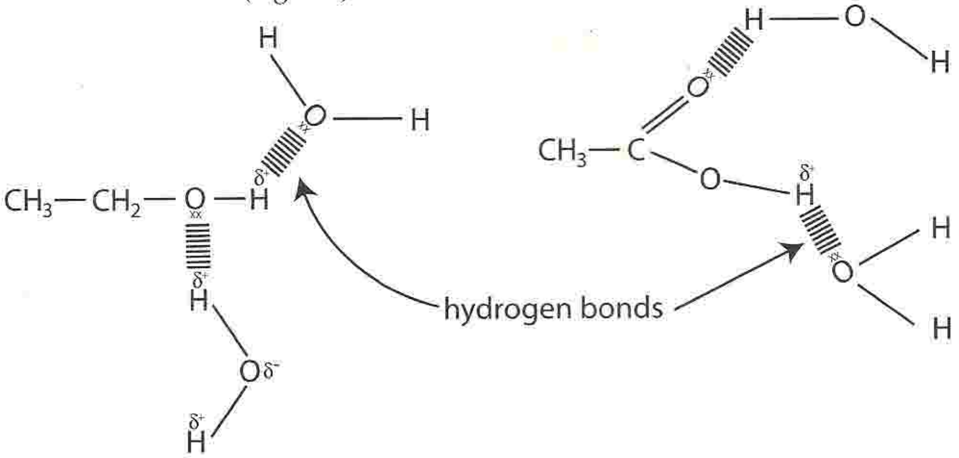
Properties of Hydrogen Bonding

- **Solubility of some substances in water**
  (a) Ammonia is very soluble in water as it forms hydrogen bonds with the water molecules (Fig 4.25).
  (b) Alcohols, carboxylic acids, amines and sugars dissolve in

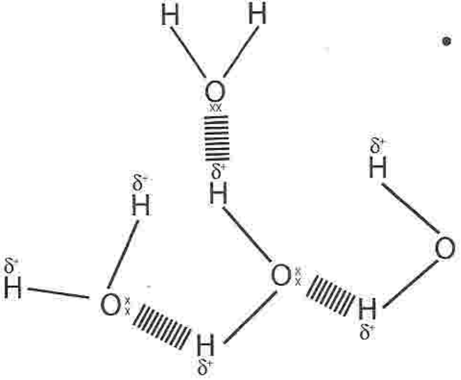


▶ Fig 4.25

water by forming hydrogen bonds with the water molecules (Fig 4.26).



▶ Fig 4.26 Ethanol and ethanoic acid in water

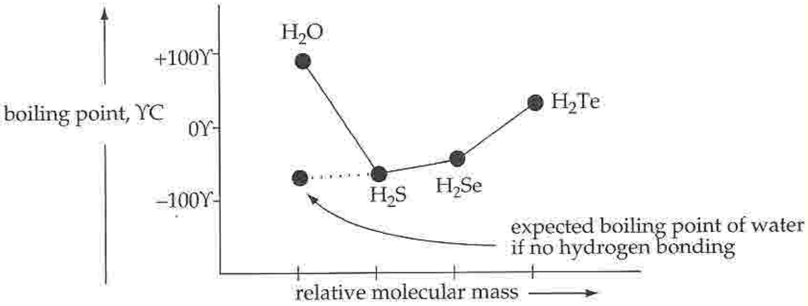


▲ Fig 4.27 Hydrogen bonds in water

- **Unusually high boiling points**

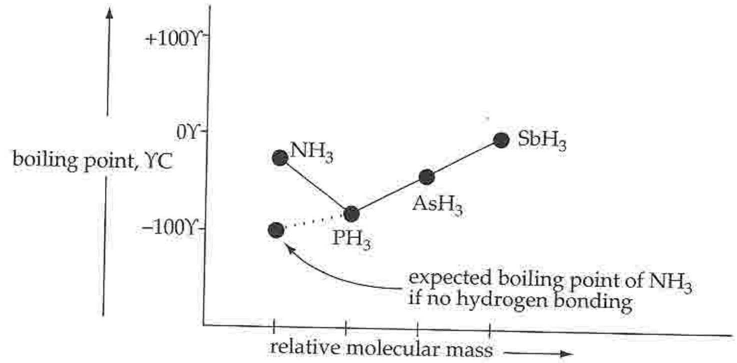
(a) Molecular substances held together by hydrogen bonds have higher boiling points than molecules held together by Van der Waals forces or ordinary dipole-dipole attractions.

(b) The hydrides of Group VI elements are molecular. Except for water whose molecules are held together by hydrogen bonds (Fig 4.27), the molecules of these hydrides are held together in the liquid state by Van der Waals forces and dipole-dipole attraction. The Van der Waals forces increase with increasing mass from H_2S to H_2Te (Fig 4.28). Water should have the lowest Mr value, but it has the highest boiling point because of relatively strong hydrogen bonds between its molecules.



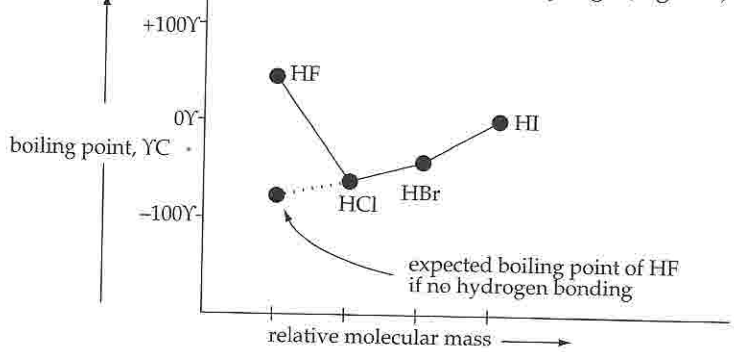
▶ Fig 4.28 Boiling points of Group VI hydrides

(c) The hydrides of Group V are molecular. Ammonia, NH_3, molecules are held together by hydrogen bonding in the liquid and solid states. Hence the boiling point of ammonia is unusually high. The other hydrides of Group V are held together by Van der Waals forces and dipole-dipole forces (Fig 4.29).



▸ Fig 4.29 Boiling points of Group V hydrides

(d) The boiling point trend for the hydrides of Group VII is similar to that of Group V and Group VI. Hydrogen fluoride molecules are held together by hydrogen bonds in the liquid. Hence the boiling point of hydrogen fluoride is unusually high (Fig 4.30).



▸ Fig 4.30 Boiling points of Group VII hydrides

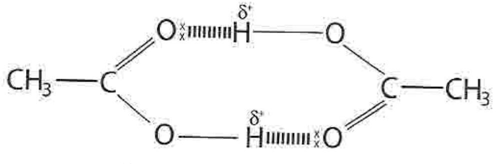
(e) Alcohols have relatively high boiling points because the molecules are held together by hydrogen bonds. Propane and ethanol have almost similar mass and size. However ethanol has a much higher boiling point because of its hydrogen bonds (Table 4.6).

compound	M_r	b.p./°C
propane	44	–42
ethanol	46	+78

▸ Table 4.6

- **Anomalous relative molecular masses**

(a) Just above its boiling point, gaseous ethanoic acid has an apparent relative molecular mass of 120 instead of the expected 60. This is because the gas particles consist of two CH$_3$COOH joined together by hydrogen bonds (Fig 4.31). This joining



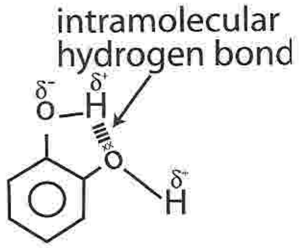
dimer of ethanoic acid

▸ Fig 4.31

together of molecules in pairs is called **dimerisation**.

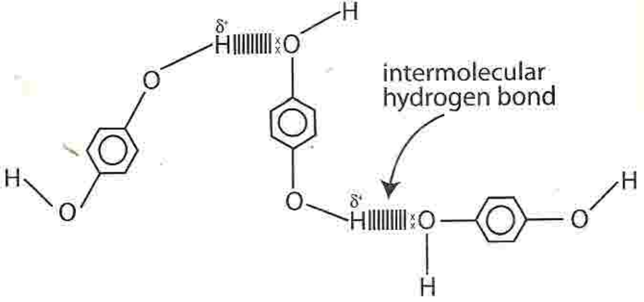
(b) Gaseous hydrogen fluoride has a larger apparent relative molecular mass than expected because the molecules are joined in twos or threes, $(HF)_2$ and $(HF)_3$, in the gaseous state by hydrogen bonding.

- **Intermolecular and intramolecular hydrogen bonding**
  (a) Hydrogen bonding between different molecules is called **intermolecular.**
  (b) Hydrogen bonding between atoms of the *same molecule* is called **intramolecular**.
  (c) An example of the difference between intermolecular and intramolecular hydrogen bonding is shown in the dihydroxybenzene isomers.
    (i) In 1,2-dihydroxybenzene the two OH groups on the same molecule can form intramolecular hydrogen bonds (Fig 4.32).



▲ Fig 4.32 Intramolecular hydrogen bonding in 1,2-dihydroxybenzene

    (ii) Intermolecular hydrogen bonds can also be formed between OH groups of different molecules.
    In 1,4-dihydroxybenzene, the two OH groups on the same molecule are too far apart to form intramolecular hydrogen bonds. They can only form intermolecular hydrogen bonds with the OH groups of other molecules (Fig 4.33).



▲ Fig 4.33 Intermolecular hydrogen bonding in 1,4-dihydroxybenzene

    (iii) The 1,4-dihydroxybenzene forms more intermolecular hydrogen bonds than the 1,2-dihydroxybenzene, so it has a higher melting and boiling point.

4.12 Co-ordinate Bonds

- In a co-ordinate bond (dative bond), one atom provides two electrons which are then shared with another atom.

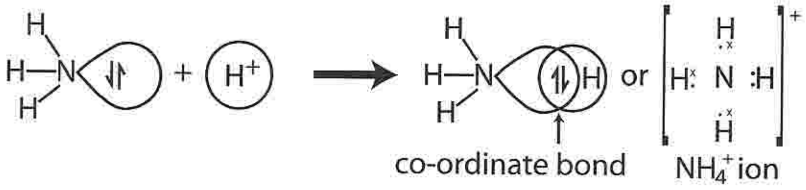
$$X: + Y \rightarrow X:Y$$

- In the formation of a co-ordinate bond:
  (a) one atom has a lone pair of electrons in the outer level;
  (b) the other atom has an empty orbital in the outer level;
  (c) the two orbitals overlap so that the electron pair is shared between the two atoms.

- A co-ordinate bond looks exactly like a normal covalent bond *after* it has been formed. A co-ordinate bond is different from a normal covalent bond in the way in which it is made.

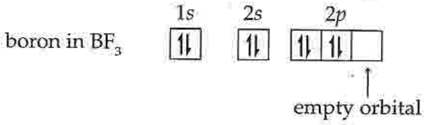
The Ammonium Ion, NH_4^+

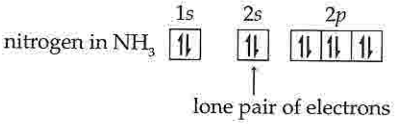
- The ammonium ion is formed from a NH_3 molecule and a H^+ ion.
- The lone pair of electrons of the nitrogen atom overlaps with the empty 1*s* orbital of the H^+ ion to form a co-ordinate bond.

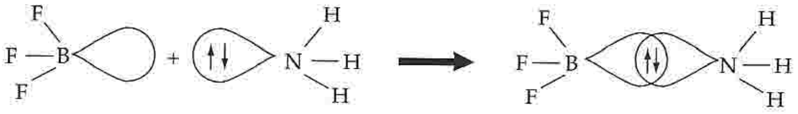


The $BF_3.NH_3$ Molecule

- The $BF_3.NH_3$ molecule can be made by mixing gaseous BF_3 and NH_3.
- The lone pair of electrons of the nitrogen atom overlaps with the empty 2*p* orbital of the boron atom.



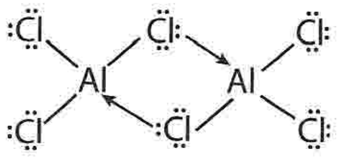




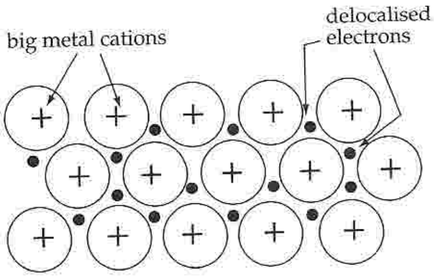
- The molecule can be written as: $H_3N \rightarrow BF_3$. The arrow represents the co-ordinate bond. The direction of the arrow indicates which atom provides the two electrons in the bond.

• The Al_2Cl_6 Molecule

The $AlCl_3$ molecule is electron deficient since there are only six instead of eight electrons around the central aluminium atom. Two $AlCl_3$ molecules dimerise by sharing two lone pairs on the chlorine atoms.



4.13 Metallic Bonds



▲ Fig 4.34 Structure of a metal

- In a metal, the atoms are closely packed together.
- The metal atoms have low electronegativities therefore they lose one or more electrons easily to become ions.
- The electrons occupy the space between the metal ions and are free to move throughout the metal (Fig 4.34). These electrons are said to be **delocalised**.
- The metallic bonds are the forces of attraction between the positive metal ions and the negative delocalised electrons.
- To form metallic bonds, elements must have
  (a) big atoms;
  (b) a relatively low ionisation energy so that they can lose electrons easily.

EXERCISE 4

Multiple Choice Questions

Section I

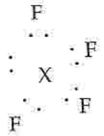
1 Which molecule has a dipole?

A BCl_3	C $BeCl_2$
B CCl_4	D NCl_3

2 Which compound forms hydrogen bonds between its molecules in the liquid state?

A CF_4	C $CHBr_3$
B NH_3	D HCl

3 The electronic structure of the molecule XF_4 is shown in Fig 4.35. Element X could be



► Fig 4.35

A phosphorus.	C oxygen.
B silicon.	D sulphur.

4 The shape of the molecule SF_6 is best described as

A planar.	C hexagonal.
B octahedral.	D pyramidal.

5 In which one of the following reactions is a co-ordinate bond formed?

A $H_2O + H^+ \rightarrow H_3O^+$
B $Cl + I \rightarrow ICl$
C $OH^- \rightarrow O^{2-} + H^+$
D $Na + \frac{1}{2}Cl_2 \rightarrow NaCl$

6 The molecules ICl and Br_2 have almost the same relative molecular mass and molecular size. However the boiling point of ICl is about 40°C higher than that of Br_2. What is the most likely explanation for this difference?

A There are hydrogen bonds between ICl molecules in the liquid state.
B There are permanent dipole-dipole forces between ICl molecules.
C The Van der Waals forces in liquid ICl are stronger than in liquid Br_2.
D The covalent bond in the ICl molecule is stronger than the covalent bond in the Br_2 molecule.

7 What type of bonds are found in solid water?

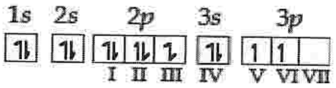
A covalent bonds only
B hydrogen bonds only
C covalent and hydrogen bonds
D co-ordinate and hydrogen bonds

8 The boiling point of methane is higher than that of neon. Which statement best explains this fact?
[H = 1; C = 12; Ne = 20]

A Methane is a polar molecule, but neon is not.
B Methane molecules form hydrogen bonds but not neon molecules.
C The intermolecular forces between molecules is stronger in methane than in neon.
D A methane molecule has a more electrons than a neon molecule.

9 Which two atoms are likely to form the most polarised bond when they join together?

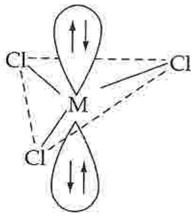
	electronegativity of the two atoms
A	0.8 and 2.0
B	1.0 and 2.0
C	1.2 and 2.6
D	2.8 and 3.0

10 

The ground state electronic configuration of silicon is shown above. Which orbitals are used by a silicon atom in the covalent bonds in a molecule of SiH_4?

A I, II, III, IV
C V, VI, VII
B IV, V, VI
D IV, V, VI, VII

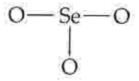
11 The structure of a molecule of a chloride of element **M** is shown in Fig 4.36. Which group in the Periodic Table is **M** in?



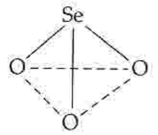
▸ Fig 4.36

A Group III
C Group VI
B Group V
D Group VII

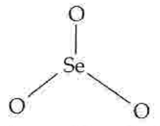
12 A gaseous molecule of SeO_3 does *not* have a dipole. Which one of the following best represents the structure of this molecule?

A 

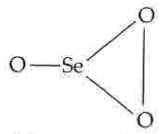
(planar, all angles 90Y)

C 

(pyramidal structure)

B 

(planar, all angles 120Y)

D 

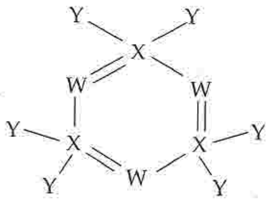
(planar, angles of 60Y and 145Y)

13 Which molecule is linear?

A H_2O
C H_2S
B CO_2
D CCl_4

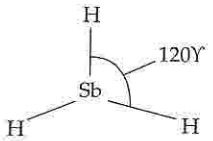
14 A molecule containing atoms of the elements **W**, **X** and **Y** has the structure shown in Fig 4.37. Which one of the following is the most likely combination of elements?

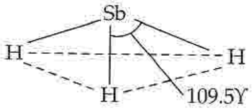
	W	**X**	**Y**
A	N	C	H
B	N	P	Cl
C	P	N	H
D	P	Si	F

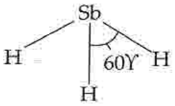


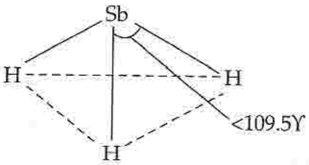
▲ Fig 4.37

15 Stibine, SbH_3, is a molecular hydride of antimony. Antimony is in Group V of the Periodic Table. Which one of the following best presents the structure of a molecule of stibine?

A 

B 

C 

D 

16 Which one of the following simple equations shows the formation of a co-ordinate bond?

A X· + ·Y → X:Y
B X + :Y → X:Y
C X: + :Y → X::Y
D X· + ·Y → $[X]^+[:Y]^-$

17 Which pair of molecules have a similar shape?

A BCl_3 and NCl_3
B $AlCl_3$ and BF_3
C SO_2 and CO_2
D BF_3 and NH_3

18 Why is the boiling point of H_2S lower than that of H_2O?

A H_2S molecules are larger than H_2O molecules.
B H_2O molecules are polar, H_2S molecules are not.
C The bonding in H_2S is covalent whereas in H_2O it is ionic.
D Liquid H_2O has hydrogen bonds, liquid H_2S does not.

Section II

Summary of directions

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

19 Which substances dissolve in water by forming hydrogen bonds?

1 NH_3 **2** CH_3COOH **3** HCl

20 Which statements are true for both phosphorus and nitrogen?

1 The elements form a chloride with a pyramidal shape.
2 There are hydrogen bonds between molecules of the hydride in the liquid state.
3 The elements can use *d* orbitals to form covalent bonds.

21 BF_3 reacts with NH_3 to form a solid with formula $BF_3.NH_3$. Which statement(s) about this solid is/are true?

1 The $BF_3.NH_3$ is a planar molecule.
2 The boron atom is surrounded by eight electrons in bonds.
3 The nitrogen atom supplies both electrons in the boron—nitrogen bond.

Structured Questions

*1 Draw 'dot and cross' diagrams for the following molecules and ions.

(a) CCl_4 (d) BCl_3
(b) Cl_2O (e) C_2H_6
(c) NCl_3 (f) N_2H_4

2 The element sulphur has atomic number 16.

(a) Write down the full electronic configuration of a sulphur atom in the ground state.

Sulphur forms a molecular chloride with molecular formula SCl_2.

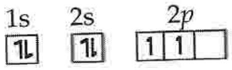
(b) Draw the electronic structure of an SCl_2 molecule, showing the electrons in the outer shells of the atoms.

(c) In a molecule of SCl_2,
  (i) how many bond pairs of electrons are arranged around the sulphur atom;
  (ii) how many lone pairs of electrons are arranged around the sulphur atom?

(d) Sketch the shape of a SCl_2 molecule. Explain your answer.

(e) Name two other molecules with a similar shape.

3 (a) The ground state electronic configuration of carbon is



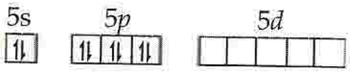
  (i) Draw a similar diagram to show the electronic configuration of the carbon *anion* in ionic Al_4C_3.
  (ii) Draw a similar diagram to show the electronic configuration of the carbon atom when it forms the bonds in CH_4.

(b) Sketch the shapes of *all* the orbitals of carbon used to form covalent bonds in CH_4.

(c) The ground state electronic configuration of antimony is (outer shell only): $5s^2\ 5p^3$.
  (i) Predict the formulae of all the possible chlorides that you might expect antimony to form.
  (ii) For the chloride in which antimony has the lowest oxidation number, give the number of:
    - bond pairs of electrons around the antimony atom;
    - lone pairs of electrons around the antimony atom.

Sketch the shape of this molecule.

4 Xenon is in Group VIII of the Periodic Table. The outer electron arrangement of xenon is



(a) Xenon forms a fluoride of formula XeF_4.
   (i) Sketch the outer electron arrangement that xenon must have to form the four covalent bonds in XeF_4.
   (ii) How many lone pairs of electrons are present in the xenon atom in XeF_4?
   (iii) What is the total number of electron pairs around the xenon atom in XeF_4?
   (iv) Sketch a possible shape for the XeF_4 molecule.

(b) Suggest the formulae of two other xenon fluorides. For each one state how many lone pairs of electrons are likely to be present in the xenon atom.

5 (a) (i) Draw 'dot and cross' electron diagrams for beryllium chloride and ammonia.
   (ii)State the number of dative bonds that may be formed between beryllium chloride and ammonia.
   (iii) Draw the shape of beryllium chloride, ammonia and of the molecule formed by the reaction between beryllium chloride and ammonia.
   (iv) Explain the change in bond angles which occurred during the reaction.
   (v) Hence,write an equation for the reaction between beryllium chloride and ammonia.

(b) The hydrogen ion can form dative bonds with ammonia as well as the hydroxide ion(OH^-). Draw diagrams to show the dative bond formation between
   (i)hydrogen ion and ammonia
   (ii)hydrogen ion and hydroxide ion.

Descriptive Questions

*1 (a) Draw 'dot and cross' diagrams to show the electronic structures of the following molecules. Use your structures to predict the shapes of the molecules, explaining your reasoning.
   (i) SF_2 (ii) PF_3 (iii) $SiCl_4$

(b) The bond angles in molecules of methane, ammonia and water are given below.

compound	*bond angle*
CH_4	109°
NH_3	107°
H_2O	104°

Explain the variation in bond angles.

*2 Explain the following observations as fully as you can. Use data from the *Data Tables* at the back of the book, where appropriate:
   (a) Phosphorus forms the chlorides PCl_3 and PCl_5, but nitrogen only forms NCl_3.
   (b) The melting point of water (0°C) is higher than that of hydrogen sulphide (–83°C).
   (c) A white solid is produced when the gases BCl_3 and NH_3 are mixed.
   (d) CI_4 decomposes on heating at a much lower temperature than CCl_4.

3 (a) In each of the following changes, the molecule underlined forms an ion. Write the formulae of these ions and explain, considering the numbers of electron pairs around the central atom, how the bond angles in the ions differ from those in the molecules.
   (i) Hydrogen chloride dissolves in water;
   (ii) ammonia dissolves in aqueous hydrochloric acid;
   (iii) potassium fluoride reacts with boron trifluoride.

(b) Explain, with one example in each case, the meaning of the following terms:
   (i) co-ordinate (dative) bond;
   (ii) metallic bond.

*4 (a) (i) How can the shape of a molecule be explained in terms of the repulsion between the electron pairs?

(b) Draw 'dot and cross' diagrams to show electronic structure of the following:
   (i)H_2O
   (ii)NCl_3
   (iii)NH_4^+

Use the electron pair repulsion theory to predict the shape of the above particles.

CHAPTER 5

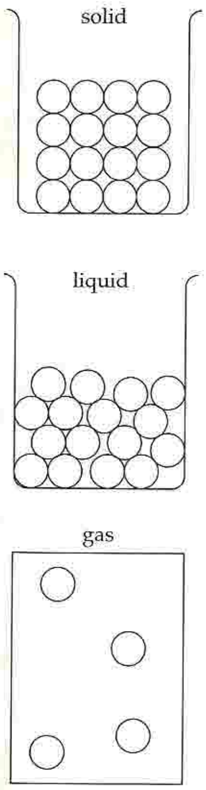
SOLIDS, LIQUIDS AND GASES

- Kinetic Theory of Matter
- Gases
- General Gas Equation
- Molar Volume of Gases
- Energy Distribution of Gas Molecules
- Calculation of M_r from the General Gas Equation
- Liquids
- Solids
- Types of Lattice Structures
- Uses of Metals
- Recycling

SYLLABUS OBJECTIVES

- Kinetic Theory of matter
- Gases
- General Gas Equation
- Molar volume of gases
- Energy Distribution of gas Molecules
- Calculation of Mr from the General gas Equation
- Liquid
- Solids
- Types of Lattice Structures
- Uses of Metals
- Recycling

5.1 Kinetic Theory of Matter



▲ Fig 5.1 Simple pictures of arrangement of particles in solids, liquids and gases

- The **Kinetic Theory** describes the particles in solids, liquids and gases and the movement of these particles.
- The main points in the Kinetic Theory are summarised below.
  - (a) All matter is made up of particles.
  - (b) **Solids**
    - (i) There are very *strong forces* between the particles, atoms, ions or molecules.
    - (ii) The particles are *packed closely* together.
    - (iii) Hence solids have high densities and *cannot be compressed easily*.
    - (iv) The particles are in an *orderly* arrangement.
    - (v) The particles can only *vibrate* and *rotate* about fixed positions. The particles cannot move throughout a solid.
    - (vi) Solids have less energy than liquids or gases.
    - (vii) Solids must gain energy to melt . The energy is required to overcome the strong forces holding the particles in fixed positions.
  - (c) **Liquids**
    - (i) There are *strong forces* between the particles.
    - (ii) The particles are *packed* less *closely* together.
    - (iii) Hence liquids have *cannot be compressed easily*.
    - (iv) The particles are in a semi *orderly* arrangement.
    - (v) The particles can *vibrate, rotate and move throughout the liquid*.
    - (vi) Liquids adopt the shape of the container.
    - (vii) Liquids have more energy than solids but less energy than gases.
    - (viii) Liquids must gain energy to boil. The energy is required to completely break the forces between the particles in the liquid.
  - (d) **Gases**
    - (i) There are *no forces* between the particles.
    - (ii) The particles are *far apart* (so that a gas consists mainly of empty space).
    - (iii) Gases have very low densities and *can be compressed easily*.
    - (iv) The particles are in a *random* arrangement.
    - (v) The particles can *vibrate, rotate and move anywhere* within the container.
    - (vi) The pressure of a gas is due to the molecules bouncing off the walls of the container.
    - (vii) Gases have no shape (except the shape of the container).
    - (viii) Gases have more energy than liquids or solids.
    - (ix) When gases condense into liquids, heat energy is given out.

5.2 Gases

Real and Ideal Gases

- An **ideal gas** has the following features:
  (a) The molecules have *no volume*, so the gas particles can move anywhere in the container.
  (b) There are *no forces* between the molecules.
  (c) When the molecules collide, the *collision* is perfectly *elastic*. This means that the molecules bounce apart when they collide, with no loss in kinetic energy. The molecules do not stick together.
  (d) The gas obeys the gas laws perfectly (eg Boyle's law and the General Gas Equation).

- A **real gas** has the following features:
  (a) The molecules have a *certain volume*. Hence the gas molecules cannot just move anywhere in the container as they cannot move into a volume of space occupied by other gas molecules.
  (b) There are *forces of attraction* between the gas molecules, though they are usually very weak. Hence the molecules tend to stick together (which reduces the pressure on the container very slightly).

- A real gas is most *like* an ideal gas under the following conditions:
  (a) *At low pressure*. The molecules are then far apart and there are relatively few molecules. Hence their volume is almost zero and the forces between them are virtually zero.
  (b) *At high temperature well above the boiling point*. The molecules then have a very large kinetic energy and cannot stick together when they collide. Near the boiling point, gas molecules tend to stick together when they collide. At a slightly lower temperature, they remain stuck together and are thus condensed to a liquid.

- A real gas is most *unlike* an ideal gas (shows the biggest deviation from ideal) under the following conditions:
  (a) *At high pressure*. When a lot of molecules are packed close together, their volume is important and there are most likely to be significant forces between them.
  (b) *At low temperature* (when the molecules tend to stick together).
  (c) *Near the boiling point* (when the molecules tend to stick together).

5.3 General Gas Equation

- The **General Gas Equation** gives the relationship between the pressure (P), the volume (V), the number of moles (n) and the temperature (T) of any quantity of gas:

$$PV = nRT$$

Useful relationships for the General Gas Equation:

$$\text{volume in m}^3 = \frac{\text{volume in cm}^3}{10^6}$$

$$\underset{\text{in K}}{\text{temperature}} = \underset{\text{in °C}}{\text{temperature}} + 273$$

$$\underset{\text{in Pa}}{\text{pressure}} = \text{pressure in kPa} \times 1000$$

1 atmosphere pressure = 101.3 kPa

R is a constant, called the *gas constant*.

In the General Gas Equation:

P = pressure in Pascals (Pa)
V = volume in cubic metres (m^3)
n = number of moles of gas
R = gas constant = 8.314 $J\ K^{-1}\ mol^{-1}$
T = temperature in Kelvin (K)

- An ideal gas obeys the General Gas Equation. This means that experimental results for a real gas closely resemble an ideal gas and agree well with theoretical results calculated using the General Gas Equation.

Partial Pressures

- The pressure of a gas on the sides of a container is due to the gas molecules bouncing off the sides. For a mixture of gases, each gas exerts its own pressure (independent of the other gases) – known as its **partial pressure**.
- The total pressure of a mixture of gases is equal to the sum of the partial pressures of each gas. For example, in a mixture of nitrogen and hydrogen gases:

  total pressure = partial pressure of N_2 + partial pressure of H_2

Question

A 2.0 dm^3 flask contains 0.2 mole of nitrogen and 0.4 mole of oxygen at 400 K. Calculate (a) the partial pressure of nitrogen, (b) the partial pressure of oxygen and (c) the total pressure in the flask.
[R = 8.31 $J\ K^{-1}\ mol^{-1}$]

Answer

(a) Applying the General Gas Equation: $PV = nRT$, the partial pressure of nitrogen is

$$P = \frac{nRT}{V} = \frac{0.2 \times 8.31 \times 400}{2.0 \times 10^{-3}}\ \text{Pa} = 332\,400\ \text{Pa} = 332.4\ \text{kPa}$$

(b) Applying the General Gas Equation, the partial pressure of oxygen is

$$P = \frac{nRT}{V} = \frac{0.4 \times 8.31 \times 400}{2.0 \times 10^{-3}}\ \text{Pa} = 664\,800\ \text{Pa} = 664.8\ \text{kPa}$$

(c) Hence total pressure = 332.4 + 664.8 = 997.2 kPa

- The partial pressure of a gas A in a mixture of gases A and B

  = mole fraction of the gas x total pressure

  $$= \frac{\text{number of moles of A}}{(\text{number of moles of A} + \text{number of moles of B})} \times \begin{matrix}\text{total}\\ \text{pressure}\end{matrix}$$

- The partial pressure of a gas A in a mixture of more than 2 gases

$$= \frac{\text{number of moles of A}}{\text{total number of moles of gases in mixture}} \text{ x total pressure}$$

Question A gas mixture consists of 0.4 mole of N_2, 0.6 mole of O_2 and 0.2 mole of argon at a total pressure of 300 kPa. Calculate the partial pressure of each gas in the mixture.

Answer Total number of moles of gas = 0.4 + 0.6 + 0.2 = 1.2 moles

Partial pressure of N_2 $= \frac{\text{no. of moles of } N_2}{\text{total no. of moles of gas}}$ x total pressure

$= \frac{0.4}{1.2}$ x 300 kPa = 100 kPa

Partial pressure of O_2 $= \frac{0.6}{1.2}$ x 300 kPa = 150 kPa

Partial pressure of argon $= \frac{0.2}{1.2}$ x 300 kPa = 50 kPa

A simple check on this type of problem is to add up the partial pressures at the end. They should be equal to the total overall pressure.

5.4 Molar Volume of Gases

- One mole of *any* (ideal) gas occupies a fixed volume, called the **molar volume**, V_m.

  The molar volume is 22.4 dm^3 (22 400 cm^3) at s.t.p. and 24 dm^3 under room conditions.

- The number of moles of gas in a known volume

  $$= \frac{\text{volume of gas}}{\text{molar volume}} \text{ mole}$$

  Hence for a volume of x cm^3 of gas, the number of moles of gas

  $$= \frac{x}{24\,000} \text{ mole at room conditions}$$

  or $$= \frac{x}{22\,400} \text{ mole at s.t.p.}$$

Question A sample of carbon dioxide has a volume of 56 cm^3 at s.t.p. Calculate (a) the number of moles of gas molecules, (b) the number of molecules, and (c) the number of oxygen atoms in the sample.
[1 mole of gas has a volume of 22.4 dm^3 at s.t.p.; Avogadro constant = 6.023×10^{23} mol^{-1}]

Answer

(a) Number of moles of gas molecules = $\frac{56}{22\,400}$ mole = 0.0025 mole

(b) Number of molecules = no. of moles x Avogadro constant
= $0.0025 \times 6.023 \times 10^{23} = 1.5 \times 10^{21}$

(c) Number of oxygen atoms in one CO_2 molecule = 2
Hence the number of oxygen atoms in 1.5×10^{21} molecules = $2 \times 1.5 \times 10^{21}$ atoms
= 3.0×10^{21} atoms

5.5 Energy Distribution of Gas Molecules

- The energy of a gas molecule is proportional to its speed.
- In a sample of gas, the molecules have a range of energies or speeds.
- The graph in Figure 5.2 is known as the **Boltzmann** distribution. It shows how the energy of particles are distributed in the gas. The graph is a histogram showing the number of particles in each small range of kinetic energy. The total number of particles is the area beneath the curve.

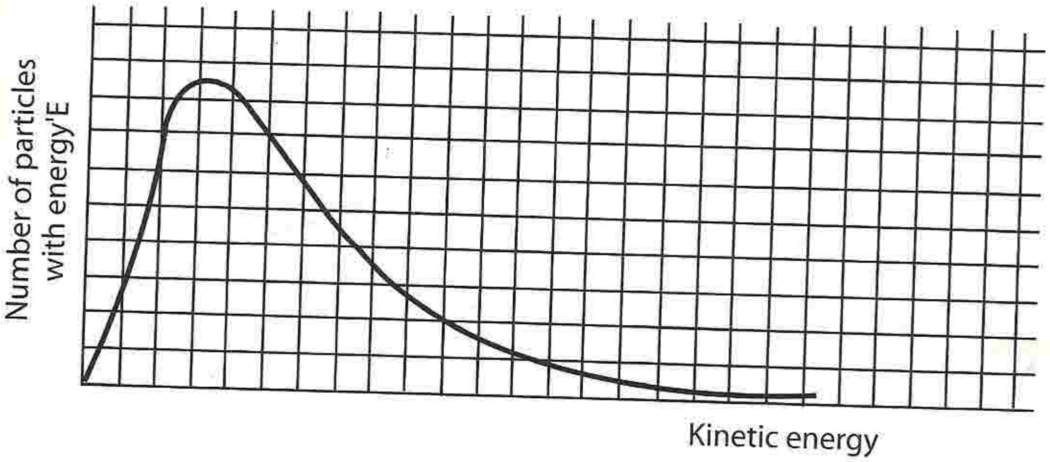


Fig 5.2 Boltzmann distribution of molecular speed

(For the *effect of temperature* on this graph, see Chapter 9.)

5.6 Calculation of M_r From The General Gas Equation

- The number of moles of gas, $n = \dfrac{\text{mass of gas in grams}}{\text{relative molecular mass}}$

$$= \frac{m}{M_r}$$

Hence the General Gas Equation can also be written as:

$$PV = \frac{mRT}{M_r}$$

This form of the General Gas Equation can be used to find the relative molecular mass, M_r, of a gas.

Question 0.400 g of a gas has a volume of 227 cm^3 at 27°C and at a pressure of 100 kPa. Calculate the relative molecular mass of the gas.
[$R = 8.31$ J K^{-1} mol^{-1}]

Answer

$P = 100\ 000$ Pa
$V = 227 \times 10^{-6}$ m^3
(1 cm^3 = 10^{-6} m^3)
$T = 27 + 273 = 300$ K
$m = 0.400$ g

Rearranging the General Gas Equation, $M_r = \dfrac{mRT}{PV}$

Substituting the given values into the equation,

$$M_r = \frac{0.400 \times 8.31 \times 300}{100\ 000 \times 227 \times 10^{-6}} = 43.9$$

Question A gas has a density of 1.70 g dm^{-3} at 127°C and at a pressure of 200 kPa. Calculate the relative molecular mass of the gas.
[$R = 8.31$ J K^{-1} mol^{-1}]

Answer

Taking 1 dm^3 of gas,
$P = 200\ 000$ Pa
$V = 1$ dm^3 = 10^{-3} m^3
$T = 127 + 273 = 400$ K
$m = 1.70$ g

Substituting into the General Gas Equation, $M_r = \dfrac{mRT}{PV} = \dfrac{1.70 \times 8.31 \times 400}{200\ 000 \times 10^{-3}} = 28.3$

Relative Molecular Mass of Volatile Liquids

- Volatile liquids have low boiling points. They are easily vaporised (ie turned into a gas) when heated. The relative molecular mass of volatile liquids can be found by applying the General Gas Equation to the vapour.

Question

In an experiment, 0.300 g of a vaporised liquid was found to have a volume of 84.0 cm^3 at 97°C and at a pressure of 105 kPa. Calculate the relative molecular mass of the vapour.
[$R = 8.31\ \text{J K}^{-1}\ \text{mol}^{-1}$]

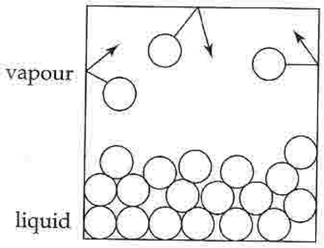
Answer

$P = 105\,000$ Pa $\quad T = 97 + 273 = 370$ K
$V = 84.0 \times 10^{-6}$ m^3 $\quad m = 0.300$ g

Substituting into the General Gas Equation, $M_r = \dfrac{mRT}{PV} = \dfrac{0.300 \times 8.31 \times 370}{105\,000 \times 84.0 \times 10^{-6}} = 105$

5.7 Liquids

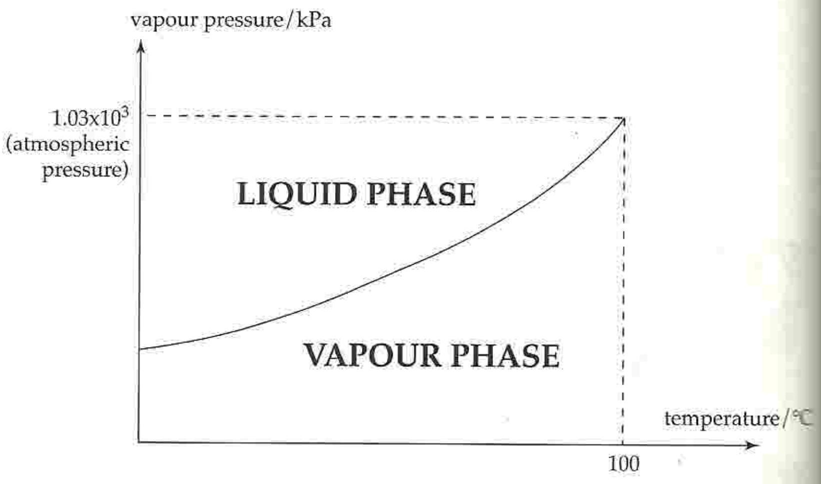
Vapour Pressure



▲ Fig 5.3 Vapour pressure of a liquid inside a closed container is caused by vapour molecules bouncing off the walls

- Liquids exert a **vapour pressure**. This is caused by molecules vaporising from the surface of the liquid to become gas (below the boiling point). These molecules of vapour exert a pressure on the walls of any container (Fig 5.3).
- Vapour pressure increases with temperature as the molecules of liquid have more kinetic energy and so can escape more easily from the surface. Thus there are more vapour molecules at higher temperatures.

  When the vapour pressure becomes equal to the atmospheric pressure, the vapour pushes back the atmosphere and the liquid boils. During boiling, the liquid turns into a gas throughout the liquid. The vapour pressure of a liquid equals the atmospheric pressure at its boiling point. Fig 5.4 shows the variation of vapour pressure with temperature for water.

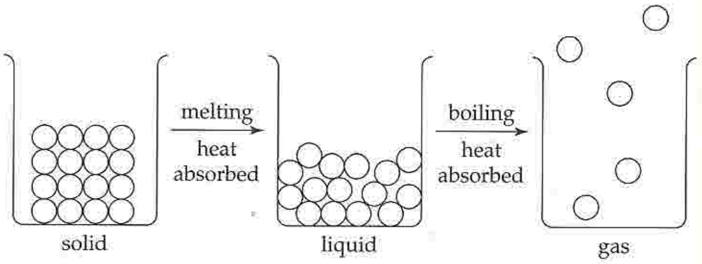


▶ Fig 5.4

5.8 Solids

Structure of Solids

- Most solids are **crystalline**. A crystalline solid consists of **lattice particles** in a regular arrangement. The lattice particles may be atoms, ions or molecules.
- In solids, the lattice particles are packed closely together. Therefore solids are relatively dense and cannot be compressed easily.
- In solids the lattice particles are in fixed positions. The particles can vibrate and rotate about their positions but cannot move throughout the solid.
- The process of melting and boiling is shown in Fig 5.5.



▶ Fig 5.5

- In melting, heat energy is absorbed to weaken some of the forces between the lattice particles. The lattice particles receive enough kinetic energy to move throughout the liquid.
- On boiling, the particles move far apart to form a gas. There are virtually no forces between gas particles; thus all the forces between lattice particles are broken when a liquid boils.
- The boiling point is a good measure of the forces between the lattice particles in a solid (and liquid), because all the lattice forces must be broken on boiling.

The stronger the lattice forces, the higher the boiling point. The weaker the lattice forces, the lower the boiling point.

- The atoms in crystals have a **coordination number**. The coordination number of an atom is the number of its nearest neighbours. In general, the larger the coordination number, the denser the solid.

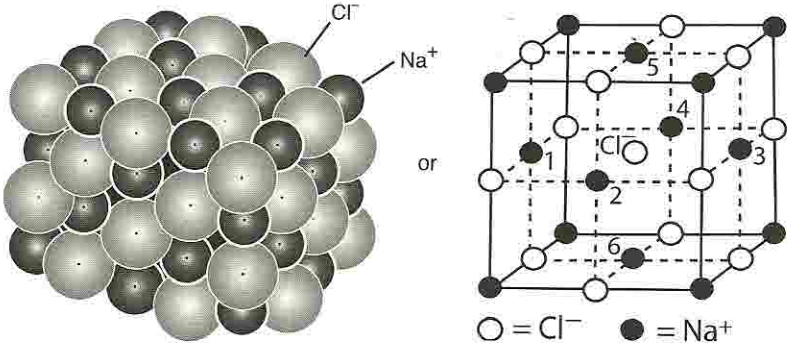
5.9 Types of Lattice Structures

- Lattice structures of solids can be classified according to the lattice particles and the lattice forces.

  The main types of lattice structures are **molecular**, **ionic**, **metallic** and **giant molecular**. These are summarised in Table 5.1.

Ionic Structures

- Sodium chloride, NaCl, is a typical compound with an ionic structure. Its structure is shown in Fig 5.6.



▶ Fig 5.6 Structure of solid NaCl

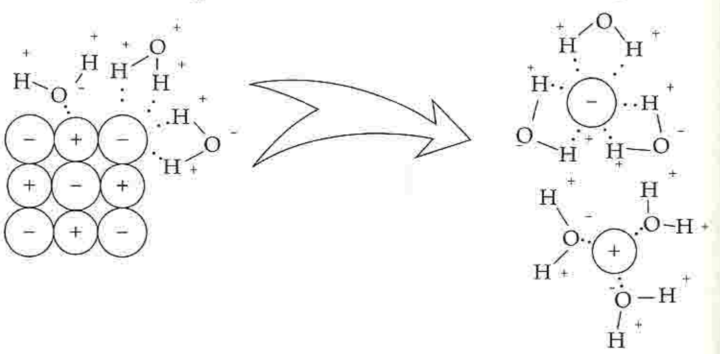
In a crystal of sodium chloride, each Na^+ ion touches six Cl^- ions. Each Cl^- ion touches six Na^+ ions. This is a **simple cubic structure**. The coordination number of Na^+ and Cl^- ions in the crystal is 6. Sodium chloride has the following properties:

(a) The lattice particles are Na^+ and Cl^- ions, held together by *strong electrovalent* bonds. The bonds act in all directions throughout the crystal.

(b) Sodium chloride has a high melting (808°C) and boiling point because a large amount of heat energy is required to weaken and break the strong electrovalent bonds.

(c) Molten sodium chloride conducts electricity. The current is carried by the ions which can move throughout the liquid. Solid sodium chloride does not conduct electricity because the ions cannot move throughout the solid.

(d) Sodium chloride dissolves in water. The water molecules are polarised and can form electrostatic bonds with the positive sodium ions. The water molecules then pull the ions off the crystal as the force between the water molecules and the ions on the edges of the crystal is greater than the force holding the ions in the crystal.

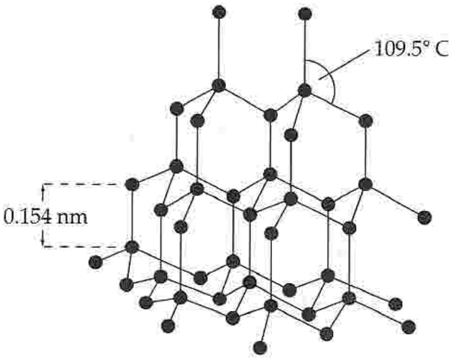


▶ Fig 5.7 Dissolving NaCl in water

- Magnesium oxide has a structure similar to that of sodium chloride. Each Mg^{2+} ion is surrounded by six O^{2-} ions, and each O^{2-} ion is surrounded by six Mg^{2+} ions.
- Refractories are solids that can resist high temperatures without melting or decomposing. Some ionic compounds are used as refractories because of their very high melting points. Two examples are:
  (a) magnesium oxide, MgO, (melting point = 2800°C) which is used to line the insides of furnaces;
  (b) aluminium oxide, Al_2O_3, (melting point = 2300°C) which is used to make heat resistant crucibles (such as for molten metals) and as an insulator in sparking plugs of motorcars. The ions of aluminium oxide cannot move and conduct electricity in the solid state.

Giant Molecular Structures

- The particles in giant molecular solids are atoms. All the atoms in the crystal are held together by *strong covalent bonds*.
  Examples of giant molecular structures are diamond, silicon dioxide and graphite.



▶ Fig 5.8 Structure of diamond

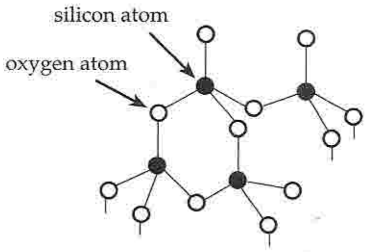
- The structure of diamond is shown in Fig 5.8. Diamond has the following properties:

▶ Table 5.1

lattice type	lattice particles	lattice forces	physical properties	electrical conductivity	examples
molecular	small molecules	Van der Waals or dipole-dipole or hydrogen bonds	weak lattice forces; low boiling point (usually below 200°C)	none	CH_4; I_2; H_2O; CH_3CH_2OH; S_8; CO_2
ionic	positive and negative ions	electrovalent bonds	strong lattice forces; high melting point (usually over 900°C) and high boiling point	not when solid; conducts when molten	NaCl; MgO; KI; Al_2O_3
metallic	atoms	metallic bonds		conducts when solid and molten	Al; Cu; Fe; Mg; Cr
giant molecular	atoms	covalent bonds		none	SiO_2; diamond

(a) The lattice particles in diamond are carbon atoms. Each carbon atom is joined by strong covalent bonds to four other atoms, in a tetrahedral arrangement. The coordination number of the carbon atoms is 4.
(b) Diamond has a very high melting point (about 4000°C) because a large amount of heat energy is required to break the strong covalent bonds.
(c) Diamond is very hard because the structure of diamond is mechanically very strong and rigid. The hardness is due to the strong carbon–carbon bonds and the tetrahedral structure.
(d) Diamond does not conduct electricity because it has no delocalised electrons. All the electrons in the outer shell of the carbon atoms are localised in the covalent bonds.
(e) Diamond does not dissolve in water because the water molecules cannot break the strong covalent bonds.

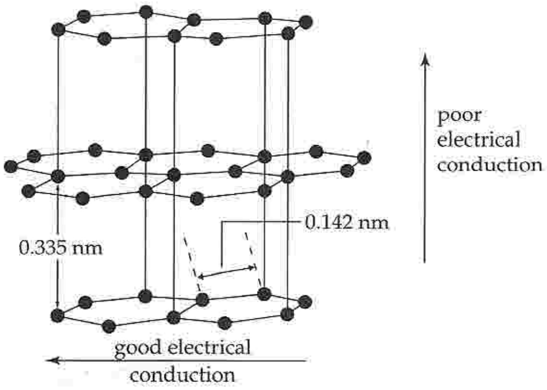
- Silicon(IV) oxide, SiO_2, has a giant molecular structure. Its structure is shown in Fig. 5.9.



▶ Fig 5.9 Structure of silicon dioxide

- Silicon(IV) oxide has the following properties.
  (a) The lattice particles are silicon and oxygen atoms. Each silicon atom is joined to 4 oxygen atoms by strong covalent bonds. Each oxygen atom is joined to 2 silicon atoms by strong covalent bonds.
  (b) SiO_2 has a high melting point because a large amount of heat energy is required to break the strong covalent bonds.
  (c) SiO_2 does not conduct electricity as it has no delocalised electrons.

- Graphite has a layer lattice, which is partly like a giant covalent structure. The structure of graphite is shown in Fig 5.10.



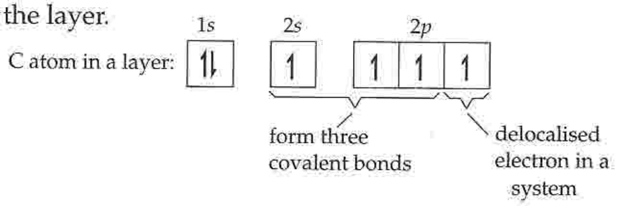
▶ Fig 5.10 Structure of graphite

Graphite has the following properties:

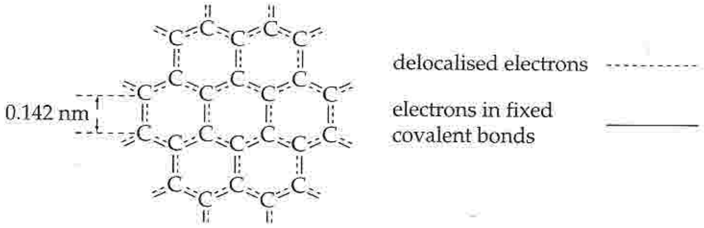
(a) The lattice particles in graphite are carbon atoms. Graphite is made up of flat layers of atoms.

(b) Within each layer, the carbon atoms are in six-membered rings. Each carbon atom forms covalent bonds with three other carbon atoms, using three of the electrons in the outer orbital of each carbon atom.

The fourth electron from the outer orbital of the carbon atom is delocalised in a giant π system that extends over the whole layer. This electron is thus able to move throughout the layer.



The structure of one layer is shown in Fig 5.10.



▸ Fig 5.11 Layer of atoms in graphite

(c) The carbon–carbon bond length *in a graphite layer* is shorter than the carbon–carbon bond length in diamond. This shows that the carbon–carbon bonds in graphite are stronger.

(d) The carbon–carbon bonds *between the layers* in graphite are longer than the bond length inside a layer. This shows that the bonds between the layers are very weak. These bonds are weak Van der Waals forces.

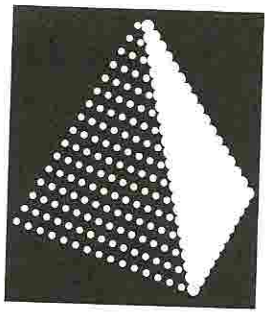
(e) Graphite is a *good electrical conductor along the layers* because the delocalised electrons can move along the layers.

Graphite is a very *poor conductor at right angles* to the layers (ie between the layers) because the delocalised electrons cannot move between the layers.

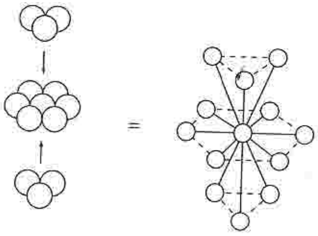
(f) Graphite has a very high melting point (about 4000°C), because the layers must be broken into small pieces on melting. To do this, very strong covalent bonds must be broken.

(g) Graphite is slippery. It is used as a lubricant and in pencils. The layers of graphite can slide over each other (as the Van der Waals forces are weak). Hence graphite is a good lubricant (particularly in machines at high temperatures, where oil lubricants decompose).

- Many ceramics have a giant molecular structure. The covalent bonds in ceramics are particularly strong and numerous. This explains why ceramics have very high melting points, are unaffected by all solvents and are good electrical and heat insulators. Ceramics are used in crockery, electrical insulators and to line the inside of furnaces.



(a) Model of Structure

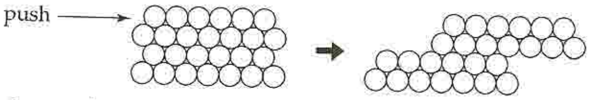


(b) Packing of atoms inside the crystal showing coordination number 12

▲ Fig 5.12 'Close-packed' structure of copper

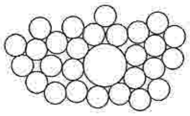
Metallic Structures

- The lattice particles in metallic solids are metal ions. The valency electrons from the metal atoms are delocalised throughout the metal structure. The lattice forces are metallic bonds. The forces of attraction are between the delocalised electrons and each ions (See *Metallic Bonds* in Chapter 4).
- In metallic solids, the metal ions are packed closely together. Hence metals are usually very dense.
- In most metals, the metal ions are packed together as closely as possible, in a **close-packed structure**. An example is copper.
  (a) In solid copper, the copper ions are packed in such a way that each copper ions touches twelve other atoms. This is shown in Fig 5.12. The coordination number of copper ions in solid copper is 12.
  (b) Copper metal conducts electricity because the delocalised electrons can move throughout the crystal. The current is carried by the delocalised electrons.
  (c) Metals such as copper have very high melting and boiling points because the metallic bonding is very strong.
- Metals are malleable because the layers of ions can slide over each other without breaking the metallic bonds (Fig 5.13). This cannot be done in ionic or giant molecular crystals without breaking the electrovalent or covalent bonds.



▶ Fig 5.13

This also makes pure metals very soft. Metals are made much harder by alloying — mixing with another metal. The atoms of the other metal have different size and disrupt the orderly arrangement of the main metal so that the layers of ions can no longer slide over each other easily (Fig 5.14).

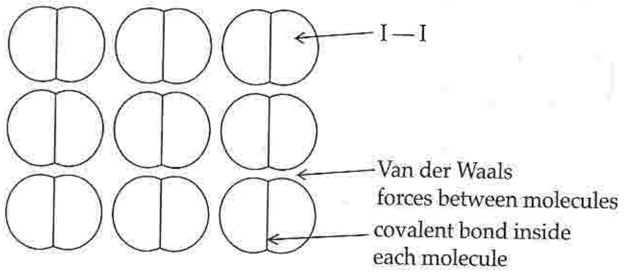


▲ Fig 5.14 Atoms cannot slide

Molecular Structures

- The lattice particles in molecular solids are small molecules. The lattice forces (ie the forces *between* the molecules) in the crystal are weak forces. These forces can be
  (a) Van der Waals forces (eg in solid I_2, S_8, CH_4, CCl_4);
  (b) dipole-dipole attractions (eg in solid SO_2) and
  (c) hydrogen bonds (eg in solid H_2O, $C_2H_5NH_2$, NH_3).
- When molecular solids melt and boil, only the lattice forces are broken. As these forces are weak, only a small amount of heat energy is required. Thus the melting and boiling points of molecular substances are low (usually the boiling point is < 200°C). If the only forces between the molecules are Van der Waals forces, the melting and boiling points are related to the size of the molecules and the number of electrons around them. The bigger the molecules and the number of electron (and hence the bigger the mass), the higher is the melting and boiling points (see *Physical Properties of Group VII Elements* in Chapter 14).

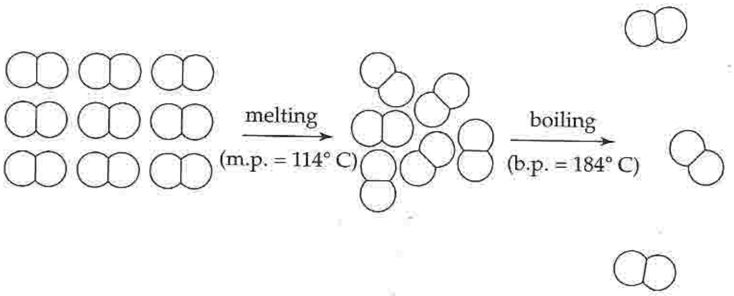
- The simplified structure of solid iodine is shown in Fig 5.15. The lattice particles are I_2 molecules. The lattice forces (between the molecules) are Van der Waals forces.



▶ Fig 5.15 Structure of molecular solid

(a) The melting and boiling of iodine is shown simply in Fig 5.16. In melting and boiling, the Van der Waals forces are broken.

The I_2 molecules ***do not*** break up into atoms during melting and boiling. The covalent bonds *inside* the molecules are not affected by melting and boiling.



▶ Fig 5.16 Melting and boiling of iodine

(b) Iodine is almost insoluble in water. Iodine molecules can only form Van der Waals forces with the water, they cannot break the hydrogen bonds between water molecules. Hence the I_2 molecules cannot push the water molecules apart to dissolve.

Most molecular solids are insoluble in water. However some molecular solids can dissolve in water by the following methods:

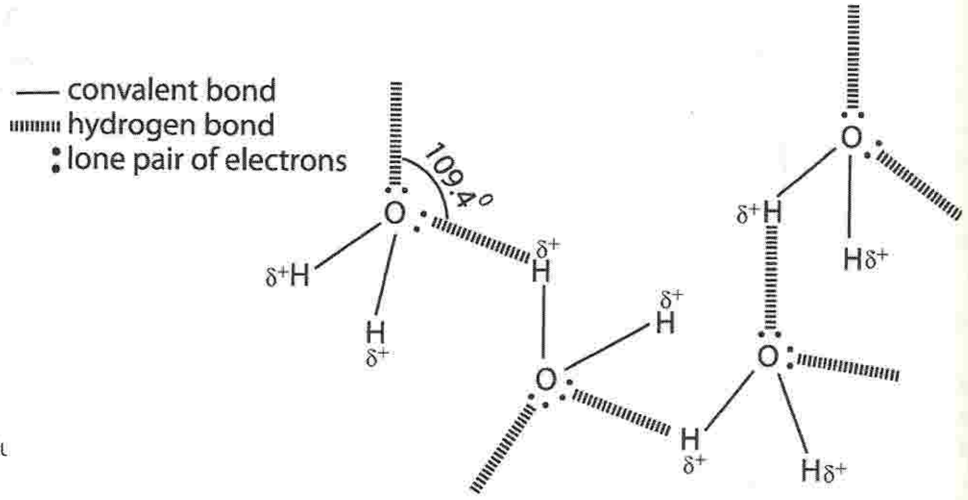
(i) forming hydrogen bonds with water (eg ethanol, ammonia)

or

(ii) reacting chemically with the water (eg HCl dissolves in water by reacting to form H_3O^+ and Cl^- ions).

(c) Iodine has no delocalised electrons, so it does not conduct electricity in any state.

- Ice is a molecular solid in which the lattice forces are hydrogen bonds. The hydrogen bonds and covalent bonds are arranged tetrahedrally around each H_2O molecule (Fig 5.17).



▶ Fig 5.17 Simplified structu

- Because of the tetrahedral direction of the hydrogen bonds, the H_2O molecules are not closely packed together and so ice contains a lot of empty space compared with most crystals.
- When ice melts, the tetrahedral arrangement is partly broken up as the molecules move around. So the molecules become closer together and thus the density of liquid water is greater than that of solid ice. Hence ice floats on water.

  This is unusual for solids. Most solids are more dense than their molten state.
- The melting and boiling points of water are low as only weak hydrogen bonds are broken to produce melting and boiling. However, the melting and boiling points are higher than many other molecular solids with similar size molecules (due to the hydrogen bonds being stronger than Van der Waals forces) (see also *Hydrogen Bonds* in Chapter 4).

5.10 Uses of Metals

- Aluminium is an important structural material. It is used for making cooking pots and aircraft because it has a low density. So such objects are relatively light. It also forms strong alloys and is corrosion resistant. Hence it is used for food containers such as soft drink cans. A comparison of the two most commonly used metals, aluminium and iron (as steel), is summarised in Table 5.2.
- Aluminium is used where lightness and corrosion resistance are important. Steel is used where strength and low cost are important.

	aluminium	steel
cost	expensive compared with steel	cheap compared with aluminium
density	low	high
corrosion resistance	good (although it is a reactive metal with a high standard electrode potential, the metal is protected by a thin coating of Al_2O_3 and so does not corrode easily)	poor (rusts easily unless in the form of 'stainless steel')

▸ Table 5.2

- Aluminium is a good electrical conductor. It is used in large electricity cables because it is much lighter than copper.

Uses of Copper

- Copper is used in electric wires because it is a very good electrical conductor. A disadvantage of copper in big electrical cables is its high density (see *Uses of Aluminium* above).
- Alloys of copper such as brass (zinc + copper) and bronze (tin + copper) are used because they are tough and corrosion resistant.

5.11 Recycling

- There are limited amounts of metals in the earth's crust. If the metals continue to be used at present rates of consumption, they will become scare and expensive to extract. Some metals may run out completely. Recycling is an important way of conserving the limited amounts of metal available so they will last for a much longer period of time.
- Recycling is also important in conserving other limited natural resources such as petroleum. Recycling plastic (made from petroleum) thus reduces oil usage and pollution due to plastic wastes.

EXERCISE 5

Multiple Choice Questions

Section I

1 In which solid are the lattice forces covalent bonds?

- **A** $I_2(s)$
- **B** $CO_2(s)$
- **C** $SiO_2(s)$
- **D** $H_2O(s)$

2 In which solid are the lattice forces Van der Waals forces?

- **A** $CO_2(s)$
- **B** $H_2O(s)$
- **C** $Mg(s)$
- **D** $NH_4NO_3(s)$

3 The General Gas Equation can be rearranged to produce an expression for the density of a gas. Which one of the following expressions is correct?

- **A** $\text{density} = \dfrac{PM_r}{RT}$
- **B** $\text{density} = \dfrac{PV}{RT}$
- **C** $\text{density} = \dfrac{RT}{PM_r}$
- **D** $\text{density} = \dfrac{mRT}{M_rPV}$

4 Which one of the following has the largest volume (all measured at 25°C and 101 kPa)?
[H = 1.00; C = 12.0; O = 16.0]

- **A** 15 g of ethane, C_2H_6
- **B** 20 g of carbon dioxide, CO_2
- **C** 9 g of methane, CH_4
- **D** 12 g of water, H_2O

5 A gas sample contains 10 g of neon and 8 g of oxygen at a total pressure of 100 kPa. What is the partial pressure of neon?
[O = 16; Ne = 20]

- **A** 33 kPa
- **B** 50 kPa
- **C** 55 kPa
- **D** 67 kPa

6 Which substance contains particles with a coordination number of 3?

- **A** sodium chloride
- **B** diamond
- **C** sodium
- **D** graphite

7 A solid melts sharply between 2000°C and 2500°C. It does not conduct electricity even when molten and is insoluble in all solvents. What structure is the solid most likely to have?

- **A** simple molecular
- **B** metallic
- **C** giant molecular
- **D** ionic

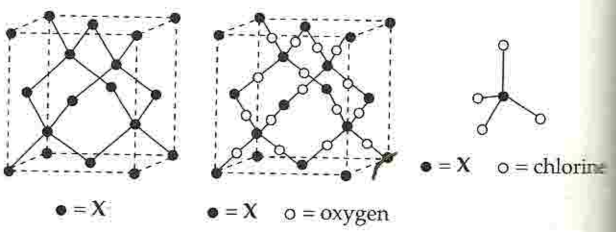
8 Solid **X** is soluble in liquid hydrocarbon solvents and has a sharp melting point just below 100°C. **X** does not conduct electricity under any conditions. What are the most likely lattice particles in **X**?

- **A** single atoms joined by metallic bonds
- **B** small covalent molecules
- **C** positive and negative ions
- **D** single atoms joined by covalent bonds

9 100 cm^3 of a gas at 127°C and 50 kPa pressure has a mass of 0.120 g. What is the relative molecular mass of the gas?
[$R = 8.31\ J\ K^{-1}\ mol^{-1}$]

- **A** 1.2
- **B** 25
- **C** 80
- **D** 367

10 Fig 5.18 shows the structures of element **X**, the oxide of **X** and the chloride of **X**. Which element is **X**?



▲ Fig 15.18

- **A** carbon
- **B** silicon
- **C** lead
- **D** phosphorus

Section II

Summary of directions

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

11 Under what conditions does a real gas behave most like an ideal gas?
  1 near the boiling point
  2 at high temperature
  3 at low pressure

12 Which relationships are correct for an ideal gas?
[P = pressure, V_m = molar volume; T = temperature]
  1 $V_m \propto P$
  2 $P \propto T$
  3 $PV_m \propto T$

13 Which of the following solids contain delocalised electrons?
  1 sodium chloride
  2 chromium
  3 graphite

14 Silicon has a diamond-type structure. Which statements about silicon are likely to be true?
  1 The coordination number of silicon in the crystal is 4.
  2 The covalent bonds in silicon have the same bond energy as the covalent bonds in diamond.
  3 1 cm^3 of solid silicon contains the same number of atoms as 1 cm^3 of diamond.

15 Which statements are true for *both* graphite and diamond?
  1 The crystal contains 6-membered rings of carbon atoms.
  2 One mole of carbon atoms burns completely to produce one mole of carbon dioxide.
  3 The solid has a very high melting point.

16 Which statements about sodium chloride are true?
  1 The bonds between the lattice particles operate in all directions.
  2 The coordination number of the sodium atoms is 6.
  3 The coordination number of the chlorine atoms is 6.

17 In a crystal of nickel, the atoms are packed together as closely as possible. Which features of solid nickel are caused by this fact?
  1 Nickel has a high density.
  2 The coordination number of nickel in the crystal is 12.
  3 Nickel is corrosion resistant.

Structured Questions

1 Complete the following table. The first one is an example.

solid	**lattice particles**	**main force between the lattice particles**
NaCl	Na^+ and Cl^- ions	electrovalent bonds
SiO_2		
CH_4		
H_2O		
NH_4Cl		
H_2		
Al_2O_3		
Cr		

2 Zinc has a boiling point of 907°C. Molten zinc is purified by fractional distillation, using a fractionating column made of silicon carbide.
  (a) (i) Predict the structure of silicon carbide.
    (ii) Give *two* reasons for your answer.
  (b) Silicon carbide has a 'diamond-type' arrangement of atoms.
    (i) Sketch a possible structure for silicon carbide.
    (ii) Predict one other property of silicon carbide and suggest how this property might be put to practical use.

*3 A 20.0 dm^3 flask at 127°C contains 0.200 mole of methane, CH_4, and 0.800 mole of oxygen, O_2.
(a) Calculate the total pressure in the flask.
(b) Calculate the partial pressure of
(i) methane and
(ii) oxygen.
(c) Write a balanced equation for the complete combustion of methane in oxygen. Include the state symbols.
(d) The mixture in the flask was sparked so that the methane completely burnt in the oxygen. What was the final pressure in the flask (measured at 127°C)?

4 Dichlorodifluoromethane, CCl_2F_2, has a melting point of –160°C and a boiling point of –28°C.
(a) What are the lattice forces in solid CCl_2F_2?
(b) What bonds exist between the atoms in a molecule of CCl_2F_2?
(c) Predict two other physical properties of CCl_2F_2 (apart from melting and boiling points).
(d) Trichlorofluoromethane, CCl_3F, has a similar structure as CCl_2F_2. How would you expect the melting and boiling points of CCl_3F to compare with those of CCl_2F_2?
(e) CCl_2F_2 is chemically inert. Suggest a possible use for this compound.

Descriptive Questions

*1 (a) Outline the kinetic theory of gases.
(b) Under what conditions does a real gas behave most like an ideal gas?
(c) State the General Gas Equation and give the units for all the quantities in the equation.
500 cm^3 of methane gas has a pressure of 40 kPa at 27°C. Calculate
(i) the number of moles of gas present, and
(ii) the total number of atoms in the 500 cm^3.

2

substance	**formula**	**relative formula mass**	**b.p. /°C**	**electrical conductivity**
propane	C_3H_8	44	–42	does not conduct in any state
ethanol	C_2H_5OH	46	78	does not conduct in any state
chromium	Cr	52	2480	conducts when solid and when molten
potassium chloride	KCl	74.5	1407	conducts when molten but not when solid

(a) What lattice particles and lattice forces are present in the above substances in the solid state?
Show how they account for the physical properties of these substances.
(b) Why is sodium chloride soluble in water but insoluble in tetrachloromethane?

3 Explain the following facts.
(a) Aluminium oxide is used as an insulator in spark plugs for motorcars.
(b) Ammonia boils at –33°C but methane, with greater relative molecular mass, boils at –162°C.
(c) Solid water (ice) has a lower density than liquid water.
(d) Ceramics are used as electrical insulators and in crucibles for molten metals.

4. (a) Describe the main type of intramolecular and intermolecular forces of attraction which are present in the following substances:
(i)sulphur dioxide
(ii)sodium
(iii)graphite
(iv)diamond
(b) Explain why, although both diamond and graphite are allotropes of carbon, they have quite different physical properties.

5. (a) Magnesium oxide has a giant lattice structure.
   (i) Draw a 'dot and cross' diagram to show bonding in magnesium oxide.
   (ii) Explain why magnesium oxide has a very high melting point and state a use of magnesium oxide based on its melting point.
   (b) Calcium oxide also consist of a giant lattice structure. But it has a lower melting point than magnesium oxide. Explain why.

6. The physical properties of a substance depends on the strength of the forces of attraction present between the particles.
   (a) Describe the type of bonding present in :
   (i) carbon dioxide
   (ii) methane
   (iii) ammonia
   (b) Explain why is ammonia expected to have a higher boiling point than methane.
   (c) Ammonia dissolves easily in water whereas methane is almost insoluble in water. Explain why.
   (d) Carbon dioxide dissolves slightly in water to form carbonic acid.
   (i) Write an equation to show the reaction between water and carbon dioxide.
   (ii) Explain the type of bond formed between carbon dioxide and water.

7. (a) State the main types of intermolecular forces of attraction that are present between the molecules in the following:
   (i) Water,H_2O
   (ii) pentane,C_5H_{12}
   (iii) trichloromethane, $CHCl_3$
   (b)The following table lists the boiling points of some organic substances

Name	Formula	Relative molecular mass	Boiling point/^{0}C
Butane	$CH_3CH_2CH_2CH_3$	58	-0.5
Pentane	$CH_3(CH_2)_3CH_3$	72	36.3
2-methylbutane	$CH(CH_3)_2CH_2CH_3$	72	27.9
2,2-dimethylpropane	$C(CH_3)_4$	72	9.5
Pent-1-ene	CH_2=$CHCH_2CH_2CH_3$	70	30.0
Hexane	$CH_3(CH_2)_4CH_3$	86	68.7

   (i) Draw the displayed formula of each of the organic substances in the table.
   (ii) Explain the trend in boiling point observed by the straight chain alkanes.
   (iii) Explain the variation in boiling points observed for the isomers of pentane.
   (iv) Why do you think the boiling point of pentane and pent-1-ene do not differ considerably?

8. (a)What do you understand by:-
   (i) an ideal gas
   (ii) a real gas
   (b)State the main assumptions made in the kinetic theory of gases.
   (i)Discuss the validity of these assumptions for a real gas.
   (ii)State the conditions under which a real gas is most likely to behave ideally.
   (c)Arrange the following gases in order of increasing degree of ideal behaviour, assuming that they are at r.t.p.
   NH_3 , CO_2, H_2 .

Explain your reasoning.
(d) While moving down group VIII elements, the noble gases deviate more from ideality. Explain why.

9. A gas cylinder of capacity 25 dm^3 contains nitrogen gas at a pressure of 150KPa and 25^{0}C.Calculate the mass of argon that must be added to the cylinder to raise the total pressure to 200 KPa at the same temperature.
   State any major assumption you made during this calculation and state whether the assumption is justified. [Molar gas constant,R=8.31J$mol^{-1}K^{-1}$]

10 (a)(i) Describe how the relative molecular mass of methanol may be determined experimentally using the ideal gas equation.

(ii)The relative molecular mass of methanol may also be determined using a mass spectrograph. Explain how this is done.

(iii)Discuss which of the above two methods is more reliable.

(b)A mixture contains sodium chloride and anhydrous sodium carbonate. When an excess of hydrochloric acid was added to 15.00g of the mixture, 3.0 dm^3 of carbon dioxide gas was liberated at a temperature of 20^0C and a pressure of 99KPa. Determine the percentage by mass of sodium carbonate in the mixture. [Molar gas constant,$R=8.31Jmol^{-1}K^{-1}$]

CHAPTER 6

CHEMICAL ENERGETICS

SYLLABUS OBJECTIVES

In this chapter you should be able to:

- explain that chemical reactions involve energy changes which can be exothermic (ΔH negative) or endothermic (ΔH positive)
- calculate enthalpy changes from experimental results, including use of the formula: enthalpy change (heat change) = $mc\Delta T$ (where m = mass of solution, c = heat capacity of solution and T = temperature change)
- explain that energy is absorbed when bonds are broken and energy is given out when bonds are formed
- explain and use the terms:
  - enthalpy change of reaction
  - standard conditions
  - enthalpy change of atomisation
  - enthalpy change of formation
  - enthalpy change of combustion
  - enthalpy change of hydration
  - enthalpy change of solution
  - enthalpy change of neutralisation
  - bond energy (ΔH is positive when a bond is broken)
  - lattice energy (ΔH is negative when an ionic crystal is formed from its gaseous ions)
- explain qualitatively the effect of ionic radius and ionic charge on the magnitude of lattice energy
- use Hess' Law to construct simple heat energy cycles and use the cycles and relevant energy terms (including ionisation energy and electron affinity) to calculate enthalpy changes of reaction
- use heat energy cycles for the following:
  - to calculate enthalpy changes that cannot be found by direct experiment (eg enthalpy change of formation of an organic compound from enthalpy changes of combustion)
  - the formation of simple ionic soilds and their aqueous solutions (eg calculation of the lattice energy of NaCl from a Born-Haber Cycle)
  - average bond energies (eg calculation of an enthalpy change of reaction from bond energies; calculation of an unknown bond energy from an enthalpy change of reaction and other known bond energies)
- explain and use the term entropy

Enthalpy Change of Reaction

Enthalpy Change of Formation, $\Delta H_f^{\ominus}$

Enthalpy Change of Combustion, $\Delta H_c^{\ominus}$

Enthalpy Change of Solution

Enthalpy Change of Hydration

Enthalpy Change of Neutralisation

Enthalpy Change of Atomisation

Hess' Law

Lattice Energy

Dissolving Ionic Solids in Water

Calculation of Enthalpy Change of Reaction From Bond Energies

Entropy

Calculation of entropy change

6.1 Enthalpy Change of Reaction

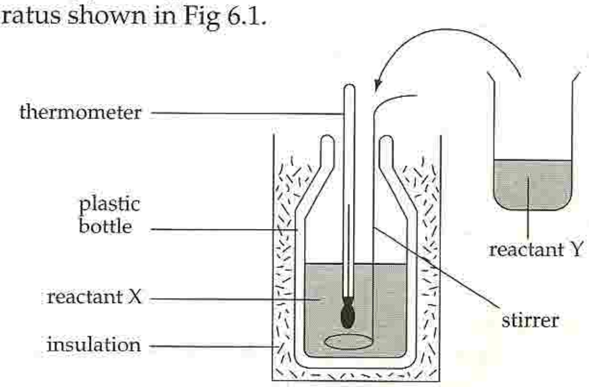
- The enthalpy change of a reaction is the heat energy absorbed or evolved in a chemical reaction, for the number of moles of reactants shown in the chemical equation.
- An example of a thermochemical equation is

  $4NH_3(g) + 3O_2(g) \rightarrow 2N_2(g) + 6H_2O(l); \quad \Delta H^{\ominus} = -1260$ kJ

  (a) ΔH = the enthalpy change of reaction.
  (b) This shows that 1260 kJ of heat energy is evolved when 4 moles of NH_3 react with 3 moles of O_2 according to the equation.
  (c) The symbol $\ominus$ means that all reactants and products are at standard state conditions. Standard state conditions are 101.3 kPa (1 atmosphere) and 298 K (25°C).
  (d) The negative sign (–) means that the reaction is exothermic, ie heat energy is given out. If a positive sign (+) is used, the reaction is endothermic and heat energy is absorbed.
- The enthalpy change of a reaction can also be stated per mole of a particular reactant. In the example above, the enthalpy change of reaction could be given as $\Delta H^{\ominus} = -315$ kJ per mol of NH_3.

To Measure the Enthalpy Change of Reaction

- The enthalpy change of a reaction can be measured using the apparatus shown in Fig 6.1.



▶ Fig 6.1

- The plastic bottle is insulated so as to reduce loss or gain of heat from the surroundings. The plastic bottle itself absorbs a negligible amount of heat (and is a poor heat conductor).
- Consider a reaction between solutions of reactants X and Y.
  (a) A known number of moles of X is placed in the plastic bottle.
  (b) The temperature of X(aq) in the bottle is measured.
  (c) The correct number of moles (or in excess) of Y(aq) is then added to the bottle. The mixture is stirred. The temperature of the product mixture in the bottle is then measured.

(d) The heat change in the reaction
= mass of the solution × temperature change × heat capacity of the solution

In practice, 1 g of solution has a volume of 1 cm^3 (like pure water).

So the heat change
= the total volume of solution in cm^3 × temperature change in °C × heat capacity of the solution in $J\ K^{-1}\ g^{-1}$

(e) The heat change in (d) is for the number of moles of X used in the reaction. By simple proportion, the heat change is then calculated for the number of moles of X shown in the chemical equation. This is the enthalpy change of reaction, ΔH:

$$\text{Enthalpy change, } \Delta H = mc\Delta T$$

(where m = mass of solution, c = heat capacity of solution and T = temperature change)

Question

In an experiment, 100 cm^3 of 0.5 mol dm^{-3} $AgNO_3$(aq) was placed in a plastic bottle. 100 cm^3 of 0.5 mol dm^{-3} KCl(aq) was then added and the mixture stirred. Both solutions were initially at the same temperature. After mixing, the temperature of the mixture was found to have risen by 7.5 C. Calculate the enthalpy change of the reaction.
[specific heat capacity of solution = 4.20 $J\ K^{-1}\ g^{-1}$]

Answer

Heat change in the reaction = volume of mixture (in cm^3) × temperature rise (in °C) × specific heat capacity (4.20 $J\ K^{-1}\ g^{-1}$)
= 200 × 7.5 × 4.20
= 6300 J

Number of moles of $AgNO_3$ used in the reaction = volume of $AgNO_3$(aq) in dm^3 × concentration in mol dm^{-3}

$$= \frac{100}{1000} \times 0.5 = 0.05 \text{ mole}$$

0.05 mole of $AgNO_3$ produces 6300 J of heat.

Hence 1 mole of $AgNO_3$ would produce $\frac{6300}{0.05}$ = 126 000 J
= 126 kJ of heat

Hence $\Delta H = -126$ kJ per mol of Ag^+ and Cl^-.
This can be shown in a thermochemical equation:

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s); \quad \Delta H^{\ominus} = -126 \text{ kJ}$$

Note: The specific heat capacity for aqueous solutions is usually taken to be equal to the specific heat capacity of pure water.

Question

In an experiment, 10 g of gallium metal (an excess) was added to 250 cm^3 of 0.2 mol dm^{-3} $CuSO_4$ in a plastic beaker. The temperature of the solution increased by 14.2°C when the reaction was complete. The equation for the reaction is

$$2Ga(s) + 3Cu^{2+}(aq) \rightarrow 2Ga^{3+}(aq) + 3Cu(s)$$

Calculate the enthalpy change of reaction, ΔH.
[specific heat capacity of the solution = 4.20 $J\ K^{-1}\ g^{-1}$]

Answer

Heat change in the reaction

$= \text{volume of solution} \times \text{temperature rise} \times \text{specific heat capacity}$

$= 250 \times 14.2 \times 4.20$

$= 14\,910 \text{ J}$

Number of moles of $CuSO_4$ used in the reaction

$= \text{volume of } CuSO_4(aq) \text{ in dm}^3 \times \text{concentration in mol dm}^{-3}$

$= \frac{250}{1000} \times 0.2$

$= 0.05 \text{ mole}$

0.05 mole of $CuSO_4$ produces 14 910 J of heat.
Hence 3 moles of Cu^{2+} (shown in the equation) would produce

$\frac{14\,910}{0.05} \times 3 = 894\,600 \text{ J}$

= 895 kJ of heat.

Hence $\Delta H^{\ominus} = -895$ kJ.

6.2 Enthalpy Change of Formation, $\Delta H_f^{\ominus}$

- The standard enthalpy change of formation of a substance is the enthalpy change which occurs when one mole of a substance is formed from its elements found in their standard state under standard conditions.
- The enthalpy change of formation of silver chloride, AgCl, is the enthalpy change of the reaction

$$Ag(s) + \frac{1}{2}Cl_2(g) \rightarrow AgCl(s); \Delta H_f^{\ominus} = -127 \text{ kJ mol}^{-1}$$

  This equation shows the formation of 1 mole of AgCl from its elements.
- The enthalpy change of formation of potassium manganate(VII), $KMnO_4$, is the enthalpy change of the reaction

$$K(s) + Mn(s) + 2O_2(g) \rightarrow KMnO_4(s); \quad \Delta H_f^{\ominus} = -813 \text{ kJ mol}^{-1}$$

  This equation shows the formation of 1 mole of $KMnO_4$ from its elements.
- Enthalpy changes of formation are often only theoretical. Such reactions may not take place in practice. For example, the enthalpy change of formation of potassium chlorate(V) is the enthalpy change of the reaction

$$K(s) + \frac{1}{2}Cl_2(g) + \frac{3}{2}O_2(g) \rightarrow KClO_3(s)$$

However, this reaction does not take place when potassium, chlorine and oxygen are mixed together.

- Enthalpy changes of formation are usually calculated indirectly from other enthalpy changes of reaction.
- Enthalpy changes of formation are commonly used to calculate the theoretical enthalpy change of a reaction, using Hess' Law. This is shown later in the chapter.
- Enthalpy changes of formation are usually negative. However some enthalpy changes of formation are positive (eg for the oxides of nitrogen).

6.3 Enthalpy Change of Combustion, $\Delta H_c^{\ominus}$

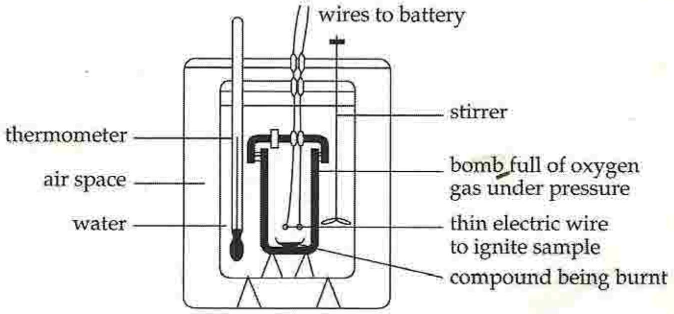
- The enthalpy change of combustion of a substance is the heat energy evolved when 1 mole of the substance is completely burnt in oxygen. The enthalpy change of combustion, $\Delta H_c^{\ominus}$, applies to the measurements of heat evolved being adjusted to standard state conditions.
- An example of the enthalpy change of combustion is the combustion of ethene. The enthalpy change of combustion of ethene is the enthalpy change of the reaction

  $C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l); \Delta H_c^{\ominus} = -1411\ kJ\ mol^{-1}$

  Note: the enthalpy change of combustion applies to the *complete* combustion of the carbon to CO_2, not to CO.
- Enthalpy changes of combustion are always negative as heat is always evolved in the combustion.

To Measure the Enthalpy Change of Combustion of a Compound

- The enthalpy change of combustion of a compound can be found by using a bomb calorimeter, as shown in Fig 6.2.



▶ Fig 6.2

- A known mass of the compound is placed in the bomb calorimete which is immersed in water.
- Oxygen gas is pumped into the bomb calorimeter. Enough oxyge is placed in the bomb to make sure that the compound completely burnt.
- The compound is set on fire by the electric wire.
- The heat from the combustion is absorbed by the water. Th amount of heat can then be found from the temperature rise the water.

Measurements

(a) Mass of compound to be burnt
(b) Volume of water
(c) Initial temperature of water (before combustion)
(d) Final temperature of water (after combustion)

Calculation

- Number of moles of compound burnt

  $$= \frac{\text{mass of compound burnt}}{\text{relative molecular mass of compound}} = x \text{ moles}$$

- Heat produced in the combustion

  $$= \frac{\text{mass of water in grams}}{(= \text{volume of water in cm}^3)} \times \frac{\text{temperature}}{\text{rise (in °C)}} \times \frac{\text{specific heat cap}}{\text{of water (4.20 J K}}$$

  $= y$ J

  $= \frac{y}{1000}$ kJ

- Hence if 1 mole of the compound was burnt, the heat produce

  $= \frac{y}{1000x}$ kJ = the enthalpy change of combustion

$$\Delta H_c^{\ominus} = -\frac{y}{1000x} \text{ kJmol}^{-1}$$

Question

1.80 g of glucose was completely burnt in oxygen. The heat produced was found to raise the temperature of 5.0 dm^3 of water by 1.34°C. Calculate the enthalpy change of combustion of glucose.
[relative molecular mass of glucose = 180; specific heat capacity of water = 4.2 J K^{-1} g^{-1}]

Answer

Heat absorbed by the water $= 5000 \times 1.34 \times 4.2$ J

$= 5000 \times 1.34 \times \frac{4.2}{1000}$ kJ

Number of moles of glucose that was burnt $= \frac{1.80}{180} = 0.01$ mole

Hence 1 mole of glucose would produce $\frac{1}{0.01} \times 5000 \times 1.34 \times \frac{4.2}{1000}$ kJ

ie the enthalpy change of combustion of glucose, $\Delta H_c^{\ominus} = -2814$ kJ mol^{-1}

6.4 Enthalpy Change of Solution

- The enthalpy change of solution of a compound is the heat change when 1 mole of the compound is dissolved in a large amount of water, so that no further heat change occurs if more water is added to the solution. All measurements are made under standard state conditions.
- The enthalpy change of solution when dissolving sodium chloride in water is the enthalpy change of the reaction

  $$NaCl(s) + water \rightarrow Na^+(aq) + Cl^-(aq)\ ;\ \Delta H^\ominus = +3.9\ kJ\ mol^{-1}$$

  Enthalpy change of the reaction = enthalpy change of solution of sodium chloride
- Enthalpy changes of solution can be positive or negative.

6.5 Enthalpy Change of Hydration

- The enthalpy change of hydration of an ion is the heat energy evolved when 1 mole of separate gaseous ions is dissolved in a large amount of water. All measurements are made under standard state conditions.
- An example of enthalpy change of hydration, is the enthalpy change obtained when dissolving gaseous sodium ions, $Na^+(g)$, in water. The equation is

  $$Na^+(g) + water \rightarrow Na^+(aq);\ \Delta H^\ominus = -406\ kJ\ mol^{-1}$$

  The enthalpy change of the reaction = the enthalpy change of hydration of $Na^+(g)$. The heat produced in the hydration of ions comes from the bonds formed between the ions and the dipole on the water molecules. This is shown in Fig 6.3 for the hydration of Na^+ and Cl^- ions.

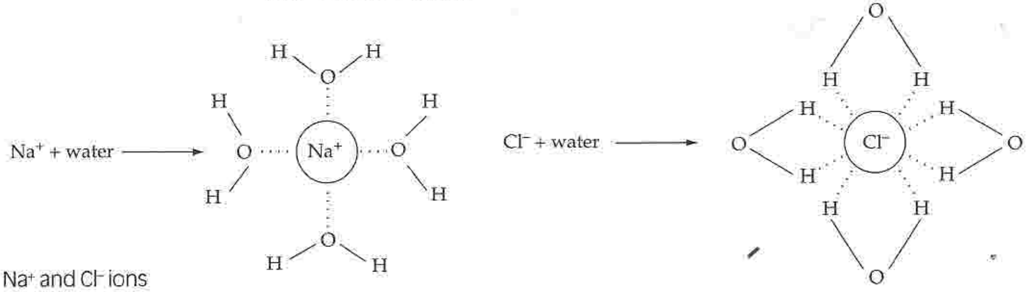


Fig 6.3 Hydration of Na^+ and Cl^- ions

- Enthalpy changes of hydration are always negative as heat energy is always evolved when the 'bonds' are formed between the solvent molecules and the ions.

6.6 Enthalpy Change of Neutralisation

- Enthalpy change of neutralisation is the heat energy evolved when an acid reacts with a base, per mole of the acid or base. All measurements are made under standard state conditions.
- Enthalpy change of neutralisation is usually applied to a particular acid and a particular base.
- An example of the enthalpy change of neutralisation is the enthalpy change obtained in the reaction between sodium hydroxide and hydrochloric acid. The equation for the reaction is

  $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l); \Delta H^{\circ} = -57.1\ \text{kJ mol}^{-1}$

  Enthalpy change of the reaction = enthalpy change of neutralisation of NaOH with HCl
- The enthalpy change of neutralisation of a strong acid with a strong alkali is almost the same for all acids and alkalis. This is because the same reaction always takes places. The reaction is

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

To determine the Enthalpy Change of neutralisation

- 25 cm^3 of 1.0 moldm^{-3} solution of hydrochloric acid is transferred in an expanded polystyrene cup.
- The temperature of the acid solution is measured.
- 30 cm^3 of 1.0 moldm^{-3} solution of NaOH is measured.
- The temperature of the alkali is measured.
- The average temperature of the solution is determined. Let it be t_1 ^{0}C.
- The alkali is carefully poured in the polystyrene cup containing the acid. The mixture is stirred and the maximum temperature reached by the mixture is noted. Let it be t_2 ^{0}C

Calculation

- Assume that to increase the temperature of 1 cm^3 of solution by 1 °C 4.5 J are required.
- Heat produced during the neutralization reaction
  $= [(25+30) \times (t_2 - t_1) \times 4.5]$ J
- Number of moles of acid used = (25 x 1.0) / 1000
  $= 2.5 \times 10^{-3}$
- Number of moles of alkali used = (30 x 1.0) / 1000
  $= 3.0 \times 10^{-3}$

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

From above, it can be deduced that the alkali is in excess.
Therefore when 2.5×10^{-3} mole of acid is neutralized,
$[(25+30)x(t_2 - t_1) \times 4.5]$ J are released.
Hence when 1 mole of acid is neutralized, energy released=

$$[(25+30)x(t_2 - t_1) \times 4.5] / 2.5\times10^{-3} \text{ J}$$

$$\therefore \Delta H^{\ominus}_{neut} = -[[(25+30)x(t_2 - t_1) \times 4.5] / 2.5\times10^{-3}] / 1000 \text{ kJmol}^{-1}$$

6.7 Enthalpy Change of Atomisation

- The enthalpy change of atomisation of an element is the heat energy change when one mole of separate gaseous atoms of the element is formed from the element under standard state conditions.
- The following equations each show atomisation of an element. In each case the enthalpy change of reaction = the enthalpy change of atomisation of the element.

$$Fe(s) \rightarrow Fe(g);\ \Delta H^{\ominus} = +418 \text{ kJ mol}^{-1}$$

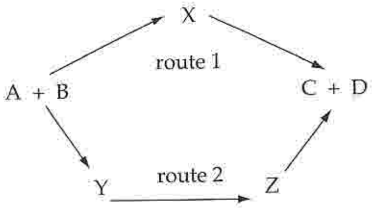
$$\frac{1}{2}Cl_2(g) \rightarrow Cl(g);\ \Delta H^{\ominus} = +121 \text{ kJ mol}^{-1}$$

- The enthalpy change of atomisation is *not* the same as the enthalpy change of vaporisation of an element. When an element is vaporised, the gas particles are usually not separate atoms.
- All enthalpy changes of atomisation of the noble gases (Group VIII elements) such as helium and argon are zero. This is because the elements are already in the form of separate gaseous atoms under standard state conditions.
- Enthalpy changes of atomisation are positive, because energy must be absorbed to pull the atoms far apart and break all the bonds between them.
- Enthalpy changes of atomisation are usually found indirectly by calculation from other enthalpy changes of reaction, using Hess' Law.

6.8 Hess' Law

Hess's Law

- Hess's law states that 'for a given overall reaction, the overall energy change is the same independent of the path taken by the reactants provided that all measurements are made under the same conditions.



- When reactants A and B are changed into products C and D by route 1 (through X), or by route 2 (through Y and Z), then according to Hess' Law the enthalpy change of the reaction in route 1 = the enthalpy change of the reaction in route 2.
- Hess' Law can be used to calculate the enthalpy change of a reaction. This is shown in the following example:

$$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \qquad (1)$$

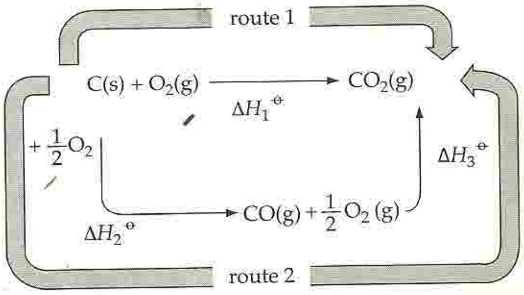
The enthalpy change of the above reaction cannot be found directly by experiment, because some CO_2 is always formed when carbon reacts with oxygen.

The enthalpy changes of combustion of carbon and carbon monoxide can be found experimentally

$$C(s) + \frac{1}{2}O_2(g) \rightarrow CO_2(g); \Delta H_c^{\circ} = -394 \text{ kJ mol}^{-1}$$
$$CO(g) + O_2(g) \rightarrow CO_2(g); \Delta H_c^{\circ} = -283 \text{ kJ mol}^{-1}$$

These two enthalpy changes of combustion can then be used to find the enthalpy change of the reaction (1).

There are two 'routes' from carbon to carbon dioxide (Fig 6.4). Route 1 is direct. In route 2, the carbon is first burnt to carbon monoxide and then burnt to produce carbon dioxide.



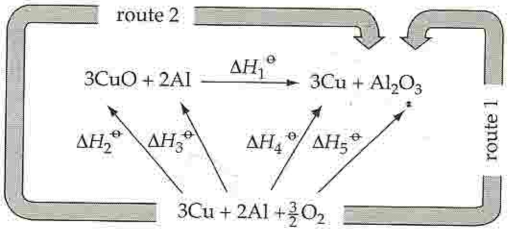
▶ Fig 6.4

By Hess' Law,
the heat energy change in route 1 = the heat energy change in route 2
If $\Delta H_1^{\ominus}$ is the heat energy change in the combustion of C to CO_2,
$\Delta H_2^{\ominus}$ for C to CO,
and $\Delta H_3^{\ominus}$ for CO to CO_2,
then $\Delta H_1^{\ominus} = \Delta H_2^{\ominus} + \Delta H_3^{\ominus}$
ie $\Delta H_2^{\ominus} = \Delta H_1^{\ominus} - \Delta H_3^{\ominus}$
$= -394 - (-283)$ kJ
$= -111$ kJ

Enthalpy Change of Reaction from Enthalpy Changes of Formation

- The enthalpy change of any reaction can be found by calculation, from the enthalpy changes of formation of all the substances in the chemical equation, using Hess' Law. For example, the enthalpy change of the reaction below can be found from the enthalpy changes of formation.

$$3CuO + 2Al \rightarrow 3Cu + Al_2O_3$$



▶ Fig 6.5

The diagram in Fig 6.5 shows two routes for making the products of the reaction from their elements. Route 1 is the direct route. In route 2, the reactants (3CuO + 2Al) are first made from their elements, then the reactants are changed into the products.
In the diagram,
$\Delta H_1^{\ominus}$ = enthalpy change of the reaction (to be calculated)
$\Delta H_2^{\ominus} = 3 \times$ enthalpy change of formation of CuO = 3(–155) kJ
$\Delta H_3^{\ominus} = 2 \times$ enthalpy change of formation of Al = zero
$\Delta H_4^{\ominus} = 3 \times$ enthalpy change of formation of Cu = zero
$\Delta H_5^{\ominus}$ = enthalpy change of formation of Al_2O_3 = –1669 kJ
By Hess' Law,
heat energy change in route 1 = heat energy change in route 2
heat energy change in route 1 $= \Delta H_4^{\ominus} + \Delta H_5^{\ominus}$
heat energy change in route 2 $= \Delta H_2^{\ominus} + \Delta H_3^{\ominus} + \Delta H_1^{\ominus}$
Hence $\Delta H_2^{\ominus} + \Delta H_3^{\ominus} + \Delta H_1^{\ominus} = \Delta H_4^{\ominus} + \Delta H_5^{\ominus}$
ie $H_1 = \Delta H_4^{\ominus} + \Delta H_5^{\ominus} - \Delta H_2^{\ominus} - \Delta H_3^{\ominus}$
$= 0 - 1669 - 3(-155) - 0$
$= -1204$ kJ

In general

$\Delta H_r = \Sigma\Delta H_f$(products) - $\Sigma\Delta H_f$(reactants)

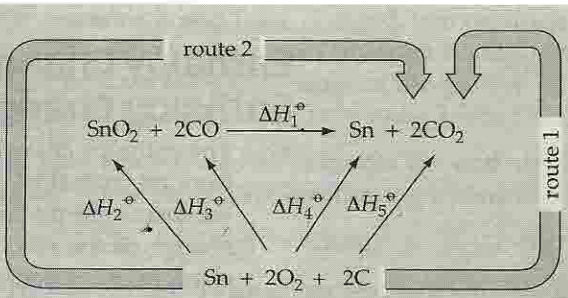
Question

$$SnO_2 + 2CO \rightarrow Sn + 2CO_2$$

Calculate the enthalpy change of the above reaction from the following enthalpy changes of formation:

$\Delta H_f^\ominus$ of SnO_2 = –581 kJ mol^{-1}
$\Delta H_f^\ominus$ of CO = –111 kJ mol^{-1}
$\Delta H_f^\ominus$ of CO_2 = –394 kJ mol^{-1}

Answer



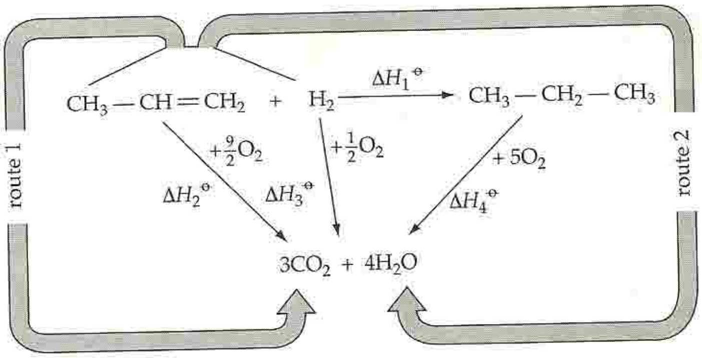
▸ Fig 6.6

$\Delta H_1^\ominus$ = enthalpy change of the reaction (to be calculated)
$\Delta H_2^\ominus$ = enthalpy change of formation of SnO_2 = –581 kJ
$\Delta H_3^\ominus$ = 2 × the enthalpy change of formation of CO = 2(–111) kJ
$\Delta H_4^\ominus$ = enthalpy change of formation of Sn = zero
$\Delta H_5^\ominus$ = 2 × the enthalpy change of formation of CO_2 = 2(–394) kJ
By Hess' Law,
heat energy change in route 2 = heat energy change in route 1
Hence $\Delta H_2^\ominus + \Delta H_3^\ominus + \Delta H_1^\ominus = \Delta H_4^\ominus + \Delta H_5^\ominus$
ie $\Delta H_1^\ominus = \Delta H_4^\ominus + \Delta H_5^\ominus - \Delta H_2^\ominus - \Delta H_3^\ominus$
$= 0 + 2(-394) - (-581) - 2(-111)\text{kJ}$
$= +15$ kJ

Enthalpy Change of Reaction from Enthalpy Changes of Combustion

- The enthalpy change can be calculated from the enthalpy chang of combustion. However, this can only be done for reactions which the substances on both sides of the equation can be bu in oxygen.
- In practice this method is only used for organic compounds.
- The enthalpy change of the reaction below can be calculated fr the enthalpy changes of combustion of propene, hydrogen propane.

$$\underset{\text{propene}}{CH_3\text{–}CH=CH_2} + \underset{\text{hydrogen}}{H_2} \rightarrow \underset{\text{propane}}{CH_3\text{—}CH_2\text{—}CH_3}$$



▶ Fig 6.7

The diagram in Fig 6.7 shows two routes for the combustion of propene and hydrogen into carbon dioxide and water. In route 1 the reactants are burnt directly in oxygen. In route 2 the reactants are first converted to propane which is then completely burnt to carbon dioxide and water.

In the diagram,

$\Delta H_1^\ominus$ = enthalpy change of the reaction (to be found)
$\Delta H_2^\ominus$ = enthalpy change of combustion of propene = –2059 kJ
$\Delta H_3^\ominus$ = enthalpy change of combustion of hydrogen = –286 kJ
$\Delta H_4^\ominus$ = enthalpy change of combustion of propane = –2220 kJ

By Hess' Law,

heat energy change in route 1 = heat energy change in route 2

$$\begin{aligned}\Delta H_2^\ominus + \Delta H_3^\ominus &= \Delta H_1^\ominus + \Delta H_4^\ominus \\ \Delta H_1^\ominus &= \Delta H_2^\ominus + \Delta H_3^\ominus - \Delta H_4^\ominus \\ &= -2059 - 286 - (-2220) \\ &= -125\text{ kJ}\end{aligned}$$

Question

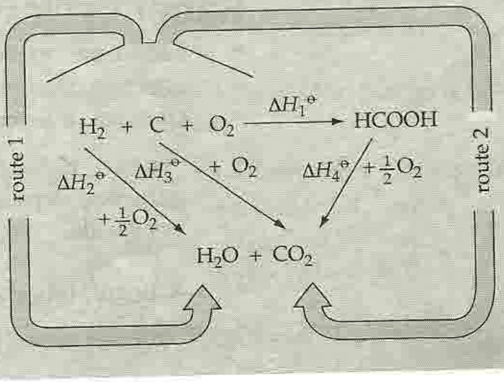
Calculate the enthalpy change of formation of methanoic acid, HCOOH, from the following enthalpy changes of combustion:

$\Delta H_c^\ominus$ of H_2 = –286 kJ mol^{-1}
$\Delta H_c^\ominus$ of carbon = –394 kJ mol^{-1}
$\Delta H_c^\ominus$ of HCOOH = –263 kJ mol^{-1}

Answer

The enthalpy change of formation of HCOOH is the enthalpy change of the reaction

$$H_2(g) + C(s) + O_2(g) \rightarrow HCOOH(l)$$



▶ Fig 6.8

Answer

In the diagram (Fig 6.8),
$\Delta H_1^{\ominus}$ = the enthalpy change of formation of HCOOH (to be found)
$\Delta H_2^{\ominus}$ = the enthalpy change of combustion of hydrogen = –286 kJ
$\Delta H_3^{\ominus}$ = the enthalpy change of combustion of carbon = –394 kJ
$\Delta H_4^{\ominus}$ = the enthalpy change of combustion of HCOOH = –263 kJ
By Hess' Law,
heat energy change in route 1 = heat energy change in route 2

Hence $\Delta H_2^{\ominus} + \Delta H_3^{\ominus} = \Delta H_1^{\ominus} + \Delta H_4^{\ominus}$

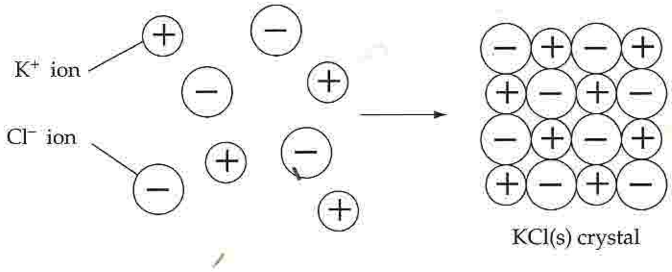
$$\Delta H_1^{\ominus} = \Delta H_2^{\ominus} + \Delta H_3^{\ominus} - \Delta H_4^{\ominus}$$
$$= -286 - 394 - (-263) = -417 \text{ kJ mol}^{-1}$$

6.9 Lattice Energy

- The lattice energy of an ionic crystal is the heat energy evolved when the separate gaseous ions are brought together to form 1 mole of solid compound under standard state conditions.
- For example, the lattice energy of potassium chloride is the enthalpy change of the reaction

  $$K^+(g) + Cl^-(g) \rightarrow K^+Cl^-(s); \Delta H^{\ominus} = -701 \text{ kJ mol}^{-1}$$

  This reaction is shown in Fig 6.9.

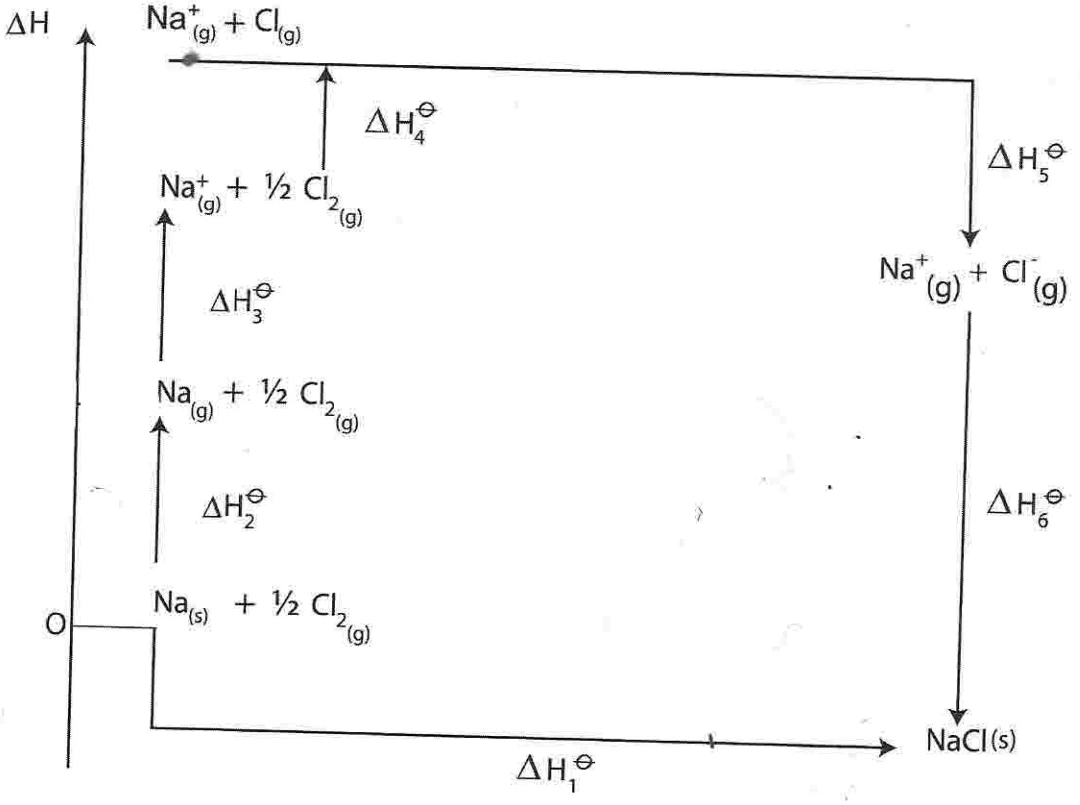


▸ Fig 6.9 Lattice energy of KCl

- All lattice energies are negative because heat energy is evolved when the ions come together to form ionic bonds.

Calculation of Lattice Energy from Born-Haber Cycles

- Lattice energies cannot be found directly from experiments. Lattice energies must be calculated indirectly from other known enthalpy changes of reaction, using a **Born-Haber cycle**.
- The Born-Haber cycle is an energy cycle which shows all the theoretical enrgetical steps in the convertion of elements into one mole of an ionic compound.
- A Born-Haber cycle for sodium chloride, NaCl, is shown in Fig 6.10.



$\Delta H_1^\ominus$ = enthalpy change of formation of NaCl = –411 kJ
$\Delta H_2^\ominus$ = enthalpy change of atomisation of sodium = +109 kJ

The standard enthalpy change of atomization is the enthalpy change which occurs when one mole of free gaseous atoms is produced from its element under standard state conditions.

$\Delta H_3^\ominus$ = enthalpy change of ionisation (ionisation energy) of sodium = +494 kJ
$\Delta H_4^\ominus$ = enthalpy change of atomisation of chlorine = +121 kJ
$\Delta H_5^\ominus$ = electron affinity of chloride = –364 kJ

$Cl(g) + \bar{e} \rightarrow Cl^-(g)\ \Delta H_r = \Delta H_{ea}(Cl) = -364\ kJ\ mol^{-1}$

The electron affinity (more strictly the first electron affinity) is the enthalpy change when each atom in one mole of gaseous atoms accepts an electron to become a negatively charged ion.

$\Delta H_6^\ominus$ = lattice energy of NaCl [ie ΔH for $Na^+(g) + Cl^-(g) \rightarrow Na^+Cl^-(s)$]

By Hess' Law,
heat energy change in route 1 = heat energy change in route 2

Hence $\Delta H_1^\ominus = \Delta H_2^\ominus + \Delta H_3^\ominus + \Delta H_4^\ominus + \Delta H_5^\ominus + \Delta H_6^\ominus$

$$\begin{aligned}\Delta H_6^\ominus &= \Delta H_1^\ominus - \Delta H_2^\ominus - \Delta H_3^\ominus - \Delta H_4^\ominus - \Delta H_5^\ominus\\ &= -411 - 109 - 494 - 121 - (-364)\\ &= -771\ kJ\end{aligned}$$

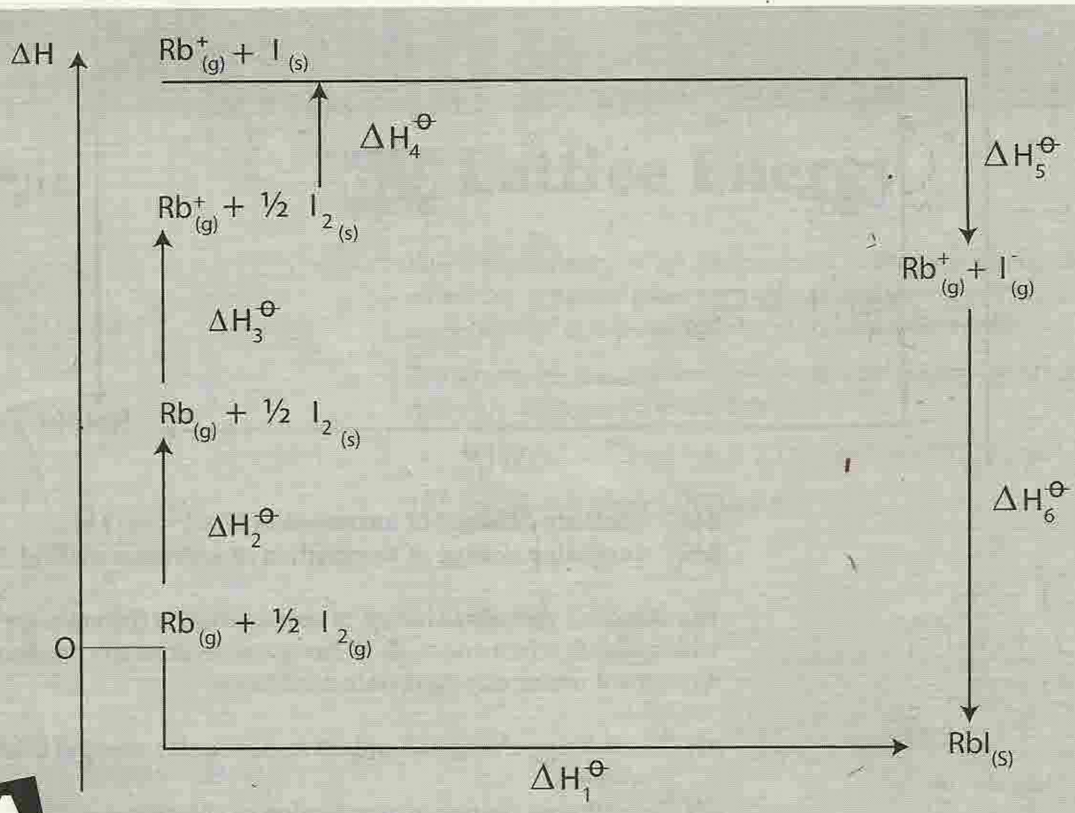
Hence the lattice energy of NaCl = –771 kJ mol^{-1}.

Question

Draw a Born-Haber cycle for rubidium iodide, RbI(s). Hence use the data below to calculate the enthalpy change of formation of RbI(s).

Enthalpy change of atomisation of rubidium = +86 kJ mol^{-1}
Enthalpy change of atomisation of iodine = +107 kJ mol^{-1}
Lattice energy of rubidium iodide = –609 kJ mol^{-1}
Ionisation energy of rubidium = +402 kJ mol^{-1}

$$I(g) + e^- \rightarrow I^-(g); \quad \Delta H^\ominus = -314 \text{ kJ}$$



Answer

$\Delta H_1^\ominus$ = enthalpy change of formation of RbI(s) (to be found)
$\Delta H_2^\ominus = +86$ kJ
$\Delta H_3^\ominus = +402$ kJ
$\Delta H_4^\ominus = +107$ kJ
$\Delta H_5^\ominus = -314$ kJ
$\Delta H_6^\ominus = -609$ kJ

By Hess' Law,
heat energy change in route 1 = heat energy change in route 2

Hence $\Delta H_1^\ominus = \Delta H_2^\ominus + \Delta H_3^\ominus + \Delta H_4^\ominus + \Delta H_5^\ominus + \Delta H_6^\ominus$
$= +86 + 402 + 107 + (-314) + (-609) = -328$ kJ

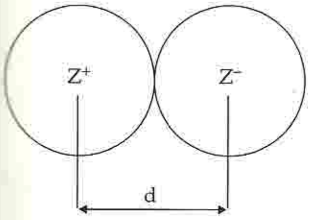
Hence the enthalpy change of formation of RbI(s) = –328 kJ mol^{-1}.

Factors Affecting the Magnitude of Lattice Energy

- The lattice energy depends on the attractive force between the ions in the crystal. The bigger the force, the bigger the lattice energy.
- The attractive force between two ions in contact (Fig 6.12) is proportional to

$$\frac{(\text{charge on positive ion}) \times (\text{charge on negative ion})}{d^2}$$

where d is the distance between the nuclei of the two ions.



▲ Fig 6.12

Therefore:

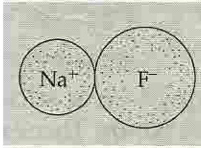
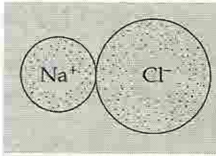
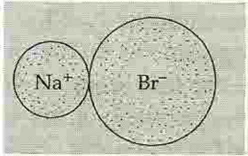
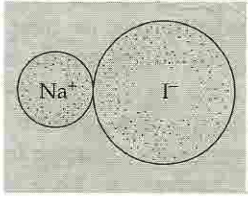
(a) The *bigger* the *charge* on the ions, the *bigger* the *lattice energy*. For example, the lattice energy of MgO(s) is much bigger than the lattice energy of NaCl(s).

Lattice energies: NaCl = –771 kJ mol^{-1}
MgO = –3830 kJ mol^{-1}

This is because in MgO the charges of the ions are +2 and –2, compared with charges of +1 and –1 in NaCl.

(b) The *smaller* the *ionic radii*, the *bigger* the *lattice energy*. For example, the lattice energies of the sodium halides (NaF, NaCl, NaBr, NaI) become smaller from F to I as the ionic radius of the halide ion becomes larger (Table 6.1).

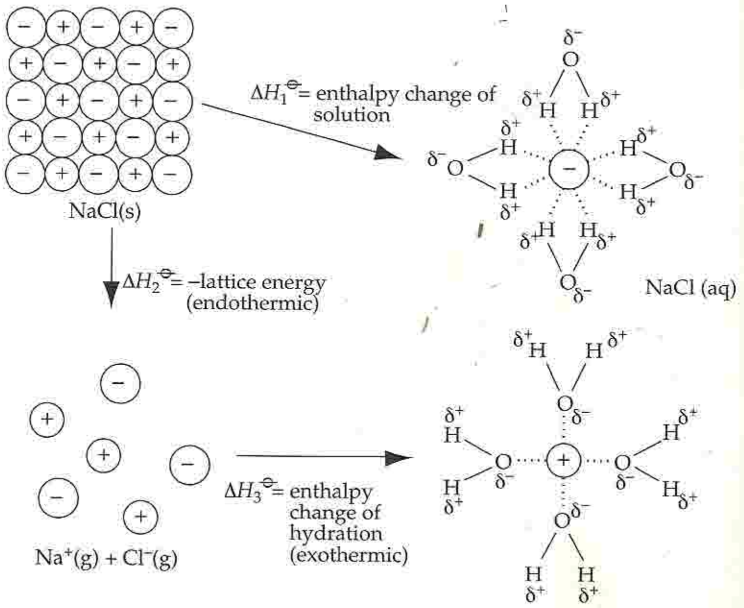
▶ Table 6.1

		distance between centres of ions nm	lattice energy kJ mol^{-1}
	0.136	0.231	–902
	0.181	0.276	–771
	0.196	0.291	–733
	0.216	0.311	-684

- The arrangement of the ions also affects the lattice energy, but this effect is small.

6.10 Dissolving Ionic Solids in Water

- Fig 6.13 shows the dissolving of sodium chloride in water. The water molecules are polarised. The oxygen atoms have a *partial negative* charge (δ–) and are attracted to the positive Na^+ ions. The hydrogen atoms have a *partial negative* charge (δ+) and are attracted to the negative Cl^- ions.



▶ Fig 6.13

- The water molecules stick to the Na^+ and Cl^- ions by forming electrostatic bonds. The water molecules then pull the ions apart to form a solution of $Na^+(aq)$ and $Cl^-(aq)$.
- The heat energy change when 1 mole of NaCl(s) dissolves in a large amount of water = the enthalpy change of solution ($\Delta H_1^\ominus$ in Fig 6.13).
- The dissolving of NaCl(s) in water can be *imagined* to consist of two stages.
  - (a) In the first stage, the ions are pulled far apart to form a gas of separate ions, $Na^+(g) + Cl^-(g)$. The heat energy change for this stage = $\Delta H_2^\ominus$ = –lattice energy. This change is *always* endothermic as heat energy is absorbed in breaking the electrovalent bonds and pulling the ions apart.
  - (b) In the second stage, water molecules are attached to the gaseous ions to form a solution of $Na^+(aq)$ and $Cl^-(aq)$. The heat energy change for this stage = $\Delta H_3^\ominus$ = enthalpy change of hydration. This change is always exothermic as heat energy is evolved in forming the electrostatic forces between the water molecules and the ions.

- By Hess' Law, $\Delta H_1^{\ominus} = \Delta H_2^{\ominus} + \Delta H_3^{\ominus}$
  So the enthalpy change of solution = $\underbrace{(-\text{lattice energy})}_{\text{endothermic}} + \underbrace{(\text{enthalpy change of hydration})}_{\text{exothermic}}$
- Conclusions:
  (a) If the lattice energy is numerically larger than the enthalpy change of hydration, the enthalpy change of solution is positive (endothermic).
  (b) If the enthalpy change of hydration is numerically larger than the lattice energy, the enthalpy change of solution is negative (exothermic).
  (c) If the lattice energy is *very much greater* than the enthalpy change of hydration, the ionic solid is insoluble in water because the water molecules cannot possibly overcome the very strong electrovalent bonds between the ions of the solid.
- For sodium chloride,
  lattice energy = –771 kJ mol^{-1}
  enthalpy change of hydration of Na^+ = –406 kJ mol^{-1}
  enthalpy change of hydration of Cl^- = –364 kJ mol^{-1}
  Hence applying Hess' Law, the enthalpy change of solution
  = (–lattice energy) + (enthalpy change of hydration of Na^+ and Cl^-)
  = +771 – 406 – 364
  = +1 kJ mol^{-1}

6.11 Calculation of Enthalpy Change of Reaction From Bond Energies

- The enthalpy change of reaction (ΔH) for gaseous covalent molecules can be calculated from bond energies.

Bond energy

- During a chemical reaction involving covalent substances, a number of covalent bonds are broken and a number of covalent bonds are formed.
- The average bond energy is the average energy required to break covalent bond between a pair of atoms in one mole of substances.

For example the bond energy for chlorine ,

Cl_2 is + 242 $KJmol^{-1}$. This implies that 242KJ are required to break the covalent bonds between each pair of atoms in one mole of chlorine.

$Cl_2(g) \rightarrow 2Cl(g)\ \Delta H_r^\circ = \Delta H_{BE}^\circ = +242\ KJmol^{-1}$

Note : $\Delta H_{BE}(Cl_2) = 2\Delta H_{at}(Cl)$ since when one mole of covalent bond breaks, two moles of chlorine atoms are produced.

- The average bond energy depends upon:-

1. the bond length

If the covalent bond is long, it will be weak and the average bond energy will be low.

Molecules	Average bond energy / $kJmol^{-1}$
Cl_2 [Cl—Cl]	+ 242
Br_2 [Br——Br]	+193
I_2 [I———I]	+ 151

2. the number of covalent bonds between the atoms

When the number of covalent bonds between the atoms increases, more energy will be required to separate the atoms. Therefore the bond energy increases.

Molecules	Average bond energy / $kJmol^{-1}$
C—C	+348
C=C	+612
C≡C	+837

3. the degree of polarity of the bond

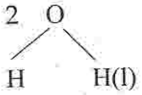
The bond energy for a polar bond is usually higher than for a non polar bond.

- The enthalpy changes of reaction calculated using bond energies are different from those calculated by using enthalpy changes of formation and combustion bond energies vary slightly between molecules (eg the O—H bond energy is different in H_2O and CH_3CH_2OH).

- For example calculate the enthalpy change for the reaction below:-

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

$$2H\text{—}H(g) + O{=}O(g) \rightarrow 2$$



$$\therefore \Delta H_r = 2\Delta H_{BE}(H\text{—}H) + \Delta H_{BE}(O{=}O) - 4\Delta H_{BE}(O\text{—}H)$$

$\Delta H_{BE}(H\text{—}H) = +436\ kJmol^{-1}$
$\Delta H_{BE}(O{=}O) = +496\ kJmol^{-1}$
$\Delta H_{BE}(O\text{—}H) = +463\ kJmol^{-1}$
$\therefore \Delta H_r = [\,2(+436) + (+496) - 4(463)\,]\ kJ = -484\ kJ$

Question

$$4NH_3(g) + 3O_2(g) \rightarrow 2N_2(g) + 6H_2O(g)$$

Calculate the enthalpy change of the reaction above from bond energies :

N–H = 390 kJ mol^{-1}; 0=0 = 496 kJ mol^{-1}; N≡N = 994 kJ mol^{-1}; O–H = 460 kJ mol^{-1}

Answer

$$4NH_3(g) + 3O_2(g) \xrightarrow{\Delta H_1} 2N_2(g) + 6H_2O(g)$$

The reaction molecules have twelve N–H bonds and three oxygen double bonds (O=O). The energy absorbed is = 12 × 390 + 3 × 496 = 6168 kJ.

The product molecule has two nitrogen with triple bonds (2N≡N) and twelve O–H bond. The energy released = 2 × 994 + 12 × 460 = 7508 kJ.

Hence, the enthalpy change of reaction

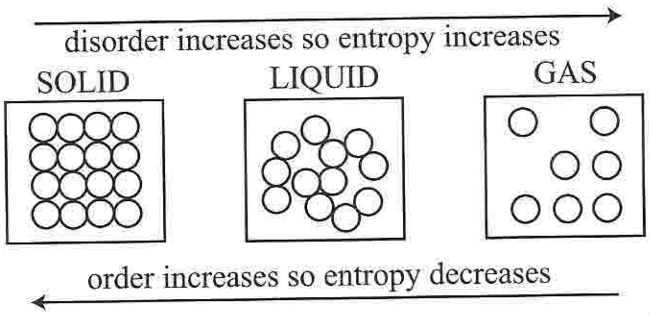
$$= \begin{bmatrix}\text{heat energy evolved} \\ \text{during bond formation}\end{bmatrix} - \begin{bmatrix}\text{heat energy absorbed} \\ \text{during bond breaking}\end{bmatrix}$$

= 7508 – 6168 = 1340 kJ

This overall heat change is exothermic because heat evolved is greater than heat absorbed, so $\Delta H = -134$ kJ.

6.12 Entropy

- Entropy[denoted by the symbol, S] is a thermodynamic quantity related to the degree of disorder in a system.
- The entropy is a quantity which measures the degree of disorder or randomness of the way particles of a system are distributed in space and the way energy is distributed between the particles.
- The greater the degree of disorder or randomness in a system, the greater will be the entropy of the system. For example comparing a crystalline solid and a gas , the gas has a greater entropy because its particles are far apart in a disorderly arrangement and moving randomly in all directions, whereas in the solid the particles have an orderly arrangement.
- The entropy increases when there is a change in state during melting or boiling.



- In general entropy increases:-

i. when a solid melts[during which the orderly arrangement of particles in the crystalline solid is replaced by the random movement of particles in the liquid]

ii. during the process of evaporation [during evaporation molecules in the vapour can move more freely than in the liquid state]

iii. when an ionic compound dissolves in a liquid [during this process a crystalline solid and a liquid is replaced by mobile ions and molecules of liquids as a result there will be a greater degree of disorder in the particles of the ionic compound].Therefore the degree of disorder and entropy increases during the dissolving process.

iv. when the number of molecules of gases increases during a chemical reaction, for example, during the decomposition of lead[II] nitrate.

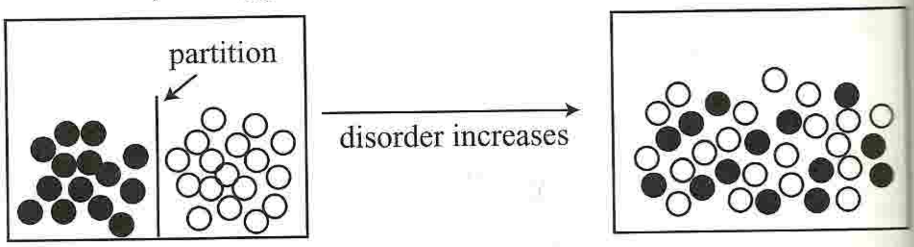
$$2Pb(NO_3)_2(s) \rightarrow 2PbO(s) + 4NO_2(g) + O_2(g)$$

An increase in the number of gas particles will increase the degree of disorder of the system.

v. when the temperature of a substance is increased[when the temperature is increased, the particles gain kinetic energy and their particles move faster.]

vi. when a spontaneous reaction occurs

vii. by mixing particles



When the partition is removed , the two sets of particles mix together **spontaneously**, increasing the degree of disorder and hence the entropy increases .

- A crystal lattice at absolute zero (0K) consists of particles which are not moving at all .Hence the particles have a perfect order and the **entropy will be zero**. As the temperature increases the mobility of the particles increases and hence the entropy increases.
- Entropy is measured in $Jmol^{-1}K^{-1}$
- The entropy for certain substances are listed in the table below:-

Substance	Standard entropy (S)/$Jmol^{-1}K^{-1}$
$H(g)$	+115.0
$H_2(g)$	+130.6
$He(g)$	+126.0
$C(graphite,s)$	+5.7
$C(diamond,s)$	+2.4
$Na(s)$	+51.0
$NaCl(s)$	+72
$H_2O(s)$	+48.0
$H_2O_{(l)}$	+69.9
$H_2O(g)$	+188.7

- The entropy change (ΔS) is the change in entropy which occurs during a process.

$$\Delta S = S_{product} - S_{reactant}$$

- By using balanced equations, it may be deduced whether the entropy of a reaction increases or decreases. For example:

[i] the decomposition of ammonium nitrate

$$2NH_4NO_3(s) \rightarrow 2N_2(g) + 4H_2O(g) + O_2(g)$$

In this reaction, a solid is producing a large volume of gas. Two moles of solid produce seven moles of gases. Hence the entropy of the system increases.

[ii] the formation of tetracarbonyl nickel[II]

$$Ni(s) + 4\,CO(g) \rightarrow Ni(CO)_4(l)$$

The number of moles of gas particles decreases. Therefore the entropy of the system decreases.

[iii] the reduction of iron(III)oxide by hydrogen

$$Fe_2O_3(s) + 3H_2(g) \rightarrow 2Fe(s) + 3H_2O(g)$$

The number of moles of gaseous particles on reactant and product sides are the same. However the entropy of hydrogen and steam are different. Hence the entropy change cannot be judged only by using the equation.

- Some common examples illustrating the entropy changes are summarized in the table below:-

change	entropy change	example
melting	increase	$H_2O(s) \longrightarrow H_2O(l)$
boiling	big increase	$Br_2(l) \longrightarrow Br_2(g)$
condensation	big decrease	$C_2H_5OH(g) \longrightarrow C_2H_5OH(l)$
freezing	decrease	$I_2(l) \longrightarrow I_2(s)$
dissolving a solid in solution	increase	$NaCl(s) + water \longrightarrow NaCl(aq)$
crystallisation from solution	decrease (crystal is more orderly)	$CuSO_4(s) \longrightarrow CuSO_4(aq)$
chemical reaction: solid/liquid → gas	big increase (gas is very disorderly)	$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$
chemical reaction: gas → solid/liquid	big decrease (solid/liquid is more orderly than gas)	$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$

- The standard entropy of different substances are available in the Data Booklet.
- Using the standard entropies of different substances, the entropy change of a reaction can be calculated.
- The entropy change, ΔS^{θ} of a reaction is equal to the sum of entropies of products minus sum of entropies of reactants.

$$\Delta S^{\theta}_{r} = \Delta S^{\theta}_{products} - \Delta S^{\theta}_{reactants}$$

6.13 To calculate entropy change of a reaction

Calculate the entropy change, DS for the reaction below:-

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

given that the entropies for $H_2(g)$, $O_2(g)$ and $2H_2O(l)$ are +131, +205 and +70 $JK^{-1}mol^{-1}$ respectively.

[Note: the unit for entropy is most frequently given as $JKmol^{-1}$ and not as $kJK^{-1}mol^{-1}$]

Answer: Using $\Delta S^{\theta}_{r} = \Delta S^{\theta}_{products} - \Delta S^{\theta}_{reactants}$

$$\Delta S^{\theta}_{r} = 2\Delta S^{\theta}(H_2O(l)) - [2\Delta S^{\theta}(H_2(g)) + \Delta S^{\theta}(O_2(g))]$$

$$\Delta S^{\theta}_{r} = ([2x70] - [(2x131) + 205])\ JK^{-1}$$

$$\Delta S^{\theta}_{r} = -327\ JK^{-1}$$

Note : the entropy change is negative. This is indeed what is expected since gases are being converted into a liquid where a decrease in degree of disorder occurs.

Entropy change for surroundings

- When water vapour condenses, it's entropy changes.
- During condensation, heat energy is lost by the water particles and the heat energy goes to the surrounding-for example in the surrounding air, on in the particles of the glass of the tube. Hence the entropy of the surrounding air and glass will increase. This entropy change is called the entropy change in the surrounding, $\Delta S_{\text{surrounding}}$.
- The entropy change in the surrounding can be calculated using the expression

$$\Delta S_{\text{surrounding}} = -\Delta H / T \qquad [1]$$

- Where, ΔH is the enthalpy change of the reaction T is the absolute temperature
  The negative sign is included since if the surrounding gains energy the chemicals must lose it.
- Therefore the total entropy change for a system must include the entropy change that occurs with the reacting particles and the entropy change in the surrounding.

- Using [1] and [2] $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$ [2]

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + -\Delta H / T$$

Multiplying by '-T', $-T\Delta S_{\text{total}} = -T\,\Delta S_{\text{system}} + \Delta H$

$$-T\Delta S_{\text{total}} = \Delta H - T\,\Delta S_{\text{system}} \qquad [3]$$

The term '$-T\Delta S_{\text{total}}$' is called the Gibbs free energy change, ΔG. Therefore'

$$\Delta G = \Delta H - T\,\Delta S_{\text{system}} \qquad [4]$$

- If measurements are conducted under standard conditions [298K and 1 atm], the energy change is referred to as the standard Gibbs free energy change of reaction, $\Delta G^{\ominus}$.

- In general,

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\,\Delta S^{\ominus}_{\text{system}} \qquad [5]$$

The term $\Delta S^{\ominus}_{\text{system}}$ is usually simply written as $\Delta S^{\ominus}$
Hence,

$$\mathbf{\Delta G^{\ominus} = \Delta H^{\ominus} - T\,\Delta S^{\ominus}} \qquad [6]$$

Equation [6] represents the standard Gibbs free energy change of reaction or Gibbs function..

- The standard Gibbs free energy change of reaction, $\Delta G^{\ominus}$ relates the enthalpy change and the entropy change of a reaction. It shows whether a process will occur spontaneously or not. Thus:-

a) if $\Delta G^{\ominus} < 0$, the process occurs spontaneously
b) if $\Delta G^{\ominus} > 0$, the process does not occur spontaneously
c) if $\Delta G^{\ominus} = 0$, the process is at dynamic equilibrium.

- From the expression for Gibbs function it can be deduced that:-

a) for an exothermic reaction which is accompanied by an increase in entropy, $\Delta G^{\ominus}$ will always be negative. Therefore the reaction will always occur spontaneously. For example the decomposition of ammonium nitrate will be an spontaneous reaction.

$$2NH_4NO_3(s) \rightarrow 2N_2(g) + 4H_2O(g) + O_2(g) \quad \Delta H^{\ominus} = -ve$$

b) for an endothermic reaction which is accompanied by an decrease in entropy, DGF will always be positive. Therefore the reaction will never occur For example the decomposition of carbon monoxide will never occur.

$$2CO(g) \rightarrow 2C(s) + O_2(g) \qquad \Delta H^{\ominus} = +ve$$

In the above reaction entropy decreases and process is endothermic. Hence reaction will not occur.

c) if a reaction is exothermic but is accompanied by a decrease in entropy, the reaction may occur provided that the temperature is so low that $\Delta H^{\ominus} > T\Delta S^{\ominus}$. In this case $\Delta G^{\ominus} < 0$.
For example during condensation, a vapour is converted into a liquid. Therefore the entropy decreases. But the process is exothermic. Hence the process may occur only at low temperature.

d) if a reaction is endothermic but is accompanied by an increase in entropy, the reaction may occur provided that the temperature is high enough such that that $\Delta H^{\ominus} < T\,\Delta S^{\ominus}$. In this case $\Delta G^{\ominus} < 0$.
For example, the convertion of a liquid into its vapour is an endothermic process. But the entropy of the process increases. Therefore at high temperature,
$T\Delta S^{\ominus} > \Delta H^{\ominus}$ .Hence $\Delta G^{\ominus} < 0$ and process will occur.
The dissolution of certain salt in water is usually an endothermic process. For example the dissolution of sodium chloride in water is an endothermic process. However the process do occur since it is accompanied by an increase in entropy.

To calculate $\Delta G^{\ominus}$ for a reaction using $\Delta G^{\ominus} = \Delta H^{\ominus} - T\,\Delta S^{\ominus}$

Q1. For the reaction

$$2Cl(g) \rightarrow Cl_2(g)$$

what are the signs of ΔH and ΔS ?

Ans: As covalent bond is formed between the atoms, energy will be released. Hence ΔH will be negative.

As there is a decreases in randomness, the entropy decreases and ΔS becomes negative.

Q2.For the reaction

$$2PCl_3(g) + O_2(g) \rightarrow 2POCl_3(l)$$

the standard enthalpy of reaction , at 298 K is –555 kJ. The molar entropies at 298 K are as follows:-

Substances	**Molar entropies, S [$Jmol^{-1}K^{-1}$**
$PCl_3(g)$	**312**
$O_2(g)$	**205**
$POCl_3(l)$	**222**

What is the value of $\Delta G^{\ominus}$ for this reaction?

Ans: Change in entropy for the reaction = entropy of products – entropy of reactants

$$\Delta S^{\ominus}_r = 2\Delta S^{\ominus}(POCl_3) - [2\Delta S^{\ominus}(PCl_3) + \Delta S^{\ominus}(O_2)]$$

$\Delta S^{\ominus}_r = 2(222) - [\,2(312) + 205\,] = -385\ JK^{-1} = -0.385\ kJK^{-1}$

Using $\Delta G^{\ominus} = \Delta H^{\ominus} - T\,\Delta S^{\ominus}$, $\Delta G^{\ominus} = (-555 - [\,298 \times -0.385]\,)\ kJ$

$$\Delta G^{\ominus} = -440\ kJ$$

Q3. The decomposition of magnesium carbonate is not spontaneous at standard state conditions:

$$MgCO_3(s) \rightarrow MgO(s) + CO_2(g) \qquad \Delta H^{\ominus} = +101\ kJmol^{-1}$$

The entropy change, ΔS, for the reaction is $+159\ Jmol^{-1}K^{-1}$.

Estimate the temperature at which the reaction will take place spontaneously.

Answer

Reaction will be spontaneous if $\Delta G^{\ominus} > 0$

The spontaneous reaction will start when $\Delta G = 0$

Using $\Delta G^{\ominus} = \Delta H^{\ominus} - T\,\Delta S^{\ominus}$, it implies that spontaneous reaction occurs when

$$\Delta H^{\ominus} - T\,\Delta S^{\ominus} = 0$$

Therefore the temperature, T at which spontaneous reaction starts

$$= \frac{\Delta H^{\ominus}}{\Delta S^{\ominus}} = \frac{101000}{159}\ \text{K} = 635\text{K}$$

So, a temperature of 635 K or 362 °C is needed for the reaction to take place.

Note:-

- The equilibrium constants K_p and Gibb's free energy are related to each other by the expression

$$\Delta G^{\ominus} = -RT\ln K_p$$

Where R = molar gas constant
T= absolute temperature(K)

- As Kp is independent of pressure, it implies that $\Delta G^{\ominus}$ will also be independent of pressure.
- As Kp as well as Kc are affected by temperature, it implies that $\Delta G^{\ominus}$ will also be affected by a change in temperature.

If a reaction is endothermic in the forward direction , it implies that according to Le Chatelier's principle, the reaction will be favoured by a high temperature. Kc or Kp will also increase and therefore $\Delta G^{\ominus}$ will also increase.

EXERCISE 6

Multiple Choice Questions

Section I

1 Which one of the following compounds would you expect to have the largest numerical lattice energy (ie most negative $\Delta H_{lattice}$)?
A NaCl C CsI
B NaI D CaO

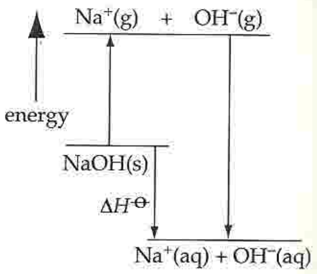
2 Which one of the following equations has an enthalpy change of reaction equal to the enthalpy change of atomisation of iodine?
A $I_2(g) \rightarrow 2I(g)$ C $\frac{1}{2}I_2(s) \rightarrow I(g)$
B $\frac{1}{2}I_2(g) \rightarrow I(g)$ D $I_2(s) \rightarrow 2I(g)$

3 Which one of the following reactions has an energy change equal to the ionisation energy of sulphur?
A $S_8(g) \rightarrow 8S^+(g) + 8e^-$
B $S_8(g) \rightarrow S^+(g) + e^-$
C $S(s) \rightarrow S^+(g) + e^-$
D $S(g) \rightarrow S^+(g) + e^-$

4 Which one of the following reactions has an enthalpy change of reaction equal to the enthalpy change of formation of sodium bromide, NaBr?
A $Na(s) + \frac{1}{2}Br_2(l) \rightarrow NaBr(s)$
B $Na(g) + Br(g) \rightarrow NaBr(g)$
C $Na(g) + \frac{1}{2}Br_2(g) \rightarrow NaBr(g)$
D $2Na(s) + Br_2(l) \rightarrow 2NaBr(s)$

5 Which enthalpy change of reaction is negative?
A $C(s) \rightarrow C(g)$
B $Na(g) \rightarrow Na^+(g) + e^-$
C $O^-(g) + e^- \rightarrow O^{2-}(g)$
D $Mg^{2+}(g) + O^{2-}(g) \rightarrow Mg^{2+}O^{2-}(s)$

6 Fig 6.14 shows an energy cycle involving sodium hydroxide.



▶ Fig 6.14

The energy change $\Delta H^\ominus$ in the diagram is best described as the

A heat of formation.
B heat of solution.
C heat of ionisation.
D lattice energy.

7 The enthalpy changes of combustion of ethyne (C_2H_2), hydrogen(H_2) and ethane(C_2H_6) are:

substance	*$\Delta H_c^\ominus$ /kJ mol^{-1}*
ethyne	–1300
hydrogen	–285
ethane	–1560

What is the enthalpy change of the reaction

$$C_2H_2 + 2H_2 \rightarrow C_2H_6?$$

A +25 kJ **C** –25 kJ
B +310 kJ **D** –310 kJ

8 The enthalpy changes of formation of aluminium oxide and copper(II) oxide are –1676 and –155 kJ mol^{-1} respectively. What is the enthalpy change of the reaction?

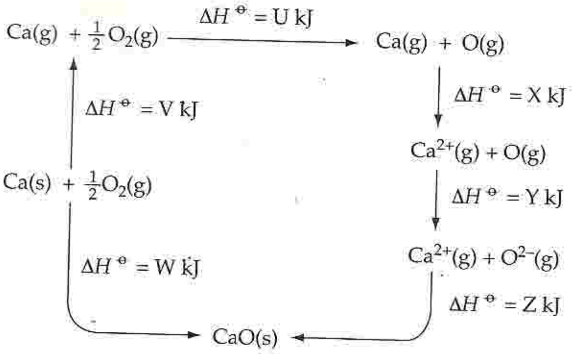
$$2Al(s) + 3CuO(s) \rightarrow Al_2O_3(s) + 3Cu(s)$$

A –1521 kJ **C** +121 kJ
B –1211 kJ **D** +2141 kJ

9 Data on iodine:
electron affinity: –297 kJ mol^{-1}
ionisation energy: +1010 kJ mol^{-1}
enthalpy change of atomisation: +107 kJ mol^{-1}
enthalpy change of hydration of the negative ion: –305 kJ mol^{-1}
enthalpy change of fusion: +8 kJ mol^{-1} of atoms
From the data above, what is the enthalpy change of the reaction

$$\frac{1}{2}I_2(s) \xrightarrow{\text{water}} I^-(aq)?$$

A –548.5 kJ **C** –495 kJ
B –540.5 kJ **D** –487 kJ



▲ Fig 6.15

Questions 10 to 12 refer to the Born-Haber cycle in Fig 6.15.

10 Which one of the following is the enthalpy change of atomisation, $\Delta H_a^\ominus$, of calcium?

A V **C** W – V
B X **D** Z – W

11 Which one of the following is the enthalpy change of formation, $\Delta H_f^\ominus$, of calcium oxide?

A W **C** Y + X
B Z **D** U + V

12 Which one of the following is the lattice energy of calcium oxide?

A W **C** Y + X
B Z **D** U + V

13 Which one of the following has an energy change equal to the lattice energy of an ionic compound, X^+Y^-?

A $X^+Y^-(s) \rightarrow XY(s)$
B $X^+(g) + Y^-(g) \rightarrow XY(s)$
C $X\cdot(g) + Y\cdot(g) \rightarrow XY(s)$
D $X(g) + Y(g) \rightarrow XY(s)$

14 Which one of the following has an energy change equal to the lattice energy of calcium bromide?

A $Ca(g) + Br_2(g) \rightarrow CaBr_2(g)$
B $Ca^{2+}(g) + 2Br^-(g) \rightarrow CaBr_2(g)$
C $Ca^{2+}(aq) + 2Br^-(aq) \rightarrow CaBr_2(s)$
D $Ca^{2+}(g) + 2Br^-(g) \rightarrow CaBr_2(s)$

15 Which one of the following quantities is *not* required in the calculation of the lattice energy of sodium chloride using a Born-Haber cycle?

A the electron affinity of chlorine
B the enthalpy change of atomisation of chlorine
C the enthalpy change of vaporisation of chlorine
D the enthalpy change of formation of sodium chloride

16 The radius and charge of each of six ions are shown in the table below.

ion	P^+	Q^+	R^{2+}	X^-	Y^-	Z^{2-}
ionic radius/nm	0.15	0.19	0.16	0.15	0.19	0.16

The ionic solids PX, QY and RZ have the same structure. What is the correct order of their lattice energies?

	largest lattice energy		*smallest lattice energy*
A	PX	QY	RZ
B	RZ	PX	QY
C	PX	RZ	QY
D	QY	RZ	PX

17 Which one of the following ions would have the largest enthalpy change of hydration?

	charge on ion	*ionic radius/nm*
A	+2	0.075
B	+1	0.105
C	+2	0.145
D	+1	0.179

18 Which one of the following equations has an enthalpy change of reaction equal to the enthalpy change of formation of carbon monoxide?

A $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$
B $C(s) + CO_2(g) \rightarrow 2CO(g)$
C $C(g) + \frac{1}{2}O_2(g) \rightarrow CO(g)$
D $C(g) + CO_2(g) \rightarrow 2CO(g)$

19 $CH_3{-}CH_3 \rightarrow CH_3{-}CH_2^{\cdot} + H^{\cdot}$; $\Delta H^\circ = +412$ kJ
$CH_3{-}CH_2^{\cdot} \rightarrow CH_2{=}CH_2 + H^{\cdot}$; $\Delta H^\circ = +168$ kJ

From the data above, what is the enthalpy change of the reaction?

$$2CH_3{-}CH_2^{\cdot} \rightarrow CH_3{-}CH_3 + CH_2{=}CH_2$$

A +580 kJ **C** –244 kJ
B +244 kJ **D** –580 kJ

Section II

Summary of directions

A	B	C	D
1, 2 and 3 are correct	**1 and 2** only are correct	**2 and 3** only are correct	**1 only is** correct

20 Which statements about magnesium and calcium are true?

1 The enthalpy change of atomisation of magnesium is larger than that of calcium.
2 The lattice energy of calcium oxide is larger than that of magnesium oxide.
3 The ionisation energy of calcium is larger than that of magnesium.

21 The enthalpy change of combustion of a compound was determined in an experiment. In the experiment, the compound was burnt in excess oxygen and the heat produced was absorbed by water. Which of the following measurements are required to calculate the enthalpy change of combustion?

1 temperature change of water
2 mass of water
3 mass of compound burnt

22 The standard enthalpy changes of formation, ΔH_f, of four hydrocarbons are given

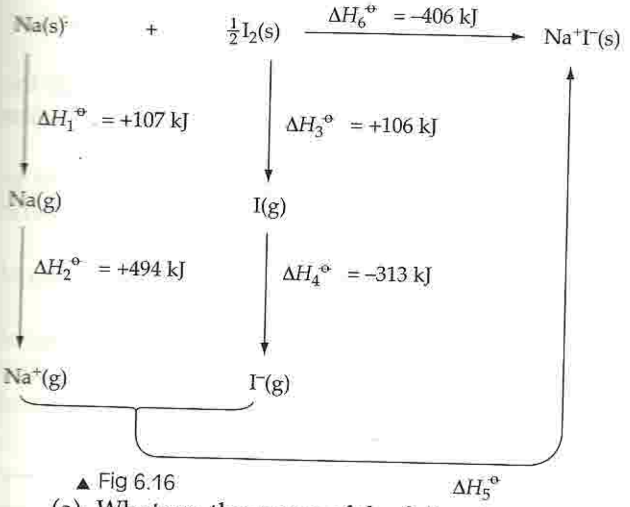
compound	C_2H_4	C_2H_6	C_4H_8	C_4H_{10}
ΔH_f, kJ mol^{-1}	+52	–85	–10	–125

Which reaction(s) is/are endothermic?

1. $2C_2H_6 \rightarrow H_2 + C_4H_{10}$
2. $C_2H_6 + C_2H_4 \rightarrow C_4H_{10}$
3. $H_2 + C_4H_8 \rightarrow C_4H_{10}$

Structured Questions

1 A Born-Haber cycle of sodium iodide is shown in Fig 6.16.



▲ Fig 6.16

(a) What are the *names* of the following energy changes?
(i) $\Delta H_1^\ominus$ (ii) $\Delta H_2^\ominus$ (iii) $\Delta H_6^\ominus$

(b) How would the following $\Delta H^\ominus$ values change, if potassium iodide is used in the Born-Haber cycle?
(i) $\Delta H_2^\ominus$ (ii) $\Delta H_4^\ominus$ (iii) $\Delta H_5^\ominus$

(c) Calculate the value of $\Delta H_5^\ominus$.

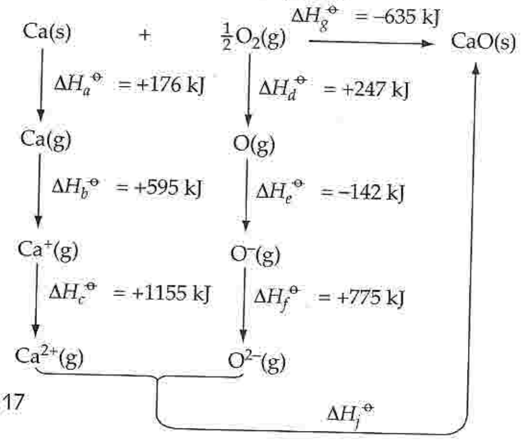
2 A Born-Haber cycle for calcium oxide is shown in Fig 6.17.

(a) Why is $\Delta H_e^\ominus$ negative and $\Delta H_f^\ominus$ positive?

(b) Why is $\Delta H_c^\ominus$ bigger than $\Delta H_b^\ominus$?

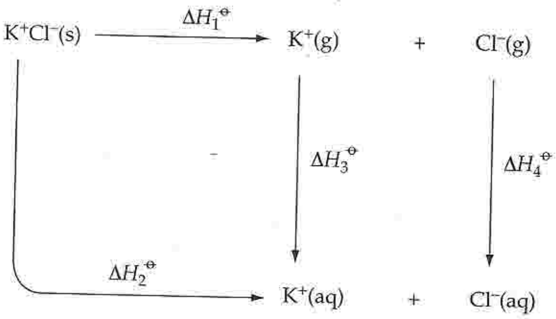
(c) Calculate the value of $\Delta H_j^\ominus$.

(d) Name an oxide of a Group II element which would have a lattice energy larger than that of calcium oxide.



▲ Fig 6.17

3 (a) What are the names of the energy changes $\Delta H_1^\ominus$, $\Delta H_2^\ominus$ and $\Delta H_3^\ominus$ in Fig 6.18?



▲ Fig 6.18

(b) For potassium chloride, the energy terms are:

enthalpy change of reaction	$\Delta H_1^\ominus$	$\Delta H_3^\ominus$	$\Delta H_4^\ominus$
energy/kJ mol^{-1}	+701	−322	−364

Calculate a value for $\Delta H_2^\ominus$.

(c) If potassium bromide were examined instead, how would you expect $\Delta H_1^\ominus$ and $\Delta H_4^\ominus$ to compare with values for potassium chloride?

4 The table below gives some data on two oxides of nitrogen and two oxides of phosphorus.

Formula of oxide	**Oxidation number of nitrogen/ phosphorus**	**Enthalpy change of formation, ΔH_f, kJ mol^{-1}**
N_2O		+82.0
NO		+90.4
P_4O_6		−1640.1
	+5	−2984.0

(a) Complete the table, adding the three missing oxidation numbers and the missing formula.

(b) (i) Write a balanced equation for the formation of the oxide NO, including the value of ΔH_f given in the table.
(ii) Use your equation to explain why this oxide is formed inside a motorcar engine.

(c) The enthalpy changes of formation of the two oxides of phosphorus are negative (like most oxides), but those of the two nitrogen oxides are *positive*. Suggest a reason for this.

(d) Use the data in the table to calculate the enthalpy change of the reaction

$$2NO(g) \rightarrow N_2O(g) + \frac{1}{2}O_2(g)$$

*5 The equation below shows the reaction between steam and flourine

$2H_2O(g) + 2F_2(g) \rightarrow 4HF(g) + O_2(g)$

(a) use the standard molar enthalpy changes of formation (ΔH_f) data below to calculate the enthalpy change for this reaction.

compound	H_2O	HF
ΔH_f, kJ mol^{-1}	–242	–269

(b) Use the average bond enthalpies from the table below to calculate the molar enthalpy change for the same reaction between steam and flourine.

Bond	O–H	F–F	H–F	O–O
bond enthalpy/ kJ mol^{-1}	460	158	562	496

(c) The answer you have calculated in (b) is different from (a). Suggest the reason for this.

*6. (a) (i) Define the standard enthalpy change of formation.

(ii)Write an equation which illustrates the standard enthalpy change of formation of solid zinc carbonate.

(b) When 1.00 g of zinc powder was made to react with 25 cm^3 of 1.0 moldm^{-3} sulphuric acid, the temperature rose by 15.0 ^{0}C.

(i) Write an equation for the reaction between zinc and sulphuric acid.

(ii) Assume that to increase the temperature of 1cm^3 of solution by 1 ^{0}C, 4.3 J are required, calculate the heat released in the experiment.

(iii) Calculate the number of moles of zinc used in the experiment.

(iv) Calculate the number of moles of sulphuric acid used in the experiment.

(v) Hence calculate the standard enthalpy change for the reaction between zinc and dilute sulphuric acid .

(c) State the main sources of error in the above experiments and how they may be overcome.

7. (a) (i) What do you understand by the term 'standard enthalpy change of combustion' of a compound?

(ii)Write an equation which represents the standard enthalpy change of combustion of ethanol, CH_3CH_2OH.

(c) Ethanol , CH_3CH_2OH can be oxidized to ethanoic acid ,CH_3CO_2H by atmospheric oxygen.

(i) Write an equation for the oxidation of ethanol to ethanoic acid.

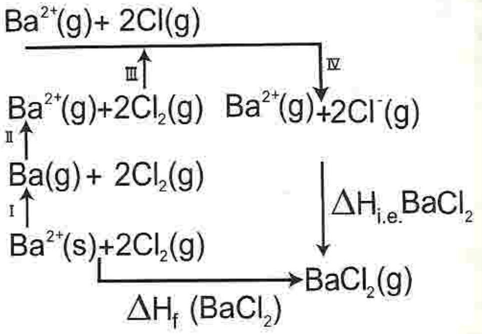
(ii) Use the following enthalpy changes of combustion to calculate the enthalpy change for the atmospheric oxidation of ethanol.

Substance	_H$_c$ /kJmol^{-1}
CH_3CH_2OH	-1371
CH_3COOH	-876

8. (a) (i) What is meant by the lattice energy of an ionic compound?

(ii) Write an equation to show the lattice energy of barium chloride.

(b) An energy cycle to show the formation of barium chloride is sketched below.



(i) Name the enthalpy changes in steps I,II,III and IV.

(ii) The enthalpy changes for steps I and IV are 176 kJmol^{-1} and –364 kJmol^{-1} respectively and the standard enthalpy change of formation of barium chloride is –860 kJmol^{-1}.

By making use of the Data Booklet and the data given above, calculate the lattice energy of barium chloride.

(c) How will you expect the magnitude of the lattice energy of magnesium chloride to be compared to magnesium oxide? Explain your reasoning.

9. (a) What do you understand by the following terms:-
   (i) the standard enthalpy of solution
   (ii) the hydration energy
   (iii) the lattice energy.

(b) (i) Using calcium fluoride as an example, draw an energy cycle to show how the enthalpy changes mentioned above are related to each other.
   (ii) Calculate the standard enthalpy change of solution of calcium fluoride using the following enthalpy changes.

Enthalpy change ($\Delta H^{\ominus}$)	$kJmol^{-1}$
Standard enthalpy change of formation of calcium fluoride	-1214
Atomisation energy of calcium	+193
Lattice energy of calcium fluoride	-2602
Hydration energy of calcium ion	-1650
Hydration energy of fluoride ion	-506

(c) Draw a Born-Haber cycle for calcium fluoride and use the above data together wit data available in the Data Booklet to calculate the electron affinity of fluorine.

Descriptive Questions

1 Calculate the enthalpy changes of the following reactions. Use the enthalpy changes of formation at the end of the question. State symbols have been omitted for simplicity. Assume that all substances are under standard state conditions.

(a) $Fe_3O_4 + 2C \rightarrow 3Fe + 2CO_2$

(b) $3MnO_2 + 4Al \rightarrow 3Mn + 2Al_2O_3$

(c) $2H_2O_2 \rightarrow 2H_2O + O_2$

(d) $2Cu(NO_3)_2 \rightarrow 4NO_2 + 2CuO + O_2$

(e) $TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl$

(f) $2NH_3 + 3CuO \rightarrow 3Cu + N_2 + 3H_2O$

Enthalpy changes of formation, in kJ mol^{-1}:

$Fe_3O_4 = -1117$
$MnO_2 = -521$
$H_2O_2 = -188$
$Cu(NO_3)_2 = -307$
$CuO = -155$
$TiO_2 = -912$
$NH_3 = -46$
$CO_2 = -394$
$Al_2O_3 = -1669$
$H_2O = -286$
$NO_2 = +34$
$TiCl_4 = -750$
$HCl = -92$

2 (a) $Am_2O_3(s) + 3Zn(s) \rightarrow 2Am(s) + 3ZnO(s)$
The enthalpy change of the above reaction is –622 kJ. Calculate the enthalpy change of formation of americium(III) oxide, Am_2O_3.

(b) $TcO_3 + 3CO \rightarrow Tc + 3CO_2$
The enthalpy change of the above reaction is –720 kJ. Calculate the enthalpy change of formation of technetium(VI) oxide, TcO_3.
Enthalpy changes of formation:
$ZnO = -348$ kJ mol^{-1}
$CO = -111$ kJ mol^{-1}
$CO_2 = -394$ kJ mol^{-1}

3 (a) Define the terms (i) *enthalpy change of atomisation*; (ii) *lattice energy*.

(b) What factors determine the magnitude of the lattice energy of an ionic compound?

(c) Draw a Born-Haber cycle for the formation of rubidium bromide and use it to calculate the lattice energy of rubidium bromide. Use the data below.

(d) How would you expect the lattice energy of rubidium iodide to compare with that of rubidium bromide? (Both compounds have the same structure.)

Data:
Enthalpy change of atomisation of bromine:

$\frac{1}{2}Br_2(l) \rightarrow Br(g); \Delta H^{\ominus} = +112$ kJ mol^{-1}

Enthalpy change of atomisation of rubidium:
$Rb(s) \rightarrow Rb(g); \Delta H^{\ominus} = +82$ kJ mol^{-1}
First ionisation energy of rubidium:
$Rb(g) \rightarrow Rb^+(g) + e^-; \Delta H^{\ominus} = +400$ kJ mol^{-1}
Electron affinity of bromine:
$Br(g) + e^- \rightarrow Br^-(g); \Delta H^{\ominus} = -325$ kJ mol^{-1}
Enthalpy change of formation of rubidium bromide:

$$\mathrm{Rb(s)} + \frac{1}{2}\mathrm{Br_2}(l) \rightarrow \mathrm{Rb^+\,Br^-(s)}$$

$$\Delta H^{\ominus} = -389\ \mathrm{kJ\ mol^{-1}}$$

4 (a) (i) State *Hess' Law.*

(ii) Outline one example of how Hess'Law can be used to determine an enthalpy change of reaction which cannot be measured directly by experiment.

(b) The enthalpy changes of combustion of but-1,3-diene (C_4H_6), hydrogen (H_2) and butane (C_4H_{10}) are –2542, –286 and –2877 kJ mol^{-1} respectively. Use these data to calculate the enthalpy change of the reaction:

$$C_4H_6(g) + 2H_2(g) \rightarrow C_4H_{10}(g)$$

5 Chlorine forms several oxides, including Cl_2O and Cl_2O_6. The oxide Cl_2O is used in bread-making to sterilise flour.

(a) Predict the shape of the Cl_2O molecule.

(b) Cl_2O_6 is a red liquid that undergoes disproportionation in aqueous alkali to produce a mixture of chlorate(V), ClO_3^-, and chlorate(VII), ClO_4^-, ions. Construct a possible equation for this reaction.

(c) Cl_2O is made by reacting chlorine with mercury(II) oxide in the reaction:

$2Cl_2(g) + HgO(s) \rightarrow HgCl_2(s) + Cl_2O(g)$
$\Delta H = -64$ kJ

Calculate the enthalpy change of formation, ΔH_f, of Cl_2O, given the additional data below.

ΔH_f for HgO = –90 kJ mol^{-1}
ΔH_f for $HgCl_2$ = –230 kJ mol^{-1}

Comment on your answer and suggest what might happen if a quantity of Cl_2O was heated.

*6 (a) Explain, with a suitable example, what is meant by the term *bond energy*.

(b) Sulphur forms the fluorides SF_4 (boiling point –40°C) and SF_6 (sublimes at –65°C). SF_6 can be made by the reaction

$$SF_4(g) + F_2(g) \rightarrow SF_6(g)$$

The average S—F bond energy is 294 kJ mol^{-1}. Use this value and the F—F bond energies from the *Data Tables* at the back of the book to calculate the enthalpy change of the reaction, ΔH.

(c) The relative formula mass of rubidium fluoride (RbF) is similar to that of SF_4. Suggest *two* major differences in the physical properties of these two compounds (other than their boiling points).

7. (a) Define

(i) enthalpy of neutralisation

(ii) enthalpy of formation

(b) When sulphuric acid is added to sodium hydroxide, a neutralisation reaction takes place.

Write an equation to show the reaction between sulphuric acid and sodium hydroxide .

(c) When 40 cm^3 of 1moldm^{-3} sodium hydroxide was added to a plastic cup containing 25 cm^3 of 1.0moldm^{-3} sulphuric acid, energy is released and the temperature change which occurred were recorded in the table below

Initial temperature of acid/^{0}C	23.0
Initial temperature of alkali / ^{0}C	23.2
Maximum temperature reached on mixing acid and alkali / ^{0}C	30.8
Temperature change / ^{0}C	

(i) Derive a suitable mean initial temperature for the reaction.

(ii) Assuming that to increase the temperature of 1 cm^3 of solution by 1^{0}C, 4.5J are required, calculate the energy released during the reaction.

(iii) Calculate the number of moles of sulphuric acid initially present in the plastic cup.

(iv) Calculate the number of moles of sodium hydroxide added to the acid in the cup.

(v) Hence calculate the standard enthalpy of neutralisation for the reaction between sodium hydroxide and sulphuric acid .

(d) In general the standard enthalpy of neutralisation for the above reaction is –57.3 KJmol^{-1}. Suggest two possible reasons for the difference between the practical value you obtained in c(v) and the theoretical value.

8. (a) Give brief explanations for the following observations.

(i) The standard enthalpy of neutralisation per mole of different acids are:

Acid	ΔH neut/ kJ mol^{-1}
Hydrochloric acid	-57.1
Sulphuric acid	-114.6
Ethanoic acid	-55.2
Chloroethanoic acid	-56.1

(ii) The standard enthalpy of neutralisation per mole of different bases are:

Bases	ΔHneut/ kJ mol^{-1}
Sodium hydroxide	-57.2
Potassium hydroxide	-57.2
Ammonia	-52.2
Barium hydroxide	-116.4

(b) (i) State the Hess's law.
 (ii) You are provided with a sample of magnesium, a sample of magnesium carbonate and dilute sulphuric acid. Describe the experiments you will carry out to determine the standard enthalpy of formation of magnesium carbonate, stating clearly in your answer all the assumptions you are making in your calculation and how you are making use of Hess's law.

9 (a) Magnesium flouride, MgF_2, is a solid of high melting point (1261°C) whereas sulphur difluoride, SF_2, is a gas.
 (i) Suggest how these two fluorides differ in their bondings and suggest a reason for the difference.
 (ii) Draw dot-and cross diagrams (outer shells only) to show the different electron arrangements in the two compounds..
(b) Using the following data, and relevant data from the Data Booklet, construct a thermochemical cycle to calculate the enthalpy change of formation of MgF_2. Include state symbols in your cycle.

	value/kJ mol^{-1}
lattice energy of $MgF_2(s)$	–2957
electron affinity of fluorine [$F(g) \rightarrow F^-(g)$]	–328
enthalpy change of atomisation of magnesium	+148

(c) The compound SF_2 readily reacts with fluorine to give SF_4. Suggest reasons why MgF_2 does not react with more fluorine to give MgF_4.

10 Lime (calcium oxide) is produced from limestone (calcium carbonate) by the following reaction.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

(a) Explain, qualitatively, what change in entropy you would expect for this reaction.
(b)

compound	**$\Delta G^{\ominus}_{formation}$ /kJ mol^{-1}**	**$\Delta H^{\ominus}_{formation}$ /kJ mol^{-1}**	**$S^{\ominus}$ /kJ mol^{-1} K^{-1}**
$CaCO_3(s)$	–1129	–1207	0.093
$CaO(s)$	–604	–635	0.0398
$CO_2(g)$	–394	–394	0.214

Use the data in the table above to calculate
 (i) the standard free energy change, $\Delta G^{\ominus}$, for the reaction;
 (ii) the standard enthalpy change, $\Delta H^{\ominus}$, for the reaction;
 (iii) the standard entropy change, $\Delta S^{\ominus}$, for the reaction.
(c) (i) Use your answers from (b) to explain why this reaction does not take place spontaneously at standard state conditions.
 (ii) Calculate the temperature at which the reaction would take place.

11 Hydrogen can be made industrially by the following reaction:

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g); \quad \Delta H^{\ominus} = +206 \text{ kJ mol}^{-1}$$

(a)

compound	**$\Delta G^{\ominus}_{formation}$ /kJ mol^{-1}**	**$\Delta S^{\ominus}$ /kJ mol^{-1} K^{-1}**
$CH_4(g)$	–50.7	0.186
$H_2O(s)$	–229	0.189
$CO(g)$	–137	0.198
$H_2(g)$	0	0.131

Use the data in the table above to calculate
 (i) the standard free energy change, $\Delta G^{\ominus}$, for the forward reaction and
 (ii) the standard entropy change, $\Delta S^{\ominus}$, for the forward reaction.
(b) Explain the **sign** of your calculated value of ΔS in (a)(ii).
(c) What is the effect on ΔG when
 (i) pressure increases?
 (ii) temperature increases?
(d) (i) What is the significance of your answer to (a)(i)?
 (ii) State and explain, using your answer to (b)(ii), how a considerable increase in temperature would be beneficial for the industrial process.

CHAPTER

7

ELECTRO-CHEMISTRY

SYLLABUS OBJECTIVES

In this chapter you should be able to:

- describe and explain redox reactions in terms of electron transfer and in terms of changes in oxidation number (oxidation state)
- construct redox equations using the relevant half-equations
- define the terms standard electrode (redox) potential and standard cell potential
- describe the standard hydrogen electrode
- describe methods used to measure standard electrode potential of
  - metals or non-metals in contact with their aqueous ions in solution
  - ions of the same element in different oxidation states (eg $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$)
- calculate a standard cell potential by combining two standard electrode potentials
- use standard cell potentials to
  - explain or predict the direction of electron flow in a simple cell
  - predict if a redox reaction will take place
- predict qualitatively how the value of an electrode potential changes when the concentration of the aqueous ion changes
- state possible advantages of other types of cell (eg the H_2/O_2 fuel cell) and improved batteries (eg for use in electric vehicles) with smaller size, lower mass and higher voltage
- state the relationship between the Faraday constant, the Avogadro constant and the charge on the electron ($F = Le$)
- predict the identity of the product liberated at electrodes during electrolysis from
  - the state the electrolyte ie molten or an aqueous solution (eg sodium metal is discharged at the cathode from molten NaCl and hydrogen from dilute aqueous NaCl)
  - position in the redox series or its electrode potential (eg copper is discharged from $Cu^{2+}(aq)$ before zinc from $Zn^{2+}(aq)$ as its electrode potential is more positive)
  - concentration of the ions (in aqueous solutions)
- calculate the quantity of electric charge passed during electrolysis (eg from the current and time or from the mass of a metal discharged)
- calculate the mass or volume (of gas) liberated during electrolysis, including hydrogen and oxygen liberated in the electrolysis of $H_2SO_4(aq)$ and $Na_2SO_4(aq)$
- explain (in terms of the electrode reactions).
  - the electrolysis of brine, using a diaphram cell
  - the anodising of aluminium
  - the electrolytic purification of copper

Oxidation and Reduction as Electron Transfer

Oxidation Number

Oxidation and Reduction as Change in Oxidation Number

Electrode Potentials

The Electrochemical Series

Electric Cells

Standard Redox Potentials

The Redox Series

Redox Potentials and Electric Cells

Practical Batteries for Use in Society and in Industry

Electrolysis

Industrial Electrolysis

7.1 Oxidation and Reduction as Electron Transfer

- Loss of electrons is oxidation.
- Gain of electrons is reduction.
- An oxidising agent is a substance that takes electrons from another substance.
- A reducing agent is a substance that gives electrons to another substance.
- Oxidation and reduction occur together in a chemical reaction. A reaction in which oxidation and reduction takes place is called a **redox reaction**.
- An example of a redox reaction is the reaction between zinc and copper sulphate solution.

  (a) The equation for the reaction is

  $$\begin{array}{lllllll} Zn & + & CuSO_4 & \rightarrow & ZnSO_4 & + & Cu \\ \underbrace{Zn}_{\text{electrons}} & + & Cu^{2+} & \rightarrow & Zn^{2+} & + & Cu \end{array}$$

  (b) In the reaction, the zinc metal gives up electrons:

  $$Zn \rightarrow Zn^{2+} + 2e^-$$ Salwe'n

  The electrons are then taken by the copper ion:

  $$Cu^{2+} + 2e^- \rightarrow Cu$$ bar kitr

  (c) The zinc metal is oxidised because it has lost electrons.

  (d) The copper ion, Cu^{2+}, is reduced because it has gained electrons.

  (e) The zinc metal is a reducing agent because it gave electrons to the copper ions.

  (f) The copper ion, Cu^{2+}, is an oxidising agent because it took electrons from the zinc metal.
- All redox reactions in which electrons are transferred can be described by two **half-equations**. One half-equation is for the oxidation and the other for the reduction. The two half-equations are then added to produce the overall redox equation.

  An example is the reaction between acidified manganate(VII) ions and iron(II) ions. The two half-equations are:

  $$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \quad \text{(reduction)}$$
  $$Fe^{2+} \rightarrow Fe^{3+} + e^- \quad \text{(oxidation)}$$

  The second half-equation is multiplied by 5 so that the number of electrons produced equals the number taken in by the MnO_4^-:

  $$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$
  $$5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^-$$

The two half-equations are then added together, producing the overall equation. In this addition, the electrons must cancel:

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$

Question

Copper metal reacts with nitric acid according to the two half-equations below:

$$Cu \rightarrow Cu^{2+} + 2e^-$$
$$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$$

(a) Write the overall ionic equation for the reaction.
(b) What is the oxidising agent in the reaction?
(c) What is the reducing agent in the reaction?
(d) What substance is oxidised in the reaction?
(e) What substance is reduced in the reaction?

Answer

(a) The first equation is multiplied by 3, and the second equation is multiplied by 2, so that the number of electrons in each half-equation is the same:

$$3Cu \rightarrow 3Cu^{2+} + 6e^-$$
$$2NO_3^- + 8H^+ + 6e^- \rightarrow 2NO + 4H_2O$$

Adding the two equations:

$$3Cu + 2NO_3^- + 8H^+ \rightarrow 3Cu^{2+} + 2NO + 4H_2O$$

(b) The NO_3^- and H^+ are the oxidising agents because they took electrons.
(c) The Cu metal is the reducing agent because it gave electrons to the NO_3^- and H^+.
(d) The Cu metal is oxidised because it lost electrons.
(e) The NO_3^- and H^+ are reduced because they took electrons.

7.2 Oxidation Number

- All atoms in elements, ions or compounds can be given an **oxidation number**. This number is obtained by applying a set of rules.

Oxidation number rules

(a) All atoms in elements have an oxidation number of zero. For example, in a piece of magnesium ribbon, the magnesium atoms have oxidation number zero.

(b) In simple ions and ionic compounds, the oxidation number = the charge on the ion.
For example, in ionic sodium chloride, NaCl:
oxidation number of sodium = charge on Na^+ ion = +1
oxidation number of chlorine = charge on Cl^- ion = −1
For example, in ionic aluminium oxide, Al_2O_3:
oxidation number of aluminium = charge on Al^{3+} ion = +3
oxidation number of oxygen = charge on O^{2-} ion = −2

For covalent molecules, the most electronegative atom is assigned a negative oxidation number.

For example in :-

(i) H_2O, oxygen is more electronegative than hydrogen. Therefore the oxygen atom is assigned a negative oxidation number, namely of **-2**.
Oxidation number of oxygen = -2
Oxidation number of hydrogen = + 1

(ii) ICl_3 , the chlorine atom is more electronegative than the iodine atom. Therefore the chlorine atom is assigned the negative oxidation state.
Oxidation number of chlorine = -1
Oxidation number of iodine = +3

(a) Some elements always have the same oxidation number in compounds (Table 7.2).

element	usual oxidation number in compounds
Group I elements (Na, K, etc)	+1
Group II elements (Mg, Ca, etc)	+2
aluminium	+3
fluorine	–1
oxygen	–2§
hydrogen	+1*

▶ Table 7.2

§ except in peroxides such as H_2O_2 where oxygen has an oxidation number of –1

* except in ionic hydrides such as NaH where hydrogen is –1

Addition of oxidation numbers

(a) In a neutral molecule, the sum of the oxidation numbers of all the atoms equals zero.

(b) In an ion, the sum of the oxidation numbers of all the atoms in the ion equals the charge on the ion.

These two rules can be used to calculate the oxidation number of an atom in a molecule or ion, if all the other oxidation numbers are known.

Question Calculate the oxidation number of uranium in K_3UF_6.

Answer

Let x be the oxidation number of uranium.
The oxidation number of potassium = +1.
The oxidation number of fluorine = −1.
Hence $3(+1) + x + 6(-1) = 0$
and $x = +3$
The oxidation number of uranium = +3.

Question

Calculate the oxidation number of chromium in CrO_4^{2-}.

Answer

Let x be the oxidation number of chromium.
The oxidation number of oxygen = −2.
Hence $x + 4(-2) = -2$
and $x = +6$
The oxidation number of chromium = +6.

7.3 Oxidation and Reduction as Change in Oxidation Number

- When the oxidation number of an atom is *increased*, the atom is *oxidised*.
- When the oxidation number of an atom is *decreased*, the atom is *reduced*.

Question

$$PbO_2 + 4H^+ + 2I^- \rightarrow Pb^{2+} + 2H_2O + I_2$$

Show where the oxidation and reduction have occurred in the above equation.

Answer

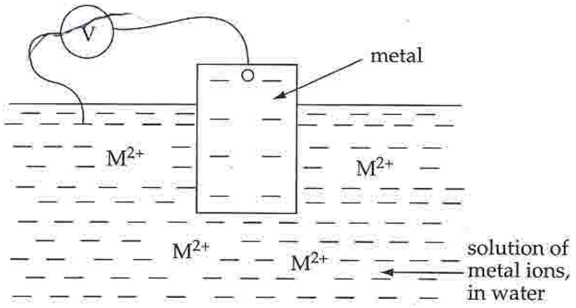
$$+4 \xrightarrow[\text{(reduction)}]{\text{decrease in oxidation number}} +2$$

$$PbO_2 + 4H^+ + 2I^- \rightarrow Pb^{2+} + 2H_2O + I_2$$

$$-1 \xrightarrow[\text{(oxidation)}]{\text{increase in oxidation number}} 0$$

The lead is reduced because the oxidation number of lead decreases from +4 to +2.
The iodine is oxidised because the oxidation number of iodine increases from −1 to zero.

7.4 Electrode Potentials



▶ Fig 7.1

- When a metal rod is dipped into a solution containing its ions, an equilibrium is set up between the metal rod and its ions.
There is a tendency for atoms of the metal to go in solution as ions

$$M(s) \rightarrow M^{z+}(aq) + Ze^-$$

There is also a tendency for metal ions to gain electrons and to deposit on the surface of metal rod as atoms

$$M^{z+}(aq) + Ze^- \rightarrow M(s)$$

An equilibrium is therefore established between the metal ant its ions in the solution

$$M^{z+}(aq) + Ze^- \rightarrow \rightleftharpoons M(s)$$

At equilibrium a potential difference is set up between the solution and the metal.

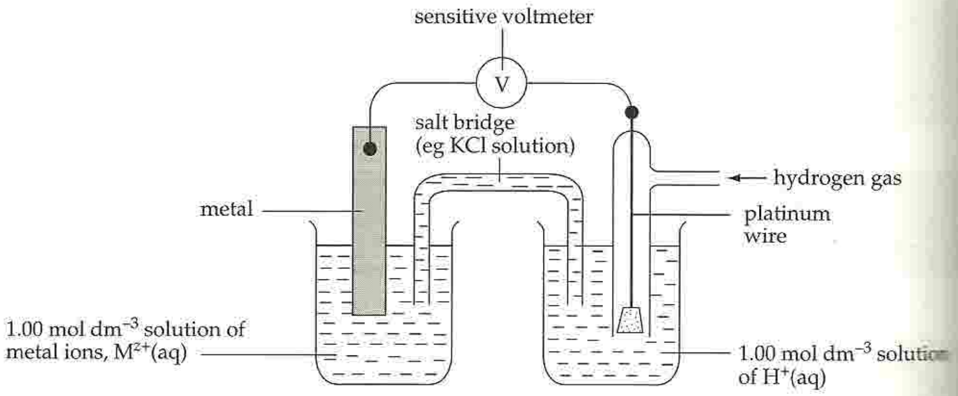
- The potential difference in Fig 7.1 *cannot be measured*. If a voltmeter is used (as shown in the diagram), a wire must be dipped in the water to measure the voltage. But the metal in this wire will also react with the water, producing another electrode potential. The reading on the voltmeter will be the *difference* of the two electrode potentials, not the true voltage of the first metal in equilibrium with its positive ions in water.

- In practice it is only necessary to make *comparisons* of potential difference. This is done by always using the *same contact* with the solution. This contact consists of a platinum wire surrounded by hydrogen gas and $H^+(aq)$ ions. The electrode potentials measured are then called **standard electrode potentials**.

Standard Electrode Potentials, $E^{\ominus}$

- The standard electrode potential of a metal is the potential difference between the metal and a 1.00 mol dm^{-3} aqueous solution of its ions, measured relative to a standard hydrogen electrode (or half-cell).

- The standard electrode potential for a metal is measured using the apparatus shown in Fig 7.2.



▶ Fig 7.2

(a) The reading on the voltmeter gives the standard electrode potentia l of the metal.
The terminal to which the metal electrode is connected will give the sign of the standard electrode potential of the metal.

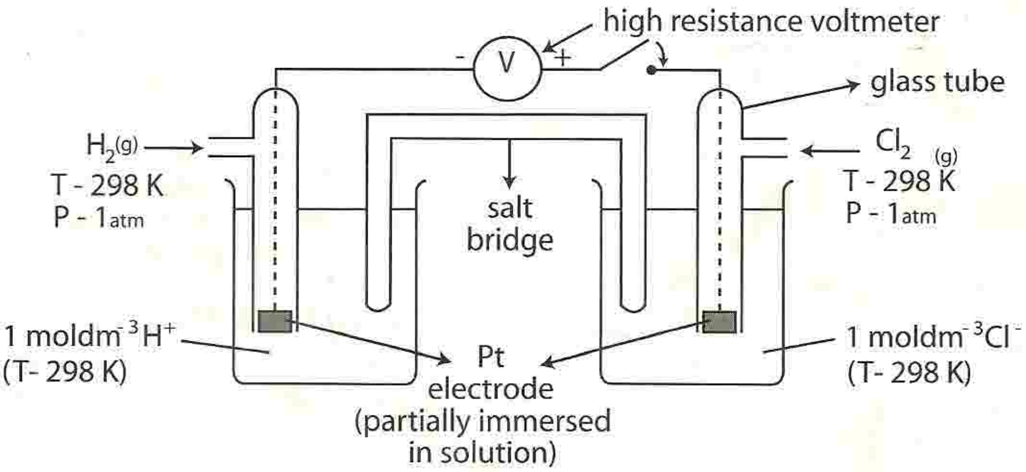
(b) The voltage is measured under standard state conditions. These conditions are: temperature at 298 K pressure of hydrogen gas at standard atmospheric pressure = 101.3 kPa

For example, the standard electrode potentials of zinc and copper are

$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s);\ E^{\ominus} = -0.76\ V$$
$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s);\ E^{\ominus} = +0.34\ V$$

A list of standard electrode potentials is included at the end of this book.

To determine the standard electrode potential of Chlorine the apparatus is set up as shown in fig 7.3



▶ Fig 7.3

A standard chlorine electrode is set up by passing chlorine gas, found at a pressure of 101.3KPa and at a temperature of 298K over a platinised platinum electrode partially immersed in a 1moldm^{3} solution containing chloride ions at a temperature of 298K.

The standard chlorine electrode is then connected to a standard hydrogen electrode via a voltmeter.

When the chlorine electrode is connected to the positive terminal of the voltmeter, a deflection of 1.36V occurs. Therefore the standard electrode potential of chlorine is +1.36 V.

Variation of Electrode Potentials with Concentration

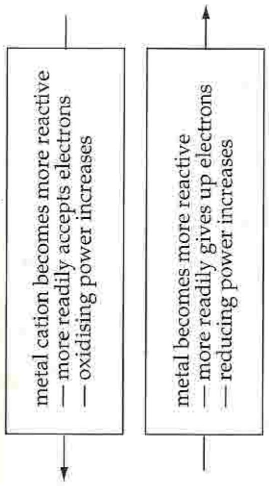
- Electrode potentials vary with concentration of the ions. If the concentration of metal ions, M^{z+}, in the equilibrium

  $$M^{z+} + ze^- \rightleftharpoons M$$

  is *increased*, the equilibrium goes to the right — ie more M^{z+} combines with electrons to produce more metal, M. Hence more electrons are removed from the electrode and it becomes *more positive*.

7.5 The Electrochemical Series

- When metals are placed in order of their standard electrode potential, the **electrochemical series** is obtained. Part of the electrochemical series is shown below.



most negative $E^{\ominus}$

metal cation				*metal*	*standard electrode potential*
Mg^{2+}	+	$2e^-$	$\rightleftharpoons$	Mg	$E^{\ominus} = -2.38$ V
Zn^{2+}	+	$2e^-$	$\rightleftharpoons$	Zn	$E^{\ominus} = -0.76$ V
Pb^{2+}	+	$2e^-$	$\rightleftharpoons$	Pb	$E^{\ominus} = -0.13$ V
H^+	+	e^-	$\rightleftharpoons$	$\frac{1}{2}H_2$	$E^{\ominus} = 0$ V
Cu^{2+}	+	$2e^-$	$\rightleftharpoons$	Cu	$E^{\ominus} = +0.34$ V
Ag^+	+	e^-	$\rightleftharpoons$	Ag	$E^{\ominus} = +0.80$ V

most positive $E^{\ominus}$

- A metal which is very 'high' in the electrochemical series (ie has a large negative $E^{\ominus}$)
  (a) readily gives up electrons (eg Mg readily reacts to become Mg^{2+});
  (b) is very reactive;
  (c) is a powerful reducing agent.

- A metal cation, M^{2+}, which is very 'low' in the electroche series (ie has a large positive $E^{\ominus}$)
  - (a) readily accepts electrons (eg Ag^+ is easily reduced to metal);
  - (b) is very reactive;
  - (c) is a powerful oxidising agent.
- A metal 'high up' in the electrochemical series will reduce (ie electrons) the cations of any metal below it.
  - (a) Hence a metal 'high up' in the series will displace from solution, any metal lower than it in the series. For exam zinc will displace lead:

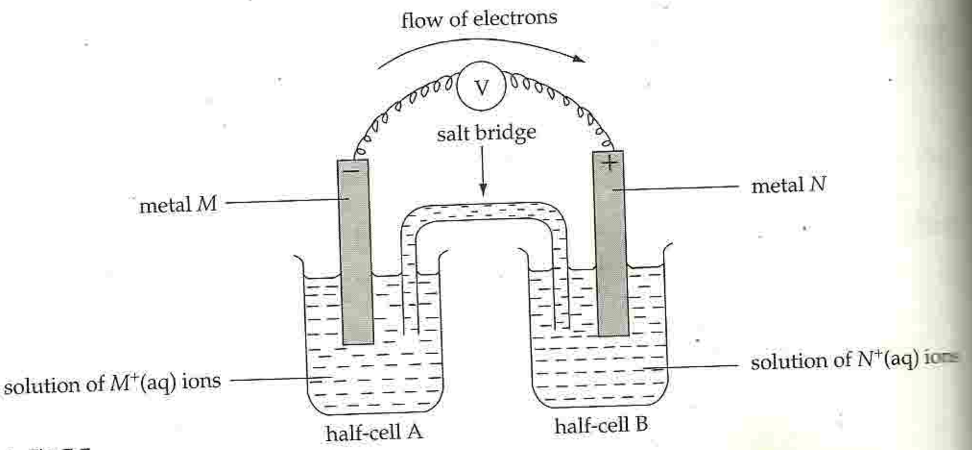
    $$Zn(s) + Pb^{2+}(aq) \rightarrow Zn^{2+}(aq) + Pb(s)$$

  - (b) A metal 'high up' in the series will displace a metal lo than it from its oxide or chloride. For example, titanium obtained by heating magnesium with titanium chloride:

    $$2Mg(s) + TiCl_4(l) \rightarrow 2MgCl_2(s) + Ti(s)$$

    Magnesium is above titanium in the electrochemical ser and thus displaces titanium from its chloride. The magnesi gives electrons to the titanium.

7.6 Electric Cells



▶ Fig 7.3

- A general diagram for an electric cell is shown in Fig 7.3. The cel is made up of two half-cells, labelled A and B in the diagram.
- Half-cell A consists of metal M in a solution of positive ions of the metal, $M^+(aq)$.
- Half-cell B consists of metal N in a solution of positive ions of the metal, $N^+(aq)$.
- The two half-cells are joined by a **salt bridge** containing potassium chloride solution. The salt bridge prevents the solutions in the two half-cells from mixing. If the solutions are allowed to mix, metal M may react with the ions of the other metal, N^+. The salt bridge also maintains electrical neutrality in the cell.

- The negative electrode is the metal with the *larger negative* standard electrode potential (in this case, metal *M*).
- At the negative electrode,
  - (a) the metal dissolves in the solution:

    $$M(s) \rightarrow M^+(aq) + e^-$$

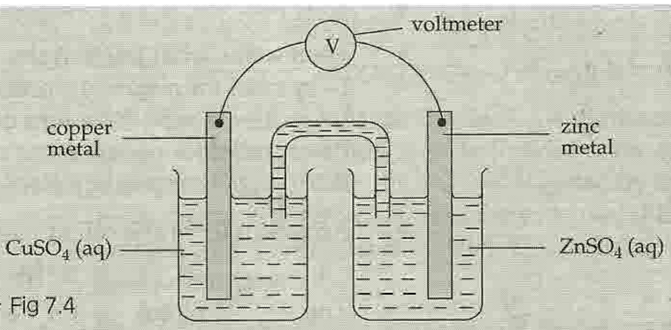
  - (b) the electrons flow through the wire (and voltmeter) to metal *N* in half-cell B;
  - (c) oxidation occurs because the metal atoms lose electrons.
- At the positive electrode,
  - (a) the electrons from half-cell A go through metal *N* and are taken by the ions of metal *N* in solution;
  - (b) the metal ions, $N^+(aq)$, accept the electrons to form the metal which is deposited on the electrode:

    $$N^+(aq) + e^- \rightarrow N(s)$$

  - (c) reduction occurs because the metal ions gain electrons.
- The equation for the cell reaction is obtained by adding the reactions in the two half-cells:

$$\begin{array}{ll} & M(s) \rightarrow M^+(aq) + e^- \\ \text{Add:} & N^+(aq) + e^- \rightarrow N(s) \\ \hline & M(s) + N^+(aq) \rightarrow M^+(aq) + N(s) \end{array}$$

Question



▸ Fig 7.4

Describe what happens in the cell in Fig 7.4.

Answer

(a) The zinc metal is the negative electrode, because the standard electrode potential of zinc ($E^\ominus = -0.76$ V) is more negative than the standard electrode potential of copper ($E^\ominus = +0.34$ V).

(b) At the zinc electrode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
The electrons go through the wire and voltmeter to the copper electrode.

(c) At the copper electrode, the copper ions in the solution accept the electrons and are deposited: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

(d) The equation for the cell reaction is: $Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$

wire [illegible]

Standard Cell potential (e.m.f.), $E^\ominus_{cell}$

- The following procedure produces the correct standard cel voltage. The cell shown in Fig 7.4 is used as an example.

  (a) Write down the standard electrode potentials for the two hal- cells.

  $$Cu^{2+} + 2e^- \rightleftharpoons Cu;\ E^\ominus = +0.34\ V$$
  $$Zn^{2+} + 2e^- \rightleftharpoons Zn;\ E^\ominus = -0.76\ V$$

  (b) Write down the reactions as they occur in the two half-cells. If the reaction is in the *opposite direction* to that the standar electrode potential, then the *sign of the voltage must be reverse*

  $$Cu^{2+} + 2e^- \rightarrow Cu;\ E^\ominus = +0.34\ V \text{ (same as } E^\ominus \text{ for copper)}$$
  $$Zn \rightarrow Zn^{2+} + 2e^-;\ E^\ominus = +0.76\ V \text{ (reverse of } E^\ominus \text{ for zinc)}$$

  (c) Then add the equations and the voltages:

  $$\underbrace{Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}}_{\text{standard cell reaction}};\ \underbrace{E^\ominus_{cell} = +1.1\ V}_{\text{standard cell voltage or e.m.f.}}$$

- All standard cell voltages for cells must be *positive*. The cell canno work if the voltage is negative.

Shorthand Description of Electric Cells

- Start with the *negative* electrode on the *left-hand* side.
- Then write, from left to right:
  I – symbol for negative electrode metal
  II – symbol for positive ions of (I)
  III – symbol for positive ions of the other half-cell
  IV – symbol for positive electrode metal.
- An example for the cell in Fig 7.4 is:

$$\overset{\text{I}}{Zn(s)}\ \Big|\ \overset{\text{II}}{Zn^{2+}(aq)}\ \Big\|\ \overset{\text{III}}{Cu^{2+}(aq)}\ \Big|\ \overset{\text{IV}}{Cu(s)};\ E^\ominus_{cell} = +1.1\ V$$

Question $Al(s)\,|\,Al^{3+}(aq)\,\|\,Pb^{2+}(aq)\,|\,Pb(s)$

(a) What is the equation for the cell reaction?
(b) What is the standard voltage of the cell?

Answer (a) The aluminium is the negative electrode (as it is on the left-hand side). This can also be deduced from the standard electrode potentials. Hence the aluminium metal must give up electrons:

$$Al \rightarrow Al^{3+} + 3e^-$$

and the lead ions must accept the electrons:

$$Pb^{2+} + 2e^- \rightarrow Pb$$

The equation for the cell reaction is:

$$2Al + 3Pb^{2+} \rightarrow 2Al^{3+} + 3Pb$$

Answer

(b) The two standard electrode potentials are:

$$Al^{3+} + 3e^- \rightleftharpoons Al;\ E^\ominus = -1.66\ V$$
$$Pb^{2+} + 2e^- \rightleftharpoons Pb;\ E^\ominus = -0.13\ V$$

The two half-equations are:

$$Al \rightarrow Al^{3+} + 3e^-;\ E^\ominus = +1.66\ V$$
$$Pb^{2+} + 2e^- \rightarrow Pb;\ E^\ominus = +0.13\ V$$

Adding the two equations and the voltages:

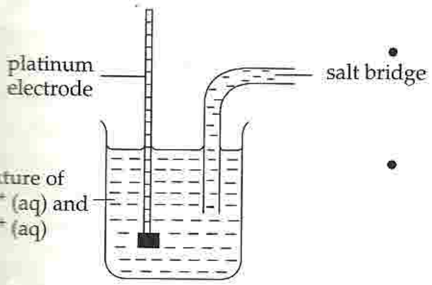
$$2Al + 3Pb^{2+} \rightarrow 2Al^{3+} + 3Pb;\ E^\ominus_{cell} = +1.53\ V$$

The standard voltage of the cell = +1.53 V.

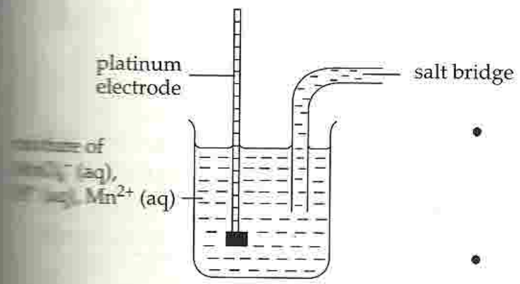
Note: The voltages are simply added. You do *not* multiply the voltages by 2 or 3 like the half-equations.

+1,66 + -0,8

7.7 Standard Redox Potentials



▲ Fig 7.5



▲ Fig 7.6

- **Standard redox potentials** are the same as standard electrode potentials. A half-cell can be made out of any redox half-equation. This half-cell has a standard redox potential.
- An example of a standard redox potential is

  $$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq);\ E^\ominus = +0.77\ V$$

  A half-cell for this is made by placing a platinum electrode in a mixture of the substances from both sides of the equation. This is shown in Fig 7.5. When the half-cell is joined by the salt bridge to a standard hydrogen electrode, the potential difference is +0.77 volts (since $E^\ominus$ for hydrogen = 0 V). This is correct under standard state conditions.
- Fig 7.6 shows a half-cell with a platinum electrode in a mixture of MnO_4^-, H^+ and Mn^{2+} ions.

  $$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O;\ E^\ominus = +1.52\ V$$
- The voltages in all standard redox potentials are measured under standard state conditions.

Use of Redox Potentials to Predict Chemical Reactions

- Many redox equations can be obtained by adding two half-equations. Each half-equation has a potential. The two potentials can be added together to obtain an e.m.f. or standard cell potential for the redox reaction.
- An example of a redox reaction is

  $$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$

This redox equation is made up from the two standard redox potentials:

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O; \; E^\circ = +1.52 \text{ V} \quad \text{...equation 1}$$

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}; \quad E^\circ = +0.77 \text{ V} \quad \text{...equation 2}$$

The first equation is unchanged, but the second equation is *reversed* to produce the two half-equations for the redox reaction:

$$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O; \; E^\circ = +1.52 \text{ V (unchanged)}$$

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-; \quad E^\circ = -0.77 \text{ V}$$ (equation and sign of voltage reversed)

The two equations are now added to produce the original redox equation. The voltages of the two half-equations are added to give the e.m.f. or cell voltage for the redox reaction:

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}; \; E^\circ_{cell} = +0.75 \text{ V}$$

- A redox reaction will take place if the e.m.f. of the reaction is positive.
- The standard cell potential of a redox reaction only indicates that the reaction is **energetically feasible,** that is the reactants possess enough chemical energy for the reaction to occur. However it does not give any indication about the rate of the reaction, that is the **kinetic feasibility** of a reaction. The cell potential of a reaction may be large and positive and still the reaction does not seem to occur when the reactants are mixed.

  For example the cell potential for the reaction between hydrogen and oxygen is +1.23V

  $$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \quad E^\circ_{cell} = +1.23 \text{ V}$$

  However when hydrogen is mixed with air/oxygen no reaction takes place. A reaction will occur only if energy is supplied in the form of heat from a burning splint.
  Hence a positive standard electrode potential does not always mean that the reaction will occur.

7.8 The Redox Series

- When standard redox electrodes are placed in order of their voltage, the **redox series** is obtained. Part of the redox series is shown below.

oxidising power of oxidising agent increases ↓

reducing power of reducing agent increases ↑

most negative voltage

oxidising agent		*reducing agent*	*standard redox potential*
$Mg^{2+} + 2e^-$	$\rightleftharpoons$	Mg	$E^\ominus = -2.38$ V
$Zn^{2+} + 2e^-$	$\rightleftharpoons$	Zn	$E^\ominus = -0.76$ V
$H^+ + e^-$	$\rightleftharpoons$	$\frac{1}{2}H_2$	$E^\ominus = 0$ V
$\frac{1}{2}I_2 + e^-$	$\rightleftharpoons$	I^-	$E^\ominus = +0.54$ V
$Fe^{3+} + e^-$	$\rightleftharpoons$	Fe^{2+}	$E^\ominus = +0.77$ V
$\frac{1}{2}Cl_2 + e^-$	$\rightleftharpoons$	Cl^-	$E^\ominus = +1.36$ V
$MnO_4^- + 8H^+ + 5e^-$	$\rightleftharpoons$	$Mn^{2+} + 4H_2O$	$E^\ominus = +1.52$ V
$\frac{1}{2}F_2 + e^-$	$\rightleftharpoons$	F^-	$E^\ominus = +2.87$ V

most positive voltage

Question

Use standard redox potentials to predict if the following reactions are likely to take place.

(a) $Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 7H_2O + 3I_2$

(b) $Cr_2O_7^{2-} + 14H^+ + 6Cl^- \rightarrow 2Cr^{3+} + 7H_2O + 3Cl_2$

Standard redox potentials:

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O;\quad E^\ominus = +1.33$ V

$I_2 + 2e^- \rightleftharpoons 2I^-;\quad E^\ominus = +0.54$ V

$Cl_2 + 2e^- \rightleftharpoons 2Cl^-;\quad E^\ominus = +1.36$ V

Answer

(a) $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O;\quad E^\ominus = +1.33$ V

$6I^- \rightarrow 3I_2 + 6e^-;\quad E^\ominus = -0.54$ V

Add: $Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 7H_2O + 3I_2;\quad E_{cell} = +0.79$ V

As the E_{cell} for this reaction (ie the e.m.f.) is *positive*, the reaction takes place.

(b) $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O;\quad E^\ominus = +1.33$ V

$6Cl^- \rightarrow 3Cl_2 + 6e^-;\quad E^\ominus = -1.36$ V

Add: $Cr_2O_7^{2-} + 14H^+ + 6Cl^- \rightarrow 2Cr^{3+} + 7H_2O + 3Cl_2;\quad E_{cell} = -0.03$ V

As the E_{cell} for this reaction is *negative*, the reaction does *not* take place.

Question

Use the standard redox potentials given at the end of this book to predict the possible reaction between nitrous acid (HNO_2) and potassium manganate(VII) solution.

Answer

Potassium manganate(VII) can only act as an oxidising agent. Hence a possible half-equation for its reaction is:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O; \quad E^\ominus = +1.52\ V$$

The equation for the oxidation of HNO_2 is

$$HNO_2 + H_2O \rightarrow NO_3^- + 3H^+ + 2e^-; \quad E^\ominus = -0.94\ V$$

Note: This is the reverse of the half-equation in the Redox Potential data table, so the voltage sign is reversed.

Adding the two equations (so that the electrons cancel):

$$2MnO_4^- + 16H^+ + 5HNO_2 + 5H_2O \rightarrow 2Mn^{2+} + 8H_2O + 5NO_3^- + 15H^+; \ E_{cell} = +0.58\ V$$

or $$2MnO_4^- + H^+ + 5HNO_2 \rightarrow 2Mn^{2+} + 3H_2O + 5NO_3^-; \ E_{cell} = +0.58\ V$$

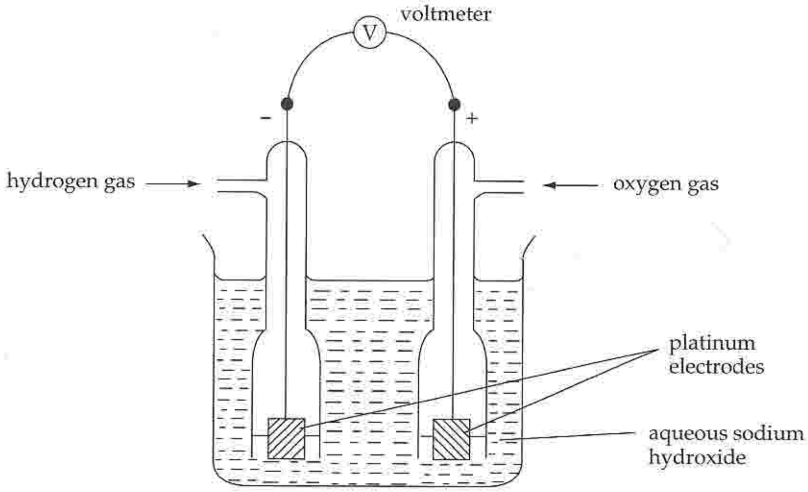
The E_{cell} value (ie e.m.f.) for this reaction is positive, so the reaction will take place.

- The redox series consists of a mixture of oxidising and reducing agents.
- An electric cell can be made from two redox potential half-cells. An example is shown in Fig 7.7.
  - (a) The more positive the voltage, the more powerful is the oxidising agent. Hence F_2 is the most powerful oxidising agent in the list above.
  - (b) The more negative the voltage, the more powerful is the reducing agent. Hence magnesium metal is the most powerful reducing agent in the list above.
- (a) Any reducing agent can reduce all the oxidising agents below it in the redox series.
  For example, in the list above, I^- can reduce Fe^{3+}, Cl_2, acidified MnO_4^- and F_2.
  - (b) Any oxidising agent can oxidise all the reducing agents above it in the redox series.

  For example, in the list above, I_2 can oxidise H_2, Zn and Mg.

  Note: A more comprehensive redox series is given in the Data Tables at the end of this book, as a list of redox potentials in order of oxidising power.

7.9 Redox Potentials and Electric Cells



▶ Fig 7.8

(a) The two standard redox potentials are:

$$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq); \quad E^\ominus = +0.77\ V$$

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l); \quad E^\ominus = +1.52\ V$$

So the platinum electrode in B is positive because that redox potential is most positive. Hence the platinum electrode in A is negative.

(b) The reaction in half-cell A is

$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-; E^\ominus = -0.77\ V$$

because electrons are added to the electrode to make it negative.

(c) The electrons from A flow through the external circuit (ie the wires and voltmeter) to the platinum electrode in B. The reaction in half-cell B is:

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l); E^\ominus = +1.52\ V$$

(d) The overall reaction is obtained by adding the two half-equations (and the voltages) to obtain the e.m.f. of the cell:

$$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l); E_{cell} = +0.75\ V$$

7.10 Practical Batteries for Use in Society and in Industry

- Batteries are used as a portable source of electricity.
- The batteries (cells) described in this chapter so far have the following disadvantages for use outside the laboratory:
  (a) the voltage is low (usually 1 – 2 volts);
  (b) they spill easily and are not portable;
  (c) they can only supply a *low* current (so they cannot be used to start a motorcar engine).
- The **dry cell** is a practical battery used in small electrical appliances such as electric torches, electric toys and portable radios. It has the following advantages:
  (a) it is sealed, so it does not leak (hence it is very portable);
  (b) it supplies a reliable voltage.

  The main disadvantages are
  (a) it provides a low voltage;
  (b) it provides a *very low* current;
  (c) it cannot be recharged.

  A high voltage (50 – 100 volts) can be obtained by joining many dry cells in series. However such a battery is not rechargeable and can only provide a very low current (so it cannot start a car engine).
- The **lead/acid battery** is used in motor vehicles. It has the following advantages:
  (a) it provides the heavy current (around 30 amperes) required to start a car engine; it can be recharged;
  (b) it provides a voltage of 12 or 24 volts by joining 6 or 12 cells in series.

  The big disadvantage of the lead/acid battery is the great weight, due to the lead.
- Electric cars run on electricity instead of fuel fossil and do not cause pollution. It requires batteries with the following properties:
  (a) they can be recharged;
  (b) they can provide the heavy current required to run the engine continuously;
  (c) they have low weight.

  At present the only practical battery to run an electric car is the lead/acid battery. This can be recharged and can provide the heavy current. The problem is the weight of the battery which must be very large in order to run the car for some distance. This heavy weight is not practical; it would make the car far too heavy.

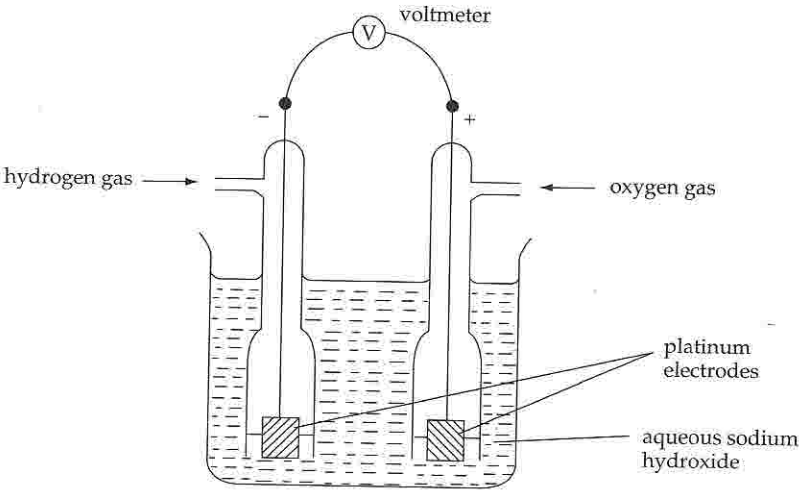
  A lot of research is being carried out to find a battery which satisfies the three conditions above *and* which is also cheap. If this can be done, it would then be possible to produce a pollution-free motorcar.

Fuel Cells

- A fuel cell consists of a fuel that is oxidised directly by an oxidant (usually oxygen). The fuel can be hydrogen or some other fuel such as methane. The energy produced in the reaction is converted *directly* into electricity *very efficiently* (in practice over 60% efficient).

  The conventional way of obtaining electricity from fuels is to burn the fuel to produce heat. This heat is used to produce steam which drives a dynamo to generate electricity. At most, only 30% of the energy released in the combustion is converted into useful electricity.

- A simple fuel cell is shown in Fig 7.8. Hydrogen (the fuel) and oxygen (the oxidant) are passed over platinum electrodes immersed in aqueous sodium hydroxide.



(a) The hydrogen gas reacts on the surface of the platinum according to the equation

$$2H_2(g) + 4OH^-(aq) \rightarrow 4H_2O(l) + 4e^-; \quad E^\ominus = +0.83\ V$$

The electrons make the platinum electrode negative. These electrons then travel through the external wire to the other platinum electrode, where they are taken by the oxygen.

(b) The oxygen gas reacts on the surface of the platinum according to the equation

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq); \quad E^\ominus = +0.40\ V$$

(c) The overall equation for the reaction is

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l); \quad E^\ominus = +1.23\ V$$

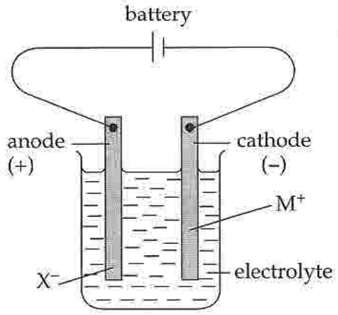
- Fuel cells differ from an ordinary battery in that the reactants are continually supplied, and the products are continually removed. Hence a fuel cell works indefinitely. An ordinary battery stops working as soon as the electrode materials are used up.
- At present, practical fuel cells have two drawbacks as portable supplies of electricity:

(a) They are expensive mainly because large amounts of nicke and platinum metals are required as catalysts for the electrod reactions.

(b) Most fuels require a high temperature to react in a fuel cel. For these reasons, fuel cells are seldom used instead o conventional batteries. At present their main use is in spacecraft. They are expected to become important in generating electricity in the future, when cheaper catalysts are developed and when hydrocarbons can be used in fue cells at room temperature.

7.11 Electrolysis

Basic Principles of Electrolysis



▲ Fig 7.9

- Electrolysis takes place in the apparatus shown in Fig 7.9. Two electrodes are placed in an electrolyte. Electrolysis takes place when the current passes through the electrolyte.
- The electrolyte is a substance containing ions that can move about. The current is carried by the ions. An electrolyte is *either* a molten ionic compound (eg molten lead(II) bromide) *or* an aqueous solution containing ions (eg copper(II) sulphate solution or dilute sulphuric acid).
- When the battery is connected to the electrodes, the positive cations (M^+) go to the negative cathode. The negative anions (X^-) go to the positive anode.
- **At the cathode**
  (a) Two different reactions can take place.
    (i) The cations are discharged: $M^+ + e^- \rightarrow M$
    Hence, when copper(II) sulphate solution is electrolysed, copper ions are discharged at the cathode, producing copper metal.

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

    (ii) In aqueous solution, cations of *very reactive* metals (with large negative electrode potentials) are not discharged.
    Hence when aqueous solutions of Group I and Group II metals are electrolysed, hydrogen gas is evolved instead at the cathode.
  (b) Reduction always takes place at cathodes because ions gain electrons.
- **At the anode**
  (a) Three different reactions can take place.
    (i) Anions of the electrolyte are discharged by giving up electrons:

    $$X^- \rightarrow X + e^-$$

    Hence, when hydrochloric acid is electrolysed using carbon electrodes, chloride ions are discharged at the anode, producing chlorine gas:

$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$$

(ii) In aqueous solution, some anions are not discharged. For example, when dilute sulphuric acid is electrolysed, using platinum electrodes, SO_4^{2-} ions are *not* discharged at the anode. Instead, oxygen gas is produced from the water:

$$4OH^-(aq) \rightarrow O_2(g) + 2H_2O(l) + 4e^-$$

(iii) The anode may dissolve in the electrolyte.
For example, when copper(II) sulphate solution is electrolysed, using copper electrodes, the copper anode dissolves:

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

(b) Oxidation always takes place at the anode because atoms or ions *lose* electrons.

Selective Discharge of Ions

- In a mixture of metal cations, the ones with the *most positive* standard electrode potential are discharged *first*.
- For example, consider a mixture of $Zn^{2+}(aq)$, $Cu^{2+}(aq)$, $Pb^{2+}(aq)$ and $Ag^+(aq)$ ions.
  The order of metal/metal ions in the electrochemical series is:

$$\begin{array}{ll} Zn^{2+} + 2e^- \rightleftharpoons Zn & \text{most negative } E^{\ominus} \\ Pb^{2+} + 2e^- \rightleftharpoons Pb & \big\downarrow \\ Cu^{2+} + 2e^- \rightleftharpoons Cu & \\ Ag^+ + e^- \rightleftharpoons Ag & \text{most positive } E^{\ominus} \end{array}$$

  When the mixture is electrolysed, the silver ions (Ag^+) are discharged first (most positive $E^{\ominus}$). The copper ions (Cu^{2+}) will be discharged, followed by the Pb^{2+} ions. Finally the Zn^{2+} ions will be discharged.
- In a mixture of anions, the anion with the *most negative* standard redox potential is discharged *first*. This anion is most easily oxidised.
- For example, in a mixture of $Cl^-(aq)$ and $I^-(aq)$ ions the order of the ions in the redox series is:

$$\begin{array}{ll} I_2 + e^- \rightleftharpoons 2I^- & \text{more negative } E^{\ominus} \\ Cl_2 + e^- \rightleftharpoons 2Cl^- & \text{more positive } E^{\ominus} \end{array}$$

  When the mixture is electrolysed, the I^- ions are discharged first (more negative $E^{\ominus}$) followed by the chloride ions (Cl^-).

Quantitative Electrolysis

- The amount of electric charge (measured in coulombs, C) that flows through an electric circuit = current in amperes × time in seconds
- The mass of substance discharged at an electrode in electrolysis is directly proportional to the amount of electric charge.

Hence mass $\propto$ current

$\propto$ time

$\propto$ number of coulombs

- The amount of charge on 1 mole of electrons = 96 500 coulom
  This amount of electric charge is called the **Faraday constant** (F
  From this, it follows that:

  $$F = L \times e$$

  where L = the Avogadro constant and
  e = the charge on the electron

- The number of coulombs required to discharge one mole of meta
  ions (M^{z+}) = 96 500 × charge on the ions.

$$\underset{\text{1 mole}}{M^{z+}} + \underset{\text{z moles}}{ze^-} \rightarrow \underset{\text{1 mole}}{M}$$

Question 30.0 g of the metal samarium (symbol Sm) was discharged by electrolysis with a current of 2.4 A flowing for 24 125 seconds. What is the formula of samarium ions? [Sm = 150]

Answer The number of moles of samarium in 30.0 g = $\frac{30.0}{150}$ = 0.2 mole

The number of coulombs that flowed = 2.4 × 24 125
= 57 900 coulombs.

0.2 mole of samarium is produced by 57 900 coulombs.

Hence 1.0 mole of samarium is produced by $\frac{57\ 900}{0.2}$ = 289 500 coulombs

Therefore the charge on samarium ions = $\frac{289\ 500}{96\ 500}$
= 3

The formula of samarium ions = Sm^{3+}.

Calculation of mass of metal deposited at cathode in electrolysis

Number of coulombs that flows through the electrolyte = current × time.

z moles of electrons produce 1 mole of metal atoms from M^{z+} ions.
Hence z × F coulombs produce 1 mole of metal atoms from M^{z+} ions.

Therefore one coulomb produces $\frac{1}{z \times F}$ mole of metal atoms.

Thus the total number of moles of metal atoms produced
= no. of coulombs that flowed through circuit × $\frac{1}{z \times F}$ moles

Hence the mass of metal produced
= no. of moles × relative atomic mass

$$= \frac{\text{Current x time x relative atomic mass}}{\text{Charge on ions (z) x Faraday constant (F)}}$$

Question A current of 4.00 A was passed through copper(II) sulphate solution for 965 seconds. What mass of copper was discharged at the cathode? [F = 96 500 C mol^{-1}; Cu = 63.5]

Answer

Number of coulombs that flowed in circuit = 4.00 × 965 C

$$Cu^{2+} + 2e^- \rightarrow Cu$$

2 × 96 500 coulombs produce 1 mole of copper atoms.

Hence 1 coulomb produces $\frac{1}{2 \times 96\,500}$ mole of copper atoms,

and 4.00 × 965 coulombs produce $\frac{4.00 \times 965}{2 \times 96\,500} = 0.02$ mole.

Therefore mass of copper discharged = 0.02 × 63.5 g = 1.27 g.

Question

Calculate the volume of oxygen gas produced (measured at s.t.p.) when 2.00 A is passed through dilute sulphuric acid, for 1830 seconds, using platinum electrodes. [1 mole of gas occupies 22 400 cm³ at s.t.p.; $F = 96\,500$ C mol⁻¹]

Answer

Number of coulombs that flowed in circuit = 2.00 × 1830 C

$$4OH^- \rightarrow \underset{\text{1 mole}}{O_2} + 2H_2O + \underset{\text{4 moles}}{4e^-}$$

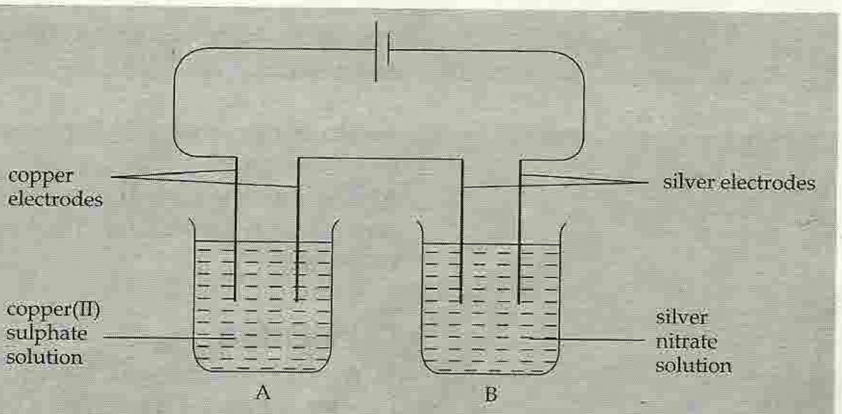
From the equation,
4 moles of electrons also produce 1 mole of O_2 gas.
ie 4 × 96 500 coulombs produces 1 mole of O_2
Hence 1 coulomb produces $\frac{1}{4 \times 96\,500}$ mole of O_2.

Therefore 2.00 × 1830 coulombs produce $\frac{2.00 \times 1830}{4 \times 96\,500}$ mole of O_2

$$= \frac{2.00 \times 1830}{4 \times 96\,500} \times 22\,400 \text{ cm}^3$$

$$= 212 \text{ cm}^3 \text{ of } O_2$$

Question



▸ Fig 7.10

A current was passed through the circuit shown in Fig 7.10. In the experiment, 5.4 g of silver metal was discharged at the cathode in electrolysis cell B. What mass of copper was discharged at the cathode in cell A?
[Cu = 63.5; Ag = 108]

Answer

The same number of coulombs must have flowed through A and B.

Number of moles of silver metal produced = $\frac{5.4}{108}$ mole

The two equations for the discharge of silver and copper ions are:

$$Ag^+ + e^- \rightarrow Ag$$
$$Cu^{2+} + 2e^- \rightarrow Cu$$

Hence the number of moles of electrons (and hence coulombs) required to produce 1 mole of copper atoms = double the number of moles of electrons required to produce 1 mole of silver atoms.
ie the number of moles of copper atoms produced by a quantity of coulombs = half the number of moles of silver atoms produced by the same quantity of coulombs

Therefore number of moles of copper atoms discharged = $\frac{1}{2} \times \frac{5.4}{108}$ mole

Hence the mass of copper discharged = $63.5 \times \frac{1}{2} \times \frac{5.4}{108}$ g = 1.59 g

Relationship between the Faraday constant, Avogadro constant and Charge on the Electron

Faraday constant (F) = Avogadro constant (L)× charge on the electron
The Avogadro constant (L) can be found from the results of electrolysis experiment, using the relationship above.

For example, the electrolysis of copper(II) sulphate solution, using copper cathode and a graphite anode can be used to determine a val for the Faraday's constant and Avogadro's constant.

Procedure

The mass of a dry copper cathode is determined. Let it be 'm_1' g
The copper cathode is dipped in a solution of copper(II)sulphate and connected to a graphite anode via a battery of cells, an ammeter, rheostat (used to maintain a constant current flow during the process and a switch.

An electric current (of 'I' A) is passed through the solution for a certa time 't' seconds.
Afterwards the switch is opened, the copper cathode is removed carefully. It is washed and dried and its new mass is determined. Let be 'm_2' g.

Calculation

Increase in mass of cathode = $(m_2 - m_1)$ g
Quantity of electricity passed = 'It' coulombs
$(m_2 - m_1)$g of copper are formed when 'It' coulombs are passed

Relative atomic mass of copper = 63.5

$\therefore$ Mass of 1 mole of copper = 63.5g

63.5g of copper will be produced when $\frac{It}{(m_2 - m_1)} \times 63.5$ coulombs of electricity are passed.

Therefore to discharge 1 mole of copper, $\frac{It}{(m_2 - m_1)} \times 63.5$ coulombs of electricity are required.

During electrolysis of copper(II)sulphate, copper is discharged at the cathode by the following process $Cu^{2+}{}_{(aq)} + 2\,e \longrightarrow Cu_{(s)}$

From the electrolytic equation above, it can be deduced that 1 mole of copper is discharged when 2 moles of electrons, that is two Faradays of electricity are passed.

$$\therefore 2F = \frac{It}{(m_2 - m_1)} \times 63.5$$

$$\boxed{F = \frac{It}{(m_2 - m_1)} \times \frac{63.5}{2}}$$

But, F=Le

$$\therefore \boxed{L = \frac{F}{e} = \frac{It}{(m_2 - m_1)e} \times \frac{63.5}{2}}$$

Knowing the value of 'e', the Avogadro's constant, L can be determined.

Hence using the electrolysis of copper(II)sulphate the Faradays constant and the Avogadro's constant can be determined.

Question

When 3860 coulombs was passed through copper(II) sulphate solution, 1.27 g of copper metal was discharged at the cathode. Calculate a value for the Avogadro constant (*L*).

[charge on the electron = 1.60×10^{-19} C; A_r for copper = 63.5]

Answer

Number of moles of copper discharged $= \frac{1.27}{63.5}$

$= 0.02$ mole

One copper ion, Cu^{2+}, is discharged by two electrons.

Hence number of moles of electrons that flowed through the circuit $= 2 \times 0.02$

$= 0.04$ mole

Number of electrons that flowed through the circuit $= \frac{3860}{1.60 \times 10^{-19}} = 2.41 \times 10^{22}$

Thus 0.04 mole must be equivalent to 2.41×10^{22} particles.

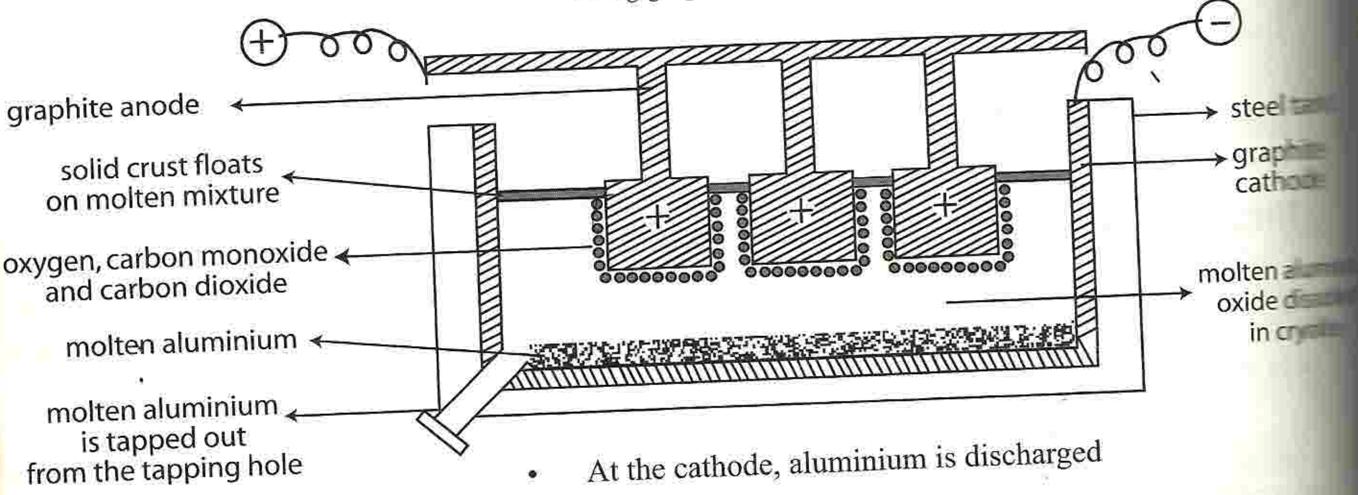
Hence 1 mole is equivalent to $\frac{2.41 \times 10^{22}}{0.04} = 6.02 \times 10^{23}$ particles.

Therefore the Avogadro constant $= 6.02 \times 10^{23}$.

7.12 Industrial Electrolysis

Extraction of aluminium

- Aluminium is extracted from its purified ore, bauxite, $Al_2O_3.2H_2O$
- The purified ore is then dissolved in molten cryolite so as to lo the temperature at which electrolysis is carried out.
- The process is carried out in the electrolytic cell shown bel using graphite electrodes:-



- At the cathode, aluminium is discharged

$$Al^{3+}(l) + 3e^- \rightarrow Al(l)$$

- At the anode oxygen gas evolves.

$$2O^{2-}(l) \rightarrow O_2(g) + 4e^-$$

- Due to the high temperature prevailing in the electroly cell, the oxygen will slowly react with the graphite anode form carbon dioxide

$$C(s) + O_2(g) \rightarrow CO_2(g)$$

Hence the graphite anode must be periodically replaced.

Anodising Aluminium

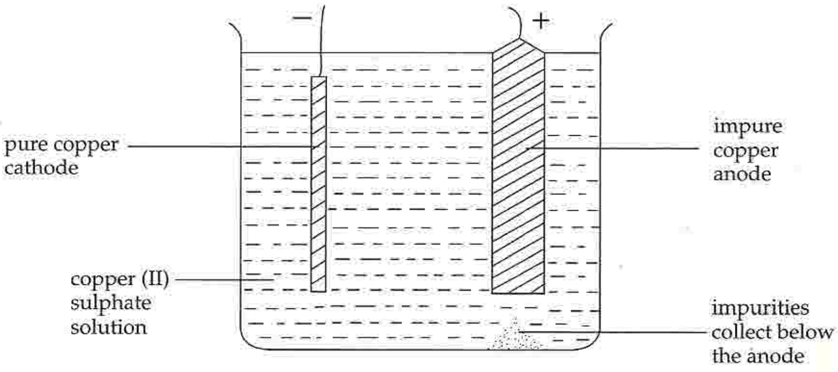
- The uses of aluminium are outlined in Chapter 5. One importa property of aluminium is its corrosion resistance, despite its hig position in the electrochemical series (ie large negative E°). The corrosion resistance of aluminium is due to a surface coating aluminium oxide that protects the metal from chemical attack air and water. This coating forms naturally in air.

- The aluminium oxide coating on aluminium objects can be increased by **anodising**. In anodising, the aluminium object is made the anode in the electrolysis of sulphuric acid. Oxygen is discharged at the anode. This oxygen reacts with the aluminium to form a thick oxide layer:

$$4Al + 3O_2 \rightarrow 2Al_2O_3$$

Purification of Copper Metal

- Impure copper is purified by electrolysis. The impure copper acts as the anode while a piece of pure copper acts as the cathode. The electrolyte is copper(II) sulphate solution (Fig 7.11).



- In the electrolysis:
  (a) The copper from the anode dissolves in the electrolyte:

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

  The impurities collect below the anode. These impurities contain valuable silver and gold which do not dissolve in the electrolyte.

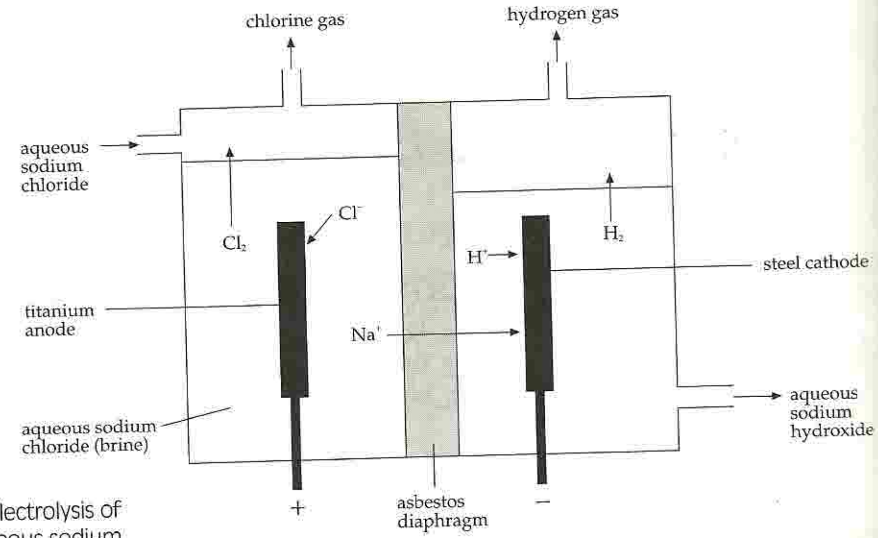
  (b) The copper ions from the solution are discharged at the pure copper cathode:

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

  (c) The overall change is the transfer of pure copper from the anode to the cathode.

Electrolysis of Brine

- Aqueous salt solution is electrolysed to manufacture sodium hydroxide (the most important product) and chlorine. Other useful chemicals are also produced from the process, including sodium chlorate(I) or NaClO, and sodium chlorate(V) or $NaClO_3$.



▶ Fig 7.12 Electrolysis of aqueous sodium chloride (simplified

(a) Aqueous sodium chloride (brine) is put into the left side of the electrolysis cell, around the titanium anode.

(b) The chloride ions go to the anode, where they are discharged:

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

Titanium is used for the anodes because it resists corrosion by the very reactive chlorine.

(b) The sodium ions go through the asbestos diaphragm to the steel cathode. They cannot be discharged to become sodium because the sodium metal would react immediately with water. Instead, hydrogen ions from the water are discharged to become hydrogen gas:

$$2H^+ + 2e^- \rightarrow H_2$$

This leaves sodium ions (Na^+) and hydroxide ions (OH^-) around the cathode. Thus aqueous sodium hydroxide flows out of the cell.

(c) The level of brine on the left (anode) side of the cell is deliberately higher than on the right (cathode) side so that the brine will slowly flow through the asbestos diaphragm towards the cathode, carrying the sodium ions with it and preventing the reverse flow of sodium hydroxide towards the cathode (where it would react with the chlorine).

(d) The initial products from the process are chlorine, sodium hydroxide and hydrogen.

- Other chemicals can be manufactured from the products of the electrolysis.
  (a) Hydrogen and chlorine can be combined to make hydrogen chloride and hence hydrochloric acid:

$$H_2 + Cl_2 \rightarrow 2HCl$$

  (b) The chlorine and *cold* aqueous sodium hydroxide can be mixed to produce sodium chlorate(I), NaClO, which is used as bleach. The equation is:

$$Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$$

EXERCISE 7

Multiple Choice Questions

Section I

1 The symbol for the element cerium is Ce. The formula of cerium(IV) oxide is

A Ce_4O **C** CeO

B Ce_2O **D** CeO_2

2 In which one of the following complex ions does the metal atom have an oxidation number of *zero*?

A $[Co(CN)_4]^{4-}$

B $[Fe(SCN)(H_2O)_5]^{2+}$

C $[Ni(CN)_5]^{3-}$

D $[Ni(NH_3)_6]^{2+}$

Refer to the following redox changes for questions 3 to 8.

In a chemical reaction, an element may

A undergo oxidation only.

B undergo oxidation and reduction .

C remain unchanged in oxidation number.

D change from two different oxidation numbers to a third oxidation number.

Which one of the above alternatives provides the best description for the change that occurs in each of the named elements in the following reactions?

3 SULPHUR, in the reaction:

$$2H_2S(g) + SO_2(g) \rightarrow 3S(s) + 2H_2O(l)$$

4 MANGANESE, in the reaction:

$$3MnO_4^{2-}(aq) + 2H_2O(aq) \rightarrow 2MnO_4^-(aq) + MnO_2(s) + 4OH^-(aq)$$

5 ALUMINIUM, in the reaction:

$$2Al(s) + 3Pb^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Pb(s)$$

6 COPPER, in the reaction:

$$[Cu(H_2O)_4]^{2+} + 4Cl^- \rightarrow [CuCl_4]^{2-} + 4H_2O$$

7 HYDROGEN, in the electrolysis of molten lithium hydride.

8 NITROGEN, in the reaction:

$2NO_2(g) + H_2O\ (l) \rightarrow HNO_3(aq) + HNO_2(aq)$

9 The same current was passed through molten potassium chloride and through molten aluminium oxide. 7.8 g of potassium was liberated in one cell. What was the mass of aluminium liberated in the other cell?

[Al = 27; K = 39]

A 5.4 g **C** 2.7 g

B 3.6 g **D** 1.8 g

10 In which one of the following particles does nitrogen have the highest oxidation number (ie most positive)?

A Li_3N **C** NH_4^+

B N_2O **D** NO_3^-

11 In which one of the following does iodine have an oxidation number of +1?

A $NaIO_4$ **C** IO_3^-

B I_3^- **D** IO^-

12 What is the oxidation number of the bromine atom in the complex $Ba[BrF_4]_2$?

A –3 **C** +1

B –1 **D** +3

13 How many electrons are required to complete the half-equation

$XO_4^-(aq) + 8H^+(aq) + \ldots e^- \rightarrow X^-(aq) + 4H_2O(l)$?

A 4 **C** 6

B 5 **D** 8

14 The thallium ion, $Tl^{3+}(aq)$, oxidises iodide ions according to the half-equation

$$I^-(aq) \rightarrow I_2 + e^-$$

In an experiment, 0.200 mole of Tl^{3+} reacts with 200 cm^3 of 2.00 mol dm^{-3} KI(aq). What is the oxidation number of thallium at the end of the reaction?

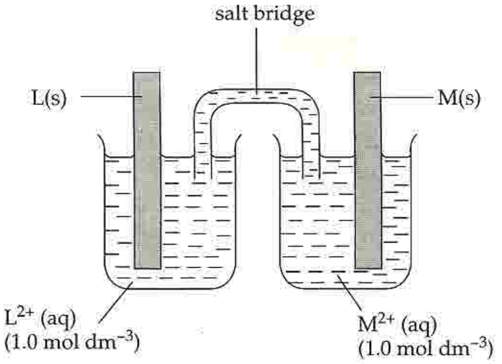
A +5 **C** +1

B +2 **D** 0

15 The standard electrode potentials for the metals L and M in Fig 7.13 are

$L^{2+}(aq) + 2e^- \rightleftharpoons L(s);\ E^{\ominus} = +0.40\ V$

$M^{2+}(aq) + 2e^- \rightleftharpoons M(s);\ E^{\ominus} = -0.60\ V$



▲ Fig 7.13

Metals L and M were combined together to make the cell shown in the diagram. Which one of the following correctly describes the cell?

	electrode at which positive ions enter the solution	*cell voltage, V*
A	L	0.20
B	M	0.20
C	M	1.00
D	L	1.00

16 Many laboratory spatulas are made of nickel. Which aqueous solution might react with a nickel spatula?

A Cu^{2+}(aq)
B Co^{2+}(aq)
C Mn^{2+}(aq)
D Pb^{2+}(aq)

17 An electric current was passed through molten calcium chloride, producing 2.0 g of calcium metal at the cathode. What mass of chlorine was produced at the anode?
[Cl = 35.5; Ca = 40]

A 1.78 g
B 3.55 g
C 4.00 g
D 7.10 g

18 When a quantity of electricity was passed through molten scandium oxide, 5.00 g of scandium and 2.67 g of oxygen were produced at the electrodes. What is the formula of scandium oxide?
[Sc = 45; O = 16]

A ScO_3
B ScO
C Sc_2O_3
D Sc_3O_2

Section II

Summary of directions

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

19 Use the standard redox potentials below to predict which of the following reagents would oxidise Fe^{2+}(aq) to Fe^{3+}(aq).

1 Co^{3+}(aq)
2 BrO_3^-(aq) + acid
3 TeO_2(s) + acid

	$E^\ominus$ /volt
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	−0.40
$TeO_2(s) + 4H^+(aq) + 4e^- \rightleftharpoons Te(s) + 2H_2O(aq)$	+0.53
$BrO_3^-(aq) + 6H^+ + 5e^- \rightleftharpoons Br_2(aq) + 3H_2O(aq)$	+1.52
$Co^{3+}(aq) + e^- \rightleftharpoons Co^{2+}(aq)$	+1.70
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77

20 $BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O$

For the above reaction, what changes occur in the oxidation numbers of the elements?

1 Oxidation number of bromine in Br^- increases.
2 Oxidation number of bromine in BrO_3^- decreases.
3 Oxidation number of oxygen in BrO_3^- decreases.

Structured Questions

1 What is the oxidation number of the following elements?

(a) manganese in MnO_2
(b) sulphur in H_2S
(c) vanadium in NH_4VO_3
(d) chlorine in $KClO_4$
(e) carbon in CH_4
(f) carbon in CO_3^{2-}
(g) aluminium in AlF_6^{3-}
(h) copper in $CuCl_4^{3-}$
(i) chromium in $Cr_2O_7^{2-}$
(j) iron in $Fe(CN)_6^{4-}$
(k) silver in $Ag(NH_3)_2^+$

2 $$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

The reaction of iodate(V) ions with iodide in the presence of acid is shown above.

(a) What are the oxidation numbers of

(i) oxygen in IO_3^-, and
(ii) iodine in IO_3^-?

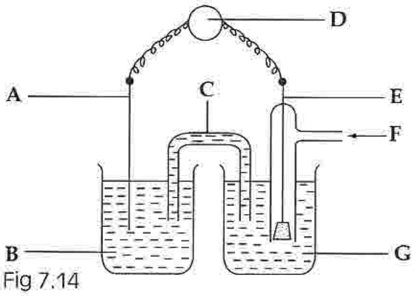
(b) What change occurs in the oxidation number of iodine in the reaction, in
(i) I^- and
(ii) IO_3^-?

(c) In an experiment, 0.02 mole of KIO_3 was reacted with excess acidified KI. The iodine produced was reacted with thiosulphate according to the reaction

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

(i) How many moles of $S_2O_3^{2-}$ are required for the reaction?
(ii) What volume of 0.1 mol dm^{-3} $Na_2S_2O_3$ is required for the reaction?

3 The apparatus shown in Fig 7.14 is used to measure the *standard electrode potential* of silver.



▸ Fig 7.14

(a) Name the chemicals or materials labelled **A** – **G**.

(b) (i) Write a balanced equation for the cell reaction.
(ii) What is the standard e.m.f. of the cell?

(c) Where do the following processes take place in the apparatus:
(i) oxidation;
(ii) reduction;
(iii) discharge of positive ions from solution?

#4 The apparatus shown in Fig 7.15 was used to investigate two electrode reactions.

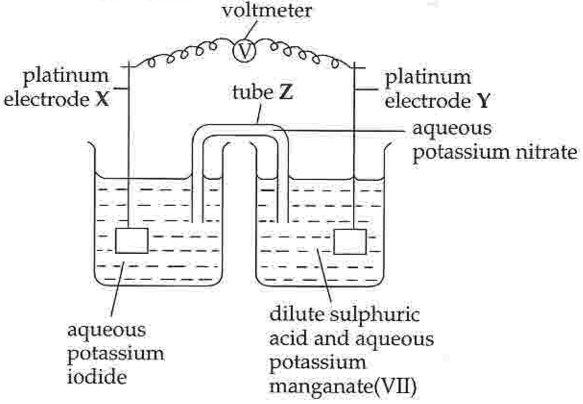
(a) What would you expect to see in the solution around electrode **X**?

(b) Write ionic equations for the reactions at
(i) electrode **X**;
(ii) electrode **Y**.

(c) Where do the electrons flow in the apparatus?

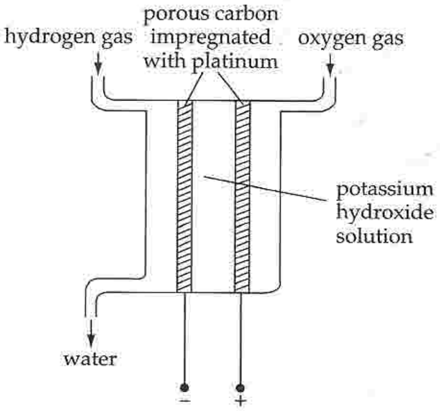
(d) (i) Write a balanced equation for the overall reaction in the apparatus.
(ii) Use the *Data Tables* at the back of this book to find the standard e.m.f. for this reaction.

(e) How would you expect the voltmeter reading to be affected by increasing the concentration of the potassium iodide solution?



▴ Fig 7.15

5 Fig 7.16 shows a simplified diagram of an oxygen/hydrogen fuel cell used to provide electricity for a manned space vehicle.



▸ Fig 7.16

(a) Suggest the sources of the oxygen and hydrogen for this fuel cell.

(b) In the fuel cell, the hydrogen gas reacts according to the equation:

$$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$$

(i) Write a similar equation for the reaction of the oxygen.
(ii) Hence write a balanced equation for the reaction in the fuel cell.

(c) Suggest the purpose of the platinum in the cell.

(d) Suggest *two* advantages of this fuel cell for a space vehicle compared with conventional batteries.

6 The standard potentials of some half-cells are as follows:

electrode reaction	E°/volts
$H_2O_2(aq) + 2H^+ + 2e^- \rightleftharpoons 2H_2O(l)$	+1.77
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.07
$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$	+0.68
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54

(a) Which of the following reactions would take place under standard conditions?

I: $H_2O_2(aq) + I_2(s) \rightarrow 2H^+(aq) + 2I^-(aq) + O_2(g)$

II: $H_2O_2(aq) + Cl_2(g) \rightarrow 2H^+(aq) + 2Cl^-(aq) + O_2(g)$

III: $2Br^-(aq) + I_2(s) \rightarrow 2I^-(aq) + Br_2(l)$

IV: $H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \rightarrow 2H_2O(l) + I_2(s)$

V: $H_2O_2(aq) + 2H^+(aq) + 2Cl^-(aq) \rightarrow 2H_2O(l) + Cl_2(g)$

(b) What reaction do you think might take place if 2.00 mol dm^{-3} HCl is mixed with 2.00 mol dm^{-3} H_2O_2?

7 (a) Define standard electrode potential.

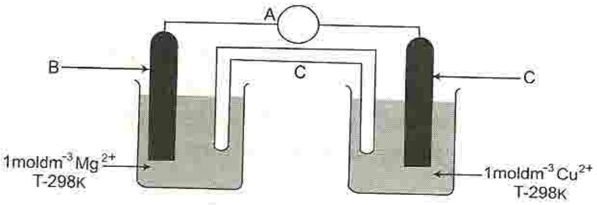
(b) Draw labelled diagrams of:-

(i) a standard chlorine electrode

(ii) a standard copper electrode

(c) (i) Describe how the standard electrode potential of zinc can be measured.

A cell is set up by connecting a standard magnesium electrode to a standard copper electrode as shown below



(i) Label the parts A,Band C in the diagram above.

(ii) State the two main functions of part C in the apparatus above.

(iii) Use the Data Booklet to ca
the cell potential set up be
the two electrodes.

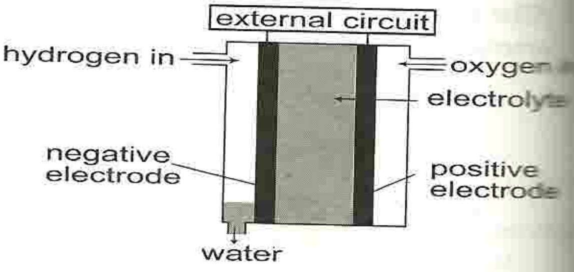
(iv) Write down a redox equati
the reaction which occurre
cell.

(v) Use the above equatio
explain the energy cha
which took place in the ele
cell.

*8 (a) (i) What is a fuel cell?

(ii) What is the main differe
between a fuel cell and
ordinary battery.

(b) A typical hydrogen fuel cell is sh
below.



(i) Explain how the fuel cell conve
chemical energy into electrical energ
(ii)Write down the half equations
the reactions which take place at ea
electrode and calculate the cell p
tential for a standard hydrogen fuel ce
(iii)Explain what will be the effect
the cell potential if the pressure of
hydrogen is higher than 1 atmosph

(c) State the main advantages a
disadvantages of the hydrogen fuel ce
as a source of energy.

Descriptive Questions

*1 (a) Define *standard electrode potential.*

(b) Outline with the aid of a diagram ho
you would measure the standard electrode potential of a metal such as copper.

(c) Use the electrode potential data at the back of this book to calculate th
standard e.m.f. of the cell

$Co(s) \mid Co^{2+}(aq) \mid Ag^+(aq) \mid Ag(s)$

and write a balanced equation for the ce
reaction.

How would you expect the e.m.f. of this cell to change, if any, if the concentration of silver ions in such a cell were increased to *double* the standard state concentration?

*2 The compound hydrazine, N_2H_4, is used as a rocket fuel.

(a) Draw a dot-cross diagram of a molecule of hydrazine.

(b) The standard redox potential for hydrazine in acid conditions is given below.

$$N_2(g) + 5H^+(aq) + 4e^- \rightleftharpoons N_2H_5^+(aq); \quad E^\circ = -0.17\ V$$

Use the *Data Tables* at the end of this book to predict the likely reaction of hydrazine with chlorine in acidic conditions and write a balanced equation for the reaction.

(c) Hydrazine is decomposed into nitrogen hydrogen by a catalyst in little rocket 'thrusters' on spacecraft. This process breaking the N—N bond. Suggest a reason why ethane, C_2H_6, doesnot behave in the same way.

*3 (a) Draw labelled diagrams to show how the standard electrode potential of the following electrode systems could be determined.

(i) $Fe^{3+}(aq) / Fe^{2+}(aq)$

(ii) $O_2(g) / OH^-(aq)$

(iii) $Mg^{2+}(aq) / Mg(s)$

(b) Explain the effect of increasing the concentration of $Fe^{2+}(aq)$ on the electrode potential value.

(c) (i) Use the standard electrode potential in the Data Booklet to calculate the standard cell potential of the cell $Mg(s)1Mg^{2+}(aq) : Zn^{2+}(aq)1Zn(s)$

(ii) Write a balanced equation for the overall reaction taking place in the cell.

*4 (a) Use your Data Booklet to answer the following questions.

(i) Is a 1.0 moldm^{-3} solution of Hydrogen ion found under hydrogen gas at r.t.p. capable of oxidising copper metal in presence of 1.0 moldm^{-3} copper(II)ion?

(ii) Is Sn^{2+} ion capable of oxidizing chromium ion, Cr^{3+} to dichromate ion, $Cr_2O_7^{2-}$ ion?

(iii) Is there any oxidising agent that can oxidize fluoride ions to fluorine?

(iv) Can magnesium be extracted from its aqueous solution by electrolysis?

(b) Describe briefly an experiment that may be used to measure the standard electrode potential of the $I_2(aq)/I^-(aq)$ system.

*5 (a) (i) What do you understand by the term 'electroplating'?

(ii) Draw a diagram to show an electrolytic cell that may be used to chromium plate a spoon.

(iii) Write down electrolytic equations for the processes that take place at the electrodes.

(b) An object is to be chromium plated. The total surface area of the object is 70cm^2 and the thickness of the layer of chromium must be 1 x 10^{-2} cm. A constant electric supply of 5A is available.

(i) Calculate the volume of chromium that must be deposited on the object.

(ii) If the density of chromium is 7.19 g/cm^3, calculate the mass of chromium that must be deposited on the object.

(iii) Calculate the quantity of electricity that must be passed to deposit the mass of chromium required.

(iv) Hence calculate the time for which the electric current must be passed through the electrolyte.

*6 (a) Describe, using a suitable diagram, how chlorine is obtained industrially.

(b) Aluminium is obtained industrially by the electrolysis of purified bauxite, in the presence of cryolite, $NaAlF_4$, using graphite electrodes.

(i) Give ion-electron equations for the processes taking place at the electrodes.

(ii) What further reaction takes place at the anode during electrolysis?

(iii) State the role of cryolite in the extraction of aluminium.

(iv) What are the factors that must be considered to select a site to set up a plant to extract aluminium?

(c) Determine whether reactions would take place between the following substances under standard conditions. If the reactions are energetically feasible, write down their ionic equations and determine their cell potentials.

(i) Zinc and copper(II)sulphate

(ii) Sulphur dioxide and acidified potassium dichromate(VI)

(iii) Iodine and iron(II)chloride

CHAPTER 8

CHEMICAL EQUILIBRIUM

- Reversible Reactions
- Dynamic Equilibrium
- Equilibrium Constant, K_c
- Equilibrium Constant, K_p
- Heterogeneous Equilibria
- Factors That Affect K_c and K_p
- Le Chatelier's principle
- Industrial Reactions

SYLLABUS OBJECTIVES

In this chapter you should be able to:

- explain what is meant by reversible reaction and dynamic equilibrium, in terms of the rates of forward and reverse reactions (eg at equilibrium, the rate forward = the rate backward)
- deduce expressions for equilibrium constants in terms of concentrations (K_c) and partial pressures (K_p)
- calculate the values of equilibrium constants from given data
- calculate the quantities present at equilibrium from given data (eg if given the value of K_c)
- state Le Chatelier's Principle and use it to deduce the qualitative effect of changes in temperature, concentration or pressure, on the composition of an equilibrium mixture
- deduce the effect of concentration, pressure, temperature and presence of a catalyst on the equilibrium constant

8.1 Reversible Reactions

- Most chemical reactions are *not* reversible, ie they cannot take place in both directions. For example, the decomposition of potassium chlorate(V) is a reaction that cannot be reversed:

$$2KClO_3(s) \xrightarrow{\text{heat}} 2KCl(s) + 3O_2(g)$$

- It is not possible to mix KCl and O_2 together to make $KClO_3$.
- The following reaction is an example of a reversible reaction:

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

Reversible reactions have the following features:

(a) The reversible sign $\rightleftharpoons$ means the reaction can go in both directions.

(b) SO_2 and O_2 can be mixed together to form SO_3. This reaction is described as the *forward reaction* — ie from left to right.

(c) SO_3 can decompose into SO_2 and O_2. This reaction is the *backward reaction* — ie from right to left.

(d) When SO_2 and O_2 are reacted together to form SO_3, they are not completely converted to SO_3. Instead, an intermediate position or **equilibrium** is reached whereby both reactants (SO_2 and O_2) and products (SO_3) are present.
Reversible reactions are never complete, *a mixture of reactants* and *products is obtained.*

8.2 Dynamic Equilibrium

- $$A + B \rightleftharpoons C + D$$

(a) When a mixture of A and B reacts to become C and D, the concentrations of A and B (the reactants) decrease with time, while the concentrations of C and D (the products) increase with time.

(b) As the concentrations of the reactants decrease, the rate of the forward reaction (from left to right) also decreases with time.

(c) At the start, the rate of the backward reaction (from right to left) is zero because there is no C and D.

As the reaction proceeds, the concentrations of C and D increase. Hence the rate of the backward reaction also increases.

(d) After a period of time, the rate of the forward reaction becomes equal to the rate of the backward reaction. This situation is called **dynamic equilibrium**. The time to reach equilibrium can vary from a fraction of a second up to several weeks.

At equilibrium in a reversible reaction:

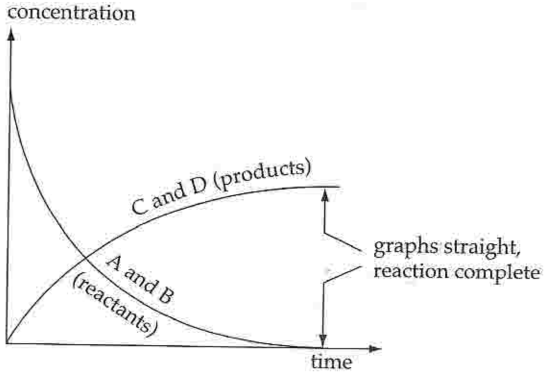
(i) the rate forward = the rate backward;

(ii) the concentrations of the reactants and the products are constant.

Graphs of Concentration Against Time

- $$A + B \rightarrow C + D$$

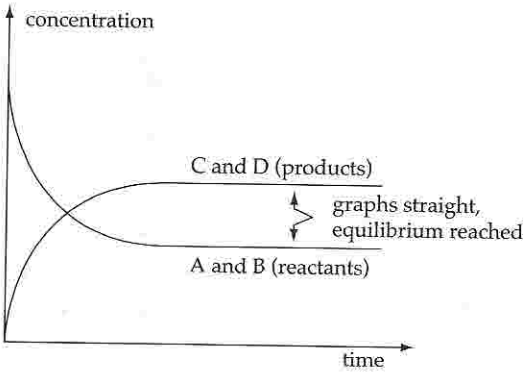
A graph of concentration of reactants and products against time, for the above non-reversible reaction, is shown in Fig 8.1. At the end of the reaction, there are *no reactants remaining* (ie concentrations of A and B = zero), and the concentrations of the products remain constant.



▶ Fig 8.1

- $$A + B \rightleftharpoons C + D$$

A graph of concentration of reactants and products against time, for the above reversible reaction, is shown in Fig 8.2. When equilibrium is reached, there is still a certain quantity of reactants remaining (ie concentrations of A and B ≠ zero). Both the concentrations of the reactants and the products remain constant at equilibrium.



▶ Fig 8.2

8.3 Equilibrium Constant, K_c

- The general equation for a reversible reaction is given by

  $$aA + bB \rightleftharpoons cC + dD$$

  The equation states that *a* moles of substance A reacts with *b* moles of substance B, to produce *c* moles of substance C and *d* moles substance D.

- At equilibrium in the above reaction,

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

  Where [A] = concentration of A, [B] = concentration of B, etc. K_c = equilibrium constant for the reaction, in terms concentrations of the reactants.

- The general equation can be written the other way round, ie

  $$cC + dD \rightleftharpoons aA + bB$$

  Then the expression for the equilibrium constant, K_c, becomes

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

  Hence the value and units of K_c depend on how the chemi equation is written.

Example

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

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

$$\text{The units of } K_c = \frac{(\text{units of concetration})^2}{(\text{units of concetration})^2 \times (\text{units of concetration})}$$

$$= \frac{\text{mol}^2\,\text{dm}^{-6}}{\text{mol}^3\,\text{dm}^{-9}} = \text{dm}^3\,\text{mol}^{-1}$$

Example

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

$$K_c = \frac{[H_2].[I_2]}{[HI]^2}$$

$$\text{The units of } K_c = \frac{(\text{units of concentration}) \times (\text{units of concentratio}}{(\text{units of concentration})^2}$$

= no units

Question

The equilibrium mixture present in a 3.0 dm³ flask at 250°C was found to contain 1.00 mole of $PCl_5(g)$, 2.00 moles of $PCl_3(g)$ and 0.3 mole of $Cl_2(g)$. Calculate the equilibrium constant, K_c, for the equilibrium

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Give the units for K_c.

Answer

$[Cl_2] = \frac{0.3}{3.0}$ mol dm^{-3}, $[PCl_3] = \frac{2.00}{3.0}$ mol dm^{-3} and $[PCl_5] = \frac{1.00}{3.0}$ mol dm^{-3}

$$K_c = \frac{[Cl_2].[PCl_3]}{[PCl_5]} = \frac{\frac{0.3}{3.0} \times \frac{2.00}{3.0}}{\frac{1.00}{3.00}} = 0.20 \text{ mol dm}^{-3}$$

Question

A sealed flask contained 2 moles of iodine, 19 moles of hydrogen iodide and 4 moles of hydrogen at equilibrium. Calculate the equilibrium constant, K_c, for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Give the units for K_c.

Answer

Let V be the volume of the flask. Hence, at equilibrium,

$$[HI] = \frac{19}{V} \text{ mol dm}^{-3}$$

$$[H_2] = \frac{4}{V} \text{ mol dm}^{-3}$$

$$[I_2] = \frac{2}{V} \text{ mol dm}^{-3}$$

$$K_c = \frac{[HI]^2}{[H_2].[I_2]}$$

$$= \frac{\left(\frac{19^2}{V}\right)}{\left(\frac{4}{V}\right).\left(\frac{2}{V}\right)}$$

$$= 45.1$$

There are no units for K_c.

Question

A quantity of dinitrogen tetraoxide, N_2O_4, was dissolved in trichloromethane. The N_2O_4 dissociates according to the equation

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

A solution of N_2O_4 and NO_2 at equilibrium in trichloromethane at 10°C was analysed. 0.5 dm^3 of the solution was found to contain 0.0014 mole of NO_2. 2.0 dm^3 of the same solution was found to contain 1.04 moles of N_2O_4.

(a) Calculate K_c for the equilibrium above and give its units.

(b) What is K_c for $2NO_2 \rightleftharpoons N_2O_4$?

Answer

(a) $$[N_2O_4] = \frac{\text{no. of moles of } N_2O_4}{\text{volume of solution in dm}^3} = \frac{1.04}{2.0} \text{ mol dm}^{-3}$$

$$[NO_2] = \frac{\text{no. of moles of } NO_2}{\text{volume of solution in dm}^3} = \frac{0.0014}{0.5} \text{ mol dm}^{-3}$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{\left(\frac{0.0014}{0.5}\right)^2}{\frac{1.04}{2.0}} = 1.51 \times 10^{-5} \text{ mol dm}^{-3}$$

(b) $$K_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{1.51 \times 10^{-5}} = 6.62 \times 10^{4} \text{ dm}^3 \text{ mol}^{-1}$$

Question

$$CH_3CH_2OH(aq) + CH_3COOH(aq) \rightleftharpoons CH_3COOCH_2CH_3(aq) + H_2O(l)$$

The equilibrium constant K_c for the above reaction is 4.00. Calculate the mass of ethanoic acid that must be mixed with 2.0 moles of ethanol to produce 1.5 moles of ethyl ethanoate at equilibrium.

Answer

Let x = no. of moles of ethanoic acid needed to mix with the 2.0 moles of ethanol
Let V = the volume of the mixture in dm^3
To produce 1.5 moles of ethyl ethanoate,

1.5 moles of H_2O will be produced;
1.5 moles of CH_3COOH is used up, so $(x - 1.5)$ mole of CH_3COOH remains;
1.5 moles of CH_3CH_2OH must be used up, so $(2.0 - 1.5) = 0.5$ mole of CH_3CH_2OH will be remaining.

Thus at equilibrium, $$[H_2O] = \frac{1.5}{V} \text{ mol dm}^{-3}$$

$$[CH_3COOCH_2CH_3] = \frac{1.5}{V} \text{ mol dm}^{-3}$$

$$[CH_3COOH] = \frac{(x - 1.5)}{V} \text{ mol dm}^{-3}$$

$$[CH_3CH_2OH] = \frac{0.5}{V} \text{ mol dm}^{-3}$$

$$K_c = \frac{[CH_3COOCH_2CH_3].[H_2O]}{[CH_3CH_2OH].[CH_3COOH]} = 4.00$$

Answer

Hence $\frac{1.5 \times 1.5}{0.5 \times (x - 1.5)} = 4.00$

ie $2x - 3 = 2.25$

$x = 2.62$ moles

Mass of ethanoic acid = no. of moles × relative molecular mass

$= 2.62 \times 60$ g

$= 157$ g

Question

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

In a flask of volume V dm^3, a moles of N_2O_4 were placed. The N_2O_4 decomposed according to the equation above. At equilibrium, x moles of N_2O_4 had decomposed. Write an expression for K_c, in terms of a, x and V.

Answer

1 mole of N_2O_4 produces 2 moles of NO_2.

Hence x moles of N_2O_4 produce $2x$ moles of NO_2 and the number of moles of N_2O_4 remaining at equilibrium = $(a - x)$ moles.

At equilibrium,

$$[NO_2] = \frac{2x}{V} \text{ mol dm}^{-3}$$

$$[N_2O_4] = \frac{(a - x)}{V} \text{ mol dm}^{-3}$$

$$K_c = \frac{[NO_2]^3}{[N_2O_4]} = \frac{\left(\frac{2x}{V}\right)}{\frac{(a - x)}{V}} = \frac{4x^2}{V(a - x)}$$

Question

In aqueous solution, ethanal undergoes the reaction

$$CH_3CHO(aq) + H_2O(l) \rightleftharpoons CH_3CH(OH)_2(aq)$$

At 0°C, 60% of the ethanal in a 1.00 mol dm^{-3} aqueous solution reacts to form $CH_3CH(OH)_2$ at equilibrium. Calculate K_c under these conditions.

Answer

At equilibrium, 1 dm^3 of aqueous solution will contain 0.6 mole of $CH_3CH(OH)_2$ and $1.00 - 0.6 = 0.4$ mole of CH_3CHO.

1 dm^3 of water contains 1000 g of water.

Number of moles of H_2O in 1000 g $= \frac{1000}{18}$ moles $= 55.6$ moles

Hence the number of moles of H_2O remaining at equilibrium

$= (55.6 - 0.6)$ moles

$= 55.0$ moles

At equilibrium, $[CH_3CHO] = 0.4$ mol dm^{-3}

$[H_2O] = 55.0$ mol dm^{-3}

$[CH_3CH(OH)_2] = 0.6$ mol dm^{-3}

$$K_c = \frac{[CH_3CH(OH)_2]}{[CH_3CHO].[H_2O]} = \frac{0.6}{0.4 \times 55.0} = 0.027 \text{ dm}^3 \text{ mol}^{-1}$$

Question

Substance A decomposes into substances B and C, according to the following equation:

$$2A(g) \rightleftharpoons 2B(g) + C(g)$$

In an experiment, a quantity of substance A was allowed to decompose into B and C. The results of the experiment are shown in Fig 8.3.

(a) At what time from the start was equilibrium reached? Give a reason for your answer.

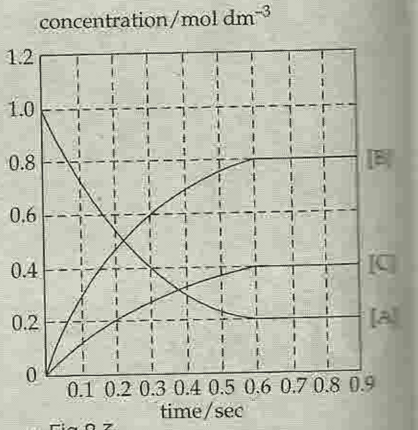
(b) What was the initial concentration of substance A?

(c) At equilibrium, what were the concentrations of (i) A, (ii) B and (iii) C?

(d) (i) Write an expression for K_c.

(ii) Calculate the value of K_c. Give its units.

(e) Give an example of one reaction that agrees with the equation above. Name substances A, B and C in your example.



▲ Fig 8.3

Answer

(a) Equilibrium was reached after 0.6 seconds. At this time, the graphs became horizontal and the concentrations of A, B and C remained constant.

(b) 1.0 mol dm^{-3}

(c) (i) 0.2 mol dm^{-3} (ii) 0.8 mol dm^{-3} (iii) 0.4 mol dm^{-3}

(d) (i) $K_c = \frac{[B]^2.[C]}{[A]^2}$ mol dm^{-3}

(ii) $K_c = \frac{(0.8)^2 \times 0.4}{(0.2)^2} = 6.4$ mol dm^{-3}

(e) An example is: $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$

A = sulphur trioxide; B = sulphur dioxide; C = oxygen

Experimental determination of K_c for hydrolysis of an ester

- Consider the hydrolysis of the ester ethyl ethanote $CH_3CO_2CH_2CH_3$. This is a reversible reaction which is catalysed by an acid.

$$CH_3CO_2CH_2CH_3 + H_2O \rightleftharpoons CH_3CO_2H + CH_3CH_2OH$$

- Mix a known mass of ester, ethyl ethanote and a known mass of water containing a small, known amount of hydrochloric acid, which catalyses the hydrolysis reaction in a stoppered flask.
- Shake the mixture vigorously for a few minutes and allow the mixture to stand for a few days [about a week] to ensure that equilibrium has been reached.
- Titrate the whole mixture *rapidly* with standardised 1.0moldm NaOH solution, using phenolphthalein as indicator. Let the volume of NaOH used = V_1 cm^3.
- The same amount of HCl that has been added in the mixture to act as catalyst is placed in another flask.

- This HCl solution is titracted with the standardized 1.0 $moldm^{-3}$ NaOH. Let the volume of NaOH used for this titration = V_2 cm^3 solution.
- Therefore the volume of NaOH used to neutralize only the ethanoic acide formed during titration = $(V_1 - V_2)$ cm^3
- The number of moles of ethanoic present at equilibrium in the mixture can be calculated. Let it be 'n' mole.
- The number of moles of ethanol will be the same as that of ethanoic acid, since during hydrolysis the same number of moles of ethanol and ethanoic acid are produced. Therefore the number of moles of ethanol = 'n'.
- Knowing the initial mass of ester and water used, the initial number of moles of ester and water used can be determined. Let the initial number of moles of ester and water be 'a' and 'b' respectively.

calculation

$$CH_3CO_2CH_2CH_3 + HO_3 \rightleftharpoons CH_3CO_2H + CH_3CH_2OH$$

Initial number of moles	a	b	—	—
Number of moles at equilibrium	a-n	b-n	n	n
Let total volume of solution be equal to V dm^3				
Equilibrium concentration	$\frac{a-n}{V}$	$\frac{b-n}{V}$	$\frac{n}{V}$	$\frac{n}{V}$

Therefore the equilibrium constant K_c for the hydrolysis of ethyl ethanoate can be calculated as show below:-

$$K_c = \frac{[CH_3CO_2H]\ [CH_3CH_2OH]}{[CH_3CO_2CH_2CH_3]\ [H_2O]} \qquad \frac{[mol\cancel{dm^{-3}}]\ [\cancel{moldm^{-3}}]}{[mo\cancel{ldm^{-3}}]\ [\cancel{moldm^{-3}}]}$$

$$= \frac{(n/\cancel{v})\ (n/\cancel{v})}{(a-n)\ /\cancel{v}\ (b-n)\ /\cancel{v}} = \frac{n^2}{(a-n)\ (b-n)}$$

$$K_c = \frac{n^2}{(a-n)\ (b-n)}$$

Where 'n' is the value determined by titration

8.4 Equilibrium Constant, K_p

- K_p is the equilibrium constant in terms of **partial pressures**. It can only be applied to gas reactions.

  $$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

  For the above gas reaction, at equilibrium,

  $$\frac{(p_C)^c.(p_D)^d}{(p_A)^a.(p_B)^b} = \text{a constant, } K_p$$

  where p_A = partial pressure of gas A, etc.

- Like K_c, the value and units for K_p depend on the way in which the chemical equation is written.

Calculate the partial pressures of hydrogen, iodine and hydrogen iodide.

$$P_{H_2} = \frac{n_{H_2}}{n_{gases}} \times P = \frac{(a-c)}{(a-c) + (b-c) + 2c} \times P = \frac{(a-c)}{(a+b)} \times P$$

$$P_{I_2} = \frac{n_{I_2}}{n_{gases}} \times P = \frac{(b-c)}{(a-c) + (b-c) + 2c} \times P = \frac{(b-c)}{(a+b)} \times P$$

$$P_{HI} = \frac{n_{H_I}}{n_{gases}} \times P = \frac{2c}{(a-c) + (b-c) + 2c} \times P = \frac{2c}{(a+b)} \times P$$

$$K_P = \frac{P^2{}_{HI}}{P_{H_2} \times P_{I_2}} \quad \frac{\cancel{atm^2}}{\cancel{atm}.\cancel{atm}.} = \frac{\left(\frac{2c}{a+b} \times P\right)^2}{\left(\frac{a-c}{a+b}\right)P \times \left(\frac{b-c}{a+b}\right)P}$$

$$\therefore K_P = \frac{4c^2}{(a-c)\,(b-c)}$$

where ‘c’ has been determined by titration

- Alternatively, the closed vessel is rapidly cooled down and the vessel is opened under a solution of potassium iodide. The iodine left will dissolve in potassium iodide solution rapidly to form a solution of iodine.

  $$I_2(s) + KI(aq) \rightarrow KI_3(aq)$$
- The aqueous iodine is then titrated with standardized sodium thiosulphate solution, whereby the number of moles of thiosulphate used and hence the number of moles of iodine found in the equilibrium mixture can be calculated and K_p is calculated as above.

8.5 Heterogeneous Equilibria

- Equilibrium reactions in which all the substances are in the same physical state (eg all gases or all liquids), are said to be **homogeneous**. Two examples of homogeneous reaction are:
  (a) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ — all gases;
  (b) $CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l)$ — all liquids
- Equilibrium reactions in which the substances are in *different* physical states (ie a mixture of solid, liquid and/or gas), are said to be **heterogeneous.**
  Two examples of heterogeneous reactions are:
  (a) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ — solid and gas;
  (b) $ICl(l) + Cl_2(g) \rightleftharpoons ICl_3(s)$ — solid, liquid and gas.
- The concentrations of solids are constants. Hence in expressions for K_c and K_p, the convention is to leave out all solids.
  For example,
  (a) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$K_p = p_{CO_2}$

$CaCO_3$ and CaO are left out because they are solid.

(b) $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

$$Kc = \frac{[H_2]^4}{[H_2O]^4}$$

Fe and Fe_3O_4 are left out because they are solid.

8.6 Factors That Affect K_c and K_p

- The equilibrium constants, K_c and K_p are affected by changes in *temperature*.
  The effect of temperature change depends on the enthalpy change of reaction, ΔH.
  For the general reaction

  $A + B \rightleftharpoons C + D$; ΔH = heat change of forward reaction

  (a) If ΔH is negative:
    (i) an increase in temperature makes K_c and K_p smaller;
    (ii) a decrease in temperature makes K_c and K_p larger.

  (b) If ΔH is positive:
    (i) an increase in temperature makes K_c and K_p larger;
    (ii) a decrease in temperature makes K_c and K_p smaller.

- The equilibrium constants, K_c and K_p are *not* affected by:
  (a) changes in concentrations of reactants and products;
  (b) changes in pressure in gaseous reactions;
  (c) presence of catalysts;
  (d) addition or subtraction of a reactant.

8.7 Le Chatelier's Principle

- Le Chatelier's Principle summarises the effect on the composition of an equilibrium mixture when conditions are changed.
- Le Chatelier's Principle states that when a system in equilibrium is disturbed, the equilibrium composition changes so as to remove the disturbance.

Factors that Affect the Composition of the Equilibrium Mixture

Concentration changes

$$A + B \rightleftharpoons C + D$$

- If extra A is added to the equilibrium mixture in the reaction above, then according to Le Chatelier's Principle the equilibrium will shift to remove (some of) the extra A. Hence more A and B react to produce C and D until a new equilibrium is attained. The new equilibrium mixture will contain more C and D but less B.

On the other hand, if some A is removed, then the equilibrium will shift to replace A. Hence more C and D will react to produce A and B in the backward reaction, until a new equilibrium is attained. The new equilibrium mixture will contain less C and D but more B.

Example: $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons \underset{\text{blood-red colour}}{[Fe(SCN)]^{2+}(aq)}$

When extra SCN^- is added to the equilibrium mixture, some of the extra SCN^- reacts with Fe^{3+} to produce more $[Fe(SCN)]^{2+}$. The solution becomes redder.

However, if some SCN^- or Fe^{3+} is removed, then more $[Fe(SCN)]^{2+}$ will be converted back to SCN^- and Fe^{3+} in the backward reaction. The solution becomes pale red.

Temperature changes

- If the temperature is increased, heat is added to the equilibrium mixture. By Le Chatelier's Principle, the equilibrium will shift to remove (some of) the extra heat.

  If the temperature is decreased, the equilibrium will shift to produce heat.

  (a) $A + B \rightleftharpoons C + D$; ΔH = endothermic (+)

  If the temperature of the equilibrium is increased, the endothermic (or heat absorbing) reaction will be favoured, so as to remove some of the extra heat. Thus the composition of the equilibrium mixture will change. The new mixture will have more C and D but less A and B in the reaction above.

  If the temperature is decreased, the exothermic reaction will be favoured. This is the backward reaction (from right to left) in the reaction above. The new equilibrium will have more A and B but less C and D.

  (b) $A + B \rightleftharpoons C + D$; ΔH = exothermic (–)

  If the temperature of the equilibrium is increased, the endothermic reaction will be favoured. This is the backward reaction. Therefore the new equilibrium will contain more A and B but less C and D.

  If the temperature is decreased, the forward exothermic reaction will be favoured. The new equilibrium will contain more C and D but less A and B.

Pressure changes

- Pressure changes *only* affect gaseous reactions.
- By Le Chatelier's Principle, if the pressure of an equilibrium mixture is increased, the mixture will try to decrease the pressure. This is done by reducing the number of moles of gas (the pressure of a gas is directly proportional to the number of moles of gas). Hence a new equilibrium will be produced, containing fewer moles of gas. For example,

$$\underbrace{2SO_2(g) + O_2(g)}_{\text{3 moles}} \rightleftharpoons \underbrace{2SO_3(g)}_{\text{2 moles}}$$

In the above reaction, when the forward reaction takes place, 3 moles of gas are changed into 2 moles of gas. Hence there is a decrease in the number of moles of gas.

Thus, when the pressure is increased, more SO_2 and O_2 combine to produce SO_3. The new equilibrium will contain more SO_3 and less SO_2 and O_2.

In a similar way, if the pressure is decreased, more SO_3 changes into SO_2 and O_2 in the backward reaction. This increases the number of moles of gas, which would increase the pressure.

- If there is no change in the number of moles of gas in a gaseous reaction, changes of pressure have *no effect* on the composition of the equilibrium mixture.

For example,

$$\underbrace{2HI(g)}_{\text{2 moles}} \rightleftharpoons \underbrace{H_2(g) + I_2(g)}_{\text{2 moles}}$$

If 2 moles of HI decompose into H_2 and I_2 in the forward reaction, 2 moles of gaseous products are obtained. There is no change in the number of moles of gas, so pressure has no effect on this equilibrium.

Presence of catalysts

- Catalysts have no effect on the composition of an equilibrium mixture.
- Catalysts only increase the rate of reaction so that equilibrium is reached more quickly.

Summary of the Effects on Equilibrium

	effect		
change	**rate of reaction**	**K_c and K_p**	**composition of equilibrium mixture**
addition of catalyst	increased	no change	no change
increase in concentration of reactant	increased	no change	changed
increase in pressure (only for gas reactions)	increased (because concentration is increased)	no change	changed
decrease in pressure (only for gas reactions)	decreased	no change	changed
increase in temperature	increased	changed	changed
decrease in temperature	decreased	changed	changed

Table 8.1

Question The reaction below is carried out at 1000°C to manufacture carbon monoxide and hydrogen gases from steam and coal. Atmospheric pressure is used.

$H_2O(g) + C(s) \rightleftharpoons CO(g) + H_2(g)$; $\Delta H = +131$ kJ

(a) What would be the effect on the amount of CO and H_2 in the equilibrium mixture if the reaction is carried out (i) using a temperature of 500°C and (ii) using a very high pressure.

(b) If extra carbon monoxide were added to the equilibrium mixture, how would this affect the amount of (i) H_2O and (ii) H_2 in the equilibrium mixture?

Answer

(a) (i) By Le Chatelier's Principle, if the temperature is lowered (ie heat is removed), the equilibrium shifts to produce more heat. As the back reaction is exothermic, this reaction would increase to produce a new equilibrium with more H_2O and C, but less CO and H_2.

(ii) By Le Chatelier's Principle, if the pressure is increased the equilibrium will shift to remove gas molecules. In the back reaction, 2 moles of gas (CO and H_2) become 1 mole of gas (H_2O). Hence a new equilibrium will be attained with more $H_2O(g)$ and $C(s)$, but less $CO(g)$ and $H_2(g)$.

(b) By Le Chatelier's Principle, when more CO is added to the equilibrium mixture, the equilibrium shifts to remove (some of) the extra CO. Hence, more CO and H_2 will react together to become H_2O and C. In the new equilibrium, there will be (i) more H_2O and (ii) less H_2.

8.8 Industrial Reactions

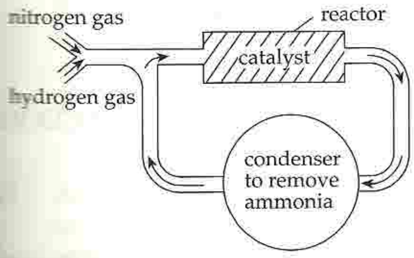
- Many important industrial reactions are reversible reactions.
- Two important principles in industrial reactions are:
  (a) the reaction must take place to produce the required product
  (b) the process must be as cheap as possible.
- The cost can be minimised by:
  (a) using the cheapest reagents (eg air and water);
  (b) making the reaction as rapid as possible (eg by using catalysts);
  (c) avoiding very high temperatures, if possible;
  (d) avoiding very high pressures, if possible.
- The actual conditions chosen in an industrial reversible reaction depend on the particular reaction. However the aim is to produce the maximum amount of product in the minimum amount of time and at the minimum cost.

Haber Process

- Ammonia is manufactured in the **Haber Process**. In the process, hydrogen and nitrogen gases are passed over an iron catalyst. The equation for the reaction is

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g);\ \Delta H^{\ominus} = -184 \text{ kJ}$$

- The conditions of the process are:
  (a) high pressure of 250 atmospheres;
  (b) moderate temperature of about 450°C;
  (c) iron catalyst;
  (d) mole ratio of N_2 to $H_2 = 1 : 3$ (same as the equation).
  The nitrogen is obtained from the air. The hydrogen is obtained from several sources — including petroleum.



▲ Fig 8.4

- An outline of the Haber Process is shown in Fig 8.4. When the mixture of nitrogen and hydrogen is passed over the catalyst, only about 15% of the reactants is converted into ammonia at equilibrium. The ammonia is removed by condensing it to a liquid at a low temperature. The unreacted nitrogen and hydrogen is recycled. It is passed over the catalyst again.
- The iron catalyst is used so that the reacting gases reach equilibrium quickly. The catalyst does not affect the percentage of ammonia in the equilibrium mixture.
- A high pressure is used, because by Le Chatelier's Principle, this produces a larger percentage of ammonia in the equilibrium mixture.
- Theoretically, a large percentage of ammonia would be produced at equilibrium if a low temperature is used. The forward reaction (from left to right) is exothermic. This reaction would be favoured by a low temperature according to Le Chatelier's Principle. However, the reaction would be too slow at low temperatures. Hence, in practice, a moderate temperature is used to speed up the reaction (although the percentage of ammonia produced at equilibrium is reduced).

EXERCISE 8

Multiple Choice Questions

Section I

1 Hydrogen iodide dissociates according to the equation:

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

0.2 mole of gaseous hydrogen iodide was placed in a 200 cm³ flask. At equilibrium, it was found that 20% of the hydrogen iodide had dissociated. What is the equilibrium constant, K_c, for the reaction?

A $\frac{1}{4}$

B $\frac{1}{8}$

C $\frac{1}{16}$

D $\frac{1}{64}$

2 Which one of the following equilibrium mixtures will not be affected by a change in pressure?

A $CH_3CH_2CH_2OH(g) \rightleftharpoons CH_3CHCH_2(g) + H_2O(g)$
B $BaCO_3(s) \rightleftharpoons BaO(s) + CO_2(g)$
C $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$
D $O_2(g) + 2Hg(l) \rightleftharpoons 2HgO(s)$

3 In an experiment, *a* moles of A placed in a flask underwent a reaction to produce B:

$$A(g) \rightleftharpoons 2B(g)$$

At equilibrium, *x* moles of A had reacted and the total pressure in the flask was *P*. What was the partial pressure of B at equilibrium?

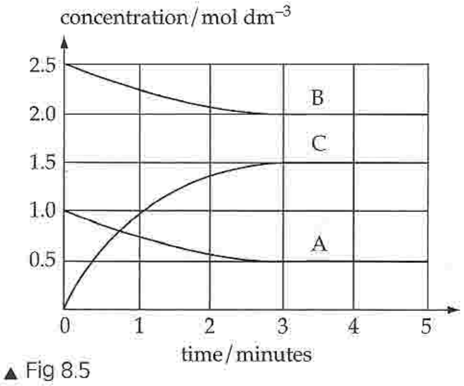
A $\dfrac{2xP}{(a+x)}$ **C** $\dfrac{2xP}{(a-x)}$
B $\dfrac{xP}{(a+x)}$ **D** $\dfrac{xP}{(a-x)}$

4 For which one of the following equilibria, does the equilibrium constant K_c have no units?

A $N_2O_5(g) \rightleftharpoons N_2O_4(g) + \frac{1}{2}O_2(g)$
B $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
C $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$
D $BaCO_3(s) \rightleftharpoons BaO(s) + CO_2(g)$

5 Quantities of substances A and B were placed in a reaction flask. A and B reacted together, according to the equation:

$$A(g) + B(g) \rightleftharpoons 3C(g)$$



▲ Fig 8.5

Fig 8.5 shows the variation in concentrations of A, B and C in the reaction flask with time. The value of the equilibrium constant, K_c, is

A $\dfrac{9}{2}$ **C** $\dfrac{8}{27}$
B $\dfrac{27}{8}$ **D** $\dfrac{2}{9}$

6 If a quantity of $^2H_2$ were added to an equilibrium mixture represented by the equation:

$$^1H_2(g) + I_2(g) \rightleftharpoons 2\,^1HI(g),$$

how many different molecules containing hydrogen would be present at equilibrium?

A 3 **C** 5
B 4 **D** 6

7 The equations below represent five equilibrium reactions under standard state conditions. Which reaction could have an equilibrium constant with units of dm^3 mol^{-1}?

A $CH_4 + H_2O \rightleftharpoons CO + 3H_2$
B $C_2H_5Br + Cl^- \rightleftharpoons C_2H_5Cl + Br^-$
C $H_2O + CH_3COOC_2H_5 \rightleftharpoons C_2H_5OH + CH_3COOH$
D $2NO_2 \rightleftharpoons N_2O_4$

8 $$2P(g) \rightleftharpoons Q(g) + 2R(g)$$

The units of K_c for the above equilibrium reaction are

A dm^6 mol^{-2} **C** mol dm^{-3}
B dm^3 mol^{-1} **D** mol^2 dm^{-6}

9 $$Ag_2CO_3(s) \rightleftharpoons Ag_2O(s) + CO_2(g)$$

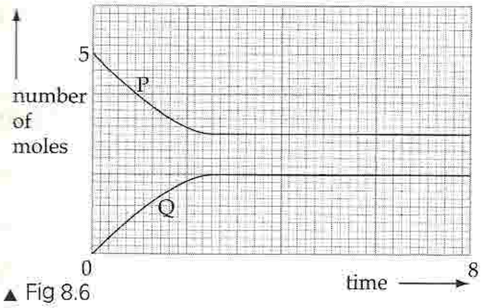
The equilibrium constant K_p for the reaction above is 1.5×10^{-1} kPa at 25°C and $3.2 \times 10^{\text{[illegible]}}$ kPa at 250°C. Which statement is correct?

A The value of K_p depends on the amount of Ag_2CO_3 used.
B The amount of CO_2 at equilibrium is larger at higher pressure.
C The forward reaction is endothermic.
D The value of ΔH for the forward reaction is almost zero.

10 Compound P decomposes according to the equation:

$$P(g) \rightleftharpoons Q(g) + R(g);\ \Delta H = \text{positive}$$

In an experiment, a quantity of P was decomposed under certain conditions inside a closed container and the results shown in Fig 8.6 were obtained.



▲ Fig 8.6

What happened in the reaction when the graphs became horizontal?

A Compound P was used up.

B The reaction stopped.

C The concentrations of P and Q had become equal.

D Rate of the forward reaction had become equal to rate of the backward reaction.

11 A mixture of nitrogen and hydrogen in the mole ratio 1 : 3 reacted according to the equation:

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

At equilibrium, 50% of the nitrogen had reacted and the total pressure was p. What was the partial pressure of the ammonia in the equilibrium mixtures?

A $\frac{1}{4}p$ **C** $\frac{1}{2}p$

B $\frac{1}{3}p$ **D** $\frac{2}{7}p$

12 The equilibrium constant K_p for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

is 40 at 100 kPa pressure and at a certain temperature. What is the value of K_p at 200 kPa pressure at the same temperature?

A 20 **C** 80

B 40 **D** 160

Section II

Summary of directions

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

13 The equilibrium constant K_p for a gaseous reaction is affected by

1 temperature.

2 the number of moles of gas.

3 the overall pressure.

14 The yield of C in the reaction

$$A(aq) + B(aq) \rightleftharpoons C(aq) + D(aq); \Delta H = \text{positive}$$

starting from a fixed amount of A, can be increased by

1 increasing the temperature.

2 removing D.

3 adding extra B.

15 $$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

ΔH is negative for the above reaction. Which of the following would *decrease* the *equilibrium constant*?

1 Raising the temperature

2 Increasing the pressure at constant temperature

3 Using a catalyst

16 Three reversible reactions are given below. For each reaction, a change in condition is stated. In which reactions will the change in condition produce an increase in the amount of products at equilibrium? All substances are gaseous.

	reaction	**change in condition**
1	$N_2O_4 \rightleftharpoons 2NO_2; \Delta H = +57.2$ kJ	temperature increased
2	$H_2 + I_2 \rightleftharpoons 2HI; \Delta H = +53.0$ kJ	pressure increased
3	$N_2 + 3H_2 \rightleftharpoons 2NH_3;$ $\Delta H = -92.0$ kJ	catalyst added

17 A mixture of carbon monoxide and hydrogen is an industrial fuel that can be produced according the following equation.

$$C(c) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

The production of carbon monoxide and hydrogen is endothermic. Which changes will produce more hydrogen in the equilibrium mixture?

1 increasing the temperature

2 increasing the pressure

3 adding more carbon

Structured Questions

1 The equation below shows the dynamic equilibrium between dinitrogen tetroxide, N_2O_4, and nitrogen dioxide, NO_2.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

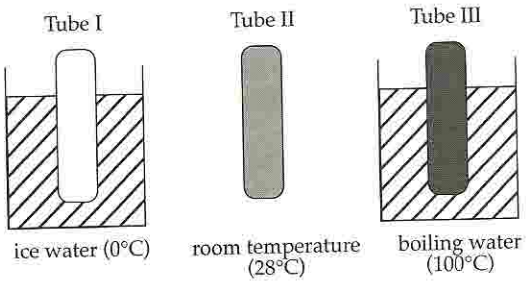
pale yellow   dark brown

(a) What is meant by the term dynamic equilibrium?

(b) (i) What would you expect to observe in the equilibrium mixture if the equilibrium shifted to the left?

(ii) What effect, if any, would an increase in pressure have on the composition of the equilibrium mixture?

(c) Figure 8.7 shows what happens when three identical sealed glass tubes containing a mixture of N_2O_4 and NO_2 are kept at different temperatures.



▲ Fig 8.7

Explain whether the forward reaction is exothermic or endothermic.

(d) The partial pressures of the gases in one of the tubes are given.

D	*partial pressure / Pa*
N_2O_4	0.42
NO_2	4.4

(i) Write an expression for the equlibrium constant, K_p, for the reaction.

(ii) Use the data from the table to calculate the value of K_p at the temperature of the tube. State the units.

2 (a) Each equation in the table shows a reversible gaseous reaction. What will be the effect of *increasing the pressure* on the amount of products obtained at equilibrium in each reaction?

Write *decrease, increase* or *no change* space provided.

reaction	amount of product(s equilibrium
$A \rightleftharpoons 2B$	
$A + B \rightleftharpoons 2C$	
$4A + 5B \rightleftharpoons 4C + 6D$	
$3A + B \rightleftharpoons 2C$	

(b) $A + B \rightleftharpoons C + D$; ΔH = endothermic
For the above reaction, what will be effect on the amounts of C and D in equilibrium mixture, if the temperature reduced?

(c) Give an example of a reaction in which substances react according to the equatio

$$3A + B \rightleftharpoons 2C$$

Give the names or formulae of A, B and C

3 $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$; $\Delta H = +180$ kJ

The equilibrium constant for the reaction above is 6.2×10^{-4} at 2000°C.

(a) (i) Write down an expression for K_c for this equilibrium.

(ii) A 25 dm^3 flask contains 0.27 mole of N_2, 0.001 mole of NO and x moles of O_2 at equilibrium. Calculate the value of x.

(b) What will happen to the composition of the equilibrium mixture in (a) if

(i) the temperature is reduced to 1500°C?

(ii) the pressure is doubled by adding helium gas to the flask?

4 Ethanol and propanoic acid react according to the equation:

$$CH_3CH_2OH(l) + CH_3CH_2COOH(l) \rightleftharpoons CH_3CH_2COOCH_2CH_3(l) + H_2O(l)$$

In an experiment, 0.500 mole each of ethanol and propanoic acid were mixed together in a sealed flask for several weeks. At the end of this time, the propanoic acid remaining required 200 cm^3 of 1.00 mol dm^{-3} NaOH for reaction.

(a) (i) How many moles of NaOH were used in the reaction?

(ii) How many moles of propanoic acid remained in the flask?

(iii) How many moles of ethanol remained in the flask?

(iv) How many moles of ethyl propanoate were produced in the reaction?

(v) How many moles of H_2O were produced in the reaction?

(b) (i) Write an expression for K_c.

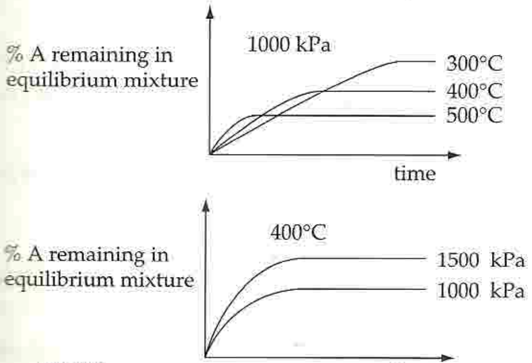
(ii) Hence, calculate the apparent equilibrium constant, K_c, for the reaction.

(c) The real value of K_c at the temperature of the experiment, is 7.5.

(i) Suggest an explanation for the difference between the real value of K_c and the experimental value.

(ii) How could you modify the experiment to obtain the real value of K_c?

5 The graphs in Fig 8.8 show the effects of temperature and pressure on the decomposition of substance **A** into two products, **B** and **C**. All three substances are gaseous.



▲ Fig 8.8

(a) From the graphs, what is the effect of

(i) pressure on the percentage of **B** and **C** in the equilibrium mixture?

(ii) temperature on the percentage of **B** and **C** in the equilibrium mixture?

(b) Is the decomposition of **A**, exothermic or endothermic? Explain your answer.

(c) Explain why the graphs in Fig 8.8 show that the reaction *cannot* be

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

(d) In an industrial process, **B** and **C** are reacted together to produce substance **A**.

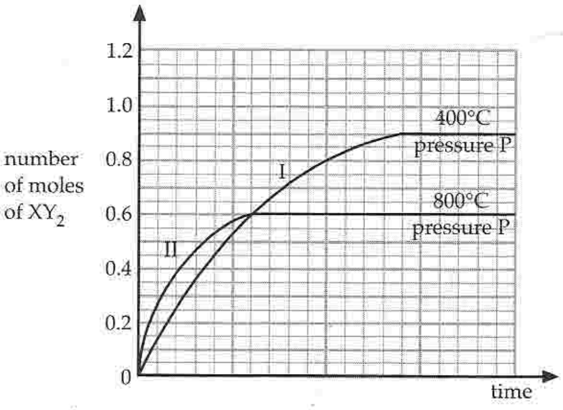
(i) Would 300°C or 500°C be more suitable for the process? Explain your answer.

(ii) Why would a temperature well below 300°C be unsuitable for the process?

6 A gas XY_2 is obtained by the reaction:

$$X_2(g) + 2Y_2(g) \rightleftharpoons 2XY_2(g)$$

In an experiment, 1.00 mole each of X_2 and Y_2 were mixed together at constant pressure P and temperature 400°C. The amount of XY_2 present in the mixture at intervals of time, was recorded. The experiment was repeated at the same pressure P, but at a temperature of 800°C. The results for both experiments are shown in Fig 8.9.



▲ Fig 8.9

(a) Why is the *initial* gradient of curve II larger than that of curve I?

(b) What conclusion can be made about each mixture when the number of moles of XY_2 becomes constant in each experiment (ie the graphs become horizontal)?

(c) What deduction can be made from the graphs about the enthalpy change of the forward reaction?

(d) Sketch on Fig 8.9 the graph you would expect if a third experiment were carried out at 400°C, in which the pressure was greater than P. Label the graph 'III'.

(e) For the experiment at 800°C (ie curve II) what are the partial pressures at equilibrium of

(i) XY_2,

(ii) X_2, and

(iii) Y_2?

(f) If the value of P is 200 kPa, what is the value of the equilibrium constant, K_p, for the reaction? Give the units and show your working.

Descriptive Questions

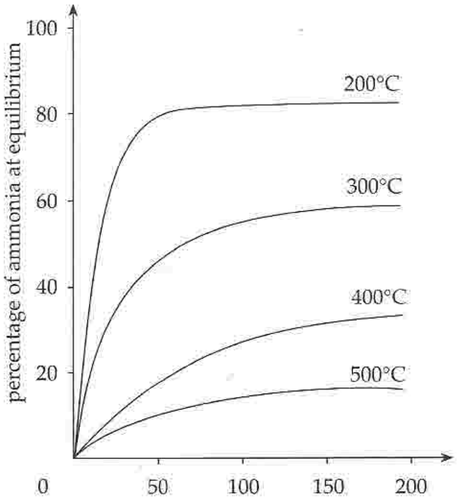
1 The Haber Process for the production of ammonia from its elements can be represented by the equation:

$$3H_2 + N_2 \rightleftharpoons 2NH_3$$

In the process, a mixture of nitrogen and hydrogen is passed over a catalyst. The ammonia is removed from the products and the unreacted gases passed through the reaction vessel again. From time to time, argon gas is removed from the reaction vessel (where it accumulates).

(a) (i) State the catalyst normally used in the Haber Process.
(ii) What are the sources of the nitrogen and hydrogen?
(iii) Suggest where the argon comes from.
(iv) Why is the ammonia removed from the products before passing the unreacted nitrogen and hydrogen over the catalyst again?

(b) Fig 8.10 shows the percentage of ammonia in the equilibrium mixture under different conditions.



▲ Fig 8.10

(i) Which temperature, 200°C or 500°C, produces a larger percentage of ammonia in the equilibrium mixture? State one disadvantage of using a temperature well below 500°C.
(ii) Which pressure, 50 or 150 atmospheres, produces a larger percentage of ammonia in the equilibrium mixture? State one disadvantage of using a pressure greater than 200 atmospheres.

2 Methanol can be manufactured by the following reaction.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g);$$
$$\Delta H = -92.5 \text{ kJ mol}$$

In industrial process, the mixture of CO and H_2 is passed over a ZnO/Cr_2O_3 catalyst at a temperature of 300°C and a pressure of 3 atmospheres.

(a) Write an expression for K_c for the reaction and state the units.
(b) In the reaction, what conditions of
(i) temperature, and
(ii) pressure are required to produce the maximum amount of CH_3OH at equilibrium? Explain your answers.
(c) 300°C is a moderate temperature for an industrial reaction.
(i) Suggest one disadvantage of using a very low temperature (below 100°C).
(ii) Use your answers from (b)(i) and (c) to explain the choice of 300°C for the reaction.
(d) Excess hydrogen is often used in the industrial reaction. Suggest one advantage of this.

3. (a) State 'LeChatelier's Principle'.
(b) Consider the following reversible reactions which are in dynamic equilibrium.

I $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92 \text{ KJmol}^{-1}$

II $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

III $Cr_2O_7^{2-}(aq) + H_2O(l) \rightleftharpoons 2CrO_4^{2-}(aq) + 2H^+(aq)$

Use Le Chatelier's Principle to predict and explain the effect of

(i) increasing the temperature on equilibrium I
(ii) increasing the pressure on equilibrium II
(iii) lowering the pH on equilibrium III
(iv) add some nitrogen to the equilibrium I

(c) Write an expression for the equilibrium constant for the reaction

$$N_2 + 2O_2 \rightleftharpoons 2NO_2$$

(d) At a certain temperature the value of the equilibrium constant for the above reaction is 80 $mol^{-1}dm^3$.

Calculate the value for the equilibrium constant for each of the reactions below

(i) $2NO_2 \rightleftharpoons N_2 + 2O_2$
(ii) $NO_2 \rightleftharpoons \frac{1}{2}N_2 + O_2$

4 When an alcohol reacts with an organic acid, an ester is produced.

(a) Write an equation for the reaction between ethane-1,2-diol and ethanoic acid.

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

(c) 6.20 g of ethane-1,2-diol was added to 6.00g of ethanoic acid.The mixture was shaken vigorously and allowed to stand for a few days . The resulting mixture was titrated rapidly with $1.00 moldm^{-3}$ sodium hydroxide.It was found that $30 cm^3$ of sodium hydroxide was required to neutralize the acid left at equilibrium.

(i) Suggest a suitable indicator for the titration.

(ii) Calculate the number of moles of sodium hydroxide used during the titration.

(iii) Deduce the number of moles of ethanoic found in the equilibrium mixture before titration.

(iv) Deduce the number of moles of ethane-1,2-diol found in the equilibrium mixture.

(v) Deduce the number of moles of water and ester found in the equilibrium mixture.

(vi) Hence calculate the equilibrium constant for the reaction between ethane-1,2-diol and ethanoic acid.

5 (a) The equilibrium constant , K_p for the reaction

$$N_2O_4 \rightleftharpoons 2NO_2$$

at 70 °C is 0.67.

If at 70 °C,the total pressure of the equilibrium mixture is 0.5 atmosphere, calculate

(i) the degree of dissociation of N_2O_4
(ii) the partial pressure of N_2O_4
(iii) the partial pressure of NO_2

(b) Describe briefly how the equilibrium constant for the reaction

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

may be determined experimentally.

CHAPTER

9

IONIC EQUILIBRIA

SYLLABUS OBJECTIVES

In this chapter you should be able to:

- understand and use the Bronsted-Lowry theory of acids and bases
- explain qualitatively the differences between strong and weak acids and bases
- explain the terms *pH*, K_a, pK_a and K_w and use them in calculations
- calculate $[H^+(aq)]$ and pH values for strong and weak acids and for strong bases
- describe the changes in pH during acid-base titrations and explain these changes in terms of the strengths of the acids and bases
- explain the choice of suitable indicators for acid-base titrations, given appropriate data (eg choose a suitable indicator from its pH range and by referring to the pH/volume graph of a titration)
- explain how buffer solutions control pH
- calculate the pH of buffer solutions
- describe and explain the uses of some buffer solutions, including the use of HCO_3^- in controlling the pH of blood
- understand and use the solubility product term, K_{sp}
- calculate K_{sp} from concentrations and *vice versa*
- understand the common ion effect

9.1 Acids and Bases

The Bronsted-Lowry Theory

- According to the Bronsted-Lowry theory of acids and bases:
  - (a) An **acid** is a substance that gives protons (hydrogen ions, H^+) to another substance. An acid is described as a **proton donor**.
  - (b) A **base** is a substance that takes a proton from another substance. A base is described as a **proton acceptor**.
- An acid always reacts with a base. The substance that loses the proton is the acid. The substance that gains the proton is the base.
- Examples of acid-base reactions:
  - (a) $HCl + H_2O$: Hydrogen chloride dissolves in water according to the equation

$$\underset{\curvearrowright\, H^+}{HCl + H_2O} \rightarrow H_3O^+ + Cl^-$$

The HCl is the acid as it gives H^+ to the water molecule. The H_2O molecule is the base because it accepts the H^+ ion.

  - (b) $NH_3 + HCl$: Hydrogen chloride gas reacts with ammonia gas to produce solid ammonium chloride. The equation for the reaction is

$$\underset{\curvearrowleft\, H^+}{NH_3(g) + HCl(g)} \rightarrow NH_4^+Cl^-(s)$$

The HCl is the acid because it gives H^+ to the NH_3 molecule. The NH_3 is the base because it accepts H^+ to become NH_4^+.

  - (c) $H_2O + CO_3^{2-}$: Sodium carbonate solution is alkaline. The carbonate ions react with the water. The equation is

$$\underset{\curvearrowright\, H^+}{H_2O + CO_3^{2-}} \rightarrow OH^- + HCO_3^-$$

The H_2O is the acid because it gives H^+ to the CO_3^{2-} ion. The CO_3^{2-} ion is the base because it accepts H^+ to become HCO_3^-.

- Acids can be classified into **weak acids** and **strong acids**.
  - (a) When a strong acid dissolves in water, virtually all the acid molecules react with the water to produce H_3O^+ ions. Examples of strong acids are HCl, HNO_3 and H_2SO_4.
  - (b) When a weak acid dissolves in water, only a *small fraction* of the acid molecules react with the water to produce H_3O^+ ions. Most of the acid molecules remain as molecules.

    An example of a weak acid is ethanoic acid. Ethanoic acid reacts with water according to the equation

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

Most of the CH_3COOH molecules remain unchanged in the water. In a 1.0 mol dm^{-3} solution of CH_3COOH, only about out of every 1000 CH_3COOH molecules react with water to become H_3O^+.

(c) Solutions of strong acids are good electrical conductors because they contain large concentrations of ions.

(d) Solutions of weak acids are poor electrical conductors because they contain small concentrations of ions.

- Bases can be classified into **weak bases** and **strong bases**.
  - (a) When a strong base dissolves in water, virtually all the base reacts with the water to produce OH^- ions. Examples of strong bases are NaOH and KOH.
  - (b) When a weak base dissolves in water, only a small fraction of the base molecules react with the water to produce OH^- ions. Most of the base molecules remain as molecules.

    An example of a weak base is ammonia, NH_3. Ammonia reacts with water according to the equation

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

In a 1.0 mol dm^{-3} solution of aqueous NH_3, only about 4 of every 1000 NH_3 molecules react with water to produce OH^-

Conjugate acids and conjugate bases

- According to Bronsted-Lowry theory, an acid is a proton donor and a base is a proton acceptor.
- Consider the reaction between sodium phenoxide solution and solution of ethanoic acid:

  $C_6H_5O^- + CH_3CO_2H \rightleftharpoons C_6H_5OH + CH_3CO_2^-$ $K_c = 1.3 \times 10^6$ moldm

In this reaction:-

a) in the forward reaction, the ethanoic acid is giving away a proton to the phenoxide ion. Hence the ethanoic acid is acting as the acid whereas the phenoxide ion is acting as a base.

b) but in the backward reaction , the phenol gives away a proton to the ethanoate ion. Hence in the backward reaction the phenol is acting as the acid and the ethanoate ion is acting as a base.

- Therefore we can deduce that when ethanoic acid gives ay a proton, the remaining ion will act as a base. The ethanoate ion will be referred to as the conjugate base of the acid. Ethanoic acid and the ethanoate ion will be referred to as a conjugate acid-base pair.
- When the phenoxide ion accepts a proton, it is converted into phenol , an acid. Phenol will be referred to as the conjugate acid of the base. Phenol and the phenoxide ion will form a conjugate acid- base pair.
- Therefore in the above equations there are two acids-ethanoic acid and phenol- and two bases-phenoxide and ethanoate ions. To determine which of the two acids and which of the two bases are the stronger and in which direction the reaction occurs preferentially the equilibrium constant, K_c for the reaction must be considered.
- For the above reaction, K_c is much greater than 1. This implies that
  - a) the forward reaction will occur to a larger extent
  - a) ethanoic acid is a stronger acid than phenol
  - b) phenoxide ion is a stronger base than ethanoate ion.

The pH Scale

- pH is a measure of the *concentration of hydrogen ions*, $H^+(aq)$, in an aqueous solution.
- The pH of a solution is the negative log to base 10 of the concentration of hydrogen ion in the solution.

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

where $[H^+]$ = concentration of hydrogen ions

- In most aqueous solutions, the pH is a number between 0 and 14.
  Dilute HCl (2 mol dm^{-3}) has a pH of about 0.
  Dilute NaOH (2 mol dm^{-3}) has a pH of about 14.

Question Calculate the pH of:
(a) a solution where concentration of hydrogen ions = 3.5×10^{-3} mol dm^{-3} and
(b) 0.01 mol dm^{-3} HCl(aq).

Answer
(a) $pH = -\log(3.5 \times 10^{-3}) = 2.46$
(b) HCl is a strong acid. Hence all the HCl reacts with water according to the equation

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

Each HCl molecule produces one $H^+(aq)$ ion.
Hence, the concentration of $H^+(aq)$ = 0.01 mol dm^{-3}.
Hence, $pH = -\log(0.01) = 2.0$

Question The pH of a solution of hydrochloric acid is 3.30. Calculate the concentration of hydrogen ions.

Answer Concentration of hydrogen ions = antilog(−3.30)
= 5.01×10^{-4} mol dm^{-3}

9.2 Ionic Product of Water

- Water is slightly ionised, according to the equation

$$H_2O \rightleftharpoons H^+ + OH^-$$

- The equilibrium constant K_c for the ionisation of water is

$$K_c = \frac{[H^+].[OH^-]}{[H_2O]}$$

The degree of ionisation of water is very small. Hence the concentra of water, $[H_2O]$, remains virtually constant.

Hence $$[H^+].[OH^-] = K_c \times [H_2O] = \text{constant} = K_w$$

The constant K_w is called the **ionic product of water**. At 25°C, $K_w = 1.0 \times 10^{-14}$ mol² dm⁻⁶.

- In pure water at 25°C, $[H^+] = [OH^-]$.

  Hence $$[H^+] = [OH^-] = (1.0 \times 10^{-14})^{\frac{1}{2}} = 1.0 \times 10^{-7} \text{ mol dm}^{-3}$$

  Therefore the pH of pure water = $-\log(10^{-7}) = 7.0$.

- In all aqueous solutions,

  $$[H^+].[OH^-] = \text{constant} = K_w$$

  Hence if $[H^+]$ becomes larger, $[OH^-]$ becomes smaller, and if [H becomes smaller, $[OH^-]$ becomes larger.

Question

Given a 2.0×10^{-3} mol dm⁻³ solution of HCl, calculate
(a) the concentration of $H^+(aq)$;
(b) the concentration of $OH^-(aq)$;
(c) the pH of the solution.
[$K_w = 1.0 \times 10^{-14}$ mol² dm⁻⁶]

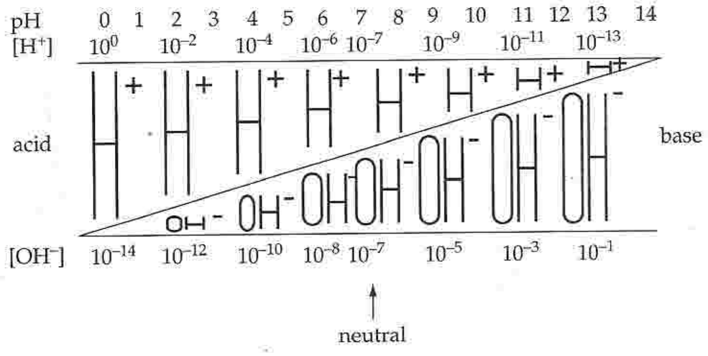
Answer

(a) As the acid is fully ionised,
$[H^+] = 2.0 \times 10^{-3}$ mol dm⁻³

(b) $$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-3}} = 5.0 \times 10^{-12} \text{ mol dm}^{-3}$$

(c) $$\text{pH} = -\log[H^+] = -\log(2.0 \times 10^{-3}) = 2.70$$

- The relationship between pH, $[H^+]$ and $[OH^-]$ is shown in Fig 9.1.



▶ Fig 9.1

- A solution is said to be *neutral* when $[H^+] = [OH^-]$. At 25°C, this occurs at a pH of 7.0.

- K_w varies with temperature. The value of K_w increases with temperature because the ionisation of water is endothermic.

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq); \quad \Delta H = \text{positive}$$

At 0°C, $K_w = 0.1 \times 10^{-14}$ mol^2 dm^{-6}. Hence a neutral solution at 0°C has a pH of 7.5.
At 100°C, $K_w = 51 \times 10^{-14}$ mol^2 dm^{-6}. Hence, $[H^+] = (51 \times 10^{-14})^{\frac{1}{2}}$

$$\text{pH} = -\log (51 \times 10^{-14})^{\frac{1}{2}}$$
$$= 6.1$$

Hence a neutral solution at 100°C has a pH of 6.1.

pH of Weak and Strong Acids and Bases

- When comparing acids of equal concentration, a strong acid has a lower pH than a weak acid. For example, 0.1 mol dm^{-3} HCl has a pH of 1 and 0.1 mol dm^{-3} CH_3COOH has a pH of 3.

9.3 Acid Dissociation Constant, K_a

- Comparing bases of equal concentration, a strong base has a higher pH than a weak base. For example, 0.1 mol dm^{-3} NaOH has a pH of 13 and 0.1 mol dm^{-3} NH_3 has a pH of 11.

- A weak acid, HA, reacts with water according to the equation

$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

At equilibrium,

$$\frac{[H^+].[A^-]}{[HA]} = \text{constant}, K_a$$

The constant K_a is called the **acid dissociation constant**. The units of K_a are mol dm^{-3}.
For example, K_a for ethanoic acid = 1.76×10^{-5} mol dm^{-3}.

- The acid dissociation constant is a measure of the *strength* of acids. The *larger* the value of K_a, the *stronger* the acid.
- A more convenient way of expressing the acid dissociation constant is pK_a.

$$pK_a = -\log K_a$$

For example, K_a for ethanoic acid = 1.76×10^{-5} mol dm^{-3}
Hence $pK_a = -\log(1.76 \times 10^{-5})$
$= 4.75$

- pK_a is a measure of the strength of acids. The *smaller* the value of pK_a, the *stronger* the acid.

- Some examples of K_a and pK_a values for acids are shown in Table 9.1.

acid	K_a	pK_a	relative strength
CH_3COOH	1.8×10^{-5}	4.7	acid becomes stronger ↓
C_6H_5COOH	6.5×10^{-5}	4.2	
$HCOOH$	1.8×10^{-4}	3.7	
$ClCH_2COOH$	1.5×10^{-3}	2.8	

▶ Table 9.1

Question

K_a for a weak monobasic acid = 1.0×10^{-5} mol dm^{-3}. In a 0.1 mol dm^{-3} solution of the acid, calculate

(a) the concentration of $H^+(aq)$ ions;

(b) the pH and

(c) the concentration of $OH^-(aq)$ ions.

[$K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6}]

Answer

(a) The acid ionises in water according to the equation

$$HA \rightleftharpoons H^+ + A^-$$

Hence $K_a = \frac{[H^+].[A^-]}{[HA]}$

Each HA molecule produces one H^+ and one A^-.

Hence $[H^+] = [A^-]$ in the solution.

We have $[H^+]^2 = [HA].K_a$

$$[H^+] = ([HA].K_a)^{\frac{1}{2}} = (0.1 \times 1.0 \times 10^{-5})^{\frac{1}{2}}$$
$$= 1.0 \times 10^{-3} \text{ mol dm}^{-3}$$

(b) $pH = -\log(1.0 \times 10^{-3}) = 3.0$

(c) $K_w = [H^+].[OH^-]$

Hence $[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-3}}$

$$= 1.0 \times 10^{-11} \text{ mol dm}^{-3}$$

Question

A 0.1 mol dm^{-3} solution of a weak monobasic acid has a pH of 4.0. Calculate (a) K_a and (b) pK_a for the acid.

Answer

$$HA \rightleftharpoons H^+ + A^-$$

$[H^+] = 1 \times 10^{-4}$ mol dm^{-3} (because pH = 4.0)

$[A^-] = [H^+] = 10^{-4}$ mol dm^{-3}

$[HA] = 0.1$ mol dm^{-3}

(a) $K_a = \frac{[H^+].[A^-]}{[HA]} = \frac{10^{-4} \times 10^{-4}}{0.1} = 1 \times 10^{-7}$ mol dm^{-3}

(b) $pK_a = -\log(1 \times 10^{-7}) = 7$

Question The acid dissociation constant, K_a, for methanoic acid is 1.8×10^{-4} mol dm^{-3}. In a 0.1 mol dm^{-3} solution of methanoic acid, calculate

(a) the concentration of hydrogen ions;
(b) the pH;
(c) the concentration of hydroxide ions;
(d) the degree of ionisation of the acid.

[$K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6}]

Answer (a) $HCOOH \rightleftharpoons HCOO^- + H^+$

$$K_a = \frac{[HCOO^-].[H^+]}{[HCOOH]}$$

$[H^+] = [HCOO^-]$

$[HCOOH] = 0.1$ mol dm^{-3} (assuming that the degree of ionisation is very small)

Hence $[H^+] = (K_a \times [HCOOH])^{\frac{1}{2}}$

$= (1.8 \times 10^{-4} \times 0.1)^{\frac{1}{2}}$

$= 4.2 \times 10^{-3}$ mol dm^{-3}

Answer (b) pH $= -\log(4.2 \times 10^{-3}) = 2.4$

(c) $[OH^-] = \frac{K_w}{[H^+]} = 2.38 \times 10^{-12}$ mol dm^{-3}

(d) The degree of ionisation = the fraction of HCOOH molecules that have ionised in solution.

$$\text{Degree of ionisation} = \frac{[H^+]}{\text{initial }[HCOOH]} = \frac{4.2 \times 10^{-3}}{0.1} = 0.042$$

The base dissociation constant, K_b

- When a weak base is in water, it ionizes slightly and it produces the OH^- ion(hydroxide ion). For example when ammonia dissolves in water, it produces a small amount of OH- ions.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

The equilibrium constant for the dissociation of a weak base is called the base dissociation constant , K_b .

For the above reaction , K_b can be expressed as follows:-

$$K_b = [NH_4^+][OH^-] \ / \ [NH_3]$$

As ammonia is a weak base, $K_b < 1$. In practice, $K_b = 1.8 \times 10^{-5}$moldm^{-3}

- The value of K_b is a measure of the strength of the weak base. The larger the value of K_b , the stronger the weak base will be.
- Usually instead of K_b, the term pK_b is used.
- The pK_b is the negative log to base 10 of the K_b of the solution.

$$pK_b = -\lg K_b$$

To calculate the pH of a weak base

Question:

The base dissociation constant of methyl amine is 4.17×10^{-4} $moldm^{-3}$. In a 0.01 $moldm^{-3}$ solution of methyl amine, calculate

(a) the concentration of OH-(aq) ions

(b) the pOH

(c) the pH of the solution

[$K_w = 1.00 \times 10^{-14}$ mol^2dm^{-6} at 25 ^0C]

Answer

[a] The base ionises according to the equation

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$$

$$K_b = [CH_3NH_3^+][OH^-]/[CH_3NH_2]$$

$$\text{but } CH_3NH_3^+ = OH^-$$

$$K_b = [OH^-]^2 / [CH_3NH_2]$$

$$[OH^-]^2 = K_b [CH_3NH_2]$$

$$[OH^-] = \sqrt{K_b [CH_3NH_2]}$$

$$\therefore [OH^-] = \sqrt{(4.17 \times 10^{-4} \times 0.01)}$$

$$[OH^-] = 2.04 \times 10^{-3}$$

[b] $pOH = -lg[OH^-]$

$$pOH = -lg\ 2.04 \times 10^{-3} = 2.69$$

[c] $pH + pOH = 14.00$

$$pH = 14.00 - pOH$$

$$pH = 14.00 - 2.69 = 11.31$$

Therefore pH of solution = 11.31

Relation between K_a, K_b and K_w for a substance

- Consider the dissociation of ammonia

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

In this reaction, in the ammonium ion and ammonia form a conjugate acid-base pair

The base dissociation constant for ammonia is expressed as

$$K_b = [NH_4^+][OH^-] / [NH_3] \qquad [1]$$

The ammonium ion is acting as a conjugate acid. Its dissociation may be represented by the equation

$$NH_4^+ \rightleftharpoons NH_3 + H^+$$

The acid dissociation constant for ammonium ion will be

$$K_a = [NH_3][H^+] / [NH_4^+] \qquad [2]$$

Multiplying [1] and [2]

$$K_b \times K_a = ([NH_4^+][OH^-] \;/\; [NH_3])\;([NH_3][H^+] / [NH_4^+])$$
$$K_a \times K_b = [H^+][OH^-] = K_w$$

In general, for any conjugate acid-base pair, the product of the acid dissociation constant and base dissociation constant is equal to the ionic product of water.

$$K_a \times K_b = K_w$$

Question

1. **The ionic product of water at 25 ^{0}C is 1.00x 10^{-14} mol^{2}dm^6. Given that the acid dissociation constant K_a for NH_4^+ ion is 5.70 x 10^{-10} moldm^{-3}, calculate the base dissociation constant, K_b, of ammonia.**

Answer

Using

$K_a(NH_4^+) \times K_b(NH_3) = Kw$

Therefore $K_b(NH_3) = Kw / K_a(NH_4^+)$

$K_b(NH_3) = 1.00\times 10^{-14} \;/\; 5.70 \times 10^{-10} = 1.75 \times 10^{-5}$ moldm^{-3}

& the base dissociation constant, K_b, of ammonia = 1.75 x 10^{-5} moldm^{-3}

9.4 Buffer Solutions

- A buffer solution is a solution whose pH remains *almost unchanged* if a little acid or alkali is added to it.
- Buffer solutions are usually one of two types:
  (a) acidic buffer — made by mixing a weak acid with the sodium salt of the weak acid. For example, a mixture of ethanoic acid and sodium ethanoate;
  (b) alkaline buffer — made by mixing a weak base with the salt of the weak base. For example, a mixture of ammonia and ammonium chloride.
- Buffers work by removing most of the extra acid or alkali added. In that way the pH remains almost unchanged.

Example

In a mixture of ethanoic acid and sodium ethanoate, the sodium ethanoate is completely ionised in water:

$$CH_3COONa(aq) \rightarrow CH_3COO^-(aq) + Na^+(aq)$$

If extra H^+ is now added, it reacts with the large concentration of CH_3COO^- present from the sodium ethanoate:

$$H^+(aq) + CH_3COO^-(aq) \rightarrow CH_3COOH(aq)$$

As CH_3COOH is a weak acid, most of the extra H^+ is removed in the reaction. If extra OH^- is added, it reacts with the large concentration of CH_3COOH present:

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

Thus most of the extra OH^- is removed in the reaction.

Applications of Buffer Solutions

- Buffer solutions are used where it is important to maintain a constant pH in a chemical reaction or experiment. Some examples are given below.

(a) Blood is a buffer. The pH of blood must be kept constant so that the enzymes in the blood can function. Enzymes only work over a narrow range of pH. The most important buffer in blood is the hydrogencarbonate ion, HCO_3^-. The HCO_3^- ion removes extra H^+ by the reversible reaction shown below:

$$HCO_3^- + H^+ \rightleftharpoons H_2O + CO_2$$

This equilibrium lies well to the right (ie it is mainly H_2O and CO_2). If the blood becomes too alkaline (ie H^+ are removed), then more H^+ is produced from the large amount of H_2O and CO_2 present.

(b) Many biochemistry experiments are carried out in a buffer solution, if acid or base is one of the reactants or products. Otherwise, the pH will change and affect the enzymes.

Calculation of pH of Buffer Solutions

- An acidic buffer solution consists of
  - (a) a large concentration of acid, HA (eg ethanoic acid);
  - (b) a large concentration of A^- ions (eg from sodium ethanoate).
- In the mixture,

$$\frac{[H^+].[A^-]}{[HA]}$$

where [HA] = the concentration of the HA acid in the mixture
$[A^-]$ = the concentration of the A^-, from the NaA, in the mixture (the amount of A^- from the HA can be ignored as it is very small)

Hence $[H^+]$ can be calculated if K_a is given.

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

The pH can then be calculated from the $[H^+]$.

Question The acid dissociation constant, K_a, for a weak monobasic acid HA is 1.0×10^{-4} mol dm^{-3}. Calculate the approximate pH of 500 cm^3 of a 0.1 mol dm^{-3} solution of HA, in which 0.05 mole of the sodium salt NaA is dissolved.

Answer For the acid HA,

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

where $[HA] = 0.1$ mol dm^{-3}

$$[A^-] \text{ (from the NaA)} = \frac{\text{no. of moles}}{\text{volume in dm}^3} = \frac{0.05}{0.5} = 0.1 \text{ mol dm}^{-3}$$

$$K_a = \frac{[H^+].0.1}{0.1} \qquad = [H^+] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$$

Hence pH = 4.0

Question Equal volumes of 0.1 mol dm^{-3} $CH_3COOH(aq)$ and 0.2 mol dm^{-3} $CHCOONa(aq)$ were mixed together. Calculate the pH of the mixture.
[K_a for ethanoic acid = 1.8×10^{-5} mol dm^{-3}]

Answer When equal volumes of solutions are mixed, the volume of the solution is doubled. Hence the concentration of each solute is halved in the mixture.

$$[CH_3COOH] \text{ in the mixture } = \frac{1}{2} \times 0.1 \text{ mol dm}^{-3}$$

$$[CH_3COONa] \text{ in the mixture } = \frac{1}{2} \times 0.2 \text{ mol dm}^{-3} = [CH_3COO^-]$$

$$K_a = \frac{[H^+].[CH_3COO^-]}{[CH_3COOH]}$$

$$[H^+] = \frac{K_a \times [CH_3COOH]}{[CH_3COO^-]} = \frac{1.8 \times 10^{-5} \times \frac{1}{2} \times 0.1}{\frac{1}{2} \times 0.2}$$

$$= 9.0 \times 10^{-6} \text{ mol dm}^{-3}$$

Hence pH = 5.0

Buffers and pH Titration Graphs

- A buffer is produced in the titration flask during the titration of a weak acid and a strong base (see *pH Changes in Acid-base Titrations* further on).

9.5 Hydrolysis of Salts

- Salts of strong acids and strong bases form neutral solutions in water, eg sodium chloride.
- Salts of weak acids and strong bases form alkaline solutions in water, eg sodium ethanoate.
  Sodium ethanoate is fully ionised in water:

  $$CH_3COONa(aq) \rightarrow CH_3COO^-(aq) + Na^+(aq)$$

  The CH_3COO^- ions react with the H^+ ions from the water:

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

  Most of the H^+ are removed in the reaction because CH_3COOH is a weak acid. Thus the $[H^+]$ becomes less, and the pH becomes larger than 7. The solution is alkaline.
- Salts of strong acids and weak bases form acidic solutions in water, eg ammonium sulphate.
  Ammonium sulphate is fully ionised in water:

  $$(NH_4)_2SO_4(aq) \rightarrow 2NH_4^+(aq) + SO_4^{2-}(aq)$$

  The NH_4^+ ions react with OH^- ions from the water:

  $$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$$

  Most of the OH^- are removed in the reaction, because NH_3 is a weak base. As OH^- ions are removed, more water ionises to keep K_w constant. Hence the $[H^+]$ becomes larger, and the pH becomes smaller than 7. The solution is acidic.
- Salts of weak acids and weak bases form neutral (or almost neutral) solutions in water, eg ammonium ethanoate.
  Ammonium ethanoate ionises in water:

  $$CH_3COONH_4(aq) \rightarrow CH_3COO^-(aq) + NH_4^+(aq)$$

The CH_3COO^- ions react with H^+ ions from the water to form CH_3COOH. The NH_4^+ ions react with OH^- ions from the water to form NH_3 and H_2O. Thus both H^+ and OH^- are removed from the water. As they are both equally removed, the pH remains the same ie 7. The solution is neutral.

9.6 pH Changes in Acid-Base Titrations

Acid-base Indicators

- Some examples of acid-base indicators are given in Table 9.2.

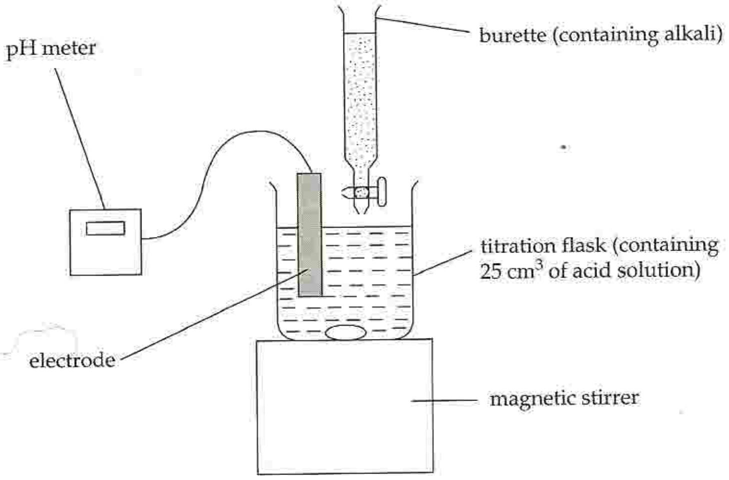
indicator	acid colour	alkaline colour	pH range
methyl orange	pink	yellow	3.1 – 4.4
bromothymol blue	yellow	blue	6.0 – 7.6
phenolphthalein	colourless	red	8.3 – 10.0
thymolphthalein	colourless	blue	8.5 – 10.5

▸ Table 9.2

- An acid-base indicator has an *acid colour* and an *alkaline* or *basic colour*.
- Each indicator has a **pH range** over which it changes colour. For example, bromothymol blue has a pH range of 6.0 – 7.6. From pH 0 to 6, bromothymol blue is yellow in colour (the acid colour) and from pH 7.6 to 14, the indicator is blue in colour (the alkaline colour). But when the pH is 6.0 – 7.6, the bromothymol blue changes colour from yellow to blue. In the middle of this pH range (at about 6.8) the bromothymol blue is green in colour (a mixture of the acid and alkaline colours).
- In titration an acid-base indicator is used to mark the end-point. For an accurate result,
  (a) the indicator must change colour sharply on addition of one or two drops of liquid from the burette;
  (b) the colour change must occur when the correct volume of liquid is added from the burette.

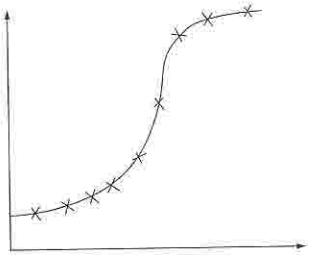
Changes in pH during an Acid-base Titration

- The change in pH during an acid-base titration can be measured using the apparatus shown in Fig 9.2.



▸ Fig 9.2

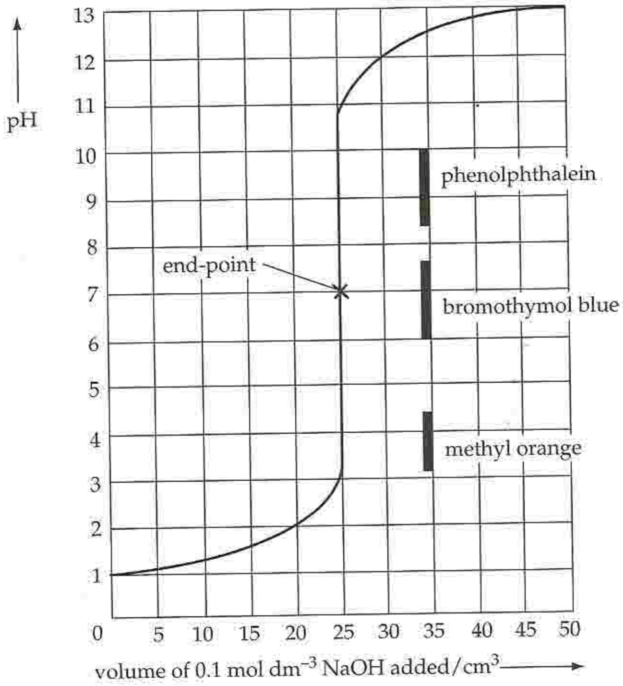
(a) The pH of the solution in the titration flask is measured with a pH meter.
(b) The alkali is added at 0.5 cm^3 intervals and the pH measured. A table of pH against volume of alkali added is then obtained, and a graph drawn (Fig 9.3).



Four Main Types of Acid-base Titrations

Strong acid + strong base

50 cm³ of 0.1 mol dm^{-3} NaOH (a strong base) is added to 25.0 cm³ of 0.1 mol dm^{-3} HCl (a strong acid). The graph of pH against volume of alkali added is shown in Fig 9.4.



▶ Fig 9.4 Strong acid + strong base

The graph has the following features:

(a) The initial pH (before addition of alkali) is about 1 for a 0.1 mol dm^{-3} acid. This shows that a strong acid is used.

(b) The pH after 50 cm³ of alkali has been added is about 13. This shows that a strong base has been added.

(c) At the end-point the solution is neutral (solution of NaCl).

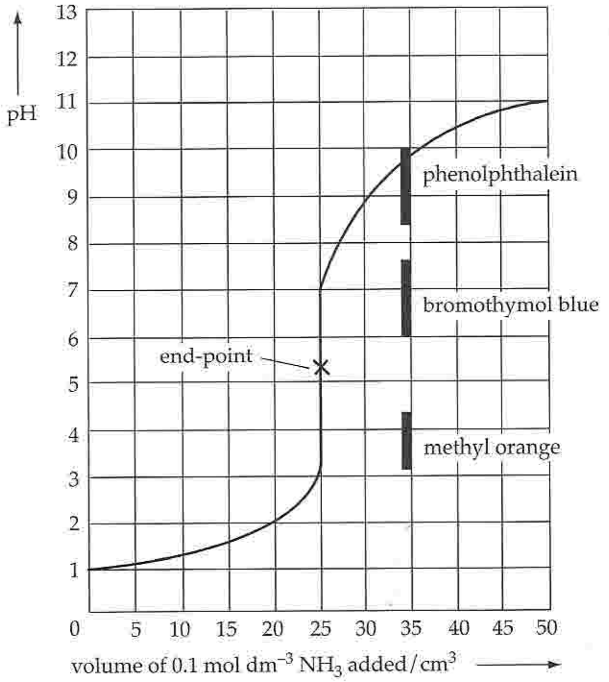
(d) There is a long, straight vertical section over the end-point. This shows that the pH changes sharply, from about 3 to 11, when one or two drops of NaOH are added from the burette at the end-point.

(e) The pH range of three indicators are shown in the graph. The end-point of the titration (at pH = 7) is in the middle of the pH range of bromothymol blue. This indicator will change colour completely when one or two drops of alkali are added at the end-point. Hence bromothymol blue is the ideal indicator for this titration.

However, phenolphthalein and methyl orange can also be used in this titration as they also will change colour completely over the straight vertical section of the graph.

Strong acid + weak base

50 cm^3 of 0.1 mol dm^{-3} NH_3 (a weak base) is added to 25.0 cm^3 of 0.1 mol dm^{-3} HCl (a strong acid). The graph of pH against volume of alkali added is shown in Fig 9.5.



▶ Fig 9.5 Strong acid + weak base

The graph has the following features:

(a) The graph starts at pH = 1 for a 0.1 mol dm^{-3} acid, showing that the acid is strong.

(b) The graph ends at pH = 11, showing that the base is weak.

(c) At the end-point the solution is acidic, with pH ≈ 5.5. This is because the NH_4Cl is hydrolysed, as it is the salt of a weak base and a strong acid (see *hydrolysis of salts* in section 9.5).

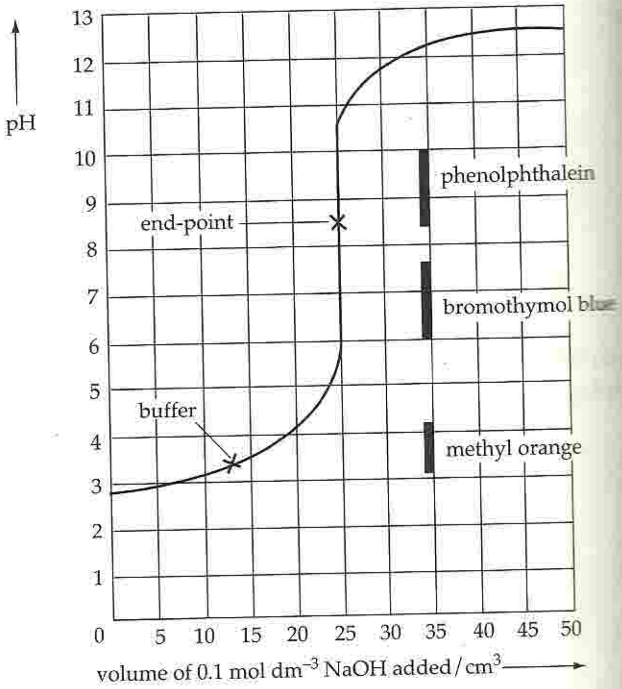
(d) The straight, vertical section of the graph is shorter than that for a titration of a strong acid with a strong base.

(e) Methyl orange is a suitable indicator because it will change colour completely over one or two drops at the end-point (ie at the vertical section).

(f) If phenolphthalein is used as the indicator, it will change colour
  (i) at the wrong volume (ie at about 30 cm^3 of NH_3), and
  (ii) over a large volume of NH_3 solution (ie over 27 – 37 cm^3).
  Hence it would be impossible to find the end-point accurately.

Weak acid + strong base

50 cm^3 of 0.1 mol dm^{-3} NaOH (a strong base) is added to 25.0 cm^3 of 0.1 mol dm^{-3} CH_3COOH (a weak acid). The graph of pH against volume of alkali added is shown in Fig 9.6.



▸ Fig 9.6 Weak acid + strong base

The graph has the following features:

(a) The graph starts at pH ≈ 3 for a 0.1 mol dm^{-3} acid, showing that the acid is weak.

(b) The graph ends at pH ≈ 13, showing that the base is strong.

(c) At the end-point the solution is alkaline, with pH ≈ 8.5. This is because the CH_3COONa is hydrolysed, as it is the salt of a strong base and a weak acid (see *hydrolysis of salts* in section 9.5).

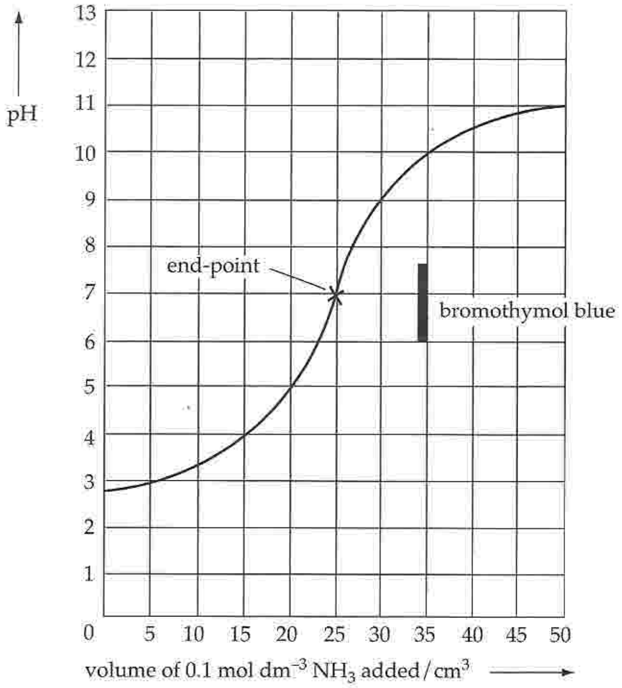
(d) The straight, vertical section of the graph is shorter than that for a titration of a strong acid with a strong base.

(e) Phenolphthalein is a suitable indicator because it will change colour completely over one or two drops at the end-point (ie at the vertical section). Bromothymol blue would also give a reasonable end-point. Methyl orange however would be completely unsuitable. It would change colour very slowly over a large volume of NaOH (ie over 8 – 21 cm^3). Thus it would be impossible to find the end-point accurately. Also the colour change would occur at the wrong volume (ie at about 15 cm^3 of NaOH).

(f) When *half* the acid has been neutralised (ie at 12.5 cm^3 of alkali in Fig 9.6), the titration flask contains an equal mixture of the weak acid CH_3COOH and its sodium salt CH_3COONa. This is a buffer solution and the pH only changes gradually around this point for that reason. Also, as $[CH_3COOH] = [CH_3COONa]$ at this point, $K_a = [H^+]$ and hence the K_a value can be found from the pH at this point.

Weak acid + weak base

50 cm^3 of 0.1 mol dm^{-3} NH_3 (a weak base) is added to 25.0 cm^3 of 0.1 mol dm^{-3} CH_3COOH (a weak acid). The graph of pH against volume of alkali added is shown in Fig 9.7.



▶ Fig 9.7 Weak acid + weak base

The graph has the following features:

(a) The graph starts at pH ≈ 3 for a 0.1 mol dm^{-3} acid, showing that the acid is weak.

(b) The graph ends at pH ≈ 11 for an approximately 0.1 mol dm^{-3} solution showing that the base is weak.

(c) At the end-point the solution (CH_3COONH_4) is approximately neutral. Although the solution of CH_3COONH_4 is hydrolysed, both H^+ and OH^- are removed from the water in the hydrolysis, so there is no net change in pH.

(d) There is no straight vertical section on the graph. This shows that the pH changes gradually throughout the titration.

If bromothymol blue is used as indicator, it would change colour over a volume of alkali (ie over 23 – 27 cm^3 on the graph). Hence it would not be possible to find the end-point accurately.

No indicator can be used for an accurate titration of a weak acid with a weak base. The colour change would always be very gradual.

To find the end-point in such a titration, a graph of pH against volume must be drawn, and the end-point determined from the graph.

Titration of Polybasic Acids

- Each acid hydrogen reacts, in turn, with the alkali. For *each* acid hydrogen there is a *separate* end-point in the titration. The end-points are marked by *inflexions* in the pH graph.
- For example, H_2SO_3 has two acid hydrogens. When NaOH is added to a solution of H_2SO_3, the first acid hydrogen reacts according to the equation

$$H_2SO_3 + NaOH \rightarrow NaHSO_3 + H_2O \qquad \text{... equation 1}$$

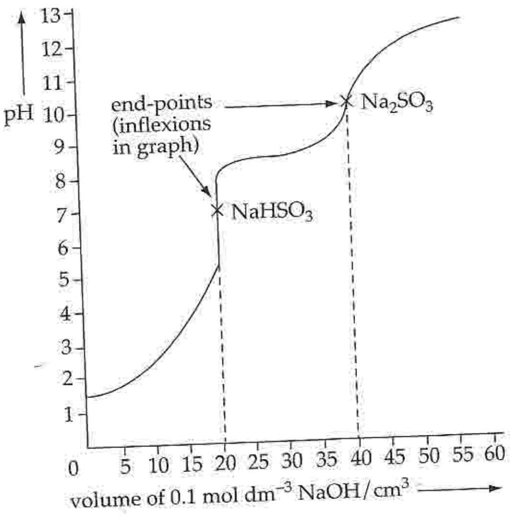
As more NaOH is added, the second acid hydrogen reacts.

$$NaHSO_3 + NaOH \rightarrow Na_2SO_3 + H_2O \quad \dots \qquad \text{equation 2}$$

The overall equation, from the start, is then

$$H_2SO_3 + 2NaOH \rightarrow Na_2SO_3 + 2H_2O \quad \dots \qquad \text{equation 3}$$

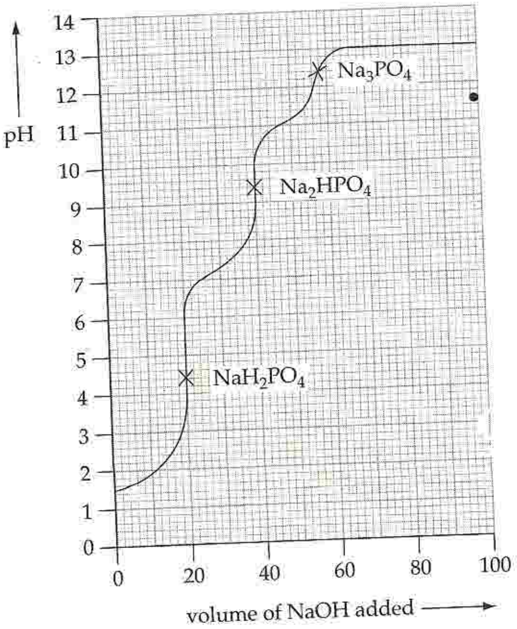
- 0.1 mol dm^{-3} NaOH is gradually added to 20 cm^3 of 0.1 mol dm H_2SO_3. The pH curve is shown in Fig 9.8.



▶ Fig 9.8

(a) The first end-point occurs after 20 cm^3 of NaOH has been added because there is a solution of $NaHSO_3$ in the titration flask (corresponding to equation 1).

(b) As more NaOH is added, the reaction as shown in equation 2 takes place. The second end-point occurs after 40 cm^3 of NaOH has been added as there is a solution of Na_2SO_3 in the titration flask.



▲ Fig 9.9

- Phosphoric acid, H_3PO_4, has *three* acid hydrogens. Each one in turn will react with NaOH, according to equations

$$H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + H_2O$$
$$NaH_2PO_4 + NaOH \rightarrow Na_2HPO_4 + H_2O$$
$$Na_2HPO_4 + NaOH \rightarrow Na_3PO_4 + H_2O$$

Hence there are *three* end-points in a titration of H_3PO_4 with NaOH in the burette. There are *three* inflexions in the pH graph for such a titration (Fig 9.9).

9.7 Solubility Product

- The general formula for an ionic compound is A_nB_m. When a slightly soluble ionic compound is shaken with water, some solid dissolves to form a saturated solution. The equation for this change is given as

$$A_nB_m(s) \rightleftharpoons nA^+(aq) + mB^-(aq)$$

When the solution is saturated, the mixture is at equilibrium.

- At equilibrium, the equilibrium constant,

$$K_c = \frac{[A^+]^n.[B^-]^m}{[A_nB_m]}$$

The concentration of any solid is constant. So $[A_nB_m]$ is constant.

Hence $[A^+]^n.[B^-]^m = [A_nB_m] \times K$
$= \text{constant} = K_{sp}$

This constant, K_{sp}, is called the **solubility product** of the ionic solid.

Question Write an expression for the solubility product of barium sulphate, $BaSO_4$. State the units.

Answer $BaSO_4$ dissolves in water according to the equation:

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

Hence $K_{sp} = [Ba^{2+}].[SO_4^{2-}]$ $mol^2\ dm^{-6}$

Question Write an expression for the solubility product of silver carbonate, Ag_2CO_3. State the units.

Answer Ag_2CO_3 dissolves in water according to the equation:

$$Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$$

Hence $K_{sp} = [Ag^+]^2.[CO_3^{2-}]$ $mol^3\ dm^{-9}$

- The expression for the solubility of an ionic compound gives the relationship between the ions in a saturated solution.
- Solubility products only apply to slightly soluble ionic compounds.
- K_{sp} values are affected by temperature. Usually, K_{sp} becomes larger when the temperature is raised.

Question The solubility of lead(II) bromide in water is x mol dm^{-3}. Write an expression for the solubility product of $PbBr_2$, in terms of x. State the units.

Answer $PbBr_2$ dissolves in water according to the equation:

$$PbBr_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Br^-(aq)$$

The solubility of $PbBr_2$, in water is x mol dm^{-3}, ie x mol dm^{-3} of $PbBr_2$ dissolves in water

$[Pb^{2+}] = x$ mol dm^{-3}

$[Br^-] = 2x$ mol dm^{-3}

in a saturated solution

Hence $K_{sp} = [Pb^{2+}].[Br^-]^2$

$= x.(2x)^2 = 4x^3$ mol^3 dm^{-9}

Question The solubility product of calcium carbonate, $CaCO_3 = 5.0 \times 10^{-9}$ mol^2 dm^{-6}. Calculate the solubility of $CaCO_3$ in g dm^{-3}.
[Ca = 40; C = 12; O = 16]

Answer $CaCO_3$ dissolves in water according to the equation:

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$$

From the equation, 1 mole of $CaCO_3$ produces 1 mole of $Ca^{2+}(aq)$ and 1 mole of $CO_3^{2-}(aq)$ when dissolved in water. So in a saturated solution,

$$[Ca^{2+}(aq)] = [CO_3^{2-}(aq)]$$

As $[Ca^{2+}] = [CO_3^{2-}]$,

$[Ca^{2+}]^2 = K_{sp} = 5.0 \times 10^{-9}$

$[Ca^{2+}] = (5.0 \times 10^{-9})^{\frac{1}{2}} = 7.1 \times 10^{-5}$ mol dm^{-3}

Hence the solubility of $CaCO_3$ $= [Ca^{2+}]$

$= 7.1 \times 10^{-5}$ mol dm^{-3}

$= 7.1 \times 10^{-5} \times M_r$ g dm^{-3}

$= 7.1 \times 10^{-5} \times 100$ g dm^{-3}

$= 7.1 \times 10^{-3}$ g dm^{-3}

Predicting Precipitation

- When solutions of cations and anions are mixed together, precipitation occursif the product of the concentration of the ions raised to their corresponding coefficients is larger than K_{sp} for the ionic compound.

- For example, if solutions of $Pb^{2+}(aq)$ and $I^-(aq)$ are mixed together, a precipitate of PbI_2 might form. The expression for K_{sp} for PbI_2 is

$$K_{sp} = [Pb^{2+}].[I^-]^2$$

If $[Pb^{2+}].[I^-]^2 = K_{sp}$, the solution is saturated, but no precipitate will form.
If $[Pb^{2+}].[I^-]^2 > K_{sp}$, a precipitate will form.
If $[Pb^{2+}].[I^-]^2 < K_{sp}$, no precipitate will form.

- Calcium ions, Ca^{2+}, are precipitated by NaOH(aq) as $Ca(OH)_2$, but not NH_3(aq). The NH_3(aq) does not precipitate the $Ca(OH)_2$ because it is a weak base and therefore has a small $[OH^-]$. Hence the product

$$[Ca^{2+}][OH^-]^2 < K_{sp}$$

Thus no precipitate is produced.

NaOH(aq) is a strong base and has a large $[OH^-]$ and therefore a precipitate is produced because $[Ca^{2+}][OH^-]^2 > K_{sp}$.

Question

Equal volumes of 0.001 mol dm^{-3} $AgNO_3$(aq) and 0.001 mol dm^{-3} K_2CrO_4 are mixed together. Will a precipitate form?
[K_{sp} for $Ag_2CrO_4 = 3.0 \times 10^{-12}$ $mol^3\ dm^{-9}$]

Answer

The precipitate would be Ag_2CrO_4.
K_{sp} for $Ag_2CrO_4 = [Ag^+]^2.[CrO_4^{2-}]$
When the two solutions are mixed together, each solution is diluted by a factor of 2.
Hence, in the mixture:

$$[Ag^+] = \frac{1}{2} \times 0.001 \text{ mol dm}^{-3}$$
$$[CrO_4^{2-}] = \frac{1}{2} \times 0.001 \text{ mol dm}^{-3}$$

Substituting into the expression for K_{sp},

$$[Ag^+]^2.[CrO_4^{2-}] = (\frac{1}{2} \times 0.001)^2.(\frac{1}{2} \times 0.001)$$
$$= 1.25 \times 10^{-10}$$

As $1.25 \times 10^{-10} > K_{sp}$, a precipitate will form.

Common Ion Effect

- The solubility of an ionic compound in a solution is decreased if the solution already contains one of the ions. For example, the solubility of AgCl in dilute HCl is less than in pure water because of the Cl^-(aq) ions from the HCl. In the equation below, $[Cl^-]$ is large so $[Ag^+]$ must become small to keep K_{sp} constant:

$$\underset{\text{small}}{\underset{\uparrow}{[Ag^+]}}.\underset{\text{big}}{\underset{\uparrow}{[Cl^-]}} = K_{sp}$$

Question K_{sp} for AgCl is 2.0×10^{-10} mol² dm⁻⁶. Calculate the solubility of AgCl in (a) water, and (b) 0.1 mol dm⁻³ HCl.

Answer

(a) $K_{sp} = [Ag^+].[Cl^-] = 2.0 \times 10^{-10}$
In water, $[Ag^+] = [Cl^-]$
Hence, $[Ag^+]^2 = 2.0 \times 10^{-10}$
and $[Ag^+] = 1.4 \times 10^{-5}$ mol dm⁻³
= solubility of AgCl in water

(b) In 0.1 mol dm⁻³ HCl, $[Cl^-] = 0.1$ mol dm⁻³ (the amount of Cl^- ions from any dissolved AgCl is very small and can be ignored).
Hence, substituting into the expression for K_{sp} of AgCl,
$[Ag^+] \times 0.1 = 2.0 \times 10^{-10}$
$[Ag^+] = 2.0 \times 10^{-9}$ mol dm⁻³
= solubility of AgCl in 0.1 mol dm⁻³ HCl

Note: This example shows that silver chloride is 10 000 times less soluble in 0.1 mol dm⁻³ HCl than in pure water.

EXERCISE 9

Multiple Choice Questions

Section I

1 The acid dissociation constant, K_a, for a weak monobasic acid is 4×10^{-5} mol dm⁻³. What is the pH of a 0.1 mol dm⁻³ solution of the acid?

A 1.00 **C** 2.70
B 2.20 **D** 4.40

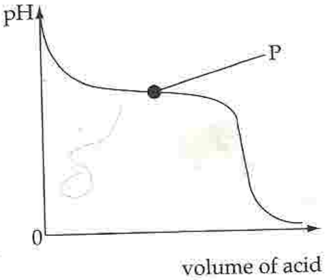
2 The pH of a 0.01 mol dm⁻³ solution of a monobasic acid is 4. What is the pK_a for the acid?

A 2 **C** 6
B 4 **D** 8

3 Which one of the following solutions has the *lowest* pH?

A 500 cm³ of 2.0 mol dm⁻³ CH_3COOH
B 10 cm³ of 0.4 mol dm⁻³ H_2SO_4
C 1 dm³ of 0.4 mol dm⁻³ HCl
D 200 cm³ of 0.5 mol dm⁻³ HCl

4 The graph shows the change in pH when quantity of aqueous ammonia is titrated w aqueous hydrochloric acid.



What is the correct explanation for the change of gradient of the graph at point P?

A The ammonia has been completely neutralised by the acid at P.
B There is a buffer at point P.
C Heat is produced in the reaction.
D The ammonia produces more hydroxide ions as acid is added.

5 A buffer solution consists of a mixture of an acid HA and the sodium salt of the acid NaA. The concentration of the acid is 0.2 mol dm^{-3}. What must be the concentration of the sodium salt, so that the pH of the solution is equal to the pK_a of the acid HA?

A 2.0 mol dm^{-3} **C** 0.1 mol dm^{-3}
B 1.0 mol dm^{-3} **D** 0.2 mol dm^{-3}

6 An acid, HA, has $pK_a = 3.20$. A quantity of the sodium salt of the acid, NaA, was added to 500 cm^3 of 0.2 mol dm^{-3} HA, producing a solution with a pH = 3.50. How many moles of NaA were added to the solution?

A 0.025 **C** 0.10
B 0.05 **D** 0.20

7 A monobasic acid has an acid dissociation constant $K_a = 2 \times 10^{-5}$ mol dm^{-3}. A 25.0 cm^3 portion of a 0.1 mol dm^{-3} solution of this acid was titrated with approximately 0.1 mol dm^{-3} NaOH. Which indicator would be most suitable for accurately determining the end-point in this titration?

	indicator	*pH range*
A	thymol blue	1.2 – 2.8
B	bromophenol blue	3.0 – 4.6
C	bromothymol blue	6.0 – 7.6
D	phenolphthalein	8.3 – 10.0

8 The acid dissociation constant for chloroethanoic acid is 1.5×10^{-5} mol dm^{-3}. What is the concentration of hydrogen ions in 0.01 mol dm^{-3} chloroethanoic acid?

A $\dfrac{1.5 \times 10^{-5}}{10^2}$ mol dm^{-3}

B $\left(\dfrac{1.5 \times 10^{-5}}{10^2}\right)^2$ mol dm^{-3}

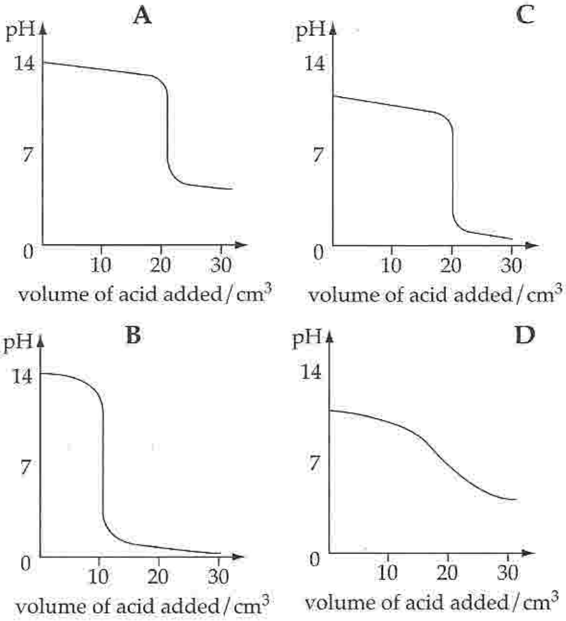
C $\sqrt{\dfrac{1.5 \times 10^{-5}}{10^2}}$ mol dm^{-3}

D $\dfrac{\sqrt{1.5 \times 10^{-5}}}{10^2}$ mol dm^{-3}

9 The concentration of hydrogen ions in an aqueous solution is 4.0×10^{-8} mol dm^{-3} and $K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6}. What is the concentration of hydroxide ions in the solution?

A 4.0×10^{6} mol dm^{-3}
B 2.5×10^{-7} mol dm^{-3}
C 1.0×10^{-7} mol dm^{-3}
D 4.0×10^{-8} mol dm^{-3}

Questions 10 – 13 are based on the graphs in Fig 9.10.
The graphs show the change in pH as 1.0 mol dm^{-3} acid is added to 20 cm^3 of 1.0 mol dm^{-3} alkali.



▲ Fig 9.10

10 Which graph could apply to the titration of nitric acid with ammonia?

11 Which graph could apply to the titration of sulphuric acid with potassium hydroxide?

12 Which graph could apply to the titration of propanoic acid with sodium hydroxide?

13 Which graph could apply to the titration of ethanoic acid with ammonia?

14 What is the pH of 0.005 mol dm^{-3} KOH?
[$K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6}]

A 9.3 **C** 11.0
B 9.5 **D** 11.7

15 What are the units of the solubility product, K_{sp}, of the metal hydroxide, $M(OH)_2$?

A mol dm^{-3} **C** mol^3 dm^{-9}
B mol^2 dm^{-6} **D** no units

16 The solubility of magnesium hydroxide is *m* mol dm^{-3}. What is the solubility product of magnesium hydroxide?

A $3m$ **C** m^3
B $3m^2$ **D** $4m^3$

17 The solubility product of iron(II) hydroxide is Z mol^3 dm^{-9}. What is the solubility of iron(II) hydroxide in mol dm^{-3}?

A C

B D

Section II

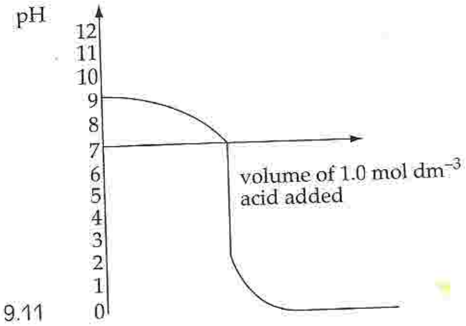
Summary of directions

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

18 Which of the following pairs of substances, when mixed together, will produce a buffer solution?

1 $CH_3COOH(aq) + NaOH(aq)$
2 $CH_3COONa(aq) + NH_3(aq)$
3 $NH_4Cl(aq) + HCl(aq)$

19 For which pairs of substances could the titration pH graph in Fig 9.11 apply?



▶ Fig 9.11

1 $NH_3(aq)/HCl(aq)$
2 $NH_3(aq)/CH_3COOH(aq)$
3 $KOH(aq)/CH_3COOH(aq)$

20 In which solution will the solubility of silver bromide be less than in pure water?

1 dilute hydrochloric acid
2 sodium bromide solution
3 silver nitrate solution

Structured Questions

*1 (a) Calculate the concentration of hydrogen ions in a solution with

(i) pH = 3.0
(ii) pH = 4.5
(iii) pH = 10.8

(b) For each of the solutions in the followi table, calculate [H$^+$], pH and [OH$^-$ The ionic product of water, $K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6}.

solution	[H$^+$]	pH	[OH$^-$
0.0001 mol dm^{-3} HCl			
0.05 mol dm^{-3} H_2SO_4			
0.01 mol dm^{-3} NaOH			
0.003×10^{-3} mol dm^{-3} HNO_3			
0.025 mol dm^{-3} KOH			

(c) The acid dissociation constant of dichloroethanoic acid, $Cl_2CHCOOH$, is 3.3×10^{-2} mol dm^{-3}. Calculate

(i) the concentration of hydrogen ions, and
(ii) the pH of a 0.003 mol dm^{-3} solution of the acid.

(d) The pH of a 0.002 mol dm^{-3} solution of a monobasic acid = 4.20. Calculate

(i) the acid dissociation constant;
(ii) the pK_a for the acid.

(e) For benzoic acid, pK_a = 4.17. What concentration of the acid, in g dm^{-3}, would have a pH = 5.0?

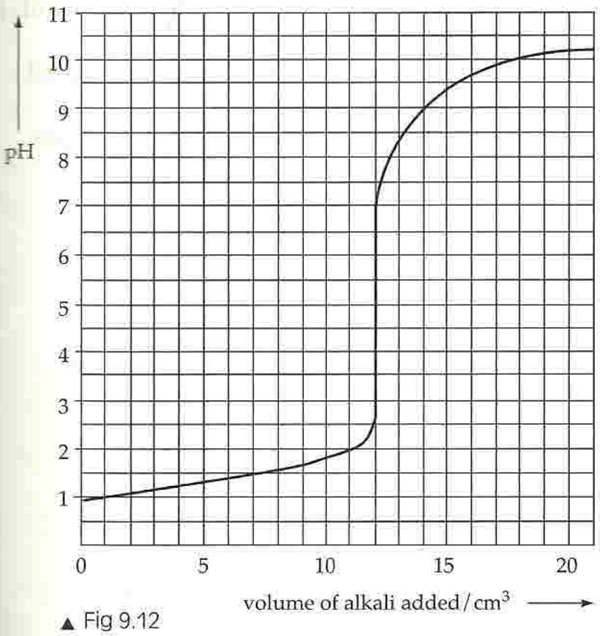
2 (a) The pH of pure water = 7.0 at 25°C. Calculate K_a for pure water at 25°C. State the units.
[$K_w = 1.0 \times 10^{-14}$ mol^2 dm^{-6} at 25°C]

(b) The acid dissociation constant for a monobasic acid = 1.0×10^{-4} mol dm^{-3}.

(i) What is the pK_a for the acid?
(ii) In a 0.01 mol dm^{-3} solution of the acid, what is the concentration of H$^+$(aq) ions and the pH?

(c) 50 cm^3 of a 0.1 mol dm^{-3} solution of the monobasic acid in (b) was mixed with 50 cm^3 of 0.4 mol dm^{-3} solution of the sodium salt of the acid. Calculate the pH.

3 20.0 cm^3 of an acid HA was titrated with an alkali. The acid and alkali were both monobasic. The concentration of the acid was 0.18 mol dm^{-3}. A total of 21 cm^3 of the alkali was added to the acid. Fig 9.12 shows the variation of the pH of the titration flask mixture as the alkali was added.



▲ Fig 9.12

(a) Was the acid weak or strong? Give a reason.

(b) Was the alkali weak or strong? Give a reason.

(c) Calculate the concentration of the alkali in mol dm^{-3}.

(d)

indicator	*pH range*
thymol blue	1.2 – 2.8
congo red	3.0 – 5.0
bromothymol blue	6.0 – 7.6
azolitmin	5.0 – 8.0
phenolphthalein	8.2 – 10.0
alizarin yellow	10.5 – 13.0

For this titration which one of the indicators above would be the most suitable to determine an accurate end-point? Give a reason for your choice.

(e) At which point in the titration did the titration flask contain the best buffer solution?

4 (a) The solubility of magnesium hydroxide, $Mg(OH)_2$, is x mol dm^{-3} at 25°C. Work out an expression for the solubility product, K_{sp} of magnesium hydroxide at 25°C in terms of x. Give the units of K_{sp}.

(b) Using your answer from (a), what is the solubility of magnesium hydroxide in 0.1 mol dm^{-3} NaOH?

(c) What is the effect on the K_{sp} for magnesium hydroxide if

(i) a little magnesium chloride is added to a saturated solution of magnesium hydroxide;

(ii) the temperature is increased?

5 Which of the following pairs of 0.002 mol dm^{-3} solutions would you expect to form a precipitate when equal volumes are mixed together?

(a) silver nitrate and potassium bromate(V)

(b) copper(II) nitrate and sodium chromate(VI)

(c) calcium nitrate and sodium fluoride

(d) copper(II) sulphate and potassium iodate(V)

(e) strontium chloride and sulphuric acid

[K_{sp} = 6.0×10^{-5} mol^2 dm^{-6} for $AgBrO_3$;
4.0×10^{-6} mol^2 dm^{-6} for $CuCrO_4$;
4.0×10^{-11} mol^3 dm^{-9} for CaF_2;
7.6×10^{-8} mol^3 dm^{-9} for $Cu(IO_3)_2$;
3.2×10^{-7} mol^2 dm^{-6} for $SrSO_4$]

6 (a) What do you understand by the pH of a solution?

(b) Calculate the pH of the following solution.

(i) A 0.1 moldm^{-3} solution of nitric acid.

(ii) A 0.1 moldm^{-3} solution of sulphuric acid

(iii) A 0.1moldm^{-3} solution of ethanoic acid

(c) A solution was made by dissolving 4.1g of sodium ethanoate in 500cm^3 of 0.1 moldm^{-3} ethanoic acid.

(i) Calculate the pH of the solution .

(ii) How do you call such a solution.

(iii) State two uses of such solution .

($K_a(CH_3CO_2H) = 1.75 \times 10^{-5}$ moldm^{-3})

7 (a) The ionic product of water is 1.00×10^{-14} mol^{2}dm^{-6} at 25 °C.

(i) Write an equation for the dissociation of water.

(ii) Write an expression for the ionic product of water.

(iii) Using the value of the ionic product of water at 25 °C, calculate the concentration of hydrogen ion in water at 25 °C.

(iv) Hence calculate the pH of pure water.

(b) (i) State 'Le Chatelier's Principle'.

(ii) Is the dissociation of water an endothermic or an exothermic process? Explain your answer.

(iii) What will be the effect of increasing the temperature of water on its degree of dissociation?

(iv)Hence determine how the pH of water will change if the temperature of pure water is increased.

8 (a) What is:-

(i) the Bronsted-Lowry theory of acids and bases?

(ii) a conjugate-acid-base pair.

(b) In each of the following equations below,name two acids and two bases

(i) $CH_3CO_2H + H_2O \rightleftarrows CH_3CO_2^- + H_3O^+$

(ii) $C_6H_5O^- + H_2CO_3 \rightleftarrows C_6H_5OH + HCO_3^-$

(iii) $C_6H_5NH_2 + H_2O \rightleftarrows C_6H_5HN_3^+ + OH^-$

State what additional information you will need to compare the relative strength of the two acids you have identified in each equation.

(c) Describe an experiment that can be carried out to determine the acid dissociation constant of ethanoic acid.

(d) Which of the two acids, ethanoic acid or chloroethanoic acid do you expect will have a higher acid dissociation constant value? Explain your answer.

Descriptive Questions

1 (a) State what is meant by the term *buffer solution*. Give one example of a buffer which is acidic and one example of a buffer which is alkaline.

Explain the effect on a buffer solution when a small volume of hydrochloric acid is added.

(b) Calculate the pH of:

(i) a 0.1 mol dm^{-3} solution of chloroethanoic acid;

(ii) a solution prepared by dissolving 0.1 mol of the sodium salt of chloroethanoic acid in 500 cm^3 of 0.1 mol dm^{-3} chloroethanoic acid.

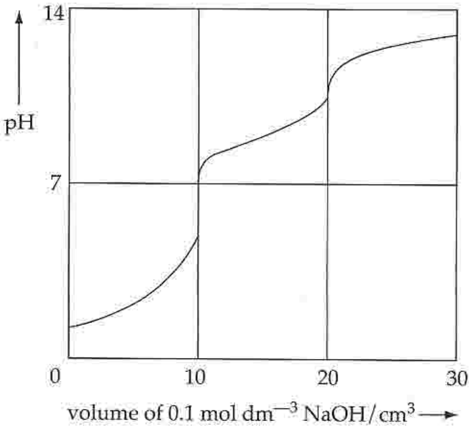
State clearly any approximations that you make in your calculations. [pK_a for chloroethanoic acid = 2.86]

2 Explain the following.

(a) The pH of pure water is 7.0 at 25°C and 6.5 at 100°C.

(b) When 25.0 cm^3 of 0.1 mol dm^{-3} ethanoic acid is titrated with 0.10 mol dm^{-3} sodium hydroxide, using methyl orange indicator, the indicator changes colour after about 10 cm^3 of alkali has been added.

(c) When 0.1 mol dm^{-3} NaOH is added slowly to 20 cm^3 of 0.1 mol dm^{-3} $SO_2(aq)$, the pH of the SO_2 solution changes as shown in Fig 9.13.



▲ Fig 9.13

3 (a) What do you understand by the term 'acid dissociation constant'?

(b) The pH of a 0.1 $moldm^{-3}$ solution of ethanoic acid at 25°C is 2.88.

(i) Calculate the concentration of hydrogen ion found in the solution of ethanoic acid.

(ii)Hence calculate the acid dissociation constant of ethanoic acid at 25°C.

(c) (i) Write an equation, including state symbols, for the reaction of ethanoic acid with zinc powder .

(ii) Calculate the volume of gas that will be produced when 5.00g of zinc powder is added to 100cm^3 of 0.1$moldm^{-3}$ ethanoic acid.

(d) (i) Calculate the pH of 0.1$moldm^{-3}$ hydrochloric acid.

(ii) Calculate the volume of gas that will be produced when 5.00g of zinc react with 100 cm^3 of 0.1$moldm^{-3}$ hydrochloric acid .

(e) Compare your results to c(ii) and d(ii). What can you deduce about the number of moles of hydrogen ions provided by each acid when they react with zinc powder? How can you explain the deduction you made?

4 (a) What do you understand by the following terms:-

(i) strong acid

(ii) weak acid

(iii) buffer solution

(b) Describe how 500cm^3 an acid buffer solution of pH 4.30 can be made using 0.1moldm^{-3} ethanoic acid and sodium hydroxide.

(c) Sketch the pH curves for each of the following titration:-

(i) 25 cm^3 of 0.1 moldm^{-3} solution of sodium hydroxide is titrated with 0.1moldm^{-3} hydrochloric acid .

(ii) 25 cm^3 of 0.1 moldm^{-3} solution of sodium hydroxide is titrated with 0.1moldm^{-3} ethanoic acid .

(iii) 25 cm^3 of 0.1 moldm^{-3} solution of aqueous ammonia is titrated with 0.1moldm^{-3} hydrochloric acid .

Label and explain any point and/or region of interest in your curve.

[acid dissociation constant of ethanoic acid, K_a= 1.75 x 10^{-5} moldm^{-3}

base dissociation constant of aqueous ammonia, K_b = 1.67 x 10 $^{-5}$moldm^{-3}]

5 (a) What do you understand by the 'solubility product' of a sparingly soluble salt?

(b) The solubility products of some of Group II sulphates are tabulated below:-

Formula of compound	K_{sp} / mol^{2}dm^{-6}
$CaSO_4$	2.4 x 10^{-5}
$SrSO_4$	3.2 x 10^{-7}
$BaSO_4$	1.3 x 10^{-10}

(i) Calculate the solubility of each of the group II sulphates tabulated above.

(ii) Explain the trend observed in solubility of GroupII sulphates down the Group.

(iii) State why magnesium sulphate has not been included in the table.

(c) Use a suitable example to explain the effect of a adding a solution containing a common ion on the solubility of the Group II sulphates.

(d) An aqueous solution contains both sodium carbonate and sodium sulphate, each of concentration 0.1 moldm^{-3}. A 0.2 moldm^{-3} solution of calcium chloride was added to the solution of sodium carbonate and sodium sulphate. Deduce what would be precipitated first given that:-

Formula of compound	Ksp / mol^{2}dm^{-6}
$CaSO_4$	2.4 x 10^{-5}
$CaCO_3$	1.69x10^{-9}

(e) The solubility product of silver chloride at 25^{0}C is 1.80 x 10^{-10} mol^{2}dm^6. Calculate the mass of silver chloride which dissolves in :-

(i) 1 dm^3 of distilled water

(ii) 1 dm^3 of 0.1moldm^{-3} hydrochloric acid

6 (a) Explain the following statements.

(i) Ethanoic acid is a strong acid in ammonia but a weak acid in water.

(ii) Trichloroethanoic acid is a stronger acid than ethanoic acid.

(iii) The pH of a solution of ethanoic acid is higher than that of methanoic acid

(b) Phenylethanoic acid dissolves slightly in water. 25 cm^3 of a saturated solution of the acid needs 17 cm^3 of 0.2moldm^{-3} sodium hydroxide for complete neutralization. What is the concentration of this saturated solution .

(c) A monobasic acid ,X,was titrated with a 0.10moldm^{-3} solution of sodium hydroxide . The pH of the solution was followed during the titration using a pH meter. The following pH readings were obtained.

Volume of NaOH added/cm^3	pH of solution
0.00	3.0
2.00	3.5
4.00	3.6
6.00	3.7
8.00	3.8
10.00	4.0
12.00	4.2
14.00	4.3
16.00	4.6
18.00	4.9
20.00	9.7
22.00	12.4
24.00	12.5
26.00	12.6

(i) Plot a graph of pH of solution on y axis against volume of alkali added on x-axis.

(ii) Comment on the shape of the curve.

(iii) Determine the volume of alkali required to neutralize10 cm^3 of the acid X, completely .

(iv) Calculate the concentration of the acid X.

(v) State whether the acid X is a strong acid or a weak acid. Give two evidences to support your statement.

7 (a) What do you understand by the term 'hydrolysis of salt'?

(b) Explain the following observations

(i) When solid ammonium chloride is dissolved in water the solution becomes slightly acidic.

(ii) When solid sodium ethanoate is dissolved in water the solution becomes weakly alkaline.

(iii) When sodium chloride dissolves in water the pH of the solution formed is 7.00 .

(iv) When propanoic acid is titrated with sodium hydroxide, at the equivalent point, the pH of the solution is greater than 7.00.

(v) The pH of a solution of iron(III) chloride or chromium(III) chloride is always slightly less than 7.00

(b) (i) Sketch the pH curve for the titration of 25cm^3 of 0.1$moldm^{-3}$ benzoic acid with 0.1$moldm^{-3}$ sodium hydroxide .

($Ka(C_6H_5CO_2H) = 6.30 \times 10^{-5} moldm^{-3}$)

(ii) Suggest a suitable indicator that may be used to carry out this titration among those suggested below:-

Indicator	pH range
Methyl orange	3.1-4.4
Bromocresol green	3.8-5.4
Bromothymol blue	6.0-7.6
Phenolphthalein	8.3-10.0

8 (a) Calculate the pH of the following solutions.

(i) 0.1 $moldm^{-3}$ sodium hydroxide

(ii) 0.1 $moldm^{-3}$ barium hydroxide solution

(b) (i) What do you understand by the 'base dissociation constant' of a substance?

(ii) Write an expression for the base dissociation constant of phenylamine.

(iii) calculate the pH of 0.1 $moldm^{-3}$ solution of phenylamine given that pK_b for phenylamine is 8.38

(c) A base buffer solution was made by dissolving 5.35 g of ammonium chloride in 500 cm^3 of 0.1 $moldm^{-3}$ aqueous ammonia.

(i) Explain the action of the base buffer solution

(ii) Calculate the pH of 0.1 $moldm^{-3}$ aqueous ammonia

(iii) Calculate the pH of the buffer solution.

($K_b(NH_3) = 1.67 \times 10^{-5} moldm^{-3}$)

CHAPTER

10

REACTION KINETICS

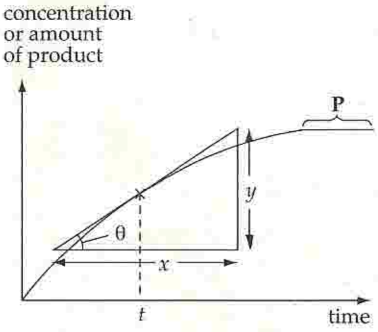
SYLLABUS OBJECTIVES

In this chapter you should be able to:

- explain and use the terms:
  - rate of reaction
  - rate equation
  - order of reaction
  - rate constant
  - half-life of a reaction
  - rate-determining step
  - activation energy
  - catalysis
- use and construct rate equations of the form, rate = $k[A]^m[B]^n$, limiting to simple cases of single-step reactions and multi-step processes with rate-determining steps, for which m and n are 0, 1 or 2
- deduce the order of a reaction by the initial rates method
- show or deduce, for zero- and first-order reactions, the order of reaction from concentration-time graphs
- show that a suggested reaction mechanism is consistent with the observed kinetics
- propose a reaction mechanism consistent with a given, or determined, order of reaction
- predict the order of reaction that would result from a given reaction mechanism
- calculate an initial rate using concentration data
- understand that the half-life of a first-order reaction is independent of concentration
- use half-life of a first-order reaction in calculations
- calculate a rate constant using the initial rates method
- devise a suitable experimental technique for studying the rate of reaction, from given information
- explain qualitatively, in terms of collisions, the effect of concentration changes on the rate of a reaction
- show understanding, including reference to the Boltzmann distribution and collision frequency, the effect of temperature change on a rate constant (and hence on a rate of reaction)
- explain that, in the presence of a catalyst, a reaction has a different mechanism, with lower activation energy (explained by reference to the Boltzmann distribution)
- explain the different modes of action of homogeneous and heterogeneous catalysis
- describe enzymes as biological catalysts

10.1 Rates of Reaction

Measurement of Rate of Reaction from Gradient of Graph

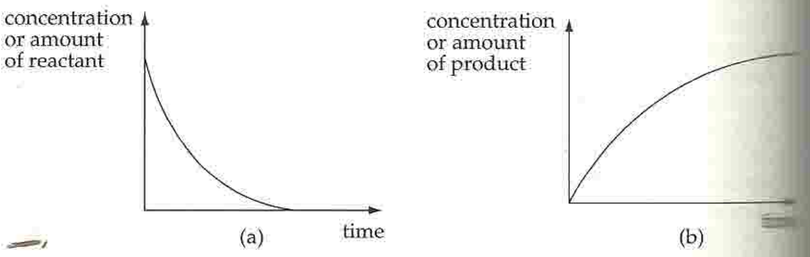


▲ Fig 10.1

- The rate of reaction is the rate of change of the concentration of the reactants and products.
- The units of rate of reaction are mol $dm^{-3} s^{-1}$.
- Fig 10.1 shows a graph of the amount of product in a reaction against time.
- The rate of reaction at any time equals the gradient of the graph at that time. For example, the rate of reaction at time t (Fig 10.1)
  = gradient of graph at time t
  = $\tan \theta$
  = $\frac{y}{x}$
- The steeper the gradient of the graph, the faster the reaction.
- When the graph is horizontal (ie the gradient is zero), the rate of reaction is zero. The reaction has stopped (section **P** in Fig 10.1).

Graphs of Concentration of Reactant and Product against Time

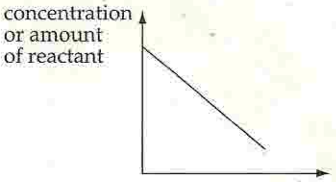
- Fig 10.2(a) shows a graph of the concentration of the reactant against time. This graph is obtained for most chemical reactions.
  - (a) The gradient of the graph decreases with time. Hence the rate of reaction decreases with time.
  - (b) The rate of reaction decreases with time because the concentration of the reactant decreases as the reaction proceeds. In most reactions, the rate of reaction is proportional to the concentration of the reactants.



(a) (b)

▶ Fig 10.2

- Fig 10.2(b) shows a graph of the concentration of product against time. This graph is obtained for most chemical reactions.
  The gradient of the graph decreases with time because the rate of reaction decreases with time, as the reactants are used up and less products are formed.



▲ Fig 10.3

- Fig 10.3 shows a graph of the concentration of the reactant against time. This graph is unusual and is only obtained for a few chemical reactions.
  - (a) The graph shows that the concentration of the reactant decreases with time, but the gradient is *constant*.
  - (b) The constant gradient means that the rate of reaction is constant.

(c) This shows that the rate of reaction is *not* affected by the concentration of the reactant (this is a *zero order* reaction; see *Order of Reaction*).

Rate of Reaction and Time for Completion of Reaction

- The rate of reaction is inversely proportional to the time for the reaction to be completed.

  $$\text{rate} \propto \frac{1}{\text{time}}$$

  For example, if reaction A takes 10 seconds to complete, and reaction B takes 20 seconds to complete, then

  $$\text{rate of A} \propto \frac{1}{10} = 0.1$$

  $$\text{rate of B} \propto \frac{1}{20} = 0.05$$

  Hence the rate of reaction A = 2 × rate of reaction B.

10.2 Rate Equations

- For the general reaction

  $$aA + bB + \ldots \rightarrow dD + eE + \ldots$$

  the rate of reaction is given by a **rate equation**:

  $$\text{rate} = k.[A]^m.[B]^n$$

  Where [ ] means concentration,
  k is the **rate constant,**
  m and *n* are numbers (usually integers).

- The rate equation is obtained *from experiment*.

- The numbers *m* and *n* are obtained from experiment. These numbers are *not* obtained from the numbers of moles written in the chemical equation. For example, for the reaction

  $$2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$$

  the rate equation is rate = $k.[I^-].[S_2O_8^{2-}]$
  and *not* rate = $k.[I^-]^2.[S_2O_8^{2-}]$

- The rate equation may not include all (or any) of the reactants written in the chemical equation.
  For example, for the reaction

  $$(CH_3)_3C\text{—}Cl(aq) + OH^-(aq) \rightarrow (CH_3)_3C\text{—}OH(aq) + Cl^-(aq)$$

  the rate equation is rate = $k.[(CH_3)_3C\text{—}Cl]$.
  The OH^- ions in the chemical equation do not appear in the rate equation.

- The rate equation may include substances that are not reactants in the chemical equation. For example, for the reaction

  $$2N(g) \rightarrow N_2(g)$$

  the rate equation has been found experimentally to be

  $$\text{rate} = k.[N]^2.[N_2]$$

  though N_2 is a *product* in the chemical equation.

Order of Reaction

- For the rate equation

  $$\text{rate} = k.[A]^n.[B]^m$$

  the sum $(n + m)$ is the **order of the reaction**.

- Definition: The order of a reaction with respect to a reactant is the power to which the concentration of the reactant is raised in the rate equation. The overall order of a reaction is the sum of the order of reaction with respect to all reactants.

- If $(n + m) = 1$, the order is one. We say that the reaction is 'first order'.
  If $(n + m) = 2$, the order is two and the reaction is 'second order'.
  If $(n + m) = 3$, the order is three and the reaction is 'third order'.

- Reaction orders can be fractions, though this is unusual.

- The order of a reaction shows the number of molecules or particles which are involved in the rate determining step of the reaction (see mechanism of reaction).

- A reaction order can be zero. A zero order reaction is independent of the concentration of the reactant; it proceeds at a constant rate.

Question

$$2A + B + C \rightarrow 2D + E$$

The rate equation for the above reaction is

$$\text{rate} = k.[A].[B]^2$$

What is the order of the reaction?

Answer

The order is 1 + 2 = 3 (third order).
Note that the reactant C does not appear in the rate equation. This shows that the rate of reaction is independent of the concentration of C. This can be shown by writing the rate equation as

$$\text{rate} = k.[A].[B]^2.[C]^0$$

(a) The reaction is first order with respect to A.
(b) The reaction is second order with respect to B.
(c) The reaction is zero order with respect to C.

Units of Rate Constants

- The units of the rate constant depend on the order of the reaction.

First order reactions

An example of a first order reaction is the reaction

$$(CH_3)_3C—Br + OH^- \rightarrow (CH_3)_3C—OH + Br^-$$

Experimentally, the rate equation is

$$\text{rate} = k.[(CH_3)_3C—Br]$$

Rearranging the rate equation

$$k = \frac{\text{rate}}{(\,CH_3\,)\,C\text{-}Br}$$

$$\text{Unit of } k = \frac{\text{Unit of rate}}{\text{Unit of conc of } (CH_3)_3C—Br}$$

$$= \frac{\text{mol dm}^{-3}\text{ s}^{-1}}{\text{mol dm}^{-3}}$$

Hence the units of $k = s^{-1}$

The unit of the rate constant for all first order reactions is s^{-1}.
The rate equation shows that in the rate determining step of the reaction only one molecule of ($(CH_3)_3C—Br$ is involved.
As hydroxide ion does not appear in the rate equation, it implies that the reaction is zero order with respect to OH^- ion. Hence the OH^- ion is not involved in the rate determining step of the reaction.

Second order reactions

An example of a second order reaction is the reaction

$$HCOOCH_3 + NaOH \rightarrow HCOONa + CH_3OH$$

Experimentally, the rate equation is

$$\text{rate} = k.[HCOOCH_3].[NaOH]$$

Rearranging the rate equation

$$k = \frac{\text{rate}}{[HCOOCH_3].[NaOH]}$$

$$\text{Hence the units of } k = \frac{\text{units of rate}}{(\text{units of concentrations})^2}$$

$$\frac{\text{mol dm}^{-3}\text{ s}^{-1}}{\text{mol}^2\text{ dm}^{-6}}$$

$$= \text{dm}^3\,\text{mol}^{-1}\text{s}^{-1}$$

The units for the rate constant of all second order reactions are $\text{dm}^3\text{ mol}^{-1}\text{ s}^{-1}$.

The rate equation shows that the rate determining step of the reaction involves one molecule of $HCOOCH_3$ and one OH- ion (as NaOH) .

Third order reactions

An example of a third order reaction is the reaction

$$2NO + Cl_2 \rightarrow 2NOCl$$

Experimentally, the rate equation is

$$\text{rate} = k.[NO]^2.[Cl_2]$$

$$\text{Hence the units of } k = \frac{\text{units of rate}}{(\text{units of concentration})^3}$$

$$\frac{\text{mol dm}^{-3}\text{ s}^{-1}}{\text{mol}^3\text{ dm}^{-9}} = \text{dm}^6\text{ mol}^{-2}\text{ s}^{-1}$$

The units for the rate constant of all third order reactions are $dm^6\ mol^{-2}\ s^{-1}$.

The rate equation shows that the rate determining step of the reaction involves two molecules of NO and one molecule of chlorine Third order reactions are quite unusual since the probability for three molecules to collide with each other with correct energy and orientation at a particular moment is very low.

Question

$$CH_3{-}CH - CH_2 + Br_2 \rightarrow CH_3{-}CHBr{-}CH_2Br$$

The rate equation for the above reaction is

$$\text{rate} = k.[CH_3{-}CH - CH_2].[Br_2]$$

The rate constant, *k*, is 30.0 $dm^3\ mol^{-1}\ s^{-1}$.

(a) What is the order of the reaction?

(b) What is the rate of reaction when the concentrations of propene and bromine are both 0.02 $mol\ dm^{-3}$?

Answer

(a) The order = 1 + 1 = 2

(b) The rate = 30.0 × 0.02 × 0.02 $mol\ dm^{-3}\ s^{-1}$ = 0.012 $mol\ dm^{-3}\ s^{-1}$

Question

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

The rate equation for the reaction is

$$\text{rate} = k.[HI]^2$$

At 629 K and at a concentration of 2.00 $mol\ dm^{-3}$, the rate of decomposition of hydrogen iodide = $24.0 \times 10^{-5}\ mol\ dm^{-3}\ s^{-1}$.

(a) Calculate the rate constant, *k*, for the reaction at 629 K. Give the units.

(b) Calculate the number of hydrogen iodide molecules that decompose per second in 1 dm^3 of gaseous hydrogen iodide at 629 K (at concentration 2.00 $mol\ dm^{-3}$).

[Avogadro constant = 6.0×10^{23} mol]

Answer

(a) $k = \dfrac{\text{rate of reaction}}{[\text{HI}]^2} \quad \dfrac{24.0 \times 10^{-5}}{2.00^2} = 6.0 \times 10^{-5}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$

(b) From the rate of reaction, 24.0×10^{-5} mole of HI is decomposing in 1 dm^3 every second.
Hence the number of molecules decomposing in 1 dm^3 every second
$= 24.0 \times 10^{-5} \times 6.0 \times 10^{23}$
$= 1.44 \times 10^{20}$ molecules

Experimental Determination of Rate Equations

Method 1 :The initial rate method

For the general equation: $aA + bB + cC \rightarrow dD + eE$

- Find out how the concentration of A affects the rate of reaction.
  - (a) Carry out two experiments and measure the *initial rate* of reaction in both.
  - (b) In the first experiment, use known concentrations of A, B and C.
  - (c) In the second experiment use double the concentration of A, but keep the concentrations of B and C the same. Hence any change in rate of reaction can only be caused by the change in the concentration of A.
  - (d) For example, if the rate is doubled in the second experiment, then rate of reaction $\propto$ [A]. If the rate of reaction increases four times, then rate of reaction $\propto [A]^2$.
- In the same way, find out how the concentrations of B and C affect the rate of reaction.

Question

$$\text{BrO}_3^-(aq) + 5\text{Br}^-(aq) + 6\text{H}^+(aq) \rightarrow 3\text{Br}_2(aq) + 3\text{H}_2\text{O}(l)$$

Four experiments were carried out to find out how the rate of the above reaction depends on the concentrations of BrO_3^-, Br^- and H^+. The results are summarised in the following table.

experiment	$[\text{BrO}_3^-]$	$[\text{Br}^-]$	$[\text{H}^+]$	initial rate of reaction
1	x	y	z	r
2	2x	y	z	2r
3	x	2y	z	2r
4	x	2y	2z	8r

(a) How does the rate of reaction depend on the concentrations of the reactants in the chemical equation?
(b) What is the rate equation for the reaction?
(c) What is the order of the reaction?
(d) What are the units of the rate constant?

Answer

(a) Comparing experiments 1 and 2: when $[BrO_3^-]$ is doubled, the rate is doubled.
Hence rate $\propto [BrO_3^-]$.
Comparing experiments 1 and 3: when $[Br^-]$ is doubled, the rate is doubled.
Hence rate $\propto [Br^-]$.
Comparing experiments 3 and 4: when $[H^+]$ is doubled, the rate is increased by a factor of 4.
Hence rate $\propto [H^+]^2$.

(b) The rate equation is rate = $k.[BrO_3^-].[Br^-].[H^+]^2$

(c) The order = 1 + 1 + 2 = 4

(d) The units of k = $\dfrac{\text{units of rate}}{(\text{units of concentrations})^4}$

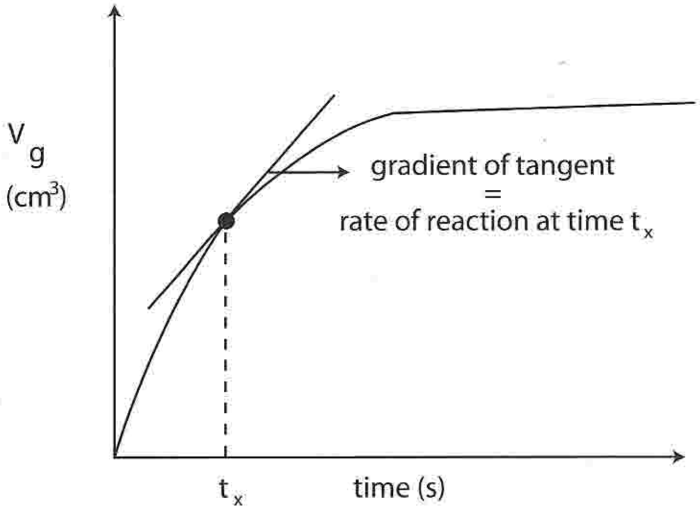
$$\frac{\text{mol dm}^{-3}\text{ s}^{-1}}{\text{mol}^4\text{ dm}^{-12}} = \text{dm}^9\text{ mol}^{-3}\text{ s}^{-1}$$

Method 2 : By determining concentration of a substance at different time.

Consider the decomposition of hydrogen peroxide
$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$
The rate of this reaction can be followed by:-

(i) determining the volume of gas produced at different time as the reaction proceeds.

A graph of volume of gas produced against time is plotted.



▲ Fig 10.4

The gradient to the graph at any time will give the rate of reaction at that time.

(ii) by determining the concentration of hydrogen peroxide left at different time as the reaction proceeds.

The concentration of hydrogen peroxide left at different time can be determined by titrating a given volume of solution with potassium manganate(VII)solution in acidic solution.

$$2MnO_4^-(aq) + 5H_2O_2(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5O_2(g) + 8H_2O(l)$$

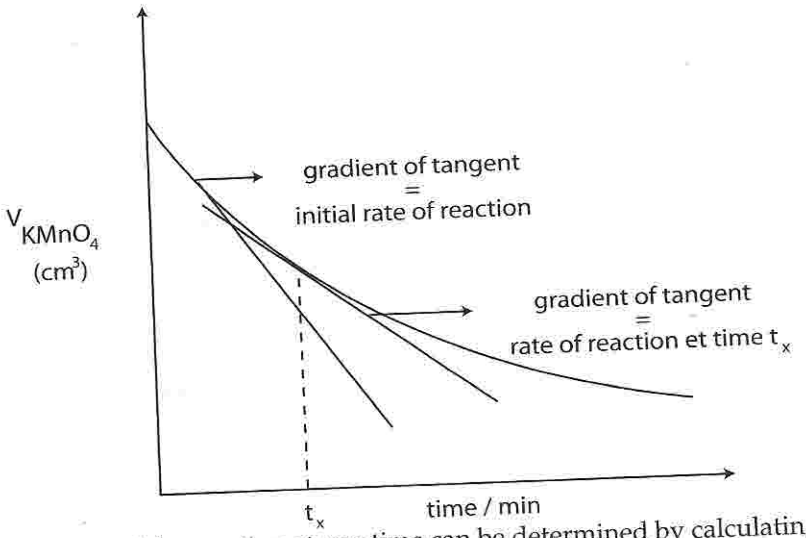
Procedure

- 10 cm³ of a solution of H_2O_2 is transferred into a titration flask containing about 25cm³ of ice-cold sulphuric acid(due to the low temperature of the ice cold sulphuric acid, the reaction is stopped, freezed or quenched).At the same time a stop watch is started.

- The hydrogen peroxide solution is titrated with standardized potassium manganate (VII) solution. The volume of $KMnO_4$ solution used is noted.
- The process is repeated at different time using fresh portions of H_2O_2 solution.
- The results are tabulated as shown below:-

Time / min	t_o	t_1	t_2	t_3	t_4	t_5	t_6	t_7	t_8
$V_{MnO_4^-}$ /cm^3	V_o	V_1	V_2	V_3	V_4	V_5	V_6	V_7	V_8

- The concentration of H_2O_2 left at any time is proportional to the volume of $KMnO_4$ solution used.
- A graph of volume of $KMnO_4$ used with time is plotted.



The rate of the reaction at any time can be determined by calculating the gradient of the tangent to the graph at that time.

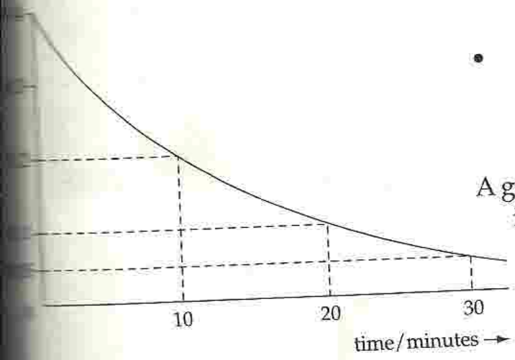
Test for First Order Reactions

- The time for the concentration of a reactant to be halved is called the **half-life**.
- In a first order reaction, the half-life is *constant for a particular experiment.*
- An example of a first order reaction is the catalytic decomposition of hydrogen peroxide.

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

A graph of concentration of H_2O_2 against time, for a typical experiment, is shown in Fig 10.4.

The initial concentration of H_2O_2 = 0.4 mol dm^{-3} (at time = 0). After the first ten minutes (ie one half-life), the concentration is 0.2 mol dm^{-3} (half the initial value). After a further 10 minutes (ie after 20 minutes) the concentration is 0.1 mol dm^{-3} (it is halved again).



▲ Fig 10.4

For this particular experiment, the time required to halve the concentration of H_2O_2 is constant (= 10 minutes). This shows that the reaction is first order.

- The half-life of a first order reaction is independent of the initial concentration of the reactants.
- The half-life of a first order reaction is related to the rate constant of the reaction by the expression

$$k = \frac{\ln 2}{t_{1/2}}$$

For example of the half-life of a reaction is 600 s, the rate constant of the reaction will be

$$k = \frac{\ln 2}{600}\,s^{-1} = 1.15 \times 10^{-3}\,s^{-1}$$

- For *any other order*, the half-life is *not constant*. It changes throughout an experiment.

Test for Zero Order Reactions

- If a reaction is zero order for one of the reactants, the rate remains constant when the concentration of that reactant is changed.
- A graph of concentration of reactant against time is a straight line if the reaction is zero order for the reactant. This is shown in Fig 10.3. For any other order the graph is a curve like Fig 10.2(a).

Determination of Rate Constants

- If the rate equation is known, the rate constant can be calculated from the known rate of reaction at a given concentration.
- For the rate equation, rate = k.[A].[B], a graph of rate of reaction against [A].[B] is a straight line. The gradient of the graph = the rate constant k.

Question

The rate equation for a certain reaction is

$$\text{rate} = k.[A]^2.[B]$$

The following experimental results were obtained:

$[A] = 3 \times 10^{-2}$ mol dm^{-3}
$[B] = 6 \times 10^{-2}$ mol dm^{-3}
Initial rate of reaction = 54×10^{-6} mol dm^{-3} s^{-1}

Calculate the rate constant. Give the units.

Answer

Rearranging the rate equation:

$$k = \frac{\text{rate}}{[A]^2.[B]} = \frac{54 \times 10^{-6}}{(3 \times 10^{-2})^2.(6 \times 10^{-2})}$$
$$= 1.00\ \text{dm}^6\,\text{mol}^{-2}\,\text{s}^{-1}$$

10.3 Mechanisms of Reactions

Effect of Concentration on Reaction Rate

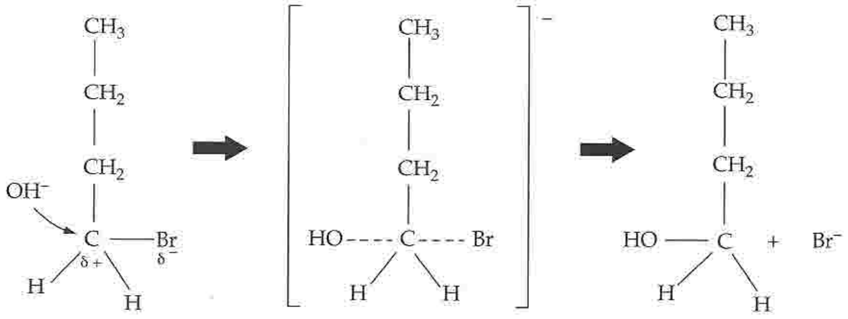
- Reactions take place when molecules or ions collide. The higher the concentration of molecules or ions, the higher the rate of collision so the rate of reaction is usually higher.

Rate-Determining Step and Rate Equation

- Most chemical reactions take place in stages. The overall reaction consists of two or more successive reactions or steps.
- Usually one of the steps is slower than the others. This slow step is called the **rate-determining step**. The overall rate of reaction depends on the rate of this slow rate-determining step.
- The rate equation for the overall reaction is obtained from the rate-determining step. The particles that collide together in the rate-determining step are the substances that appear in the rate equation.
- An example of a *single step* reaction is

  $$CH_3CH_2CH_2CH_2{-}Br + OH^- \rightarrow CH_3CH_2CH_2CH_2{-}OH + Br^-$$

  (a) The C—Br bond is polarised with a small positive charge (δ+) on the carbon atom, as bromine is more electronegative than carbon. The OH^- ion is attracted to the small positive charge on the carbon atom. The OH^- ion forms a bond with the carbon atom, and at the same time, the C—Br bond is broken (Fig 10.5).



▸ Fig 10.5

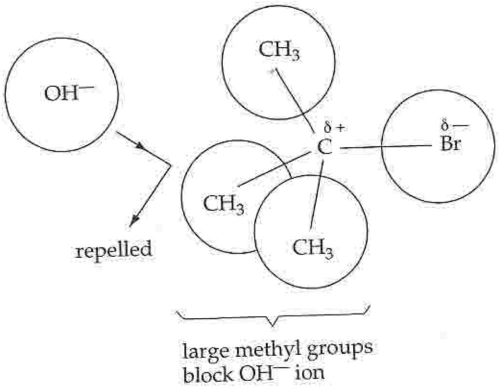
  (b) This reaction consists of one step. The rate of reaction depends on the rate of collision between the OH^- ion and the $CH_3CH_2CH_2CH_2Br$. The rate of collision depends on the concentration of the OH^- ions and the concentration of the $CH_3CH_2CH_2CH_2Br$. Hence the rate equation is

  $$\text{rate} = k.[CH_3CH_2CH_2CH_2Br].[OH^-]$$

- An example of a *multi-step* reaction is

$$(CH_3)_3C\text{—}Br + OH^- \rightarrow (CH_3)_3C\text{—}OH + Br^-$$

(a) Although the OH^- ion is attracted to the small positive charge on the carbon atom that is joined to the bromine atom, the OH^- ion is prevented from reaching this carbon atom by the big methyl groups (Fig 10.6).



▶ Fig 10.6

Hence the mechanism for the reaction is different from the hydrolysis of 1–bromobutane.

(b) The actual mechanism is a two-step reaction:
The Br^- ion has to first break away from the molecule.

$$(CH_3)_3C\text{—}Br \rightarrow (CH_3)_3C^+ + Br^- \qquad \text{step 1 (slow)}$$

The OH^- ion is then able to reach the carbon atom.

$$(CH_3)_3C^+ + OH^- \rightarrow (CH_3)_3C\text{—}OH \qquad \text{step 2 (fast)}$$

The slow (first) step is the rate-determining step. The overall rate of reaction depends on this slow step. The only reactant in this slow step is the $(CH_3)_3C$—Br, so the rate equation for the overall reaction is

$$\text{rate} = k.[(CH_3)_3C\text{—}Br]$$

(c) The OH^- does not appear in the rate equation because it does not take part in the slow, rate-determining step.

Example

$$X(aq) + Y(aq) \rightarrow Z(aq)$$

The mechanism for the above reaction is:

$X + H^+ \rightarrow XH^+$ (slow)
$XH^+ + Y \rightarrow Z + H^+$ (fast)

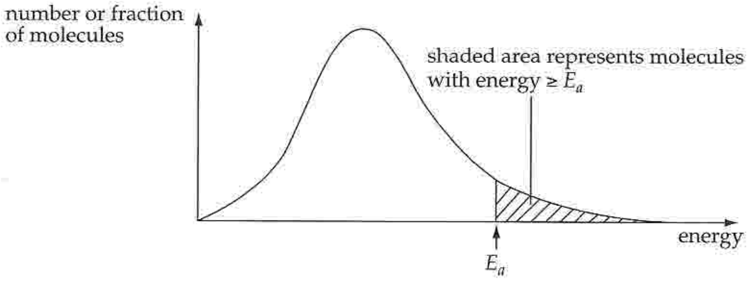
Which one of the following rate equations is most likely to be correct for this reaction?

A rate = $k.[X].[Y]$
B rate = $k.[X]$
C rate = $k.[X].[H^+]$
D rate = $k.[XH^+].[Y]$
E rate = $k.[Y]$

The correct answer is C. This is because this rate equation contains all the reactants in the slow rate-determining step (and *only* those reactants).

Activation Energy, E_a

- In a chemical reaction, molecules react together if
  - (a) they collide and
  - (b) the molecules in the collision have a certain minimum energy.
- The minimum energy for a reaction to take place when the molecules collide is called the **activation energy (E_a)**.
- In practice, only a very small fraction of colliding molecules have energy the activation energy. This is shown on the Boltzmann Distribution diagram in Fig 10.7.

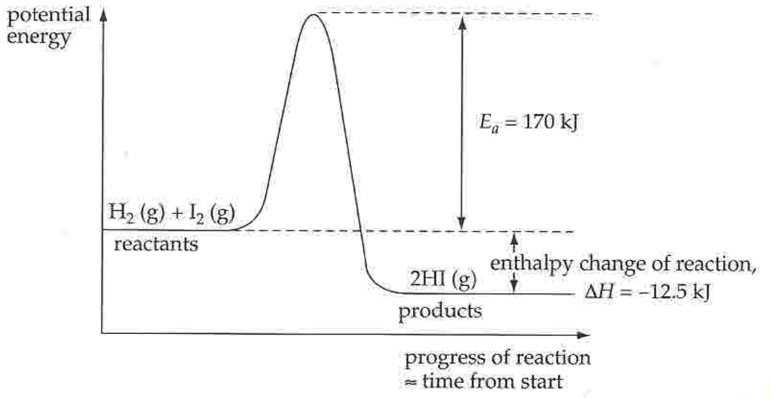


▸ Fig 10.7

- The activation energy is used to break the bonds in the reacting molecules, so that new bonds can be formed in the products.
- For example, in the reaction

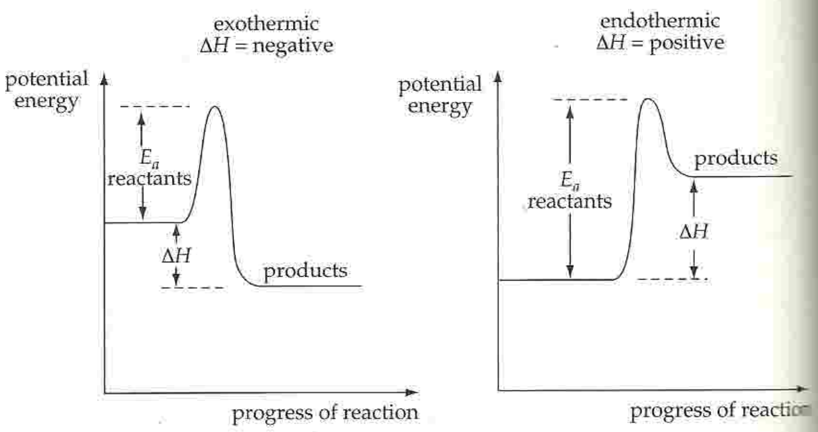
$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

(a) the activation energy is about 170 kJ per mole;
(b) when a H_2 molecule collides with an I_2 molecule, a reaction takes place if the molecules have energy 170 kJ;
(c) when a reaction occurs, 170 kJ of kinetic, heat and other energy is absorbed and used to break the H—H and I—I bonds;
(d) as the H—H and I—I bonds break; new H—I bonds form. Energy is given out when the new bonds are formed. The overall energy changes are summarised in Fig 10.8.



▸ Fig 10.8 Potential energy changes in a chemical reaction

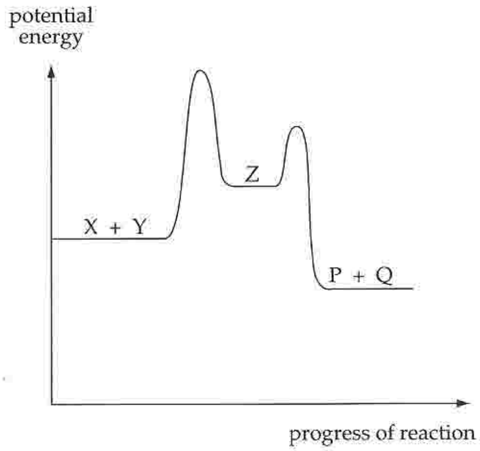
- A comparison of the energy changes in endothermic an exothermic reactions is shown in Fig 10.9.



▶ Fig 10.9

- An example of a potential energy diagram for a two-step reactio is shown in Fig 10.10. The two steps are:

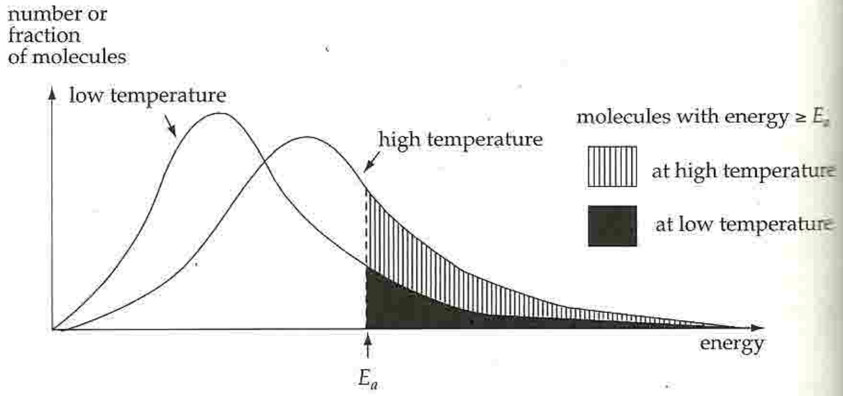
$$X + Y \rightarrow Z;\ \Delta H = \text{positive}$$
$$Z \rightarrow P + Q;\ \Delta H = \text{negative}$$



▲ Fig 10.10

Effect of Temperature on Rate of Reaction

- When the temperature of the reactants is increased by 10°C,
  (a) the rate of collision increases by about 2% and
  (b) the rate of reaction increases by about 100%.
  From these facts, the increase in rate of reaction *cannot* be due t an increase in the rate of collision only, as the increase in rate o reaction is 50 times the increase in the rate of collision.
- An increase in temperature increases the average energy o reacting molecules. Hence at a higher temperature, the number or fraction of colliding molecules with energy the activation energy, is increased. That is why the reaction rate increases a higher temperatures (Fig 10.11).



▶ Fig 10.11 Effect of temperature on the energy of the molecules (E_a = activation energy)

- A change in temperature affects the rate constant, k, of a reaction. When the temperature is increased, k usually increases.

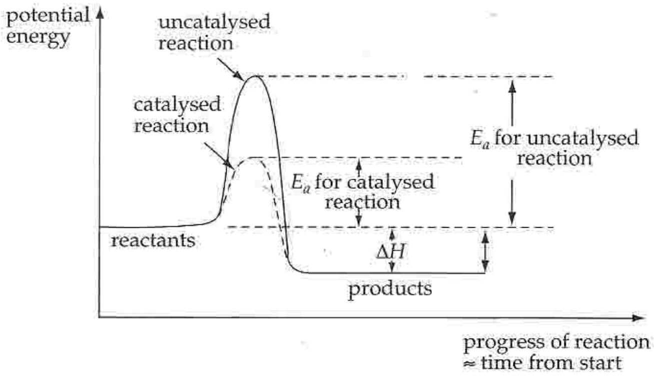
10.4 Catalysts

Properties of Catalysts

- Catalysts increase the rate of reaction.
- The rate of reaction is proportional to the amount of catalyst used.
- Catalysts may change the order of the reaction and the rate equation.
- Catalysts generally increase the rate constant, *k*, for a reaction.
- Catalysts are usually required in small amounts.
- Catalysts are usually chemically unchanged at the end of the reaction.
- Catalysts do not affect the enthalpy change of the reaction, ΔH.
- If no reaction takes place, addition of a catalyst will not cause any reaction to proceed.

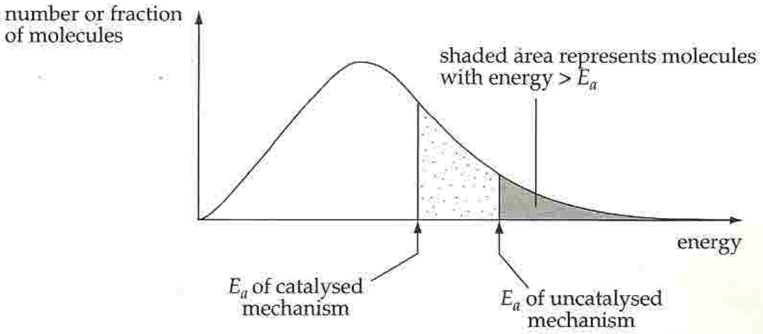
How Catalysts Work

- Catalysts work by providing an *alternative mechanism* for a reaction. The alternative mechanism has a *lower* activation energy (Fig 10.12).



▶ Fig 10.12

- Because of the lower activation energy in the catalysed mechism, a larger number or fraction of molecules have energy greater than the activation energy, therefore more molecules react when they collide (Fig 10.13).



▶ Fig 10.13 Effect of activation energies of uncatalysed and catalysed mechanism on fraction of molecules that are able to react in a collision

- There are two types of catalysts:
  (a) **Homogeneous catalysts**, in which the catalyst and reac
  are in the same physical state (usually in solution).
  (b) **Heterogeneous catalysts**, in which the catalyst is in a ph
  state different from that of the reactants (usually the cata
  is solid and the reactants are liquids, solutions or gases
  The reacting molecules are adsorbed on the surface of
  solid catalyst where their bonds are broken and the
  bonds formed. The product molecules then leave the cata
  surface.

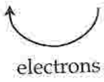
Homogeneous Catalyst

- Many homogeneous catalysts are transition metal ions, whic
  as catalysts by varying their oxidation states.
- An example of a homogeneous catalyst is the reaction betwee
  and $S_2O_8^{2-}$ ions:

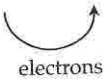
$$2I^- + S_2O_8^{2-} \rightarrow I_2 + 2SO_4^{2-}$$

In the reaction, electrons are transferred from the I^- to the S
The reaction is slow because of the repulsion between the
negative ions.
The reaction is catalysed by Fe^{3+} ions in two steps:

Step 1: $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$



Step 2: $2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$



The iron catalyst works by changing its oxidation state from +
+2 and back to +3.

- Sulphur dioxide causes acid rain. The sulphur dioxide reacts w
  water in the atmosphere to form sulphuric acid. The reaction
  catalysed by nitrogen dioxide.

Step 1: Sulphur dioxide reacts with nitrogen dioxide, NO
(from fires and car exhausts).

$$SO_2 + NO_2 \rightarrow SO_3 + NO$$

Step 2: The SO_3 reacts with water to form sulphuric acid.

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Step 3: The NO from step 1 reacts with atmospheric oxyge
to produce more NO_2.

$$2NO + O_2 \rightarrow 2NO_2$$

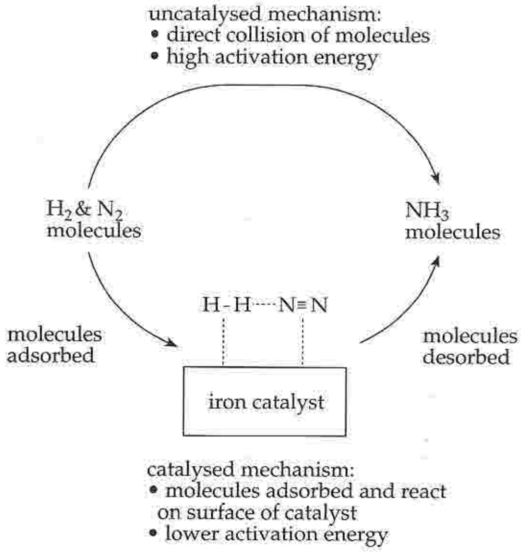
The nitrogen acts as a catalyst in the reaction by varying
oxidation state from +4 to +2 and back to +4.

Heterogeneous Catalyst

- An example of a heterogeneous catalyst is the use of iron as the catalyst in the **Haber Process** (see *Haber Process* in Chapter 8). Pellets of solid iron catalyse the reactions

$$3H_2(g) + H_2(g) \rightleftharpoons 2NH_3(g)$$

The catalyst adsorbs the H_2 and N_2 molecules on its surface, forming weak bonds with the molecules. This weakens the bonds within the H_2 and N_2 molecules, which can then break more easily to form new bonds with each other and form NH_3. Because the bonds within the H_2 and N_2 molecules are weakened, the activation energy decreases, and the rate of reaction increases. The NH_3 molecules then escape from the catalyst surface.



▶ Fig 10.14

- **Catalytic converter** fitted to motocar exhaust is another example of a heterogeneous catalysed reaction. A catalytic converter contains a thin layer of a platinium/rhodium alloy spread over a ceramic support. The gases from the car engine contain pollutants, including carbon monoxide and nitrogen dioxide. These two pollutants react together very rapidly on the surface of the alloy catalyst, according to the equation:

$$\underbrace{2NO_2 + 4CO}_{\text{from car engine}} \rightarrow \underbrace{N_2 + 4CO_2}_{\text{released into the air}}$$

The N_2 and CO_2 are relatively harmless and are released into the atmosphere.

Enzymes

- Enzymes catalyse reactions in living organisms and are known as biological catalysts.
- Enzymes are *polypeptide* molecules, consisting of large numbers of amino acid molecules condensed together (see *Proteins* in Chapter 23).
- Enzymes only work well within a narrow pH range (about 5 – [illegible] and within a narrow temperature range (about 20°C – 40°C).
- Most enzymes only catalyse a very specific biochemical reaction which no other enzyme will catalyse.
- Enzymes are very effective catalysts compared with non-enzyme catalysts. For example, the enzyme nitrogenase catalyses the conversion of N_2 gas into nitrogen compounds in nitrogen-fixing bacteria at room temperature. By comparison, the iron catalyst in the Haber Process requires a temperature of 500°C to convert N_2 and H_2 into ammonia.

Summary

▶ Table 10.1 Changes that affect the rate of reaction and the rate constant

change	effect on rate of reaction	effect on rate constant, *k*	notes
increase in concentration	increased	no change	
increase in to pressure	increased	no change	only applies gaseous reactants
increase in temperature	increased	increased	
use of a catalyst the	increased	increased	a catalyst can also change rate equation

EXERCISE 10

Multiple Choice Questions

Section I

1 The rate equation for a reaction is

$$\text{rate} = k.[A]^2$$

The units of the rate constant, *k*, are

A s^{-1}.
B mol dm^{-3} s^{-1}.
C dm^6 mol^{-2} s^{-1}.
D dm^3 mol^{-1} s^{-1}.

2 The kinetics of the acid-catalysed reaction of iodine with propanone were investigated by reacting dilute aqueous iodine with known concentrations of propanone and acid. In one experiment, a large excess of propanone was used. What could be the reason for this?

A To keep the rate of reaction constant.
B To keep the concentration of propanone almost constant.
C To keep the iodine dissolved in solution.
D Because the rate is not affected by the concentration of propanone.

3 The kinetics of the reaction:
$A + B + C \rightarrow D + \ldots$ etc, were investigated.
The results are given in the following table.

experiment	[A]	[B]	[C]	rate
1	x	y	z	s
2	$4x$	y	z	s
3	$2x$	$2y$	z	$4s$
4	$2x$	$2y$	$2z$	$8s$

What is the rate equation for the reaction?

A rate = $k.[A].[B].[C]$
B rate = $k.[B].[C]$
C rate = $k.[B]^2.[C]$
D rate = $k.[A].[B]^2.[C]$

4 Which general statement about the rate constant, *k*, of chemical reactions is *not* true?

A The rate constant increases when a catalyst is used.
B The rate constant increases if the activation energy is increased.
C The rate constant remains the same if the concentration of reactants is increased.
D The rate constant can have different units.

5 Which one of the following statements about a first order reaction is true?

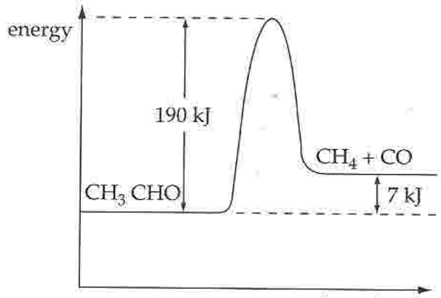
A The time required for the concentration of a reactant to be halved is constant.
B The units of the rate constant are mol dm^{-3} s^{-1}.
C A graph of concentration of reactant against time is a straight line.
D At a given temperature, the rate of reaction is constant.

6 The energy diagram for the reaction

$$CH_3CHO \rightarrow CH_4 + CO$$

is shown in Fig 10.15. What is the activation energy of the *reverse* reaction?

A 7 kJ
B 183 kJ
C 190 kJ
D 197 kJ



▲ Fig 10.15

7 The uncatalysed thermal decomposition of hydrogen peroxide as shown,

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

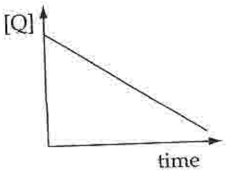
is a *second order* reaction. Which one of the following graphs is a straight line?

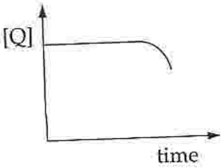
A $[H_2O_2]$ against (rate of reaction)^2
B $[H_2O_2]^2$ against (rate of reaction)
C $[H_2O_2]$ against (time)^2
D $[H_2O_2]^2$ against time

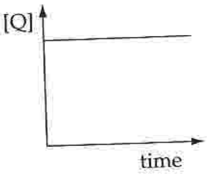
8 In the reaction $P + Q \rightarrow R + S$, the rate equation is found experimentally to be

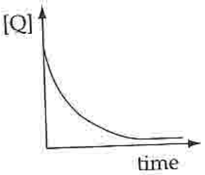
$$\text{rate} = k.[P]$$

If a quantity of Q was added to a *large* excess of P, which one of the following graphs showing the change in concentration of Q with time, is likely to be correct?

A 

C 

B 

D 

9 The reaction of diazonium ions with iodide ions is a two-step process:

$C_6H_5{-}N_2^+ \xrightarrow{slow} C_6H_5^+ + N_2$ (step 1)

$C_6H_5^+ + I^- \xrightarrow{fast} C_6H_5{-}I$ (step 2)

Which one of the following rate equations best agrees with this mechanism?

- **A** rate = $k.[C_6H_5{-}N_2^+].[I^-]$
- **B** rate = $k.[C_6H_5^+].[I^-]$
- **C** rate = $k.[C_6H_5^+]$
- **D** rate = $k.[C_6H_5{-}N_2^+]$

10 Which statement is true about the effect of a catalyst on reacting molecules?

- **A** The fraction of molecules with energy greater than the activation energy is increased.
- **B** The maximum in the Boltzmann Distribution graph is shifted to the right (to a higher energy).
- **C** The average energy of the colliding molecules is increased.
- **D** The bonds in the molecules become stronger.

11 The rate of the reaction,

$$X(aq) + Y(aq) \rightarrow XY(aq)$$

in the presence of a dilute aqueous alkali, is given by the rate equation

$$rate = k.[Y(aq)].[OH^-(aq)]$$

Which one of the following mechanisms best agrees with these results?

A $X(aq) + OH^-(aq)$ $XOH^-(aq)$
$XOH^-(aq) + Y(aq)$ $XY(aq) + OH^-(aq)$

B $X(aq) + OH^-(aq)$ $XOH^-(aq)$
$XOH^-(aq) + Y(aq)$ $XYOH^-(aq)$
$XYOH^-(aq)$ $XY(aq) + OH^-(aq)$

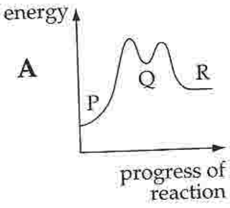
C $Y(aq) + OH^-(aq)$ $YOH^-(aq)$
$YOH^-(aq) + X(aq)$ $XYOH^-(aq)$
$XYOH^-(aq)$ $XY(aq) + OH^-$

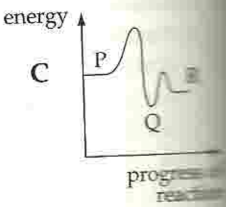
D $Y(aq) + OH^-(aq)$ $YOH^-(aq)$
$YOH^-(aq) + X(aq)$ $XY(aq) + OH^-$

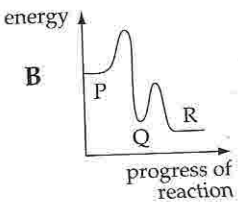
12 In the conversion of compound P compound R, it was found that the reacti proceeded by way of compound Q, wh could be isolated. The steps involved were

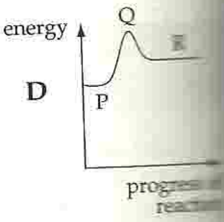
$P \rightarrow Q; \Delta H =$ negative
$Q \rightarrow R; \Delta H =$ positive

Which one of the following reaction pro agrees with this data?

A 

C 

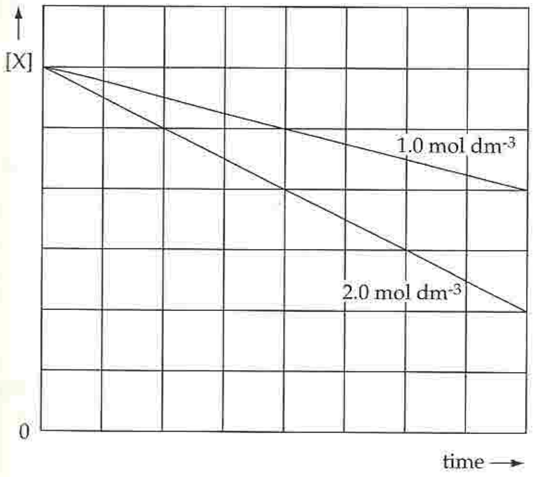
B 

D 

13 $$X + Y \rightarrow C$$

The above reaction was carried out in aque solution. In one experiment, a small quanti of X was added to excess Y, of concentrati 1.0 mol dm^{-3}. In another experiment, the sam quantity of X was added to excess Y but a concentration 2.0 mol dm^{-3}. The results are shown in Fig 10.16. Which one of the followin rate equations best agrees with these resul

- **A** rate = $k.[X]$
- **B** rate = $k.[Y]$
- **C** rate = $k.[Y]^2$
- **D** rate = $k.[X].[Y]^2$



▲ Fig 10.16

14 Which one of the following statements about the activation energy of a reaction is *not* true?

A It is the same for the forward and backward reactions.

B It is the minimum energy that colliding molecules must have before reacting.

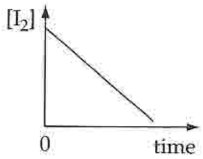
C It is mainly used in breaking bonds in reacting molecules.

D In general, the bigger the activation energy, the slower the reaction.

15 A quantity of iodine was reacted with a large excess of propanone and dilute acid. The equation for the reaction is

$$I_2 + CH_3COCH_3 \rightarrow ICH_2COCH_3 + HI$$

The concentration of iodine in the reaction mixture was recorded at regular time intervals and the result is shown in Fig 10.17.



▶ Fig 10.17

Which one of the following deductions can be made from this graph?

A The rate of reaction is directly proportional to $[I_2]$.

B The rate of reaction is inversely proportional to $[I_2]$.

C The rate of reaction is independent of $[I_2]$.

D The rate of reaction is independent of $[H^+]$.

16 In a chemical reaction the rate-determining step is

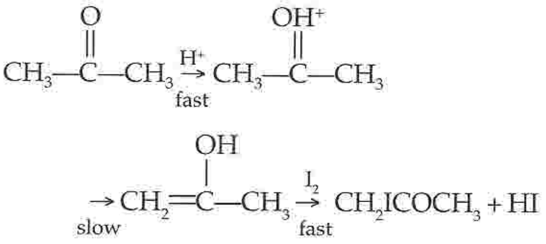
A the one with the largest activation energy.

B the one with the smallest activation energy.

C the fastest step.

D the last step.

17 Propanone reacts with a mixture of iodine and acid. The mechanism for this reaction is as follows:



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \xrightarrow[\text{fast}]{H^+} CH_3-\overset{\overset{\displaystyle OH^+}{\|}}{C}-CH_3$$

$$\xrightarrow[\text{slow}]{} CH_2{=}\overset{\overset{\displaystyle OH}{|}}{C}-CH_3 \xrightarrow[\text{fast}]{I_2} CH_2ICOCH_3 + HI$$

What are the orders of reaction with respect to propanone and iodine?

	propanone	*iodine*
A	1	0
B	1	1
C	2	0
D	0	1

Section II

Summary of directions

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

18 Which statements about a catalysed reaction is/are true?

1 A catalyst does not change the enthalpy change of reaction, ΔH.

2 A catalyst only speeds up the forward reaction, but not the backward reaction.

3 A catalyst increases the kinetic energy of the reacting particles.

19 The rate equation for the reaction of CH_3Cl with aqueous NaOH is

$$\text{rate} = k.[CH_3Cl].[OH^-]$$

Which statement(s) about this reaction is/are true?

1 Both CH_3Cl and OH^- are reactants in the rate-determining step.
2 The units of the rate constant, k, are $dm^3\ mol^{-1}\ s^{-1}$.
3 The OH^- is a nucleophile in this reaction.

Structured Questions

1 $$2NO(g) + 2H_2(g) \rightarrow 2H_2O(g) + N_2(g)$$

A series of experiments were carried out to find the rate equation for the above reaction. The results are shown in the following table.

experiment	$[H_2]$ mol dm^{-3}	[NO] mol dm^{-3}	rate mol $dm^{-3}\ s^{-1}$
1	1×10^{-3}	6×10^{-3}	6.0×10^{-3}
2	2×10^{-3}	6×10^{-3}	12.0×10^{-3}
3	3×10^{-3}	6×10^{-3}	18.0×10^{-3}
4	6×10^{-3}	1×10^{-3}	1.0×10^{-3}
5	6×10^{-3}	2×10^{-3}	4.0×10^{-3}
6	6×10^{-3}	3×10^{-3}	9.0×10^{-3}

(a) How does the rate of reaction depend on
(i) the concentration of H_2 and
(ii) the concentration of NO?
(b) (i) Write a rate equation for the reaction.
(ii) What is the order of the reaction?
(iii) What are the units of the rate constant?
(iv) What is the value of the rate constant?

2 Iodine reacts with propanone according to the equation

$$I_2 + CH_3COCH_3 \rightarrow ICH_2COCH_3 + HI$$

The kinetics of this reaction were investigated in four experiments at constant temperature. The *initial* rate of reaction was measured at different concentrations of propanone, iodine and hydrogen ions. The results are shown in the following table.

experiment	$[CH_3COCH_3]$ mol dm^{-3}	$[H^+]$ mol dm^{-3}	$[I_2]$ mol dm^{-3}	rate mol $dm^{-3}\ s^{-1}$
1	3.0	0.2	0.02	18×10^{-6}
2	3.0	0.4	0.02	36×10^{-6}
3	4.0	0.4	0.02	48×10^{-6}
4	4.0	0.2	0.04	24×10^{-6}

(a) How does the rate of reaction depend on the concentration of
(i) propanone,
(ii) iodine and
(iii) hydrogen ions?
(b) What should be the rate of reaction (at the same temperature) when the concentrations are as follows:

$[CH_3COCH_3] = 1.5$ mol dm^{-3}
$[H^+] = 0.1$ mol dm^{-3}
$[I_2] = 0.01$ mol dm^{-3}

(c) (i) Write a rate equation for the reaction.
(ii) What is the order of the reaction?
(iii) Calculate the value of the rate constant, k.
(iv) What are the units of the rate constant?
(d) Why was the *initial* rate measured in the four experiments?

3 $$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

The rate equation for the above reaction is

$$\text{rate} = k.[NO]^2.[O_2]$$

(a) What are the units of the rate constant?
(b) If the rate of the reaction under certain conditions is y, write expressions for the rate of reaction, in terms of y, when the following changes are made:
(i) the pressure of O_2 is doubled (the pressure of NO is unchanged);
(ii) the pressure of both O_2 and NO are doubled;
(iii) the volume of the mixture is doubled but the pressure is unchanged;
(iv) a quantity of argon is added to the mixture so as to double the total pressure (you may assume that the argon plays no part in the reaction).

4 Hydrogen peroxide decomposes according to the equation
$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$
This decomposition can be speeded up by many catalysts.

The catalysed decomposition was studied in an experiment.

The initial rate of reaction was measured for different concentrations of hydrogen peroxide. The following results were obtained.

concentration /mol dm^{-3}	initial rate of reaction /mol dm^{-3} s^{-1}
0.06	0.35×10^{-3}
0.13	0.75×10^{-3}
0.19	1.10×10^{-3}
0.27	1.55×10^{-3}
0.32	1.80×10^{-3}

(i) Plot the results on graph paper (rate of reaction against concentration).
(ii) From the graph, what is the order of the reaction? Give a reason.
(iii) Write a rate equation for the reaction.
(iv) Calculate the value of the rate constant and state the units. Show your working.
(v) Name a suitable catalyst for this reaction and state whether it is homogeneous or heterogeneous.

5 (a) What is meant by
  (i) the rate of the reaction
  (ii) the order of a reaction
(b) Hydrogen peroxide decomposes slowly in sunlight.
  (i) Write an equation , including state symbols to show the decomposition of hydrogen peroxide.
  (ii) You are provided with a fresh supply of hydrogen peroxide, potassium manganate(VII)solution , dilute sulphuric acid. Describe an experiment that may be carried out to determine the initial rate of the reaction and the order of the reaction.
(c) The catalytical decomposition of hydrogen peroxide is relatively fast.
  (i) Name a suitable catalyst that may be used to decompose hydrogen peroxide.
  (ii) Draw an apparatus that may be used to collect the gas evolved during the catalytical decomposition of hydrogen peroxide.
  (iii) Discuss how the order of the reaction for the decomposition of hydrogen peroxide can be determined using the apparatus you have drawn in c(ii).
(d) Do you think that the order of the reaction for the decomposition of hydrogen peroxide will be different in the presence and in the absence of a catalyst?

6 (a) What is a
  (i) homogeneous catalyst
  (ii) heterogeneous catalyst.
(b) Using suitable examples , describe the action of
  (i) a homogeneous catalyst
  (ii) a heterogeneous catalyst.
(c) In certain reactions, the reaction is first order with respect to a heterogeneous catalyst if the concentration of the reactants are low, but is zero order if the concentration of the reactants are high. Suggest a possible explanation for this observation.
(d) (i) What do you understand by a 'first order reaction' ?
  (iii) A first-order reaction is 50% complete after 5.0 minutes.Calculate the rate constant for the reaction.

7 (a) Explain the following terms:-
  (i) the activation energy
  (ii) the activated state.
(b) With the aid of a sketch of the Boltzmann distribution, explain how the presence of a catalyst increases the rate of a chemical reaction.
(b) Suggest experimental methods that may be used to determine the initial rate of reaction for the following reactions:-

(i) $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$
(ii) $CH_3COCH_3(l) + I_2(aq) \rightarrow CH_3COCH_2I(l) + HI(aq)$
(iii) $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$

8 (a) (i) Describe how the rate of a reaction is affected by a change in temperature.
  (ii) With the aid of a sketch of the Boltzmann distribution, explain why a small increase in temperature may lead to a large increase in the rate of a chemical reaction.
(b) Two substances A and B react according to the following equation

$$2A(aq) + B(aq) \rightarrow A_2B(aq)$$

A set of experiments were performed at a constant temperature in order to determine the order of this reaction and a value for the rate constant of the reaction. The results obtained were recorded in the table below.

Experiment number	Initial concentration of A in mol dm^3	Initial concentration of B in mol/dm^3	Initial rate of reaction/ $moldm^{-3}s^{-1}$
1	0.1	0.1	0.002
2	0.2	0.1	0.004
3	0.1	0.2	0.008
4	0.4	0.3	

(i) What is the order of this reaction with respect to(i) A and (ii) B?

(ii) Write down a rate equation for the reaction between A and B.

(iii) Calculate a value for the rate constant of the reaction.

(iv) What is the unit of the rate constant?

(v) Calculate the initial rate of the reaction for the experiment 4.

Descriptive Questions

1 (a) Explain what is meant by the term *rate-determining step.*

(b) In the gaseous state, hydrogen iodide decomposes according to the equation

$$2HI(g) \rightarrow I_2(g) + H_2(g)$$

In an investigation of this reaction, the following experimental results were obtained at 300°C.

experiment	**[HI]/mol dm^{-3}**	**initial rate of reaction /mol dm^{-3} s^{-1}**
1	0.010	13.30×10^{-10}
2	0.008	8.50×10^{-10}
3	0.005	3.32×10^{-10}
4	0.002	5.32×10^{-11}

(i) From the table of results, deduce the order of reaction with respect to the concentration of HI.

(ii) Hence, use the results of experiment 1 to calculate the rate constant at 300°C. State the units.

2 (a) State and explain, using a diagram, the effect of a catalyst on the *activation energy* of a reaction.

(b) (i) What is meant by the terms *homogeneous catalyst*?

(ii) $S_2O_8^{2-}(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$
The reaction above is slow at room conditions but the rate can be increased by many transition metal catalysts, including Fe^{3+} ions.

Outline the mechanism of the reaction catalysed by Fe^{3+} ions. What feature of transition metals is used in this reaction?

(c) (i) Outline how a solid heterogeneous catalyst increases the rate of a gas reaction.

(ii) A heterogeneous catalyst is used in a catalytic converter to remove the pollutants carbon monoxide and nitrogen dioxide from car exhaust gases.

Name the catalyst, write the equation for the reaction removing the named pollutants, and give one way in which the rate of reaction is made very high.

3 (a) Explain the following terms:

(i) the order of a reaction

(ii) the half-life of a reaction.

(b) The decomposition of hydrogen peroxide is a first-order reaction.

(i) Write an equation for the decomposition of hydrogen peroxide.

(ii) Write a rate equation for the decomposition of hydrogen peroxide.

(c) The rate of decomposition of a 0.5 $moldm^{-3}$ solution of hydrogen peroxide was followed by withdrawing 10 cm^3 portions of the solution at different times and placing them in titration flasks containing ice-cold sulphuric acid. Afterwards each mixture was titrated with 0.05 $moldm^{-3}$ solution of potassium manganate(VII) solution. The following results were obtained.

Time/min	Volume of 0.05 $moldm^{-3}$ $KMnO_4(aq)$ / cm^3
0	40.00
5	30.80
10	24.80
15	19.20
20	15.60
25	12.00
30	9.60
35	8.00
40	6.80

(i) State two reasons why the hydrogen peroxide solution were placed in ice cold sulphuric acid.

(ii) Explain why the volume of $KMnO_4$ used at a particular time may be taken as a measure of the concentration of hydrogen peroxide at that time.

(iii) Plot a graph of volume of potassium manganate(VII) solution used against time . Use the graph to confirm that the decomposition of hydrogen peroxide is a first order reaction.

(iv) Calculate the rate constant for the reaction.

4 (a) Propanone reacts with iodine in presence of sulphuric acid . The rate of the reaction can be followed by measuring the time required for the brown colour of iodine to disappear.

A set of solutions was prepared and the time taken for the brown colour of iodine to disappear in each case was recorded. The results are tabulated below.

Experiment number	Volume of propanone used/cm^3	Volume of iodine used/cm^3	Volumeof sulphuric acid used/cm^3	Volume of water added	Time/s
1	10.0	5.0	5.0	15.0	60
2	20.0	5.0	5.0	5.0	30
3	10.0	10.0	5.0	10.0	60
4	20.0	5.0	10.0	0.0	15
5	20.0	10.0	5.0	0.0	

(i) Write an equation for the reaction between propanone and iodine in acidic medium.

(ii) Name the type of reaction which takes place between iodine and propanone in acidic medium.

(b) Deduce the order of reaction with respect to:-

  (i) propanone
  (ii) iodine
  (iii) hydrogen ions

(c) (i) Write a rate equation for the reaction .

  (ii) What does the rate equation suggest about the mechanism of the reaction between iodine and propanone in acidic medium.

  (iii) Fill the empty grid in the table above for experiment 5.

(b) How will the rate of the reaction change if aqueous bromine is used instead of aqueous iodine?

  (iv) Suggest another method that may be used to follow the rate of the above reaction.

5 (a) Sodium thiosulphate reacts with dilute sulphuric acid according to the following equation

$$Na_2S_2O_3(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + S(s) + SO_2(aq) + H_2O(l)$$

The rate of this reaction can be followed by determining the time taken for a certain amount of sulphur to be formed, at which time, a cross drawn on a sheet of paper below the flask will disappear.

A set of experiments was carried out to determine the order of the reaction with respect to hydrogen ions and to the thiosulphate ions. The results obtained were recorded in the table below:

Experiment number	Volume of $S_2O_3^{2-}$ /cm^3	Volume of H^+ (aq)/cm^3	Volume of $H_2O(l)$ / cm^3	Time /s
1	20	10	10	70 .
2	20	20	0	34
3	10	20	10	68

(i) Why was water added in experiments 1 and 3?

(ii) Deduce the order of the reaction with respect to the thiosulphate ion and the hydrogen ion.

(b) Why is it important to determine the orders of reaction and the rate equations ?

(c) How do you expect the rate of the above reaction to change when the temperature is increased?

Explain your answer.

6 (a) (i) What do you understand by 'the mechanism of a reaction'?

  (ii) How can a study of the rate of a reaction be used to determine a possible mechanism for the reaction?

(b) A zero order reaction is 50% complete after 30minutes. How long after the start of the reaction will it be 70% complete.

(c) In a first order reaction

$$A \rightarrow B + C$$

Sketch a graph of :-

(i) concentration of A at different time against time

(ii) rate of reaction against concentration of A.

(d) Substance X reacts with Y according to the equation below

$$2X + 2Y \rightarrow X_2Y_2$$

The initial rate of reaction is determined for several different initial conditions. The results obtained are recorded in the table below.

Experiment number	[X]/ moldm^{-3}	[Y] moldm^{-3}	Initial rate/ moldm^{-3}s^{-1}
1	0.2	0.1	0.063
2	0.2	0.2	0.125
3	0.4	0.1	0.254
4	0.4	0.2	0.525

(i) What is the order of reaction with respect to X?

(ii) What is the order of reaction with respect to Y?

(iii) What is the overall order of reaction?

(iv) Write a possible mechanism for the reaction between X and Y.

7 (a) (i) What do you understand by the activation energy of a reaction.

(ii) Explain how a knowledge of the activation energies of the forward reaction and the backward reaction can help us to predict the effect of temperature on the position of equilibrium for a reversible reaction.

(b) The reaction between two substances A and B is represented by the following equation

$$2A + B \rightarrow C$$

Experiments were carried out to determine a value for the rate constant. The results are recorded in the table below.

Initial concentration of A, [A$_0$] / moldm^{-3}	Initial concentration of B, [B$_0$]/ moldm^{-3}	Initial concentration of C, [C$_0$]/ moldm^{-3}	Time/min	Final concentration of C , [C]/ moldm^{-3}
0.20	0.10	0.00	40.0	0.040
0.20	0.20	0.00	21.0	0.039
0.40	0.20	0.00	11.0	0.075

(i) Determine the order of the reaction with respect to A.

(ii) Determine the order of the reaction with respect to B.

(iii) Write a rate equation for the reaction.

(iv) Write a possible mechanism for the reaction.

CHAPTER

11

THE PERIODIC TABLE

SYLLABUS OBJECTIVES

In this chapter you should be able to:

- for the third Period elements (sodium to argon), describe qualitatively the variations (including the periodicity in these properties) in their atomic radius; ionic radius; melting point; electrical conductivity
- explain qualitatively the variation in atomic radius and ionic radius (eg of Na^+, Mg^{2+}, Al^{3+}) of the elements in the third Period
- interpret the variation in melting point and electrical conductivity of the elements of the third Period in terms of their structure and bonding (ie simple molecular, giant molecular or metallic bonding)
- explain the variation in the first ionisation energy of the elements in the third Period
- describe the reactions (if any) of the third Period elements with oxygen (to give Na_2O, MgO, Al_2O_3, P_4O_{10}, SO_2, SO_3), with chlorine (to give $NaCl$, $MgCl_2$, Al_2Cl_6, $SiCl_4$, PCl_5) and with water
- state and explain the variation in oxidation number of the oxides and chlorides of the third Period elements, referring to bonding and electronegativity
- describe the reactions of the oxides of the third Period elements with water (eg compare reactions of Na_2O and SO_3 with water), referring to bonding and electronegativity
- describe and explain the acid/base behaviour of the oxides and hydroxides of the third Period elements, including amphoteric behaviour in reaction with sodium hydroxide and acids (eg describe the reaction of aluminium oxide with aqueous NaOH and HCl), referring to bonding and electronegativity
- describe and explain the reactions of the chlorides of the third Period elements with water, referring to bonding and electronegativity
- suggest the types of chemical bonding in chlorides and oxides from their given chemical and physical properties
- predict the characteristic properties of an element in a given Group by using knowledge of chemical periodicity (eg predict properties of Astatine from knowledge of the other Group VII elements)
- make deductions with regard to the nature, possible position in the Periodic Table, and identity of unknown elements from given information of physical and chemical properties (eg an unknown element M that reacts vigorously with water to form a strongly alkaline solution containing M^+ ions, is probably in Group I)

Predicting Positions of Elements

Changes in Physical Properties of Elements in a Period

Chemical Reactions of the Elements Sodium – Argon

Properties of the Oxides of the Elements Sodium – Sulphur

Properties of the Chlorides of the Elements Sodium – Phosphorus

11.1 Predicting Positions of Elements

Common Properties of a Group of Elements

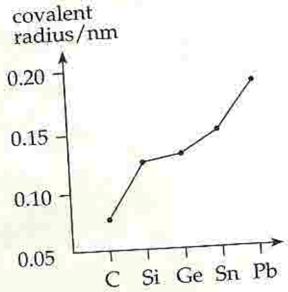
- All elements in a group have the same number of electrons in the outer shell which is the same as the group number, and have a similar outer shell electronic configuration.
  For example, the outer shell electronic configuration of all Group IV elements is

- Because of a similar outer electronic configuration, all elements in the group have the following properties:
  (a) The elements have similar metal/non-metallic properites (eg all Group VII elements are non-metals which are very poor conductors of electricity).
  (b) They form ions with the same charge (eg all Group II elements form an ion with a charge of +2).
  (c) They form compounds with similar formulae as they form the same number of bonds (eg all Group III elements form a chloride with the formula MCl_3).
  (d) The elements usually have the same type of oxides (eg all Group I oxides are basic). However, the oxides become more basic down the Group so, although in Group III aluminium is amphoteric, thallium (at the bottom of the Group) is basic.

Trends in Properties in a Group

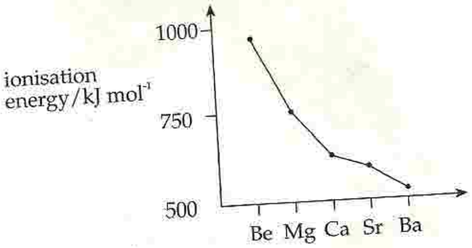
- Going down a group in the Periodic Table (ie with increasing proton number), there is a *gradual change* in the properties of the elements. This change in properties is small for groups on the edge of the Periodic Table (ie in Groups I, II, VII and VIII). The change in properties is large for groups in the middle of the Periodic Table (eg in Group IV).

- The *atomic radius increases* down the group. This is due to the increasing number of electron shells. For example, the increase in the covalent radius of the Group IV elements is shown in Fig 11.1.

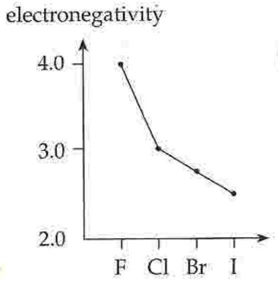


▲ Fig 11.1

- The *ionisation energy decreases* down the group. This is because the atomic radius becomes larger, so the outer electrons are further from the nucleus and thus become less strongly attracted by the positive nucleus. Although the nuclear charge increases, extra shells of electrons are added. Thus the increase in nuclear charge is largely cancelled by the extra shells of electrons, going down the group, making it easier for electrons to be removed. The decrease in ionisation energy down a group is shown for Group II in Fig 11.2.



▲ Fig 11.2



▲ Fig 11.3

- The *electronegativity* of the elements *decreases* down the group. This is due to the increase in atomic radius. The decrease in electronegativity down Group VII is shown in Fig 11.3.

- The elements become *more metallic* as the proton number increases. This is because the atomic radius becomes larger and the outer electrons become less strongly held. Hence the outer electrons can more easily be given up by the atoms to form delocalised electrons in metallic bonds.

- *Covalent bonds* become *weaker*, as the proton number increases. For example, the hydrides of Group VII (HCl, HBr and HI) become less stable to heat as the atomic number of the Group VII element increases. This is because the covalent bonds in the HX molecules become weaker.

- *Van der Waals forces* become *stronger* as the proton number increases. This is because the atoms become bigger. For example the melting and boiling points of the Group VII elements increase from F_2 to I_2, as the molecules become bigger and the Van der Waals forces between the molecules become stronger (Table 11.1).

▶ Table 11.1 Melting and boiling points of Group VII elements

element	m.p./°C	b.p./°C	
fluorine	–220	–188	Van der Waals forces stronger ↓
chlorine	–101	–34	
bromine	–7	58	
iodine	114	183	

Predicting Position of an Element in the Periodic Table

- The position of an element in the Periodic Table can be found from the Group and Period it is in.
  - (a) The likely Group can be found from the formula of its compounds, such as its oxide or chloride, or the charge on its ion. For example, a chloride XCl_2, indicates that X is in Group II.
  - (b) The Period an element is in and its identity can then be found from its approximate relative atomic mass.

11.2 Changes in Physical Properties of Elements in a Period

- The physical properties of the elements in the Period sodium to argon are summarised in Table 11.2.

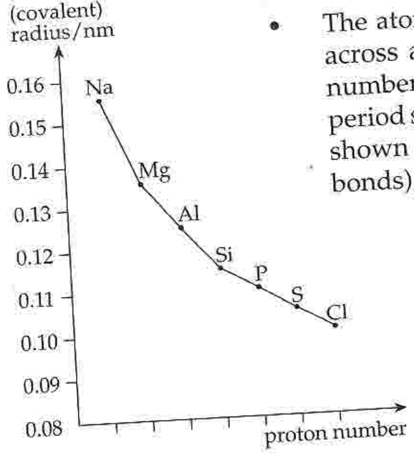
property \ element	Na	Mg	Al	Si	P*	S*	Cl	Ar
proton number	11	12	13	14	15	16	17	18
ionisation energy kJ mol^{-1}	500	740	580	790	1010	1000	1260	1520
covalent bond radius nm	0.156	0.136	0.125	0.117	0.110	0.104	0.099	–
electronegativity	1.0	1.25	1.45	1.74	2.05	2.45	2.85	
structure	← metallic →			giant molecular	← molecular → P_4	S_8	Cl_2	Ar
density g cm^{-3}	0.97	1.74	2.70	2.33	1.82	2.07	(gas)	(gas)
melting point °C	98	651	660	1410	44	119	–101	–189
boiling point °C	890	1117	2447	2355	280	445	–35	–186
electrical conductivity of the solid	← good →			← very poor →				

*data for phosphorus applies to white phosphorus, while data for sulphur applies to rhombic sulphur

▲ Table 11.2 Physical properties of the elements in the third Period

Atomic Radius

- The atomic radius of elements decreases across a period, with increasing proton number. This is shown in Fig 11.4 for the period sodium to argon (argon itself is not shown because it does not form covalent bonds).

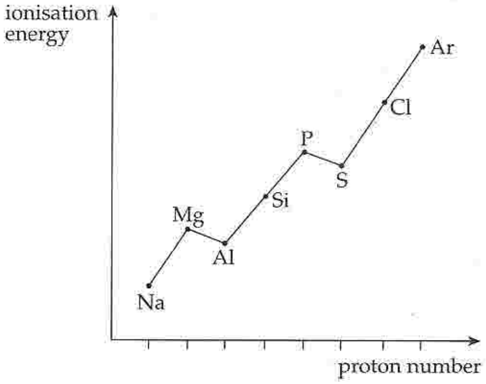


▶ Fig 11.4

- The decrease in radius is due to the increase in the nuclear charge, so that the outer electrons are more strongly attracted to the nucleus.
- The decrease in radius becomes smaller with increasing proton number because of increased repulsion between electrons in the outer shell.

Ionisation Energy

- The ionisation energy of elements increases across a period, with increasing proton number. This is shown in Fig 11.5 for the period sodium to argon.



▶ Fig 11.5

- The increase in ionisation energy is due to the increase in nuclear charge. This increases the force of attraction on the outer electrons, so they are more strongly held.
- The rather low ionisation energy for aluminium compared to magnesium is due to the electron being lost from the 3*p* subshell which is further from the nucleus than the 3*s* subshell.

	3*s*	3*p*		
Al atom:	↑↓	↑		

  Also, more energy is required to break up the electron pair in the 3*s* in magnesium.

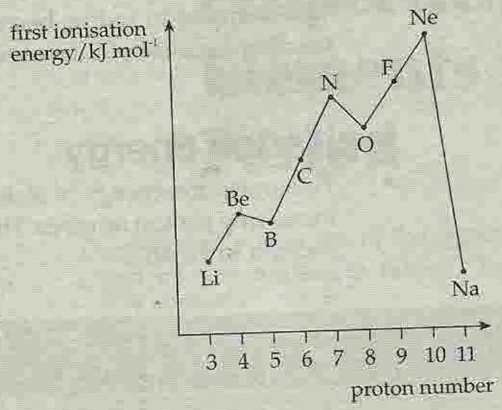
- The rather low ionisation energy for sulphur is due to increased repulsion between the two electrons occupying the same 3*p* orbital — so one electron is more easily lost.

	3*s*	3*p*		
S atom:	↑↓	↑↓	↑	

  In phosphorus, the 3*p* electrons are all single electrons.

Question

Explain the shape of the graph in Fig 11.6.



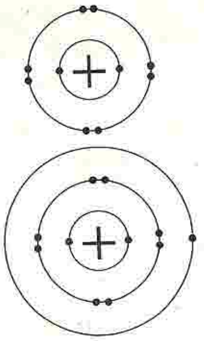
▶ Fig 11.6

Answer

(a) The increase in ionisation energy from Li to Ne is due to increase in nuclear charge across the period. Thus the outer electrons are more strongly held and so the ionisation energy increases. The low ionisation energy for B is due to the 2*p* subshell (from which the electron is removed) which is further from the nucleus than the 2*s* subshell.

The low ionisation energy for O is due to the increased repulsion between the paired 2*p* electrons so less energy is required to lose one of these electrons.

(b) The big decrease in ionisation energy from Ne to Na is because the outer electron of sodium is in the *third* shell (ie in the 3*s* orbital), as shown in Fig 11.7. The 3*s* electron of sodium is further from the nucleus than the outer electrons of neon (in the 2*s* and 2*p* orbitals). The *second shell* of electrons is in *between* the nucleus and the 3*s* electron, so it cancels out or shields much of the positive charge of the nucleus.



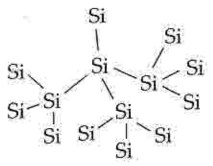
▲ Fig 11.7 Atoms of neon and sodium

Electronegativity

- Electronegativities of the elements increase across a period with increasing atomic number.
- In the period Na to Ar, the elements change from metals to non-metals (like in the Period Li to Ne). Because the atoms are larger than those in the second period, more of the elements are metallic. Only the metals sodium, magnesium and aluminium conduct electricity well. The conductivity increases from sodium to aluminium as the number of electrons in the outer shell (which can be delocalised) increases from 1 to 3.

Structure and Melting Point

- The melting point and (particularly) the boiling point depends on the bonds that must be weakened and broken for melting and boiling.



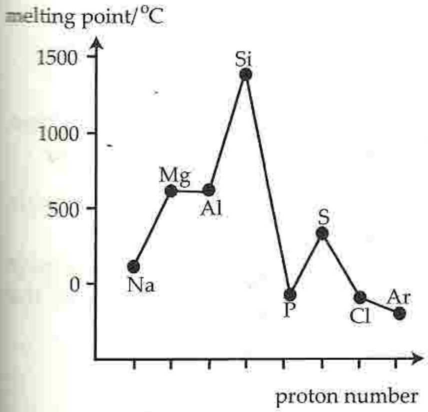
▲ Fig 11.8 Giant molecular structure of silicon

- **In the period Na – Ar**
  (a) Sodium, magnesium and aluminium have metallic structures. Their melting points increase from sodium to aluminium. This happens because the metallic bonds become stronger due to
  (i) decreasing atomic radius;
  (ii) increasing nuclear charge;
  (iii) increasing number of delocalised electrons.
  (b) Silicon has a giant molecular structure, like diamond. It has a high melting point as strong covalent bonds must be broken to melt it. The melting point of silicon is less than the melting point of diamond, because Si—Si bonds are weaker than C—C bonds.
  (c) From phosphorus to argon, the elements have a molecular structure. They all have low melting and boiling points as little energy is required to break the very weak Van der Waals forces between the molecules. The melting and boiling points are in the same order as the mass and size of the molecules, as shown in Table 11.3. This is because the strength of Van der Waals forces depends on the size of the molecules.

▶ Table 11.3

molecular formula	P_4	S_8	Cl_2	Ar
relative molecular mass	124	256	71	40
m.p./°C	44	119	–101	–189
b.p./°C	280	445	–35	–186

(d) A graph of melting point against atomic number for Na to Ar is shown in Fig 11.9. A graph of boiling point against atomic number has a similar shape.



▲ Fig 11.9

Ionic Radii

- (a) The ionic radii of the ions formed by Na, Mg and Al in compounds are as follows:

ion	Na^+	Mg^{2+}	Al^{3+}
ionic radius	0.095 nm	0.065 nm	0.050 nm

All the ions have the same electronic configuration ($1s^2\ 2s^2\ 2p^6$). The only difference between them is the nuclear charge, which increases from Na to Al. This increasing nuclear charge increases the attractive force on the outer electrons and hence causes a decrease in ionic radii.

(b) The ionic radii of the ions formed by P, S and Cl in compounds are as follows:

ion	P^{3-}	S^{2-}	Cl^+
ionic radius	0.212 nm	0.184 nm	0.181 nm

All the ions have the same electronic configuration ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$). The decrease in ionic radii is due to the increasing nuclear charge.

(c) The radii of the negative ions in (b) are larger than the radii the positive ions in (a), because there is an extra shell electrons in the negative ions.

11.3 Chemical Reactions of the Elements Sodium – Argon

element	oxide product
Na	Na_2O
Mg	MgO
Al	Al_2O_3
Si	SiO_2
P	P_4O_{10}
S	SO_2
Cl, Ar	–

▲ Table 11.4 Products of combustion of Na – Ar in oxygen

Reaction with Oxygen

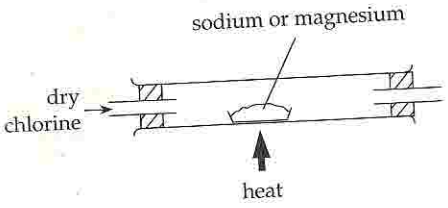
- All the elements (except argon and chlorine) react wth oxygen Usually the powdered element is heated strongly in oxygen.
- The products of combustion of the elements in oxygen summarised in Table 11.4.
- Sulphur burns in oxygen to produce sulphur dioxide, SO_2. In the presence of vanadium(V) oxide or platinum catalyst, the SO_2 reacts with oxygen to produce SO_3 in a reversible reaction.

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

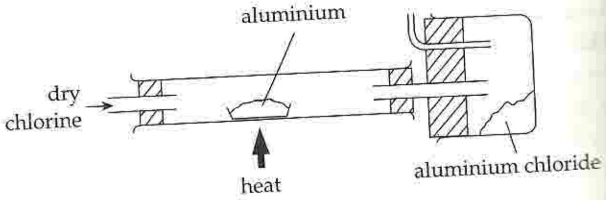
- In all the reactions, the oxygen is an oxidising agent and the other element is the reducing agent.

Reaction with Chlorine

- All the elements (except argon and chlorine) react with chlorine Usually the powdered element is heated strongly in chlorine.
- The apparatus used for the reaction depends on the chloride product.
  - (a) For sodium and magnesium, the chloride product is ionic with a high melting point. The chlorides are prepared in the apparatus shown in Fig 11.10.



▲ Fig 11.10



► Fig 11.11

  - (b) For the other elements, the chloride product is molecular Because of the high temperature of the reaction, the chloride is produced as a gas. To obtain the solid product, the chloride must be collected in a cool container. Fig 11.11 shows the apparatus for preparing solid Al_2Cl_6.
  - (c) The products of reaction of the elements with chlorine summarised in Table 11.5.

element	chloride product
Na	$NaCl$
Mg	$MgCl_2$
Al	Al_2Cl_6
Si	$SiCl_4$
P	PCl_5

▲ Table 11.5 Products of reaction of Na – Ar with chlorine

11.4 Properties of the Oxides of the Elements Sodium – Sulphur

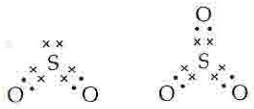
- The properties of the oxides of Na – S in the third Period are summarised in Table 11.6.

element	Na	Mg	Al	Si	P	S
atomic number	11	12	13	14	15	16
formula of oxide	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_6 P_4O_{10}	SO_2 SO_3
oxidation number	+1	+2	+3	+4	+3 +5	+4 +6
structure	←—— ionic ——→			giant molecular	←molecular →	
m.p./°C	0	2900	2040	1610	24 580	−75 17
b.p./°C	sublimes	3600	2980	2230	175 sublimes	−10 45
acid/base nature	←—— basic ——→		amphoteric	←—— acidic ——→		
effect of water on oxide	alkaline solution pH ≈ 13	dissolves slightly pH ≈ 9	insoluble		strongly acidic solution pH ≈ 2	

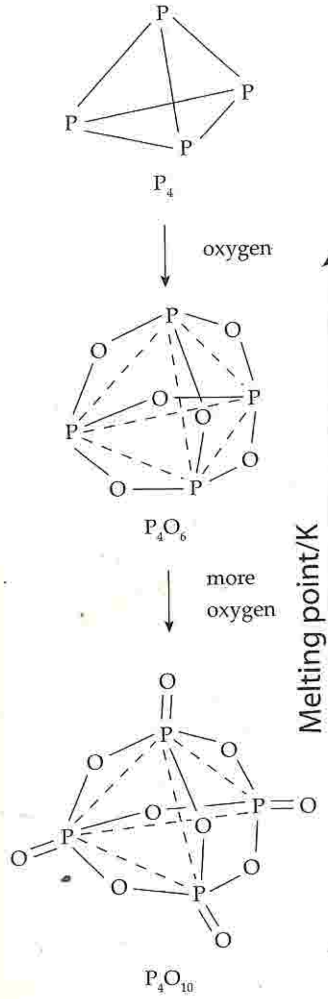
▸ Table 11.6 Oxides of elements in the third Period

Oxidation Number

- The oxidation number of the element in its oxide corresponds to the number of electrons used for bonding. The maximum oxidation number increases across the period from +1 for Na to +6 for S. This corresponds to the total number of outer shell electrons — all being used in the bonding. This is the same as the group number.
- In P and S other oxidation numbers are obtained, depending on the number of electrons used for bonding. For example, sulphur only uses four electrons (out of a possible six) for bonding in SO_2. Hence in SO_2, sulphur has an oxidation number of +4 (see *Covalent Bonds* in Chapter 4).



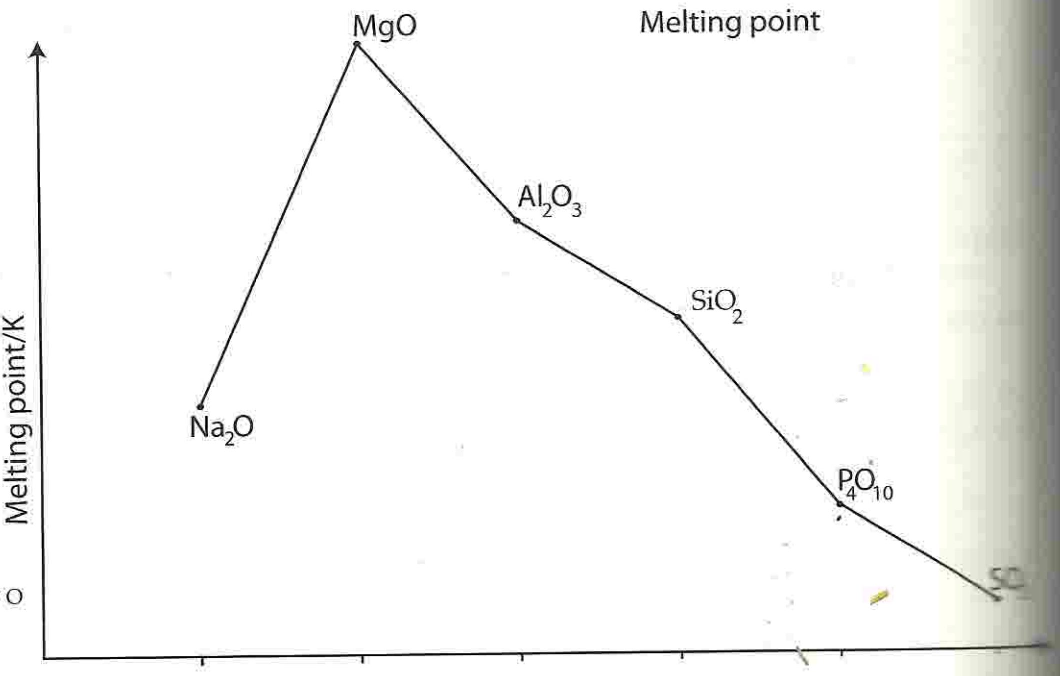
▲ Fig 11.12

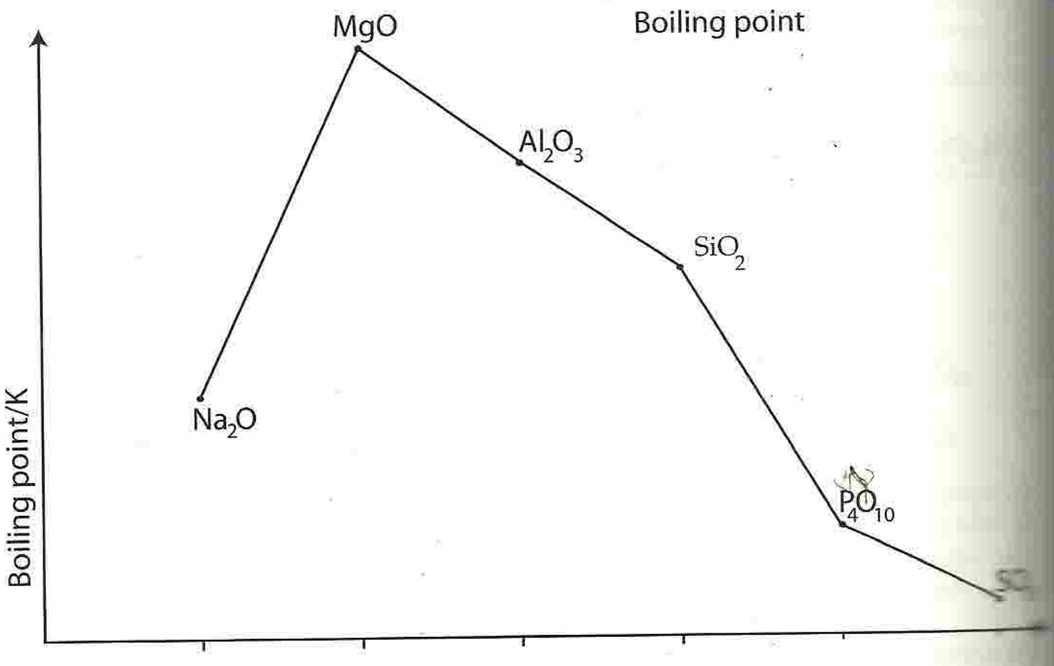


▲ Fig 11.13

Structure and Bonding

- The bonds change from ionic to covalent across the period, because the difference in electronegativity between the element and oxygen decreases.
- The oxides of sodium and magnesium are ionic. Hence they have high melting and boiling points, as strong electrovalent bonds must be broken for melting and boiling to occur.





Aluminium oxide is mainly ionic. However due to the high charge density of aluminium ion (Al^{3+}), it will polarize the oxide ion slightly as a result of which the aluminium oxide will have a small degree of covalency.

- SiO_2 has a giant covalent structure (see Chapter 5). It has a high melting and boiling point, as strong covalent bonds must be broken. The oxides of P and S have molecular structures. They have low melting and boiling points as only weak dipole-dipole forces need to be broken.

  The different structures of the oxides of phosphorus can be seen, starting from a P_4 molecule of white phosphorus, as shown in Fig 11.13.

Acid/base Nature of the Oxides

- The oxides become more acidic across the period, as atomic number increases.
  (a) Sodium oxide reacts with water to form a strongly alkaline solution:

$$Na_2O + H_2O \rightarrow 2NaOH$$

  (b) Aluminium oxide is amphoteric. It does not react with water, but reacts with acid (H^+ ions) and alkali (OH^- ions):

$$Al_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2Al(OH)_4^-(aq)$$

  (c) Phosphorus(V) oxide, P_4O_{10}, reacts with water to form a strongly acidic solution of phosphoric acid:

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

  (d) Sulphur trioxide reacts with water to form a strongly acidic solution of sulphuric acid:

$$SO_3 + H_2O \rightarrow H_2SO_4 \rightarrow 2H_3O^+ + SO_4^{2-}$$

11.5 Properties of the Chlorides of the Elements Sodium – Phosphorus

- The properties of the chlorides of Na – P in the third Period are summarised in Table 11.7.

element					
proton number	11	12	13	14	15
formula of chloride	NaCl	$MgCl_2$	Al_2Cl_6	SiO_4	PCl
oxidation number	+1	+2	+3	+4	+5
bonding and structure	ionic		covalent molecular		Cl Cl ions
state at room conditions	solids			liquid	soli
m.p./°C	808	714	sublimes at 180°C	−70	sublim at 162
b.p./°C	1465	1418		57	
effects of water	neutral solution	slightly acidic solution	fumes of HCl acidic solution products such as Al(OH)		
approximate pH of solution	7	6.5	2	1	1

*phosphorus also form the chloride PCl_3 (see *Covalent Bonds* in Chapter 4).

▶ Table 11.7 Chlorides of elements in the third Period

Oxidation Number

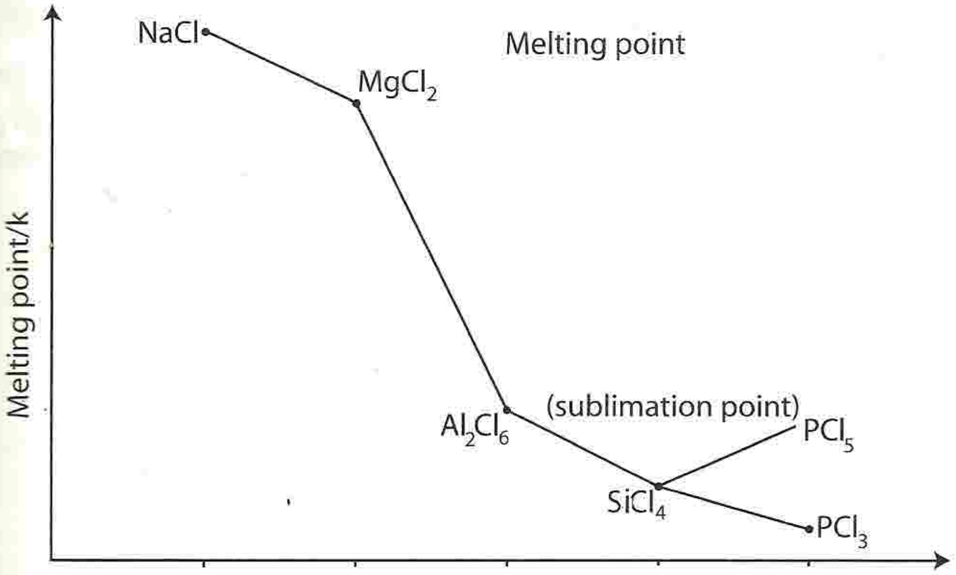
- The oxidation number of the element in the chloride corresp to the number of electrons used for bonding. The maxim oxidation number increases across the period from +1 for Na +5 for P (in PCl_5) like in the oxides. This corresponds to the number of outer shell electrons, and is the same as the g number.

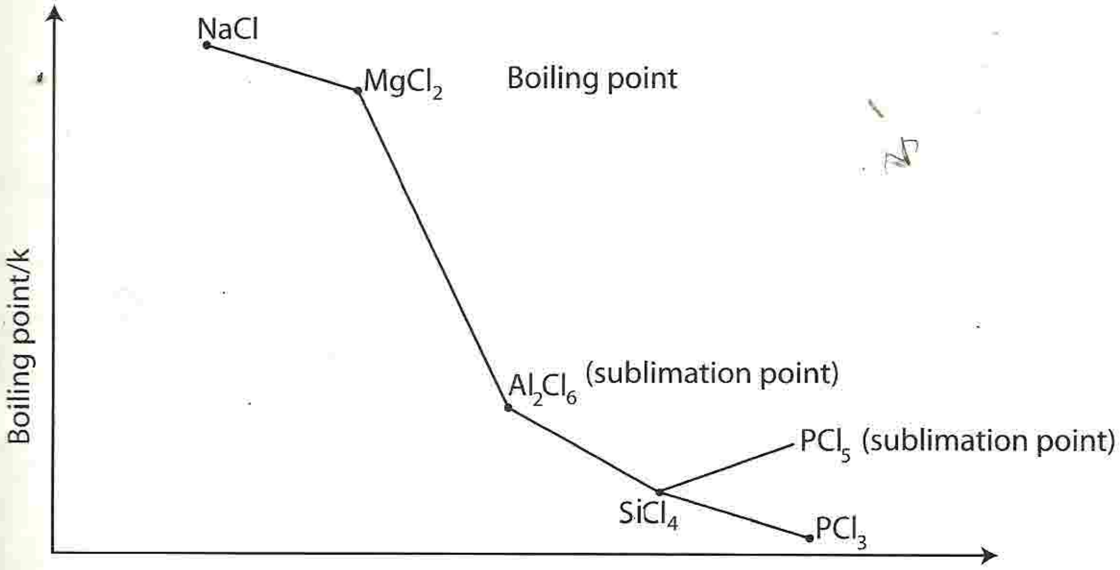
Structure and Bonding

- The bonds change from ionic to covalent across the Period, beca the electronegative difference between the element and chlo decreases.
- The chlorides of sodium and magnesium are ionic. Hence have high melting and boiling points, as strong electrova bonds must be broken for melting and boiling to occur.
- $AlCl_3$ consists of covalent molecules, joined together by dative bonds. It sublimes at a low temperature because these bonds easily break to produce small molecules.

- The chlorides of Si and P are all molecular. The forces between the molecules are weak. Hence their melting and boiling points are low.

  The variation in melting point and boiling point of the chlorides of third period elements will be as shown below:-





Acid/Base Nature of the Chlorides

- The chlorides become more acidic across the Period, with increasing atomic number.
- The chlorides of Al – P react with water, producing HCl. In the reactions, the Cl atom is replaced with OH. The final product may be an oxide or an acid. Some examples of the reaction with water are given below:

$$AlCl_3(s) + 6H_2O(l) \longrightarrow [Al(H_2O)_5OH]^{2+}(aq) + H^+(aq) + 3Cl^-(aq)$$

$$SiCl_4(l) + 2H_2O(l) \longrightarrow SiO_2(s) + 4H^+(aq) + 4Cl^-(aq)$$

$$PCl_3(l) + 3H_2O(l) \longrightarrow H_3PO_3(aq) + 3HCl(aq)$$

$$PCl_5(s) + 4H_2O(l) \longrightarrow H_3PO_4(aq) + 5HCl(aq)$$

Question

Z4

A chloride of element E has melting point –18°C and boiling point 130°C. A 'cross-dot' structure of the chloride is shown in Fig 11.14.

(a) Describe the lattice structure of this chloride.

(b) In which group of the Periodic Table does element E belong? Explain your answer.

▶ Fig 11.14

(c) The chloride reacts with water producing white fumes. Write a balanced equation for the reaction.

(d) Predict the formula of *one* oxide of element E and state the oxidation number of E in the oxide.

Answer

(a) Because of its low melting and boiling points, the chloride has a molecular structure. The crystal consists of covalent ECl_3 molecules held together by weak Van der Waals forces.

(b) E is in Group V because it has five outer shell electrons (3 in the covalent bonds and 2 in a lone pair in an ECl_3 molecule).

(c) $ECl_3 + 3H_2O \rightarrow E(OH)_3 + 3HCl$ (other equations are possible, but the simplest one is obtained by replacing each Cl with OH).

(d) E_2O_5 (or E_2O_3) with oxidation number of +5 or +3.

Question 0.05 mole of a chloride of element X was reacted with excess silver nitrate solution. 28.7 g of silver chloride was produced when the reaction was complete. Deduce the empirical formula of the chloride and predict which group of the Periodic Table element X belongs.
[Cl = 35.5; Ag = 108]

Answer Number of moles of AgCl $= \dfrac{\text{mass of AgCl}}{M_r \text{ of AgCl}}$

$$= \frac{28.7}{143.5}$$

$$= 0.2 \text{ mole}$$

0.05 mole of the chloride of X produces 0.2 mole of AgCl and so must contain 0.2 mole of Cl atoms.

Hence, 1 mole of the chloride of X must contain $\frac{0.2}{0.05} = 4$ moles of Cl atoms.

Therefore the empirical formula of the chloride is XCl_4.
X is probably in Group IV as all Group IV chlorides have a similar formula.

EXERCISE 11

Multiple Choice Questions

Section I

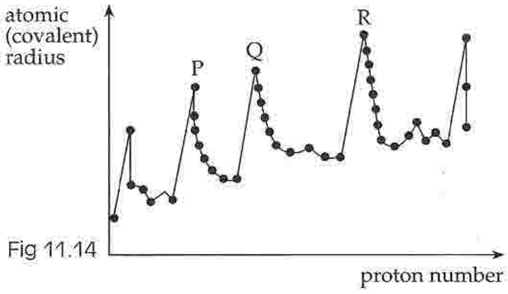
Which one of the following oxides has the highest melting point?

A SiO_2 C SO_2
B P_4O_{10} D SO_3

Which change takes place in a period of elements, with increasing proton number?

A The atomic radius becomes larger.
B The electronegativity increases.
C The elements become more metallic.
D The oxides of the elements become more basic.

Fig 11.14 shows a graph of the atomic (covalent) radius for the first 60 elements.
The elements labelled P, Q and R belong to

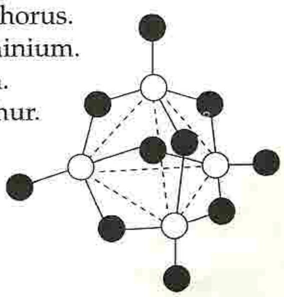


▶ Fig 11.14

A Group I. C Group VII.
B Group III. D Group VIII.

4 Fig 11.15 shows the structure of a molecule of

A an oxide of phosphorus.
B a chloride of aluminium.
C an oxide of silicon.
D a chloride of sulphur.



▶ Fig 11.15

5 Which one of the following chlorides has an ionic structures?

A Al_2Cl_6 C $MgCl_2$
B $SiCl_4$ D HCl

6 The following elements are all in the same period of the Periodic Table. Which element has the highest melting point?

A phosphorus C magnesium
B aluminium D silicon

7 Which one of the following oxides is amphoteric?

A sodium oxide, Na_2O
B magnesium oxide, MgO
C aluminium oxide, Al_2O_3
D phosphorus(V) oxide, P_4O_{10}

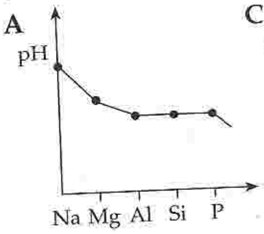
8 Tellurium (symbol Te) is below sulphur in Group VI. Which one of the following predictions does not describe tellurium?

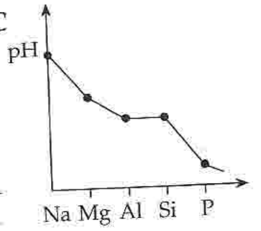
A Tellurium forms a covalent oxide.
B Tellurium oxide is more ionic than sulphur oxide.
C Tellurium forms a fluoride, TeF_6.
D Tellurium oxide is a basic oxide.

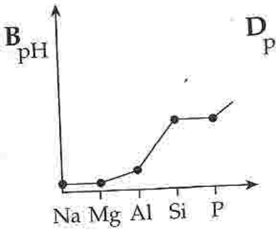
9 Which one of the following ions has the *smallest* radius?

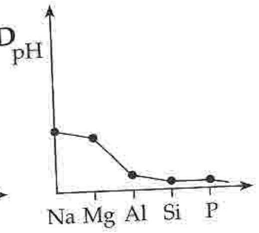
A O^{2-} C Na^+
B F^- D Al^{3+}

10 One mole of the chloride of each of the following elements was mixed separately with 1 dm^3 of water. Which one of the following graphs shows the pH of the solutions produced?

A


C


B


D


11 The particles Cl^-, Ar and K^+ are isoele
(This means that they have the same
of electrons). What is the correct order f
radii?

	smallest	⟶	*largest*
A	K^+	Cl^-	Ar
B	Cl^-	K^+	Ar
C	K^+	Ar	Cl^-
D	Ar	Cl^-	K^+

12 Which oxide is **not** ionic?

A Al_2O_3 C Na_2O
B MgO D SiO_2

13 Four pairs of elements are given bel
which pair does the *second* element
smaller ionisation energy than the first el

A Na, Mg C Mg, Al
B Cl, Ar D S, Cl

Section II

Summary of directions

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

14 Which of the following statements abou
oxides SiO_2, P_4O_{10} and SO_3 are true?

1 They are all acidic.
2 They are all covalent.
3 SiO_2 is the only one with a giant mole
structure.

15 Which are correct descriptions of the proper
of anhydrous aluminium chloride?

1 It fumes in moist air producing hydr
chloride.
2 Its vapour has a covalent molecular structure.
3 Its solid is ionic.

16 The aluminium ion, Al^{3+}, contains the
number of electrons as

1 the Mg^{2+} ion.
2 the Ar atom.
3 the Cl^- ion.

tructured Questions

The first eight successive ionisation energies of element **Z** (in kJ mol^{-1}) are

790, 1600, 3200, 4400, 16 100, 19 800, 23 800, 29 200

(a) What group is element **Z** in? Explain your answer.

(b) What is the formula of the chloride of **Z**, and what is the oxidation number of **Z** in this chloride?

(c) Write a balanced equation for the reaction of the chloride of **Z** with water.

2 Some information is given on an oxide of each of four elements, **A – D**, which are in the third period (sodium to argon). In each case,

(i) give the oxidation number of the element in the oxide;

(ii) name the oxide;

(iii) give a brief explanation for your answer to (ii).

A The oxide of element **A** has the formula AO and melts well above 1000°C.

B The oxide of element **B** dissolves in water to produce a strongly acidic solution containing BO_4^{2-} ions.

C The oxide of **C** is a white solid. Ammonia gas is liberated from ammonium salts when they are warmed with an aqueous solution of the oxide.

D In the oxide of **D**, the atoms of **D** and oxygen are in the mole ratio 1 : $2\frac{1}{2}$. The oxide reacts with water to produce an acid with relative molecular mass 98.

3 Gallium (symbol Ga) is below aluminium in Group III. Use your knowledge of the chemistry of aluminium and the Periodic Table to answer the following questions. Where possible, give reasons for your answers.

(a) How does the atomic radius of gallium compare with that of aluminium?

(b) How does the electronegativity of gallium compare with that of

(i) aluminium;

(ii) germanium (next to gallium, in Group IV)?

(c) How does the ionisation energy of gallium compare with that of

(i) germanium;

(ii) indium (below gallium in Group III)?

(d) Gallium chloride melts at 79°C and boils at 201°C.

(i) What type of bonds are present in the chloride?

(ii) Predict the oxidation number of gallium in the chloride.

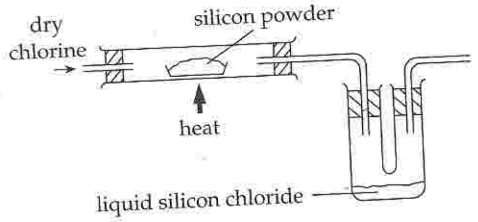
(iii) Write an equation to show the likely effect of water on the chloride.

(e) (i) Give the expected formula of gallium oxide.

(ii) Predict the likely acid/base nature of this oxide.

(iii) How would you expect the lattice energy of gallium oxide to compare with that of aluminium oxide?

*4 (a) The chlorides of the elements in the period Na to Ar, can be prepared by heating the element wth chlorine gas. The apparatus shown in Fig 11.16 was used to prepare a sample of silicon chloride in the laboratory.



▲ Fig 11.16

(i) Write a balanced equation, with state symbols, for the reaction.

(ii) Why must *dry* chlorine be used for the reaction? Explain your answer with an equation.

(iii) Name one other chloride which could be prepared using the same apparatus.

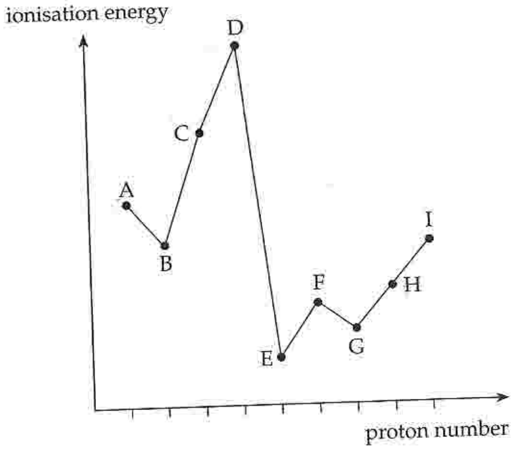
(b) A chloride of sulphur was found to contain 47.4% sulphur and has a boiling point of 136°C.

(i) Calculate the empirical formula of this chloride.

At a pressure of 100 kPa and a temperature of 500 K, 0.100 g of the chloride was found to have a volume of 30.8 cm^3.

(ii) Calculate the relative molecular mass, M_r, of the chloride.
(iii) Deduce the molecular formula of the chloride.
(iv) From the data given, comment on the bonding in this chloride.

5 The ionisation energies of nine successive elements, **A – I**, in the Periodic Table are shown in Fig 11.17.



▲ Fig 11.17

(a) Which two elements are in the same group?
(b) Using the letters **A – I**, write the formulae of
  (i) a molecule of element **C**;
  (ii) a molecule of element **D**;
  (iii) the oxide of element **G**;
  (iv) the chloride of element **H**.
(c) Which element has the largest atomic radius?
(d) Explain why the ionisation energy of
  (i) **A** is higher than that of **B**;
  (ii) **A** is higher than that of **I**.
(e) Draw a 'dot and cross' diagram for a chloride of element **I** and state the shape of this molecule.
(f) Which element forms the most basic oxide?

6 (a) Describe and explain the difference in electrical conductivity of the elements aluminium and sulphur.
(b) Write equations for the reactions, if any, of oxides of these elements with aqueous alkali and with aqueous acid.

(i) With aqueous sodium hydroxide

magnesium oxide	
one of the sulphur oxides	

(ii) With aqueous hydrochloric acid

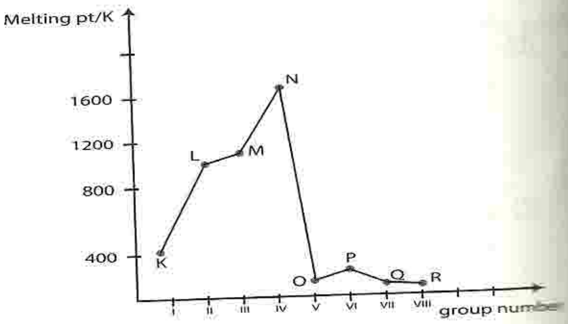
magnesium oxide	
one of the sulphur oxides	

Descriptive Questions

1 (a) For each of the elements sodium to sulphur in the third period, give the formula of the oxide with the highest oxidation number. State the oxidation number of the element in each oxide and briefly account for the variation.
(b) Write balanced equations for the reactions of water with an oxide of sodium and an oxide of phosphorus. State the difference in the pH of the solutions produced.

*2 Element **Q** forms an oxide with formula **Q_2O**. 1.00 g of the **Q_2O** reacts with water to form a solution that requires 42.6 cm^3 of 0.500 mol dm^{-3} HCl for complete reaction.
(a) Write equations for both reactions.
(b) Calculate the relative atomic mass of **Q** and suggest its identity.

3 The sketch below shows the melting points for the elements across a Period of the Periodic Table.



(a) Identify the Period represented by the sketch.

(b) Write the symbol of each element in the Period.

(c) Discuss in terms of structure and bonding the trend of the melting points across the Period. Give diagrams of structures where possible.

4 (a) Give the formulae of the chlorides of the elements from sodium to sulphur.

(b) With reference to their electronegativities to chlorine, explain concisely the type of bonding in the chloride.

(c) Give the structure of Al_2Cl_6 and $GeCl_4$.

(d) (i) Explain the dimerisation of aluminium chloride.

(ii) Explain what happens when solid Al_2Cl_6 is heated gradually beyond 450 °C.

(e) How do the chloride of Period 3 elements (Na to S) behave with water. Write equations where appropriate and estimate the ptt of the resulting solutions.

5 An element across Period 3 from Na to S, forms a chloride YCl_n. It dissolves and reacts with water to form an acidic solution. When 0-20 mole of YCl_n is reacted with water and aqueous silver nitrate added, 143.5 g of silver chloride is precipitated.

(a) Calculate a value for n.

(b) (i) Is y a metal or a non-metal, explain.

(c) (i) Identify Y, write the formula of YCl_n and its structure using dot and cross.

(d) Write the equation of the reaction of YCl_n with water and estimate the pH of the solution.

(e) Y exhibits another valency, write the formula of its chloride.

(f) Using orbitals explain why the element Y exhibits two valencies.

6 (a) Across a Period 3 from left to right, the proton number increases but the atomic radius decreases.
Explain as fully as you can.

(b) Why is the second ionization energy of an element larger than the first ?

(c) Account for the general trend of the electronegativities across Period 3 and the change in the nature of the element.

(d) Describe briefly the change in structure of the element from Na to S.

7 (a) (i) Use data booklet to plot a graph of the first ionization energy (y-axis) against the atomic number (x-axis).

(ii) Comment on the general trend.

(iii) Explain concisely the discrepancies between magnesium and aluminium and between nitrogen and phosphorus.

(b) An oxide of an element of Period 3 form an oxide X_aO_b. When 300 cm^3 of gaseous X was made to react with 1050 cm^3 of oxygen, two moles of X_aO_b was formed.

(i) Find the value of *a* and *b*.
(ii) Suggest the identity of X.
(iii) Write the formula of X_aO_b.
Write an equation for its reaction with water.

8 (a) Name an ore from which magnesium is extracted.

(b) Explain why electrolysis is used for the extraction of magnesium from its molten ore.

(c) Sodium Chloride forms anhydrous crystals but the crystals of magnesium chloride contains water of crystallization.
Explain as fully as you can.

(d) When a solution of magnesium chloride is evaporated to dryness, the product formed has the following composition by mass :

52.6% Cl, 35.5% Mg and 11.9% O.

(i) Calculate the empirical formula of the compound.
(ii) Suggest the actual formula of the solid.
(iii) Explain why anhydrous magnesium chloride is not formed when its hydrated crystals are strongly heated. Write a balanced equation.

CHAPTER

12

GROUP II ELEMENTS

General Characteristics of Group II Elements

The Elements Mg – Ba

Oxides of Group II Elements

Carbonates and Nitrates of Group II Elements

Uses of Compounds of Group II Elements

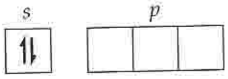
SYLLABUS OBJECTIVES

In this chapter you should be able to:

- describe similarities and trends in the properties of Group II elements (Mg – Ba) and their compounds and uses.
- describe the reactions of the elements with oxygen and water
- describe the behaviour of the oxides with water
- describe the thermal decomposition of the nitrates and carbonates
- explain qualitatively the trend in the thermal stability of the nitrates and carbonates in terms of the charge density of the cation and the polarisability of the large anion
- make predictions from the trends in physical and chemical properties of the elements and their compounds (eg predict properties of radium from known properties of Mg – Ba)
- know the use of magnesium oxide as a refractory lining (eg of furnaces) and of carbonates as building materials (eg calcium carbonate [limestone] in making cement)
- describe the use of lime in agriculture (ie in neutralising acidity in soils)

12.1 General Characteristics of Group II Elements

- Atoms of Group II elements have two electrons in the outer shell



- The elements have the following features:
  (a) large atomic radius;
  (b) relatively low ionisation energy;
  (c) small electronegativity and
  (d) they usually form M^{2+} ions in compounds (most compounds are ionic).
- The elements are all metals with similar properties.
- The elements are all very reactive and are powerful reducing agents.
- The Group II elements have only the oxidation state of +2 in their compounds.
- The oxides of Group II elements are all basic (except beryllium oxide, which is amphoteric).

12.2 The Elements Mg – Ba

- The elements are all powerful reducing agents, because when they react they readily give up electrons to form M^{2+} ions. This is also shown by their high negative standard electrode potentials (see below).
- As the proton number of Group II elements increases (going down the Group),
  (a) the atomic radius increases;
  (b) the ionisation energy decreases;
  (c) the standard electrode potential becomes more negative:

$$Mg^{2+} + 2e^- \rightleftharpoons Mg;\ E^\circ = -2.38\ V$$
$$Ca^{2+} + 2e^- \rightleftharpoons Ca;\ E^\circ = -2.87\ V$$
$$Ba^{2+} + 2e^- \rightleftharpoons Ba;\ E^\circ = -2.90\ V$$

(d) because of the above changes, the elements become more reactive and more powerful reducing agents as the proton number increases.

- The elements burn in oxygen with a bright flame. The general equation is:

  $$2M + O_2 \rightarrow 2MO$$

  Because of the increasing reactivity down the Group, barium must be stored under oil to protect it from reacting with oxygen and water vapour in the air.

- The elements react with cold water to produce hydrogen gas and metal hydroxides. The general equation is:

  $$M + 2H_2O \rightarrow M(OH)_2 + H_2$$

  The reactivity of the elements with water increases down the Group.

12.3 Oxides of Group II Elements

- The elements magnesium to barium all form basic oxides with the general formula MO.
- The lattice energies of the oxides decrease down Group II. The lattice energies decrease because of the increasing ionic radius of the cation (Table 12.1).

oxide	cation	ionic radius of cation/nm	lattice energy/kJ mol^{-1}
MgO	Mg^{2+}	0.065	3933
CaO	Ca^{2+}	0.099	3523
SrO	Sr^{2+}	0.113	3310
BaO	Ba^{2+}	0.135	3125

▶ Table 12.1

- Because the lattice energies decrease down the Group, the solubilities of the oxides *increase* down the Group. So magnesium oxide is insoluble in water but calcium oxide and barium oxide both react with water to form alkaline solutions of metal hydroxides. For example:

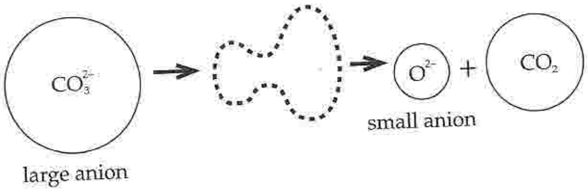
$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s) \xrightarrow[\text{water}]{\text{excess}} Ca(OH)_2(aq)$$

12.4 Carbonates and Nitrates of Group II Elements

- Group II elements form carbonates with the general formula MCO_3, and nitrates with the general formula $M(NO_3)_2$.
- The carbonates are all insoluble in water. The nitrates are all soluble in water.
- The carbonates and nitrates of Group II elements decompose on heating to leave a metal oxide residue. The general equations are:

$$MCO_3 \rightarrow MO + CO_2$$
$$2M(NO_3)_2 \rightarrow 2MO + 4NO_2 + O_2$$

- The thermal stability of the Group II compounds *increases* down the Group from calcium to barium. Hence the carbonate and nitrate of calcium decompose more easily on heating than the carbonate and nitrate of barium.
- The radius of the dipositive cation increases down the group. Charge density ($\frac{\text{charge}}{\text{radius}}$) decreases and the polarization of the carbonate and nitrate ions decreases and decomposition to form the smaller oxide ion becomes more difficult such that higher temperatures are required.



▶ Fig 12.1

12.5 Solubility of Sulphates of Group II Elements

- The solubility of an ionic solid is a measure of the relative magnitude of its reverse enthalpy change of lattice and the enthalpy change of hydration of its ions.

$$\Delta H^\ominus_{\text{solution}} = -\Delta H^\ominus_{\text{lattice}} + \Delta H^\ominus_{\text{hydration}}$$

- The solubility of Group II metal sulphates decreases down the group. Magnesium sulphate is soluble, calcium sulphate is sparingly soluble but strontium and barium sulphates are insoluble

- Since the radius of the SO_4^{2-} is large, the rate of decrease of $-\Delta H^{\ominus}_{lattice}$ lattice is slower than the rate of increase of $\Delta H^{\ominus}_{hydration}$ hydration of the separate ions.

$$\Delta H^{\ominus}_{lattice} \; \alpha \; \frac{\text{product of charges on ions}}{r^{+} + r^{-}}$$

- Therefore, less hydration energy is made available to meet up the reverse lattice energy and solubility decreases.

12.6 Uses of Compounds of Group II Elements

▾ Table 12.2

compound	use	reason for use
magnesium oxide	refractory (heat resistant) lining of furnaces	magnesium oxide has a very high melting point
calcium oxide and calcium hydroxide	spread onto agricultural land to neutralise excess acidity	calcium oxide and hydroxide are basic
calcium carbonate (marble and limestone)	used to make cement for concrete in buildings	—
calcium sulphate $CaSO_4.\frac{1}{2}H_2O$	plaster casts for broken limbs	absorbs water and sets to a hard solid

EXERCISE 12

Multiple Choice Questions

Section I

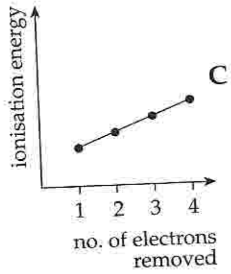
1 Which change is correct for the elements barium, calcium and magnesium, with decreasing proton number?
A The ionisation energy decreases.
B The lattice energy of the oxides becomes greater.
C The electronegativity decreases.
D The elements become more reactive.

2 Which statement best explains the difference in thermal stabilities of calcium nitrate and barium nitrate?
A The lattice energy of calcium nitrate is smaller than that of barium nitrate.
B The ionic radius of the calcium ion is larger than that of the barium ion.
C The ionisation energy of calcium is greater than that of barium.
D The calcium ion has a greater charge density than the barium ion.

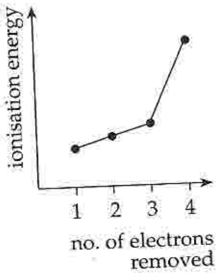
3 Radium is in Group II and has proton number 88. Which statement about radium is *not* likely to be true?
A Radium nitrate decomposes more easily than barium nitrate when heated.
B The radium ion, Ra^{2+}, has the greatest polarizing power of the Group II cations.
C Radium oxide dissolves in water to form an alkaline solution.
D Radium metal reacts vigorously with water to produce hydrogen gas.

4 Which graph shows the variation of the first four successive ionisation energies for a Group II element?

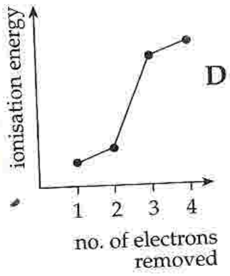
A



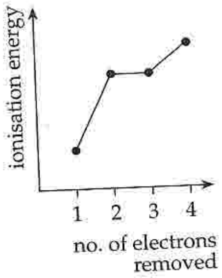
C



B



D



5 Which property of beryllium is *typical* of the other elements in Group II?

- **A** Beryllium oxide is amphoteric.
- **B** Beryllium fluoride contains Be^{2+} ions.
- **C** Beryllium chloride is covalent.
- **D** Beryllium does not react with water.

6 Barium and radium have proton numbers 56 and 88 respectively. Some properties of barium and radium are given below.

Element	barium	radium
Ionic radius M^{2+} ion/nm	0.143	0.157
Sum of first ionisation energies /kJ mol^{-1}	1468	1488
Enthalpy of vaporisation /kJ mol^{-1}	151	137
Standard electrode potential/V	–2.90	–2.92

Which property of radium, compared with that of barium, is unexpected?

- **A** ionic radius
- **B** sum of the first two ionisation energies
- **C** enthalpy of vaporisation
- **D** standard electrode potential

Section II

Summary of directions

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

7 Anhydrous calcium nitrate and anhydrous magnesium nitrate both decompose on heating, producing nitrogen dioxide and oxygen. Which statements about these two decomposition reactions are correct?

1 Nitrogen dioxide and oxygen produced from magnesium nitrate are at a lower temperature than that from calcium nitrate.

2 The volume of oxygen produced is half the volume of nitrogen dioxide produced for both nitrates.

3 Both nitrates leave a residue of metal oxide.

Structured Questions

1 Barium and magnesium are both Group II elements.

(a) Magnesium carbonate decomposes when it is heated. Write an equation, with state symbols, for this reaction.

(b) (i) Compare the thermal stabilities of barium carbonate and magnesium carbonate.

(ii) Explain your answer to (i) above.

(c) (i) Write an equation to show the reaction when a little water is added to barium oxide.

(ii) Would you expect a similar reaction with magnesium oxide? Explain your answer.

(d) Magnesium compounds have important uses.

(i) Name one such compound.

(ii) State one use for the compound.

(iii) Explain why it is used for the purpose.

2 Strontium is a Group II element with proton number 38.

(a) How would you expect the ionisation energy of strontium to compare with that of
  (i) calcium, and
  (ii) rubidium (proton number 37)?

(b) (i) What would you expect to observe if a piece of strontium were added to cold water?
  (ii) Write an equation for the reaction.

(c) (i) How would you expect the solubility of strontium sulphate to compare with that of calcium sulphate?
  (ii) Give a reason for your answer.

(d) (i) Write the formula of strontium nitrate.
  (ii) Construct a balanced equation for the thermal decomposition of strontium nitrate.
  (iii) How easily would you expect strontium nitrate to decompose compared with calcium nitrate?
  (iv) Give a reason for your answer to (iii) above.

3 The table below shows the metallic and ionic radii of group II elements.

Elements	Metallic radii/nm	Ionic radii (M^{2+})/nm
Beryllium	0.112	0.030
Magnesium	0.160	0.065
Calcium	0.197	0.094
Strontium	0.215	0.110
Barium	0.211	0.134

(a) Explain why the metallic radius increases down the group.

(b) Why are the ionic radii smaller than the atomic radii.

(c) K^+ and Ca^{2+} are isoelectronic but the radius of k^+ is larger.
  (i) Explain the term isoelectronic.
  (ii) Why is the radius of k^+ larger than Ca^{2+}?

(d) Explain with reasons which of the ion in the table has the least hydration energy.

4 (a) The atomic number of barium is 56. Write its electronic configuration.

(b) Use the databooklet to sketch the first for ionization energies of barium. Account for the shape in terms of the quantum levels occupied.

(c) Compare the reaction of calcium and barium with water at room temperature. Write balanced equations.

(d) Explain as fully as you can why barium carbonate decomposes at a higher temperature than calcium carbonate. Write balanced equations.

Descriptive Questions

1 Suggest explanations for the following facts. Write equations for any chemical reactions.

(a) Barium carbonate must be heated to a much higher temperature than magnesium carbonate to evolve carbon dioxide.

(b) Magnesium ribbon is stored in air but barium metal is stored under oil.

(c) Bottles of beryllium nitrate must be stored in a cool dark place.

2 (a) The chemistry of beryllium is very different from that of the other metals of group II. For example :
  (i) $BeCl_2$ is covalent but the other chlorides are ionic.
  (ii) BeO is amphoteric but the other oxides are basic.
  (iii) $Be(OH)_2$ dissolves in excess NaOH but the other hydroxides do not.
  (iv) Beryllium ressembles more aluminium than the other elements of group II.

Explain the above statements as fully as you can. Where appropriate give diagrams and equations.

(v) Give a concise account of the trend of the solubility of group II hydroxides from $Mg(OH)_2$ to $Ba(OH)_2$.

CHAPTER 13

GROUP IV ELEMENTS

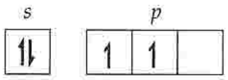
SYLLABUS OBJECTIVES

In this chapter you should be able to:

- outline the variation in melting point and electrical conductivity of Group IV elements and explain the variation in terms of structure and bonding
- describe and explain the bonding, molecular shape, melting points and boiling points of the tetrachlorides of Group IV elements
- describe and explain the reactions of the tetrachlorides of Group IV elements with water in terms of structure and bonding (eg explain the considerable reactivity of $SiCl_4$ compared with the lack of reactivity of CCl_4)
- describe and explain the bonding, acid-base nature and thermal stability of the oxides of Group IV elements, in oxidation states of II and IV
- describe and explain the relative stability of higher and lower oxidation states of Group IV elements in their oxides and aqueous cations, using $E^{\ominus}$ values where relevant (eg Sn^{2+} is readily oxidised to the more stable Sn^{4+}, but Pb^{4+} is readily reduced to the more stable Pb^{2+})
- show awareness of the properties and uses of ceramics based on silicon(IV) oxide

13.1 General Characteristics of Group IV Elements

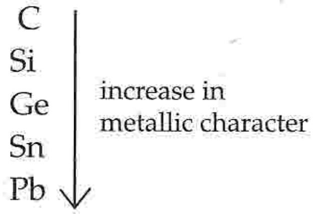
- Group IV elements have four electrons in the outer shell.



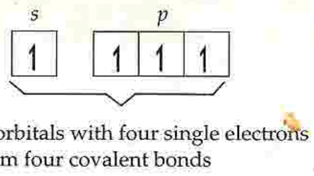
$_{6}C$: [He] $2s^2\ 2p^2$
$_{14}Si$: [Ne] $3s^2\ 3p^2$
$_{32}Ge$: [Ar] $3d^{10}\ 4s^2\ 4p^2$
$_{50}Sn$: [Kr] $4d^{10}\ 5s^2\ 5p^2$
$_{82}Pb$: [Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^2$

- Group IV elements change from a typical non-metal (carbon) at the top of the group, to a typical metal (lead) at the bottom of the group.

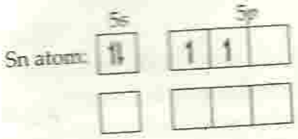
  Silicon and germanium are on the borderline between metals and non-metals and are called **metalloids**. These elements have some properties of metals and some properties of non-metals.



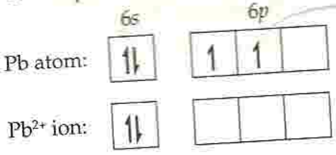
- All the elements can form four covalent bonds in compounds, by moving an *s* electron to the empty *p* orbital in the outer shell.



- All the elements form covalent hydrides with the formula MH_4 and covalent chlorides with the formula MCl_4. In these compounds the Group IV element forms four covalent bonds.
- **Ionic compounds**
  (a) Except for a few metal carbides (containing C^{4-} ions), carbon and silicon do not form ionic compounds.
  (b) Towards the bottom of Group IV, the atoms become large and can lose electrons to form positive ions.
    (i) Tin and lead can lose the four outer electrons to form 4+ ions in some compounds (eg Sn^{4+} in SnO_2).



(ii) Tin and lead can also form 2+ ions in some compounds, by losing only the outer *p* electrons (eg Pb^{2+} in PbO).



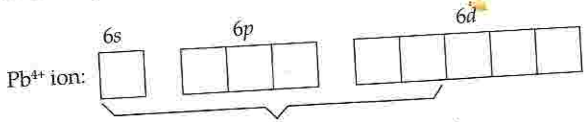
This happens because the two outer *s* electrons are unwilling to be involved in bonding. This is known as the **'inert pair effect'**. The inert pair effect is stronger in lead than in tin. Hence, lead usually forms Pb^{2+} rather than Pb^{4+} in ionic compounds. Pb^{2+} is more stable than Pb^{4+}. In tin compounds, tin usually forms Sn^{4+} rather than Sn^{2+} in ionic compounds. Sn^{4+} is more stable than Sn^{2+}.

13.2 Distinctive Chemistry of Carbon

- The first element in a Periodic Table group often has properties very different from the other elements in the group. In Group IV, carbon has some properties which are very different from the other elements in Group IV.
- The outer shell of carbon is the second shell — made up of the 2*s* and 2*p* orbitals. There are no 2*d* orbitals. Thus carbon only has four orbitals in the outer shell for bonding.

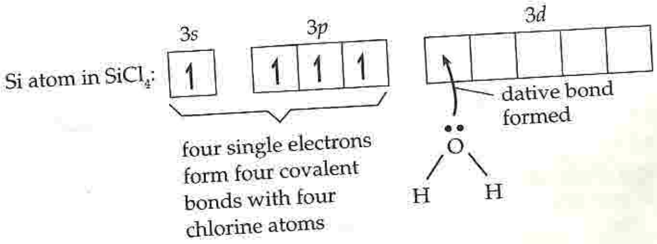
  The other elements of Group IV all have *d* orbitals in the outer shell which can be used for dative bonding.

  (a) The other Group IV elements can form octahedral complex ions such as SiF_6^{2-} and $PbCl_6^{2-}$. In these complex ions, two of the outer *d* orbitals can be used for forming dative bonds. For example, to form $PbCl_6^{2-}$:



six Cl^- ions form six dative bonds by using six empty orbitals in outer shell of lead

  (b) CCl_4 does not react with water unlike $SiCl_4$. $SiCl_4$ reacts rapidly with water because a water molecule can form a dative bond with the silicon atom, using an empty 3*d* orbital:



This cannot happen with CCl_4, as the carbon atom has no 2*d* orbitals.

Furthermore, the carbon atom is the smallest atom in the group. It is bonded to four large chlorine atoms. Therefore the water molecule cannot approach the carbon atom sufficiently to start a reaction.

- Large numbers of carbon atoms can join together in long chains. This is called **catenation**. As a result carbon can form a large number of *organic* compounds.

  Although catenation can occur in other Group IV elements, only a few compounds are formed, and these are unstable to heat.

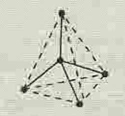
  Catenation occurs in carbon because the C—C bond is very strong compared to Si—Si, Ge—Ge, Sn—Sn and Pb—Pb bonds. The C—C bond energy is double that of Si—Si.

- Carbon forms multiple bonds such as C—C, C=C, C=O and C≡N in many compounds. Other elements rarely form multiple bonds.

  Carbon forms multiple bonds because their bond energy is large, thus the bonds and their compounds are stable.

13.3 Properties of the Elements

- The main physical properties of the Group IV elements are summarised in Table 13.1.

element	allotropes	electrical conductivity	structure	m.p./°C	b.p./°C
carbon	graphite	good (along layers)	giant molecular (layer lattice)	about 3730	(sublimes
	diamond	very poor	giant molecular 	3550	about 4800
silicon	–	very poor (when pure)	giant molecular (diamond-type)	1410	2355
germanium	–	very poor (when pure)	giant molecular (diamond-type)	937	2830
tin	white tin	good	giant metallic	232	2270
	grey tin	very poor	giant molecular (diamond-type)	changes into white tin	–
lead	–	good	giant metallic	327	1744

▶ Table 13.1
Main physical properties of Group IV element

Structure of the elements

(a) Carbon has two main allotropes — graphite and diamond. The structures of these are considered in detail in Chapter 5. A third allotrope of carbon has recently been discovered . It is called buckminsterfullerene. It consists of balls of carbon atoms (C_{60}).

(b) Silicon has a diamond-type structure. It has a lower melting point than diamond and is softer than diamond because the Si—Si bonds are longer and weaker than the C—C bonds.

(c) Germanium has a diamond-type structure. The melting point and hardness of germanium are less than that of diamond or silicon because the Ge—Ge bond is even longer and weaker than the C—C and Si—Si bonds.

(d) The main allotrope of tin is called *white tin* and is metallic. At low temperatures, a non-metallic form of tin is obtained. This form is called *grey tin* and has a diamond-type structure.

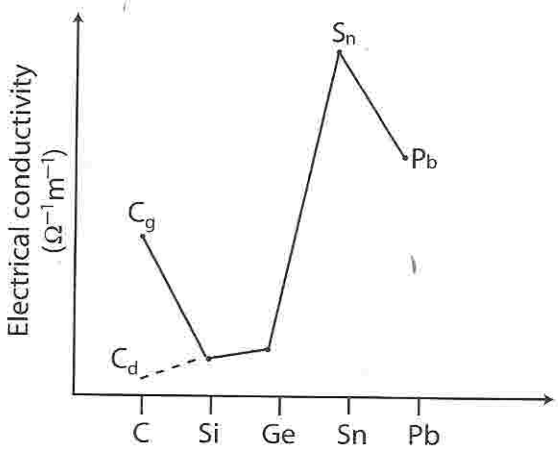
(e) Lead only exists as a metallic structure.

Electrical conductivity

(a) Carbon (diamond) is a very poor conductor of electricity. The other allotrope, graphite, is a fair conductor (see *Solids* in Chapter 5).

(b) Silicon and germanium conduct electricity slightly. This conductivity can be increased by adding impurities. These *impure* elements become semiconductors and are used in the electronic industry.

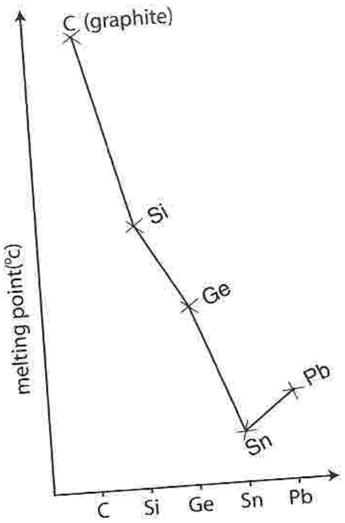
(c) Tin and lead are good conductors of electricity.



13.4 Melting point

- The melting point of an element depends on the magnitude of the force of attraction which hold the particles together in the solid state.
- Carbon(diamond), silicon and germanium consists of a giant molecular structure in which each atom is held to four other atoms by relatively strong covalent bonds. Hence they have high melting points.
- However while moving from carbon(diamond) to germanium the bond length increases. The bond weakens. Therefore the melting point decreases from diamond to germanium(Table 13.1)

- Tin and lead consists of a giant metallic structure in which the metal ions are found in a cloud of mobile electrons. However the metallic bond in tin and lead are weaker than the covalent bonds in germanium. Hence tin and lead have a lower melting point than germanium.



13.4 Uses of the Elements

- Diamond is used in saws and drills, for cutting through rock because it is very hard.
- Very pure silicon is used in the semiconductor industry to make silicon 'chips' for calculators and computers.
- Very pure germanium is used in the semiconductor industry for electronic components (pure silicon is far more important).
- Tin is mainly used in tin-plating of steel (eg tin cans) to prevent rusting, and in low melting-point electrical solder.

Stability of oxidation states

The two oxidation states of Group IV elements in compounds are +II and +IV. Going down the group, the +II oxidation state becomes more stable and the +IV oxidation state less stable. This is a result of the inert pair effect, which becomes stronger down the group. This change is responsible for the following characteristics of Group IV.

(a) Virtually all carbon and silicon compounds contain carbon(IV) or silicon(IV). The +II oxidation state is almost unknown in carbon and silicon.

(b) Tin forms tin(II) and tin(IV) compounds. The tin(IV) compounds are more stable. Hence tin(II) compounds are powerful reducing agents, as they are readily oxidised to tin(IV) compounds.

For example, $SnCl_2(aq)$ reduces $Fe^{3+}(aq)$ to $Fe^{2+}(aq)$:

$$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}; \qquad E^\ominus = +0.15\ V \;\ldots\ldots\; 1$$

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}; \qquad E^\ominus = +0.77\ V \;\ldots\ldots\; 2$$

Reversing the first electrode potential reaction:

$$Sn^{2+} \rightleftharpoons Sn^{4+} + 2e^-; \quad E^\ominus = -0.15\ V \ \ldots\ldots\ 3$$

So, adding equations 2 and 3:

$$Sn^{2+} + 2Fe^{3+} \rightarrow Sn^{4+} + 2Fe^{2+}; \quad E^\ominus = +0.62\ V$$

This reaction takes place as the $E^\ominus$ value is positive (see Chapter 7).

(c) Lead forms lead(II) and lead(IV) compounds. The lead(II) compounds are more stable. Hence lead(IV) compounds are powerful oxidising agents, as they are readily reduced to lead(II) compounds. For example, PbO_2 oxidises iodide ions, I^-, to iodine, I_2. This can be seen from the following electrode potentials:

$$Pb^{4+} + 2e^- \rightleftharpoons Pb^{2+}; \quad E^\ominus = +1.69\ V \ \ldots\ldots\ 4$$

$$I_2 + 2e^- \rightleftharpoons 2I^-; \quad E^\ominus = +0.54\ V$$

Reversing the second electrode potential:

$$2I^- \rightleftharpoons I_2 + 2e^-; \quad E^\ominus = -0.54\ V \ \ldots\ldots\ 5$$

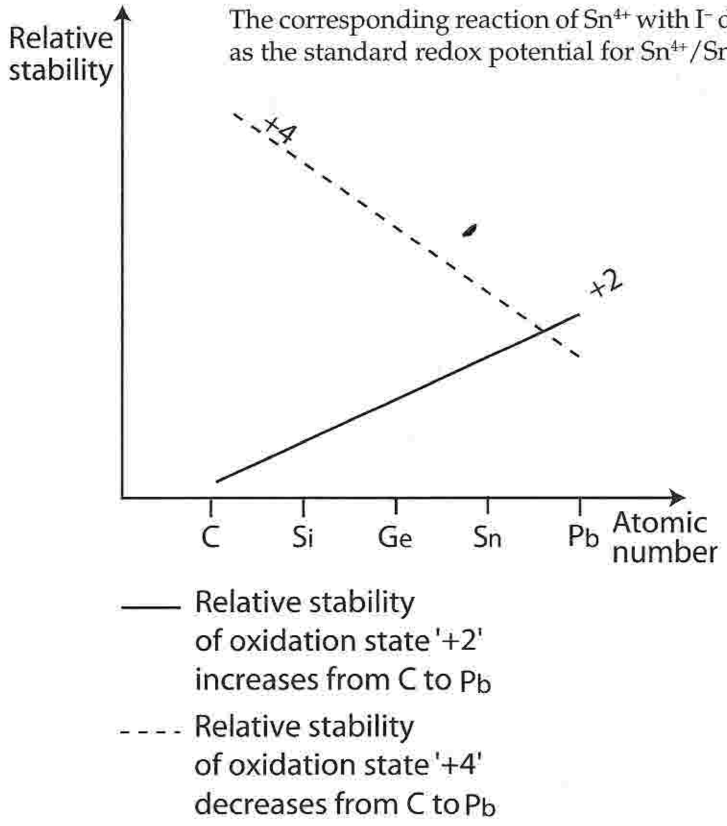
So, adding equations 4 and 5:

$$Pb^{4+} + 2I^- \rightarrow Pb^{2+} + I_2; \quad E^\ominus = +1.15\ V$$

This reaction takes place because the $E^\ominus$ value is positive (see Chapter 7). In practice, acid is required for this reaction, so the actual equation is:

$$PbO_2 + 2I^- + 4H^+ \rightarrow Pb^{2+} + I_2 + 2H_2O$$

The corresponding reaction of Sn^{4+} with I^- does not take place as the standard redox potential for Sn^{4+}/Sn^{2+} is too small:



Question 5.00 g of a sample of impure lead(IV) oxide was shaken with excess aqueous potassium iodide and dilute acid. The iodine produced in the reaction required 200 cm^3 of 0.2 mol dm^{-3} sodium thiosulphate solution for complete reaction. Calculate (a) the mass of lead(IV) oxide in the sample, and (b) the percentage purity of the sample. [O = 16.0; Pb = 207]

Answer (a) Number of moles of $S_2O_3^{2-}$ used in the titration $= \frac{200}{1000} \times 0.2$ mol

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

From the equation, $\frac{\text{no. of moles of } I_2}{\text{no. of moles of } S_2O_3^{2-}} = \frac{1}{2}$

Hence number of moles of $I_2 = \frac{1}{2} \times$ no. of moles of $S_2O_3^{2-}$

$$= \frac{1}{2} \times \frac{200}{1000} \times 0.2 \text{ mol}$$

$$PbO_2 + 4H^+ + 2I^- \rightarrow Pb^{2+} + 2H_2O + I_2$$

From the equation, number of moles of PbO_2 = no. of moles of I_2

$$= \frac{1}{2} \times \frac{200}{1000} \times 0.2 \text{ mole}$$

Hence mass of PbO_2 = no. of moles × relative molecular mass

$$= \frac{1}{2} \times \frac{200}{1000} \times 0.2 \times 239 = 4.78 \text{ g}$$

(b) Percentage purity $= \frac{\text{mass of } PbO_2 \text{ in sample}}{\text{mass of sample}} \times 100\%$

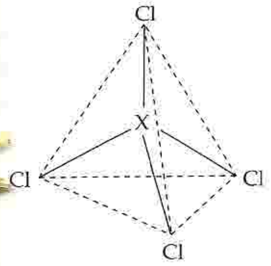
$$= \frac{4.78}{5.00} \times 100 = 95.6\%$$

13.5 Tetrachlorides

- All the Group IV elements form chlorides with the formula XCl_4
- All the compounds have a molecular structure, consisting of XCl_4 molecules held together in the liquid state by weak Van der Waals forces. Hence all the compounds have low boiling points and are liquids under room conditions.
- The boiling points of the compounds increase down Group IV as the molecules become larger and Van der Waals forces become stronger.
- The volatility of the tetrachlorides decreases from CCl_4 to $PbCl_4$
- The XCl_4 molecule has a tetrahedral shape (Fig 13.1).

- The thermal stability of the tetrachlorides decreases down Group IV because
  - (a) the covalent bonds become longer and weaker as the Group IV atom becomes larger;
  - (b) the inert pair effect makes the +IV oxidation state less stable down the group.
- CCl_4 is very stable to heat.
- $PbCl_4$ is a yellow liquid which slowly decomposes at room temperature to lead(II) chloride and chlorine gas:

$$\underset{\text{yellow liquid}}{PbCl_4} \rightarrow \underset{\text{white solid}}{PbCl_2} + \underset{\text{yellowish-green gas}}{Cl_2}$$



▲ Fig 13.1 Shape of XCl_4 molecule

Hydrolysis with water

(a) CCl_4 does *not* react with water.
(b) $SiCl_4$ reacts with cold water:

$$SiCl_4 + 4H_2O \rightarrow 4HCl + SiO_2.2H_2O$$

(c) $GeCl_4$ can be hydrolysed by water to GeO_2.
(d) $SnCl_4$ and $PbCl_4$ are only partially hydrolysed by water.

13.6 Oxides

- The Group IV elements form oxides with the formulae XO and XO_2. Lead also forms an oxide with the formula Pb_3O_4. These oxides are summarised in Table 13.2.

	+II oxidation state			+IV oxidation state		
element	**formula**	**structure**	**state at room conditions**	**formula**	**structure**	**state at room conditions**
carbon	CO	molecular	gas	$\boxed{CO_2}$	molecular	gas
silicon	SiO	molecular	(unstable)	$\boxed{SiO_2}$	giant molecular	solid; high m.p.
germanium	GeO	–	(unstable)	$\boxed{GeO_2}$	molecular/ ionic	solid
tin	SnO	ionic	solid	$\boxed{SnO_2}$	ionic	solid; high m.p.
lead	$\boxed{PbO}$	ionic	solid	PbO_2	ionic	solid, decomposed when heated

☐ = *most stable oxide*

▲ Table 13.2 Oxides of Group IV elements

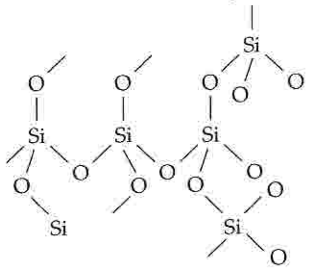
- The +4 oxidation state becomes less stable down the group. Hence from carbon to tin, the most stable oxide is the +4 oxidation state oxide (XO_2). But for lead the most stable oxide is the +2 oxidation state oxide (PbO).

- Lead(IV) oxide is a powerful oxidising agent and decomposes on heating to form the more stable lead(II) oxide, PbO, and oxygen gas. It also oxidises iodide ions to iodine (see earlier).
- Comparison of structures of CO_2 and SiO_2:
  (a) CO_2 is molecular. The molecule is non-polar, so the bonds between the molecules are weak Van der Waals forces. Thus CO_2 sublimes at very low temperatures and is a gas under normal room conditions.
  (b) SiO_2 has a giant molecular structure. All the atoms in a crystal of SiO_2 are held together by strong covalent bonds. The structure is shown in Fig 13.2.

  In SiO_2, each silicon atom forms four covalent bonds with four oxygen atoms. Each oxygen atom forms two covalent bonds with two silicon atoms.

  SiO_2 has a high melting point because a lot of heat energy is required to break these strong covalent bonds to cause melting.

  SiO_2 is an important component of ceramics, where these properties are important (see Chapter 5).



▲ Fig 13.2 Structure of SiO_2

Acid/base nature of oxides

The oxides change from acidic oxides at the top of Group IV (CO_2 and SiO_2), to amphoteric oxides at the bottom of Group IV (PbO and PbO_2).

(a) CO_2 and SiO_2 oxides are acidic oxides. They react with alkalis:

$$CO_2(g) + 2NaOH(aq) \longrightarrow Na_2CO_3(aq) + H_2O(l)$$

$$SiO_2(s) + NaOH(s) \xrightarrow{\text{fused}} Na_2SiO_3(s) + H_2O(l)$$

(b) The oxides of germanium, tin and lead are amphoteric oxides. They behave as acidic oxides — dissolving in aqueous alkalis, and as basic oxides — dissolving in acids.
For example, lead(II) oxide dissolves in hot aqueous NaOH and in hot dilute nitric acid:

$$PbO + 2OH^- \rightarrow PbO_2^{2-} + H_2O$$
$$PbO + 2H^+ \rightarrow Pb^{2+} + H_2O$$

(c) Lead(IV) oxide, PbO_2, does not react with nitric acid. However, it dissolves in concentrated hydrochloric acid:

$$PbO_2 + 4HCl \rightarrow \underset{\substack{\text{yellow}\\\text{liquid}}}{PbCl_4} + 2H_2O$$

The yellow liquid is unstable. It decomposes as shown below:-

$$PbCl_4(l) \longrightarrow PbCl_2(s) + Cl_2(g)$$

overall equation

$$PbO_2(s) + 4HCl(\text{conc.}) \longrightarrow PbCl_2(s) + Cl_2(g) + 2H_2O(l)$$

The $PbCl_4$ decomposes slowly at room temperature.

(d) Pb_3O_4 is an ionic oxide made up of Pb^{2+}, Pb^{4+} and O^{2-} ions. It behaves in chemical reactions as if it is a mixture of 2PbO and PbO_2. Hence with nitric acid, the PbO part dissolves while the PbO_2 does not. The equation for the reaction is

$$\underset{\text{red solid}}{Pb_3O_4(s)} + 4HNO_3(aq) \rightarrow 2Pb(NO_3)_2(aq) + 2H_2O(l) + \underset{\text{dark brown solid}}{PbO_2(s)}$$

13.7 Cations of Group IV Elements

- The cations of tin and lead are given in Table 13.3.

▶ Table 13.3 Cations of Group IV elements

element	cations	comments
tin	Sn^{2+}	powerful reducing agent; readily oxidised to Sn^{4+}
	Sn^{4+}	most stable form of tin
lead	Pb^{2+}	most stable form of lead
	Pb^{4+}	powerful oxidising agent; readily reduced to Pb^{2+}

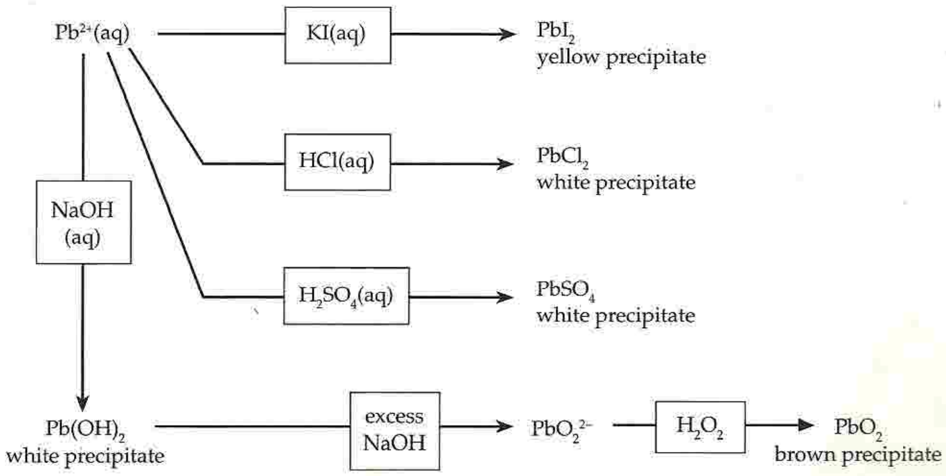
- **Reactions of Pb^{2+}**

(a) Almost all lead(II) compounds are insoluble in water (except lead(II) nitrate and lead(II) ethanoate). Thus most reagents give precipitates with solutions of $Pb^{2+}(aq)$.

(b) $Pb^{2+}(aq)$ can be oxidised to lead(IV) oxide by alkaline H_2O_2 or alkaline OCl^-.

$$Pb^{2+}(aq) + H_2O_2(aq) + 2OH^-(aq) \rightarrow PbO_2(s) + 2H_2O(l)$$

(c) A summary of some reactions of Pb^{2+} is given below.



Ceramics

- Ceramics are materials made from clays and non-metallic minerals that have been permanently hardened by using a high temperature.
- They are strong, brittle and resistant to heat and attack by chemicals.
- Ceramics, like glass, are based on silicates. But glass can be melted and remelted several times, whereas once a ceramic has been hardened, it will remain resistant even to extremely high temperatures
- Examples of ceramic materials are silicon nitride (Si_3N_4used as abrasive powder), silicon carbide(SiC, used in microwave furnaces in abrasive and as refractory materials) , ferrite (Fe_3O_4, used in the core of electrical transformers and magnetic core) and silicates(ceramics based on SiO_2) .
- Ceramics are usually ionic , covalently bonded materials or both.

Properties of ceramics:-

i. They have high melting points
ii. They are good thermal and electrical insulators
iii. They have greater rigidity, hardness and temperature stability than organic polymers
iv. They are resistant to heat and chemical attack

Uses of ceramics

i. In manufacture of glass, bricks , tiles, dinnerware
ii. As refractory materials in the lining of furnaces
iii. As powerline insulators
iv. In making of glasses for solar panels

EXERCISE 13

Multiple Choice Questions

Section I

1 Which one of the following statements about the tetrachlorides of the Group IV elements is *not* true?

A All the elements form a chloride with formula MCl_4.
B All the tetrachlorides are covalent.
C The tetrachlorides become more stable as the proton number of the Group IV element increases.
D The covalent bonds in the tetrachlorides become weaker from carbon to lead.

2 Which one of the following changes occurs in the Group IV elements as the proton number increases?

A The oxides become more basic.
B The electronegativity of the elements increases.
C The +4 oxides become more stable than the +2 oxides.
D The melting point of the tetrachloride decreases.

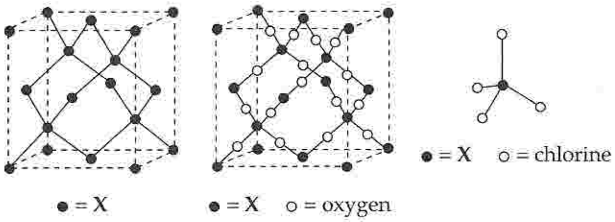
3 The first six successive ionisation energies for four elements are given below. Which one is a Group IV element?

A 1400, 2900, 4600, 7500, 9400, 53 300 kJ mol^{-1}
B 740, 1500, 7700, 10 500, 13 600, 18 000 kJ mol^{-1}
C 1260, 2300, 3800, 5200, 6500, 9300 kJ mol^{-1}
D 790, 1600, 3200, 4400, 16 100, 19 800 kJ mol^{-1}

4 Germanium is between silicon and tin in Group IV. Which one of the following statements about germanium chemistry is *least likely* to be true?

A The element has a diamond-type structure.
B The oxide will dissolve in aqueous sodium hydroxide.
C The element is a better electrical conductor than tin.
D Germanium-oxygen covalent bonds will be weaker than silicon-oxygen bonds.

5 Fig 13.3 shows the structures of element **X**, the oxide of **X** and the chloride of **X**. Which element is X?



▲ Fig 13.3

A carbon
B silicon
C lead
D phosphorus

6 Tin(II) chloride decolourises an acidified solution of potassium manganate(VII). Lead (II) chloride has no effect on the potassium manganate(VII). Which one of the following is the best explanation for this difference between tin(II) chloride and lead(II) chloride?

A Tin(IV) compounds are more stable than tin(II) compounds.
Lead(II) compounds are more stable than lead(IV) compounds.
B Tin manganate(VII) is a stable compound.
Lead manganate(VII) is an unstable compound.
C Tin(II) compounds are powerful oxidising agents.
Lead(II) compounds are powerful reducing agents.
D Potassium manganate(VII) can reduce tin(II) chloride to metallic tin.
Potassium manganate(VII) cannot reduce lead(II) chloride to metallic lead.

7 What would be the products of the complete combustion of plumbane, PbH_4, in oxygen gas?

A Pb and H_2O
B PbO_2 and H_2O
C PbO and H_2O
D PbO and H_2

8 Which change is most likely to be brought about by acidified aqueous potassium iodide?

A $Pb^{2+} \rightarrow Pb^{4+}$
B $Sn^{2+} \rightarrow Sn^{4+}$
C $Pb^{4+} \rightarrow Pb^{2+}$
D $Sn^{4+} \rightarrow Sn^{2+}$

Section II

Summary of directions

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

9 Which statements about the oxides of Group IV elements are true?

1 All the Group IV elements form an oxide MO_2.

2 All the oxides are either amphoteric or basic.

3 All the oxides are thermally stable.

10 Which of the following have a giant molecular structure?

1 Si(s)

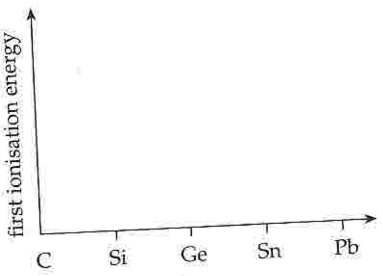
2 $SnCl_4$(s)

3 PbO(s)

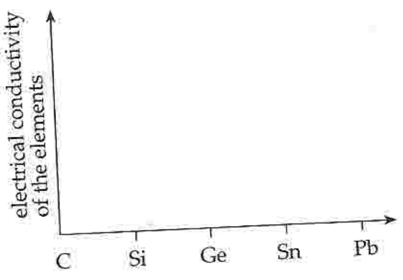
Structured Questions

1 Sketch graphs on the following axes to show how each property changes for the Group IV elements. Give a brief explanation for the shape of each graph.

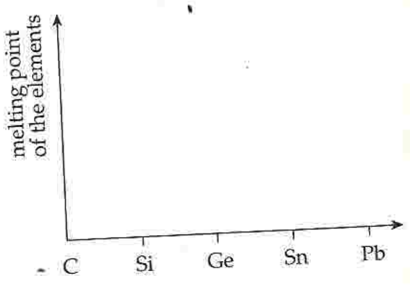
(a) First ionisation energy of the elements



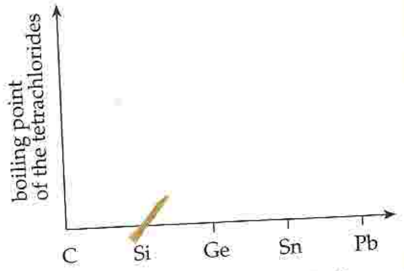
(b) Electrical conductivity of the elements



(c) Melting point of the elements



(d) Boiling point of the tetrachlorides



2 Germanium (symbol Ge) is below silicon in Group IV.

(a) How would you expect the ionisation energy of germanium to compare with that of silicon?

(b) Germanium forms two oxides, GeO and GeO_2.

(i) Which oxide is produced when germanium burns in air?

(ii) Give a reason for your answer in (i).

(iii) Briefly outline the likely structure and bonding of the oxide chosen in (i).

(c) (i) State and explain the shape of a molecule of germanium(IV) chloride.

(ii) Germanium(IV) oxide is produced when germanium(IV) chloride is mixed with water. Write a balanced equation for the reaction.

3 (a) (i) Explain using bond energy the unique ability of carbon to catenate as compared to the other elements of group IV.

(ii) Explain, with reference to structure and bonding, why graphite is a conductor but diamond is an cusulator.

(iii) Account as fully as you can for the difference in behaviour of CCl_4 and $SiCl_4$ towards water. Give balanced equation where appropriate.

(b) (i) What do you understand by the inert pair effect.

(ii) Use the concept of the inert pair effect to explain the different stability of the +2 and +4. States from carbon to lead. Support your arguments with E° values and examples.

Descriptive Questions

1 (a) Write the full electronic configuration of
  (i) a carbon atom in the ground state and
  (ii) a carbon atom when it forms four covalent bonds.

(b) Briefly explain why carbon usually forms covalent bonds in its compounds, rather than electrovalent bonds.

(c) Explain *each* of the following observations in terms of structure and bonding.
  (i) Carbon dioxide is a gas at room temperature but silicon(IV) oxide is a solid with a high melting point.
  (ii) Silicon has a 'diamond-type' structure, but is not as hard as diamond.

2 According to current theory, the element with atomic number 114 should be placed below lead in Group IV. The name suggested for this element is *unquadium* (symbol Unq). From your knowledge of the elements in Group IV, predict the following properties of the element unquadium and unquadium compounds. Give reasons for your answers.

(a) Predict the electrical conductivity of unquadium.

(b) Sketch the likely shape of the tetrachloride of unquadium. Comment on the thermal stability of this chloride.

(c) Give the formula of and the bonding in the most stable oxide of unquadium. What would you expect to be the effect of nitric acid on this oxide?

(d) Describe, with equations, the expected effect of aqueous sodium hydroxide on an aqueous solution of unquadium(II) nitrate.

(e) How would you expect the standard electrode potential of unquadium to compare with that of lead?

Write a concise account of the following chemistry of the Group IV elements and their compounds.

(a) The electrical conductivity of the elements.

(b) The thermal stability of the tetrachlorides.

(c) The acid/base nature of the oxides.

**4* (a) Lead, lead(IV) chloride and lead(II) chloride have melting points of 327°C, –15°C and 498°C respectively.
Describe the bonding in these three substances and explain how it accounts for these melting points.

(b) When tin(IV) oxide and lead(IV) oxide are strongly heated, only lead(IV) oxide produces oxygen gas. Suggest an explanation for this.

(c) Lead is no longer used for water pipes because it can cause lead poisoning. The lead reacts with water to form a layer of solid lead(II) hydroxide inside the pipe, which is slightly soluble in water.

Use the *Data Tables* at the end of the book to write an ionic equation for this reaction of lead metal and find the standard redox potential (e.m.f.) for the reaction. Explain how the lead(II) hydroxide is formed in the pipe for the lead tocorrode in this way.

5 (a) Use structure and bonding to explain why carbon melts at 4000 C but tin melts at 232 C.

(b) lead (ii) chloride is insoluble in dilute hydrochloric acid but dissolves in concentrated hydrochloric acid. Write balanced equation.

(c) Use structure and bonding to explain the acid/base behaviour of the oxides of the elements of group IV in the +4 oxidation state.

(d) Use E° values from the data booklet to suggest what happens when aqueous iron (iii) nitrate is separately added to solutions of :

(i) Tin (II) nitrate
(ii) lead (II) nitrate

CHAPTER

14

GROUP VII ELEMENTS

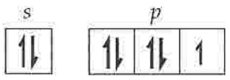
SYLLABUS OBJECTIVES

In this chapter you should be able to:

- describe the trends in volitility (melting point, boiling point) and colour of chlorine, bromine and iodine in the Group
- explain the trend in melting points and boiling points of the elements in terms of changes in the strength of Van der Waals forces
- describe and deduce the relative reactivity of the elements as oxidising agents by referring to their E° values
- describe and explain the reactions of the elements with hydrogen
- describe and explain the relative thermal stabilities of the hydrides (ie due to changes in the H—X bond energy from HCl to HI)
- describe and explain the reactions of the halide ions (ie Cl^-, Br^-, I^-) with aqueous silver ions followed by ammonia
- describe and explain the reactions of the halide ions (ie Cl^-, Br^-, I^-) with concentrated sulphuric acid
- outline the manufacture of chlorine from aqueous sodium chloride by electrolysis in a diaphragm cell (including the electrode reactions)
- describe the reactions of chlorine with cold, and with hot, aqueous sodium hydroxide (including the changes in oxidation numbers)
- explain the use of chlorine in water purification
- show awareness of the industrial importance and environmental significance of the halogens (eg uses of halogens in the manufacture of bleach, PVC and halogenated hydrocarbons as solvents, refrigerants and in aerosols; environmental harm caused by CFCs)

14.1 General Characteristics of Group VII Elements

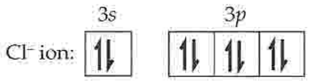
- Group VII elements have seven electrons in the outer shell:



- The elements are all typical non-metals, with similar properties.
- The elements are all very reactive and are powerful oxidising agents.

Ionic compounds

(a) The halogen elements can gain one electron to form the X^- ion, which has a stable electron arrangement. For example:



(b) Halogens commonly react with metals to form ionic halides such as NaBr, KI, $CaCl_2$, which contain X^- ions. This happens because of the high electron affinity of the halogens.

Covalent bonding

(a) All the elements can use the single unpaired *p* electron in the outer shell to form a single covalent bond. For example, bromine forms a single covalent bond in the HBr molecule:

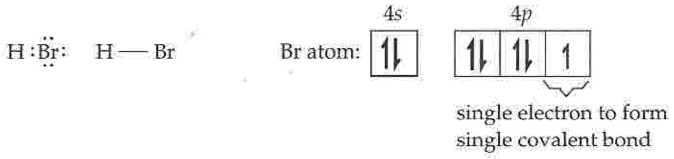
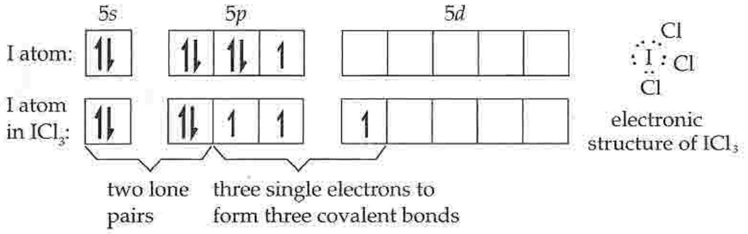


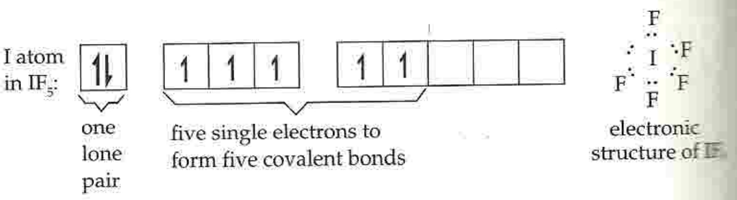
Fig 14.1 Electronic structure of the HBr molecule

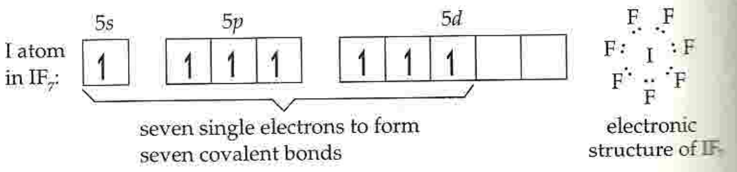
(b) Except for fluorine, the other elements can also use the outer *d* subshell to form 3, 5 or 7 covalent bond in compounds. Examples for iodine are shown below and on the next page.



5s 5p 5d

(continued)





(c) Fluorine can only form *one* covalent bond in compounds, because it has no *d* orbitals in its outer shell. The outer shell of fluorine only contains the 2*s* and 2*p* orbitals.

- The elements all have a molecular structure, made up of X_2 molecules, and have low boiling points (below 200°C).

- The diatomic molecules cohere via Weak Van Der Waal's Forces. These forces become stronger as the number of electrons around the molecule increases from F_2 to I_2. Therefore, volatility decreases down the group. At room temperature and pressure, fluorine and chlorine are gases, bromine is a volatile liquid but iodine is a solid.

- As the atomic number increases, the X^- ions become more powerful reducing agents, as the X^- ion gives up electrons more easily. Thus I^- is readily oxidised to I_2. Cl^- can only be oxidised to Cl_2 by powerful oxidising agents (such as $KMnO_4$). F^- cannot be oxidised to F_2 by any chemical oxidising agent (it is necessary to use electrolysis to oxidise F^- to F_2.)

- Because of variable covalency, the Group VII elements have variable oxidation numbers in their compounds (from –1 to +7). Fluorine is an exception, the oxidation number of fluorine in all compounds is –1.
  The variation in the oxidation number of chlorine in chlorine compounds is shown in Table 14.1.

▶ Table 14.1 Variable oxidation number of chlorine in compounds

oxidation number	example
–1	NaCl, $CaCl_2$ (containing Cl^- ions), ICl (covalent)
+1	ClF, ClO^- in NaClO
+3	ClF_3
+5	ClF_5, ClO_3^- in $NaClO_3$
+7	ClO_4^- in $NaClO_4$

- The halide ions, X^-, are often found as ligands in complex ions. The X^- ion has four electron pairs:a pair forms a dative bond with an empty orbital of the central atom in the complex ion.

  Examples of complex ions with halide ions as ligands are:
  AlF_6^{3-} (important in the extraction of aluminium by electrolysis);
  $CuCl_4^{2-}$ (important in the copper chemistry);
  $CoCl_4^{2-}$ (important in the cobalt chemistry).

14.2 The Elements

Physical Properties

- The physical properties of the Group VII elements are summarised in Table 14.2.

▶ Table 14.2 Physical properties of Group VII elements

element	molecular formula	colour	m.p./°C	b.p./°C	solubility in water
fluorine	F_2	pale yellow	–220	–188	soluble
chlorine	Cl_2	yellow-green	–101	–35	moderately soluble
bromine	Br_2	dark red	–7	58	slightly soluble
iodine	I_2	black	113	183	insoluble

- The elements have a molecular structure. Halogens consist of X_2 molecules held together by Van der Waals forces.
  The melting and boiling points increase down Group VII as the molecules become larger and the Van der Waals forces become stronger.

- As the number of electrons in the molecules of the halogens increases the magnitude of the Van der Waals forces of attraction increases. Therefore the melting point, boiling point and the standard enthalpy of vaporisation of the halogens will also increase down the group.

- Furthermore due to an increase in Van der Waals forces, the vapour pressure of the halogens decreases down the group. The halogen will therefore become less volatile down the group.

- The physical state of the halogens changes gradually from gases (fluorine and chlorine) through liquid(bromine) to solid(iodine and astatine).

- The solubility of the elements in water decreases as the molecules become larger.

- The elements become darker down the group from fluorine to iodine. This is due to absorption of part of the wavelength of light to bring about electronic excitation. With increase in atomic number from fluorine to iodine, the last occupied quantum level has higher energy. Therefore the wavelength absorbed from white light gets longer such that shorter wavelength of more intense colour are transmitted.

- The elements are soluble in organic solvents, such as hydrocarbons and chloroalkanes. Bromine usually forms a *red* or *orange* solution and iodine usually forms a *violet* solution.This is because in such solvents they exist as their simple diatomic molecules.

Chemical Properties

- The elements readily react with metals, forming compounds which are ionic (containing X^- ions).
- The reactivity of the elements *decreases* down the group because
  (a) the electron affinity decreases from chlorine to iodine so less energy is evolved when ionic compounds are formed;
  (b) covalent bonds with other elements become weaker from chlorine to iodine, so less energy is evolved when covalent compounds are formed.
- All the elements react with hydrogen to form covalent hydrides with the formula HX. As the atomic number of the halogen increases,
  (a) the rate of reaction decreases;
  (b) the ease of reaction decreases and
  (c) the extent of reaction decreases (eg the reaction with iodine to form HI is incomplete).
  This is summarised in Table 14.3.

▶ Table 14.3 Reaction of Group VII elements with hydrogen

element	reaction
fluorine	explodes with hydrogen under all conditions
chlorine	hydrogen burns in chlorine; H_2 and Cl_2 explode in the presence of light
bromine	bromine reacts with hydrogen when heated to 200°C in the presence of platinum catalyst
iodine	Iodine will react with hydrogen only at a relatively high temperature of about 450° C and in the presence of platinum which acts as a catalyst. The reaction is reversible

- The oxidising power of the elements *decreases* down Group VII. This is because the elements become less reactive as atomic number increases and the electron affinity decreases. As atomic radius increases, effective nuclear charge decreases. Then, the uptake of the incoming election is less readily.

The decrease in oxidising power is shown by the standard redox potentials of the halogens:

$$\frac{1}{2}Cl_2 + e^- \rightleftharpoons Cl^-;\ E^{\ominus} = +1.36\ \text{V}$$
$$\frac{1}{2}Br_2 + e^- \rightleftharpoons Br^-;\ E^{\ominus} = +1.07\ \text{V}$$

$$\frac{1}{2}I_2 + e^- \rightleftharpoons I^- \qquad E^\ominus = +0.54\ V$$

- The decrease in oxidising power of the elements is shown by their reaction with thiosulphate ions.

(i) Chlorine and bromine oxidise thiosulphate to sulphate (in which the sulphur has an oxidation number of +6):

$$S_2O_3^{2-} + 4Cl_2 + 5H_2O \rightarrow 2SO_4^{2-} + 10H^+ + 8Cl^-$$

(ii) Iodine is a weaker oxidising agent and oxidises thiosulphate to $S_4O_6^{2-}$ (in which the sulphur has an average oxidation number of +2):

$$2S_2O_3^{2-} + I_2 \rightarrow 2I^- + S_4O_6^{2-}$$

- The reaction of halogens with solution containing Fe^{2+} ion also indicates the trends in their oxidizing power.

(i) . Chlorine and bromine will oxidise Fe^{2+} ion to Fe^{3+} ion.

$$2Fe^{2+}(aq) + Cl_2(g) \longrightarrow 2Fe^{3+}(aq) + 2Cl^-(aq)$$

But iodine will not react with Fe^{2+} ions

(ii) Chlorine can displace bromine or iodine from a solution of their salt. This shows that chlorine is a more powerful oxidizing agent than bromine and iodine.

$$Cl_2(g) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$$

Bromine can displace iodine from a solution of its salt. Therefore bromine is a more powerful oxidizing agent than iodine.

$$Br_2(l) + 2I^-(aq) \rightarrow 2Br^-(aq) + I_2(aq)$$

14.3 Hydrides of Chlorine, Bromine and Iodine

- All the Group VII elements form covalent hydrides with the formula HX.
- The hydrides react with water to form strongly acidic solutions:

$$HX + H_2O \rightarrow H_3O^+ + X^-$$

The strength of the acids *increases* down the group from HCl to HI. The reason for this is the decrease in the strength of the H—X bond (Table 14.4). Hence the H—X bond is more easily broken, from HCl to HI, so the H_3O^+ and X^- can be formed more easily.

bond	bond energy/ kJ mol^{-1}
H—Cl	431
H—Br	364
H—I	299

Table 14.4

- The hydrides become less stable to heat from HCl to HI. HI can be decomposed into H_2 and I_2 by putting a red-hot platinum wire in the gas. This decrease in thermal stability of the hydrides from HCl to HI is because of the decrease in the H—X bond energy.

14.4 Reactions of the Halide Ions, Cl^-, Br^- and I^-

Reaction with Silver Nitrate Solution

- Solutions of the X^- ions produce precipitates with silver nitrate solution:

$$Ag^+(aq) + Cl^-(aq) \rightarrow \underset{\text{white}}{AgCl(s)}$$

$$Ag^+(aq) + Br^-(aq) \rightarrow \underset{\text{cream-coloured}}{AgBr(s)}$$

$$Ag^+(aq) + I^-(aq) \rightarrow \underset{\text{yellow}}{AgI(s)}$$

- The silver chloride precipitate readily dissolves in dilute ammonia due to the formation of $[Ag(NH_3)_2]^+$.
  The silver bromide only dissolves in concentrated ammonia. The silver iodide is insoluble in ammonia.

While moving from AgCl to AgI the solubility product of the silver halide decreases.

Silver halide	Solubility product /mol^2dm^{-6}
AgCl	1.8×10^{-10}
AgBr	7.7×10^{-13}
AgI	8.3×10^{-17}

Therefore the concentration of silver ion found in a saturated solution of the silver halide decreases from silver chloride to silver iodide.

The concentration of Ag^+ ion in a saturated solution of silver chloride is large enough to allow for the formation of the complex ion, diammine silver(I) ion.

$$AgCl(s) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$$

But in a saturated solution of silver bromide, the concentration of Ag^+ ion is not large enough to allow for the formation of the complex ion, diammine silver(I) ion. Hence, AgBr does not dissolve in aqueous ammonia. But it will dissolve in concentrated ammonia.

Reaction with Concentrated Sulphuric Acid

- Solid ionic halides react with concentrated sulphuric acid to produce HX:

$$NaX + H_2SO_4 \rightarrow NaHSO_4 + HX$$

- The concentrated sulphuric acid is also an oxidising agent. The ease of oxidation of X^- to X_2 increases from Cl^- to I^-. Concentrated sulphuric acid cannot oxidise Cl^- to Cl_2, but can oxidise some Br^- to Br_2, and oxidises a large percentage of any I^- to I_2.

$$NaBr + H_2SO_4 \longrightarrow NaHSO_4 + HBr$$

$$2HBr + H_2SO_4 \longrightarrow Br_2 + SO_2 + 2H_2O$$

- The effect of concentrated sulphuric acid on NaCl, NaBr and NaI is summarised in Table 14.5.

Table 14.5 Reaction of NaX with concentrated H_2SO_4

salt	products	observations
NaCl	HCl gas	white fumes of HCl gas
NaBr	HBr gas, and some Br_2	white fumes of HBr gas and red-brown fumes of Br_2 gas
NaI	mainly I_2, and some HI gas	solid black iodine and purple I_2 gas, and some white fumes of HI gas

With sodium chloride

$$NaCl(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HCl(g)$$

With sodium iodide

$$NaI(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HI(g)$$

$$2HI(g) + H_2SO_4(l) \rightarrow I_2(s) + SO_2(g) + 2H_2O(l)$$

Overall equation

$$2NaI(s) + 3H_2SO_4(l) \rightarrow 2NaHSO_4(s) + I_2(s) + SO_2(g) + 2H_2O(l)$$

Oxidation of Aqueous Solutions of Halide Ions

- The ease of oxidation of $X^-(aq)$ to $X_2(aq)$ increases down the group. Hence $I^-(aq)$ is oxidised to $I_2(aq)$ by almost all common oxidising agents, including atmospheric oxygen. However $Cl^-(aq)$ is only oxidised to $Cl_2(aq)$ by powerful oxidising agents such as potassium manganate(VII).

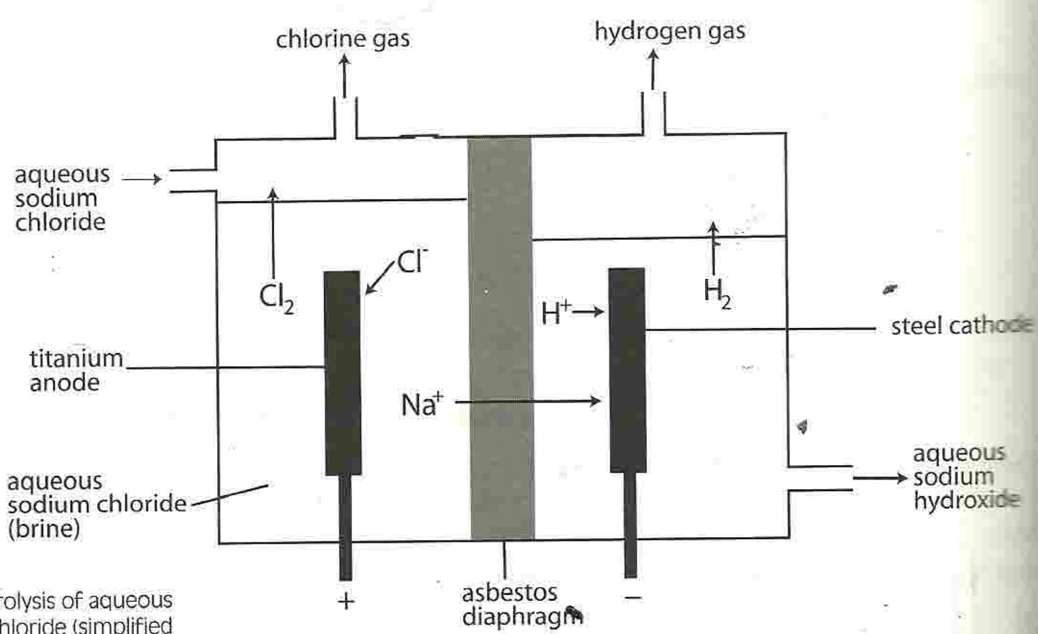
14.5 Electrolysis of Salt Solution (Brine)

- Aqueous salt solution is electrolysed to manufacture sodium hydroxide (the most important product) and chlorine. Other useful chemicals are also produced from the process, including sodium chlorate(I) or NaClO, and sodium chlorate(V) or $NaClO_3$.
  (a) Aqueous sodium chloride (brine) is put into the left side of the electrolysis cell, around the titanium anode.
  (b) The chloride ions go to the anode, where they are discharged:

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

  Titanium is used for the anodes because it resists corrosion by the very reactive chlorine.
  (c) The sodium ions go through the asbestos diaphragm to the steel cathode. They cannot be discharged to become sodium because the sodium metal would react immediately with water. Instead, hydrogen ions from the water are discharged to become hydrogen gas:

$$2H^+ + 2e^- \rightarrow H_2$$



▶ Fig 14.2 Electrolysis of aqueous sodium chloride (simplified industrial method)

  This leaves sodium ions (Na^+) and hydroxide ions (OH^-) around the cathode. Thus aqueous sodium hydroxide flows out of the cell.
  (d) The level of brine on the left (anode) side of the cell is deliberately higher than on the right (cathode) side so that

the brine will slowly flow through the asbestos diaphragm towards the cathode, carrying the sodium ions with it and preventing the reverse flow of sodium hydroxide towards the cathode (where it would react with the chlorine).

(e) The initial products from the process are chlorine, sodium hydroxide and hydrogen.

$$\underset{\text{1 mole}}{NaCl} + H_2O \longrightarrow \underset{\text{1 mole}}{NaOH} + \underset{\text{0.5 mole}}{\tfrac{1}{2}Cl_2} + \underset{\text{0.5 mole}}{\tfrac{1}{2}H_2}$$

Other chemicals can be manufactured from the products of the electrolysis.

(a) Hydrogen and chlorine can be combined to make hydrogen chloride and hence hydrochloric acid:

$$H_2 + Cl_2 \rightarrow 2HCl$$

(b) The chlorine and *cold* aqueous sodium hydroxide can be mixed to produce sodium chlorate(I), NaClO, which is used as bleach. The equation is:

$$Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$$

In this reaction, chlorine undergoes disproportionation. The oxidation number of chlorine changes from zero in Cl_2 to –1 in Cl^- (reduction) and from zero in Cl_2 to +1 in ClO^- (oxidation).

(c) The chlorine and *hot* aqueous sodium hydroxide can be mixed to produce sodium chlorate(V), $NaClO_3$. The equation is:

$$3Cl_2 + 6OH^- \rightarrow 5Cl^- + ClO_3^- + 3H_2O$$

This reaction is also disproportional. The oxidation number of chlorine changes from zero in $C1_2$ to +5 in ClO_3^- (oxidation)

14.6 Uses of Halogens and Halogen Compounds

- Sodium chlorate(I), NaClO, is used as a bleach for clothes.
- Chlorine is used to purify water for drinking and swimming (it kills bacteria).

  Chlorine dissolves slightly in water to form a mixture of hydrochloric acid and chloric(I)acid.

$$Cl_2(g) + H_2O(l) \rightleftharpoons HClO(aq) \text{ -------} ①$$

The choric acid,HClO is an oxidisising agent. It oxidizes the living material in germs, microbes and bacteria. Therefore it kills all pathogenic organisms.

The chloric(I)acid is a weak acid and ionizes very slightly

$$HClO(aq) \rightleftharpoons H^+(aq) + ClO^-(aq) \text{ -------} ②$$

The HClO molecule is 80 times more effective than the OCl^- ion in killing bacteria . However:-

(i) if the pH is very high the concentration of H+ ion is very low. According to Le Chatelier's Principle equilibrium (2) will shift in the forward direction and more HClO molecule will ionize

(ii) if the pH is too low, it implies that the concentration of H^+ion is the solution is high. Therefore equilibrium (2) will shift in the backward direction and more HClO molecule will be formed. But at the same time as more HClO molecules are formed equilibrium(1) will shift in the backward direction, leading to loss of chlorine.

Therefore the pH of water must be carefully monitored to ensure a higher concentration of HClO in water .

Chlorination must be carefully monitored because excess chlorine can undergo substitution reaction with traces of organic compounds to make poisonous chloro-compounds. For example, alkanes react with chlorine to produce toxic chloroalkanes.

- Chlorine is used to make organic solvents such as CCl_4, polymers such as PVC and refrigerator fluids, and aerosol propellants such as Freon 11 ($CFCl_3$) and Freon 12 (CF_2Cl_2).
- Silver chloride, bromide and iodide are used in photographic films and paper (silver salts are decomposed by light).
- Iodine is used as a disinfectant (dissolved in KI solution and in alcohol), and in 'iodoform' (CH_3I).
- Organic chlorocompounds are used as insecticides. A well-known example is DDT.
- Sodium chlorate(I), NaClO, is used as a bleach for clothes.

EXERCISE 14

Multiple Choice Questions

Section I

1 Which one of the following changes does not occur in Group VII elements as the proton number increases?

A Reactivity with hydrogen decreases.
B H—X bond becomes stronger.
C The X^- ion is more easily oxidised.
D The ionisation energy of the elements becomes smaller.

2 Why is concentrated sulphuric acid *not suitable* for preparing a sample of hydrogen iodide from potassium iodide?

A It dehydrates the hydrogen iodide.
B It is a reducing agent.
C It is an oxidising agent.
D It is a strong acid.

Pollution problems of halogenocompounds (see page 400)

3 In some Periodic Tables hydrogen is placed in Group VII. Which property of hydrogen could justify this?

A It has one outer shell electron.
B It forms the ionic hydride Na^+H^-.
C It forms the ion H_3O^+ in acids.
D It contains a single electron shell.

4 Astatine, symbol At, is at the bottom of Group VII. Astatine has proton number = 85. Which statement about astatine and its compounds is *not* likely to be true?

A The hydride of astatine is a strong acid.
B The ion of astatine in compounds has 86 electrons.
C Astatine can have an oxidation number of +5 in compounds.
D The astatine anion is the weakest reducing agent of all the Group VII anions.

5 Which reagent will increase the oxidation number of bromine in a solution of potassium bromide?

A dilute sodium hydroxide
B chlorine solution
C ammonia solution
D hydrochloric acid

6 Which one of the following hydrides most easily decomposes into its elements when heated with a hot glass rod?

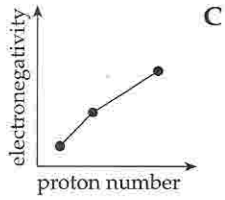
A ammonia
B methane
C hydrogen iodide
D hydrogen chloride

7 Fluorine is above chlorine in Group VII. Which one of the following statements about fluorine and fluorine compounds is correct?

A The electronegativity of fluorine is less than that of the other Group VII elements.
B Fluorine is the most powerful oxidising agent of the Group VII elements.
C Hydrogen fluoride is the strongest acid of all the Group VII hydrides.
D Hydrogen fluoride is easily decomposed into its elements.

8 Which one of the following graphs best shows the change in the electronegativity of the elements chlorine, bromine and iodine?

A



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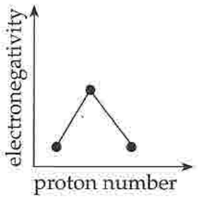
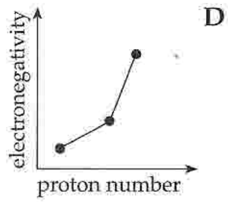


B



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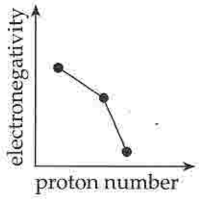


9 In which one of the following pairs of substances does the chlorine have the largest difference in oxidation number?

A NaCl, ClO_3^-
B ClO^-, $KClO_3$
C $MgCl_2$, ClO_4
D $Cl_2O_7^{2-}$, ClO_3^-

Section II

Summary of directions

A	B	C	D
1, 2 and 3 are correct	**1 and 2** only are correct	**2 and 3** only are correct	**1 only** is correct

10 Which properties become *greater/higher* for the series of elements F → Cl → Br → I?

1 size of the ion X^-
2 melting point of the element
3 oxidising power of the element

11 Which statements about the hydrides of Group VII elements are correct?

1 They form silver salts that are soluble in water.
2 They react with water to form H_3O^+ ions.
3 They react with ammonia to form white solids.

12 For the hydrides HCl, HBr and HI, what properties of these hydrides increase as the relative molecular mass increases?

1 their boiling points
2 the ease of oxidation
3 the thermal stability

Structured Questions

1 Some data of Group VII elements is given in Table 14.6.

(a) Predict the data for astatine.

(b) Answer the following questions about the likely properties of astatine and its compounds.

(i) Predict the appearance and physical state of astatine at room conditions.

(ii) Astatine forms the ionic compound KAt. How does the lattice energy of this compound compare with those of the other potassium salts of Group VII?

(iii) Write the formula of the hydride of astatine. What would be the effect of heat on this hydride?

(iv) Write a balanced ionic equation for the reaction of astatine hydride with water.

element	fluorine	chlorine	bromine	iodine	astatine
molecular formula	F_2	Cl_2	Br_2	I_2	
outer electronic configuration	$2s^2\,2p^5$	$3s^2\,3p^5$	$4s^2\,4p^5$	$5s^2\,5p^5$	
m.p./°C	−220	−101	−7	113	
ionic radius/nm	0.136	0.181	0.195	0.216	
first ionisation energy	1680	1250	1140	1010	
electronegativity	4.0	3.0	2.8	2.5	

▲ Table 14.6

Descriptive Questions

1 Suggest explanations for the following facts:

(a) Neon and hydrogen fluoride have the same relative molecular mass, but the boiling point of hydrogen fluoride is about 200°C higher.

(b) When concentrated sulphuric acid is added to solid potassium bromide, a brown gas is seen in addition to white fumes of a colourless gas.

(c) When a red hot platinum wire is plunged into a gas jar of hydrogen iodide, purple and brown fumes are seen.

2 (a) Give the formulae of the chlorine containing compounds with the following oxidation number :

+ 1, - 1, + 5, + 7

(b) When chlorine reacts with cold and hot aqueous sodium hydroxide, the chlorine molecules disproportionate.

(i) What do you understand by disproportionation ?

(ii) Write balanced equation for the reaction of chlorine with Cold and hot NaOH. Indicate the disproportionation of the chlorine molecules.

(c) A solution of potassium iodide of 0.060 mol/dm^3 was titrated with an alkaline solution of potassium manganate (VII), 0.106 mol/dm^3. 25.0 cm^3 of the potassium iodide solution needed 28.30 cm^3 of the potassium manganate (vii) solution for complete reaction.

(i) Calculate the molar ratio of $KMnO_4$: KI that reacted.

(ii) Assuming that MnO_2 precipitated during the titration, deduce the final oxidation number of iodine.

3 (a) Give concise explanation for each of the following :

(i) The intensity of the colour of the halogen molecules increases from fluorine to iodine.

ii) The electronegativities of the elements are :

Element /ion	$F \rightarrow F^-$	$Cl \rightarrow Cl^-$	$Br \rightarrow Br^-$	$I \rightarrow I^-$
Electro-negativity	-333	-364	-342	-295

(iii) AgCl dissolves in dilute aqueous ammonia.

AgBr dissolves only in concentrated ammonia.

AgI is insoluble in both dilute and concentrated aqueous ammonia.

(b) (i) Give a concise description of the electrolysis of brine using the diaphragm cell.

(ii) Write one equation to show the products of the electrolysis of brine.

(iii) Give the molar ratio of the anodic and cathodic products.

CHAPTER

15

NITROGEN AND SULFUR

SYLLABUS OBJECTIVES

In this chapter you should be able to:

- explain the lack of reactivity of nitrogen (ie because of the strong N≡N bond)
- describe the structure and formation of the ammonium ion (NH_4^+)
- describe the displacement of ammonia (NH_3) from ammonium salts (ie by warming with strong alkalis)
- describe the Haber Process, giving essential operating conditions and their kinetics and equilibria in applying Le Chatelier's Principle
- know the industrial importance of ammonia and nitrogen compounds produced from ammonia particularly nitrogen fertilizer compounds such as ammonium sulphate and ammonium nitrate
- know the harm to the environment caused by the uncontrolled use of nitrate fertilizers
- describe and explain the occurrence of oxides of nitrogen in car exhaust gases and their removal by catalytic converters
- explain simply why atmospheric oxides of nitrogen are pollutants, including the catalytic role of oxides of nitrogen in oxidising atmospheric sulphur dioxide to sulphuric acid
- describe the formation of atmospheric sulphur dioxide from the combustion of sulphur-containing fossil fuels (eg from burning coal)
- state the role of sulphur dioxide in forming acid rain and effect on the environment caused by acid rain
- describe the Contact Process for the manufacture of sulphuric acid
- realise the industrial importance of sulphuric acid
- describe the use of sulphur dioxide in food preservation

General Properties of Nitrogen

Nitrogen Element

Ammonia

Nitrogen Fertilizers

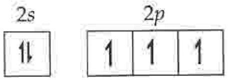
Nitrogen Oxide Pollution

Sulfur Dioxide

Sulfuric Acid

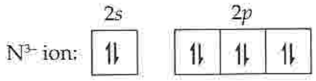
15.1 General Properties of Nitrogen

- The outer electronic configuration of nitrogen is



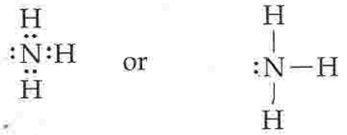
- The element is a typical non-metal.
- In compounds, nitrogen can form bonds in the following ways:

(a) Gain three electrons to fill the outer shell and achieve the octet structure by forming the N^{3-} ion:

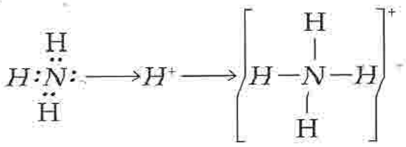


For example, magnesium reacts with nitrogen gas to form magnesium nitride, Mg_3N_2, which contains N^{3-} ions. In these compounds, nitrogen forms electrovalent bonds.

(b) Use the three unpaired electrons in the 2*p* orbitals to form three covalent bonds. This is the most common bonding of nitrogen. The ammonia molecule is an example of this:



(c) *Use the 2s electron pair (lone pair) to form a co-ordinate bond.* One example is the ammonium ion:



(d) Form hydrogen bonds with suitable hydrogen atoms, because nitrogen is a very electronegative element (see *Properties of Ammonia* further on).

- Other elements in Group V can form compounds with five covalent bonds, such as phosphorus in PCl_5. Nitrogen cannot form NCl_5 because it has only 2*s* and 2*p* orbitals (a total of four orbitals) in the outer shell. Nitrogen has no 2*d* orbitals.

  The other elements in Group V can form five covalent bonds by using the *d* orbitals in the outer shell.

15.2 Nitrogen Element

- Much of the nitrogen is found in the air. Nitrogen makes up about 79% of the atmosphere.
- Nitrogen has a molecular structure. The molecular formula is N_2. In the molecule, the two nitrogen atoms are held together by a very strong triple covalent bond:

$$:N\vdots N: \qquad \text{or} \qquad :N\equiv N:$$

- Nitrogen is obtained from the air by fractional distillation of liquid air. In this process purified air is freed from carbon dioxide and water vapour is compressed to about 200atm, and cooled by passing through a pipe surrounded by cold water. The cooled and compressed air is then passed through a spiral tube and escapes through a very small nozzle. The air expands into a region of lower pressure as a result of which it cools down. The cooled air passes around the spiral tubes where it cools down further. The cooled air is further cooled by expansion and cooling. This process is continued until the air liquefies. A pale blue liquid, characterisric of the blue colour of liquid oxygen is formed.
  Fractional distillation is then carried out.
- Compared with other elements, nitrogen is unreactive. This is due to the very strong N≡N bond in N_2. This bond must be broken before nitrogen can react with other elements to form compounds. A lot of energy is required to break the bond.

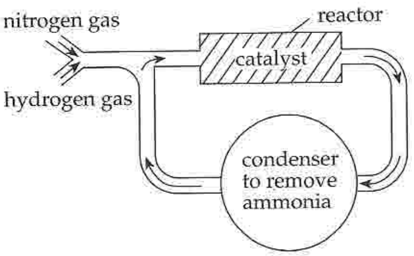
$$\Delta H_{BE}(N\equiv N) = +944KJmol^{-1}$$

- Nitrogen has very few reactions only (because of the strong N≡N bond). The more important reactions are summarised below. The conversion of N_2 into nitrogen compounds is called **nitrogen-fixation**.
  (a) Nitrogen reacts with hydrogen to form ammonia, in the Haber Process (see Section 15.3):

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

  (b) Nitrogen reacts with oxygen in the air in the presence of an electric discharge, such as lightning. This produces oxides of nitrogen. The oxides react with water to form nitric acid which is added to the soil in rain. This is how some nitrogen is added to the soil for plant growth.
  (c) Nitrogen reacts with oxygen in the air in motorcar engines (see Section 15.5).
  (d) Nitrogen is absorbed by 'nitrogen-fixing' plants. An enzyme in the plant converts the nitrogen into nitrogen compounds before they are absorbed by the plants.

15.3 Ammonia



▲ Fig 15.1 Simplified Haber Process

Manufacture of Ammonia

- Ammonia is manufactured by the **Haber Process**. In the process, hydrogen and nitrogen gases are passed over an iron catalyst. The equation for the reaction is

  $$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \quad \Delta H^{\ominus} = -92 \text{ kJ}$$

- The conditions of the process are:
  (a) high pressure of 250 atmospheres;
  (b) optimum temperature of about 450°C;
  (c) finely divided iron promoted by alumina catalyst;
  (d) mole ratio of N_2 to H_2 = 3:10.

  The nitrogen is obtained from the air. The hydrogen is obtained from several sources, including petroleum.

  An outline of the Haber Process is shown in Fig 15.1. When the mixture of nitrogen and hydrogen is passed over the catalyst, only about 15% of the reactants is converted into ammonia at equilibrium. The ammonia is removed by condensing it to a liquid at a low temperature. The unreacted nitrogen and hydrogen is recycled and passed over the catalyst again.

- The iron catalyst allows the reacting gases to reach equilibrium quickly. The catalyst does not affect the percentage of ammonia in the equilibrium mixture.

- A high pressure is used. When a high pressure is applied, according to Le Chatelier's principle, the equilibrium will shift in such a direction so as to lower the pressure. Therefore the equilibrium will shift in the direction which is accompanied by a decrease in the number of moles of gases, that is in the forward direction. Therefore a high pressure favours the formation of ammonia.

- Theoretically, a high percentage of ammonia would be produced at equilibrium if a low temperature is used because the forward reaction (from left to right) is exothermic according to Le Chatelier's Principle. However, the reaction is too slow at low temperatures. Hence, in practice, a moderate temperature is used to speed up the reaction (although the percentage of ammonia produced at equilibrium is reduced).

  Note: For an explanation of *Le Chatelier's Principle*, see Chapter

Laboratory Production of Ammonia

- Ammonia can be prepared by adding a strong alkali or a basic oxide to an ammonium salt. For example, ammonia gas is produced when ammonium chloride is warmed with aqueous sodium hydroxide or solid magnesium oxide. The equations for the reactions are

$$NH_4Cl + NaOH \rightarrow NH_3 + H_2O + NaCl$$

$$2NH_4Cl(s) + MgO(s) \longrightarrow 2NH_3(g) + MgCl_2(s) + H_2O(l)$$

- Ammonia is also produced when a nitrate is heated with a mixture of aluminium powder and excess aqueous sodium hydroxide. In this reaction, the nitrate ions are reduced to ammonia.

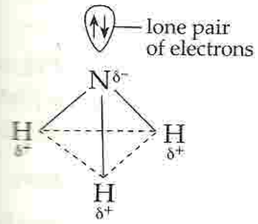


Fig 15.2

Properties of Ammonia

- The ammonia molecule has the following properties:
  - (a) it is a polar molecule;
  - (b) it has a pyramidal shape as the four electron pairs stay as far apart as possible (Fig 15.2).
- In liquid and solid ammonia, the NH_3 molecules are held together by hydrogen bonds (Fig 15.3).

  Because of the hydrogen bonds, the boiling point of liquid ammonia is higher than the boiling points of the other hydrides of Group V. The boiling points of the hydrides of Group V are shown in Fig 4.29 in Chapter 4.

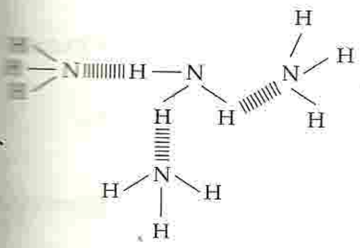


Fig 15.3 Hydrogen bonding in liquid ammonia

- Ammonia is very soluble in water, because it forms hydrogen bonds with the water molecules (see Fig 4.25 in Chapter 4).
- Ammonia is a base.
  - (a) Ammonia is a weak alkali. It reacts with water to form OH^- ions.

    $$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

    In the reaction, the NH_3 molecule accepts a proton from the H_2O molecule.
  - (b) Ammonia reacts with acids to form ammonium salts. For example, ammonia reacts with nitric acid to form ammonium nitrate:

$$NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq) \quad \text{or} \quad NH_3(aq) + HNO_3(aq) \rightarrow NH_4NO_3(aq)$$

In the reaction, the NH_3 molecule accepts a proton from the acid.

- Ammonia forms complex ions with several metal ions. For example, when ammonia solution is added to a solution of copper ions, Cu^{2+}, a blue precipitate of copper(II) hydroxide is first formed:

$$Cu^{2+}(aq) + 2OH^-(aq) \rightarrow Cu(OH)_2(s)$$

The precipitate dissolves in *excess* ammonia due to the formation of a complex ion:

$$Cu(OH)_2(s) + 4NH_3(aq) + 2H_2O(l) \longrightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 2OH^-(aq)$$

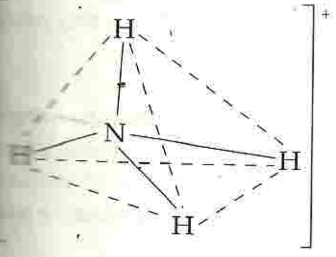


Fig 15.4 Shape of the ammonium ion

Ammonium Ion

- The ammonium ion, NH_4^+, is tetrahedral as it has four electron pairs around the central nitrogen atom (Fig 15.4).

Uses of Ammonia

- Ammonia is mainly used for fertilizers, such as ammonium sulphate (see section 15.4).
  Ammonia is used as a degreasing agent in laundries and oven cleaners.

- Some ammonia is oxidised to nitric acid, by the steps below:
  (a) a mixture of ammonia and oxygen is passed over a platinum catalyst at about 900°C. The equation for the reaction is

  $$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g); \quad \Delta H = \text{negative}$$

  (b) the NO is allowed to cool in the presence of air. It reacts with oxygen to form NO_2:

  $$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

  (c) The NO_2 gas dissolves in water, in the presence of excess air to form nitric acid:

  $$4NO_2(g) + O_2(g) + 2H_2O(l) \rightarrow 4HNO_3(aq)$$

- The main uses of nitric acid are:
  (a) manufacture of nitrate fertilizers, particularly ammonium nitrate;
  (b) manufacture of explosives, such as 2,4,6-trinitromethyl-benzene ('TNT');
  (c) manufacture of organic dyes (see azo dyes in *Reactions of Phenylamine* in Chapter 23).

15.4 Nitrogen Fertilisers

Environmental Problems (Nitrate Fertilisers)

- If excess nitrate fertiliser is added to soil, leaching may occur when the excess is washed off the land by rain and goes into nearby rivers and lakes. The fertiliser causes excessive growth of weeds and algae in the fresh water. This clogs the waterways with vegetation and limits the amount of light that reaches the aquatic plants. Less photosynthesis occurs and less oxygen is produced by the aquatic plants. The concentration of dissolved oxygen in water decreases. This is further decreased when the weeds , aquatic plants or algae die. Some of the dissolved oxygen is used up during their decay.This consumption of oxygen is measured as the biological oxygen demand(BOD). The BOD can become very large. This process is referred to as eutrophication. During this process fish and aquatic animals die out .

- Nitrates in rivers can also get into tap water. Nitrate ions are poisonous because they can oxidise iron(II) in haemoglobin to iron(III). The iron in haemoglobin must be in the +2 oxidation state to absorb oxygen into the blood. Therefore excessive use of nitrate fertilizers can indirectly reduce the body's ability to absorb oxygen in the lungs (see *Haemoglobin* in Chapter 16).

- The pollution effects of nitrate fertiliser can be reduced by using less fertiliser and utilizing other methods to increase the yield of food crops (eg using natural fertilisers from animal waste, manure from decomposing vegetation and selecting more productive strains of wheat and rice etc).

15.5

Nitrogen Oxide Pollution

- Nitrogen and oxygen in the air combine together at high temperatures to form nitrogen oxide, NO:

  $$N_2(g) + O_2(g) \rightarrow 2NO(g); \Delta H = +180\ kJ$$

  The high temperature due to the combustion of fuel in the car engine is required to break the strong triple bond in N_2 for this reaction to take place. This is why ΔH is positive.

  The NO then combines with more oxygen in the air to form nitrogen dioxide, NO_2:

  $$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g); \quad \Delta H = -113\ kJ$$

  This reaction takes place as the exhaust gases cool down. At high temperatures, the equilibrium is displaced to the left as ΔH is negative and NO_2 is not produced.

  The two oxides, NO and NO_2, are commonly described simply as 'NO_x'.

- Most NO_x in the air comes from motor car engines. Some NO_x is also produced by electricity-generating stations and industries and from the combustion of (particularly) coal and oil.

- NO_x damages the environment in the following ways:
  (a) NO_2 reacts with water to form a mixture of nitrous acid (HNO_2) and nitric acid (HNO_3):

  $$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$$

  The nitrous acid is then oxidised by atmospheric oxygen to nitric acid, HNO_3.

  The overall equation for the conversion of NO_2 into nitric acid by atmospheric water and oxygen can be written as:

  $$2NO_2(g) + H_2O(l) + \frac{1}{2}O_2(g) \longrightarrow 2HNO_3(aq)$$

  Nitric acid is a major cause, together with SO_2, of **acid rain** (see *Acid Rain* further on).

  (b) NO_x reacts with other air pollutants to form ozone. Ozone irritates the eyes.

  Acid rain and the ozone produced from NO_x are killing the trees in many European forests.

  (c) NO_x catalyses the oxidation of atmospheric SO_2 to sulphuric acid, producing acid rain (see *Acid Rain* further on).

Preventing NO_x Pollution

- The production of NO_x from motor car engines can be greatly reduced by using a catalytic converter in the exhaust. The mixture of NO_x, CO and unburnt hydrocarbons is passed over a platinum catalyst and is converted into harmless N_2, CO_2 and steam. 'Lead-free' petrol must be used because lead poisons the platinum catalyst, making it ineffective.

  Typical reactions in the converter are:

$$\underbrace{2NO + 2CO}_{\text{pollutants}} \rightarrow \underbrace{N_2 + 2CO_2}_{\text{relatively harmless products}}$$

$$2NO_2(g) + 4CO(g) \longrightarrow N_2(g) + 4CO_2(g)$$

- Catalytic converters in motor cars are expensive because:
  - (a) it uses the relatively expensive platinum;
  - (b) engines that use 'lead-free' petrol are less efficient, so more fuel is used.
- The amount of NO_x produced from burning fuel can be reduced by lowering the temperature. This is done in power stations by spraying water onto the burning fuel.

15.6 Sulfur Dioxide

Sources of Atmospheric Pollution

- Human related sources of atmospheric sulfur dioxide are:
  - (a) burning coal and oil causes sulfur to be oxidised to SO_2 and released into the atmosphere:

$$S + O_2 \rightarrow SO_2$$

  - (b) release of sulfur dioxide from industries, such as roasting of metal sulfide ores in the extraction of metals.

Uses of Sulfur Dioxide

- Sulfur dioxide is an antioxidant Sulfur dioxide is used as a perservative in food. It is added to sauces and some drinks to kill any harmful microorganisms that might breed in the food.
- Sulphur dioxide is used to bleach wood pulps.

SULPHURIC

15.7 Sulfuric Acid

Manufacture of Sulfuric Acid

- Sulfuric acid is manufactured by the **Contact Process**:

  Stage 1: Sulfur is burnt in air to produce SO_2 (or the SO_2 is obtained from other sources):

$$S + O_2 \rightarrow SO_2$$

Stage 2: Sulfur dioxide is reacted with excess air over a vanadium(V) oxide catalyst to produce SO_3 at about 450°C:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g); \quad \Delta H = -191 kJ$$

The conversion of SO_2 into SO_3 is 98% complete.

Stage 3: The sulfur trioxide is reacted with concentrated sulfuric acid to produce $H_2S_2O_7$, 'oleum':

$$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$$

Stage 4: The $H_2S_2O_7$ is reacted with water to produce concentrated sulfuric acid:

$$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$$

The SO_3 is not reacted directly with water because the reaction is very vigorous producing polluting mists of sulfuric acid droplets.

Importance of Sulfuric Acid

- Sulfuric acid is one of the most important industrial chemicals. Some of its major uses are:
  (a) manufacture of fertilizers, particularly soluble phosphate fertilizers and ammonium sulphate (this is the major use);
  (b) manufacture of paint, particularly titanium(IV) oxide for white paints and to make other paints opaque;
  (c) removal of rust from steel before painting;
  (d) manufacture of other acids, such as hydrochloric acid;
  (e) manufacture of organic chemicals such as dyes, drugs and explosives.

Acid Rain

- Acid rain is caused mainly by sulfur dioxide in the atmosphere. Some acid rain is also caused by oxides of nitrogen in the atmosphere.
- Sulfur dioxide reacts with oxygen and water in the air to form sulfuric acid causing acid rain. This reaction is catalysed by oxides of nitrogen:

  Stage 1: Sulfur dioxide reacts with nitrogen dioxide, NO_2 (from fires and car exhausts):

  $$SO_2 + NO_2 \rightarrow SO_3 + NO$$

  Stage 2: The SO_3 reacts with water to form sulfuric acid:

  $$SO_3 + H_2O \rightarrow H_2SO_4$$

  Stage 3: The NO from stage 1 reacts with atmospheric oxygen to produce more NO_2:

  $$2NO + O_2 \rightarrow 2NO_2$$

  The NO_2 can then react with more SO_2 to repeat stage 1.
- Nitrogen dioxide reacts with oxygen and water in the air to form

nitric acid, which also becomes acid rain:

$$2NO_2 + H_2O + \frac{1}{2}O_2 \rightarrow 2HNO_3$$

- Some of the harm caused by acid rain are:
  - (a) Corrosion of buildings, eg sulfuric acid reacts with calcium carbonate in marble and limestone:

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$$

  - (b) Corrosion of steel, eg sulfuric acid reacts with iron in vehicles and steel structures:

$$H_2SO_4 + Fe \rightarrow FeSO_4 + H_2$$

  - (c) Acidification of fresh water lakes. This kills fish.
  - (d) Acidification of agricultural land. This lowers the pH of the soil and reduces the yield of food crops, which requires neutralisation by applying 'lime', calcium hydroxide, to the soil.
  - (e) When acid rain comes into contact with soil, it causes heavy metal ions as well as aluminium ion (Al^{3+}) to dissolve. The dissolved ions may enter nearby lakes and rivers or may be absorbed by plants. But aluminium ion are toxic to plants. Hence aquatic plants as well as trees may be damaged.

- Acid rain can be prevented by:
  - (a) burning less sulfur-containing fuels, particularly coal;
  - (b) treating the exhaust gases from industries and power stations with SO_2-absorbing chemicals such as heated limestone. Calcium oxide from the decomposing calcium carbonate together with air reacts with the SO_2 to produce solid particles of calcium sulphate which is trapped by filters.

EXERCISE 15

Multiple Choice Questions

Section I

1 The lack of reactivity of nitrogen gas is due to

A the lack of 2*d* orbitals in the outer shell.
B the strength of the covalent bond in the N_2 molecule.
C the high ionisation energy of nitrogen compared with oxygen.
D the very low solubility of nitrogen in water.

2 When ammonia reacts with substance X, the ammonium ion, NH_4^+, is formed. What type of substance is X?

A an acid
B an oxidising agent
C a base
D a reducing agent

3 Which one of the following does *not* involve the lone pair of electrons on the nitrogen atom of ammonia?

A Reaction of ammonia with HCl(aq) to produce ammonium and chloride ions.
B Reaction of ammonia with potassium metal to produce $K^+NH_2^-$ and H_2.
C Hydrogen bonding between ammonia and water in $NH_3(aq)$.
D Dissolving of silver chloride in $NH_3(aq)$.

4 How does nitrogen dioxide catalyse the production of acid rain from sulphur dioxide?
- A By oxidising the sulphur dioxide to sulphur trioxide
- B By changing water molecules into $H^+(aq)$ ions
- C By reacting with water vapour to form nitric acid
- D By removing hydrogen from water to release oxygen

5 Ammonia is very soluble in water. What is the *main* reason for this?
- A Ammonia reacts with the water to form NH_4^+ and OH^- ions.
- B Ammonia forms hydrogen bonds with the water molecules.
- C Ammonia molecules are very small so they can occupy empty space between the water molecules.
- D Ammonia forms complex ions with the water molecules.

6 Phosphorus and nitrogen are in the same group in the Periodic Table. The compound PCl_5 is known, but no chemist has been able to make NCl_5. What is the most likely explanation for this?
- A The covalent bond in the N_2 molecule is too strong.
- B There is no space for five large chlorine atoms to fit around one small nitrogen atom.
- C Nitrogen-chlorine covalent bonds are very weak.
- D Nitrogen has only four orbitals in its outer shell.

Section II

Summary of directions

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

7 In which of the following reactions is ammonia reacting as a base?
- 1 Reaction with water to produce $NH_4^+(aq)$ and $OH^-(aq)$.
- 2 Reaction with hydrogen chloride to produce $NH_4^+Cl^-(s)$.
- 3 Reaction with oxygen to produce NO(g) and $H_2O(g)$.

8 The damage caused by nitrogen oxides from motor car exhausts is known to include
- 1 'acid rain'.
- 2 the 'greenhouse effect'.
- 3 destruction of the 'ozone layer'.

9 Which of the following statements about ammonia are true?
- 1 An ammonia molecule forms a dative bond with a H^+ ion to produce an NH_4^+ ion.
- 2 In liquid ammonia, the main force between the molecules is hydrogen bonding.
- 3 In aqueous solution, most ammonia is present in the form of molecules.

Structured Questions

*1 (a) Magnesium reacts with nitrogen at a very high temperature to produce a yellow solid, **S**. Solid **S** contains 28% nitrogen by mass.
- (i) Suggest why the reaction only takes place at a high temperature.
- (ii) Calculate the empirical formula of solid **S**.
- (iii) Suggest the type of bonding present in solid **S**.

(b) When water is added to solid **S**, the products are ammonia and a white solid.
- (i) Suggest the name of the white solid.
- (ii) Construct a balanced equation for the reaction.

2

nitrogen compound	**enthalpy change of formation, ΔH_f, kJ mol^{-1}**	**oxidation number of nitrogen**
NO	+90	+2
NH_3	– 46	
N_2O	+82	+1
NO_2	+34	
N_2H_4	+50	

Some data on nitrogen compounds is given in the table above.

(a) Complete the table by adding the missing oxidation numbers.

(b) (i) Which compound is produced *inside* a *hot* car engine?

(ii) Suggest a reason why the activation energy for this reaction is very high.

(iii) The compound in (i) changes into another compound in the table in *cold* air outside a car exhaust. What is the other compound?

(iv) Explain why the compound in (iii) is only produced at low temperatures.

(c) One of the compounds reacts with air and moisture to produce an acid that is a component of acid rain. Construct an equation for this reaction.

(d) Under the right conditions, hydrazine (N_2H_4) reacts with hydrogen to produce ammonia. Construct an equation for this reaction and use the ΔH_f values from the table above to calculate the enthalpy change of this reaction.

(e) Aqueous hydrazine, like aqueous ammonia, is alkaline. Write an equation to show this.

3 The Haber Process for the production of ammonia from its elements can be represented by the equation:

$$3H_2 + N_2 \rightleftharpoons 2NH_3$$

In the process, a mixture of nitrogen and hydrogen is passed over a catalyst. The ammonia is removed from the products and the unreacted gases passed through the reaction vessel again. From time to time, argon gas is removed from the reaction vessel (where it accumulates).

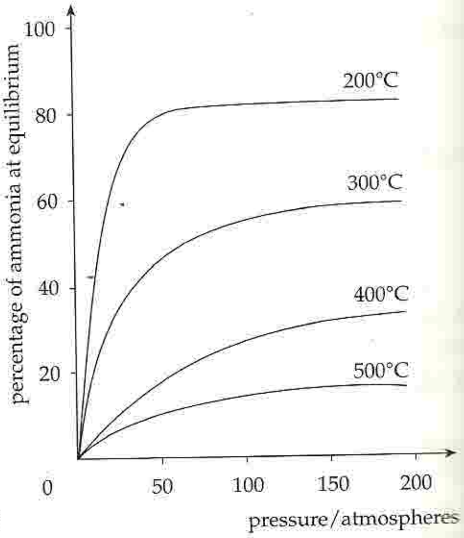
(a) (i) State the catalyst normally used in the Haber Process.

(ii) What are the sources of the nitrogen and hydrogen?

(iii) Suggest where the argon comes from.

(iv) Why is the ammonia removed from the products before passing the unreacted nitrogen and hydrogen over the catalyst again?

(b) Fig 15.5 shows the percentage of ammonia in the equilibrium mixture under different conditions.



▶ Fig 15.5

(i) Which temperature, 200°C or 500°C, produces a larger percentage of ammonia in the equilibrium mixture? State one disadvantage of using a temperature well below 500°C.

(ii) Which pressure, produces a larger percentage of ammonia in the equilibrium mixture, 50 or 150 atmosphere?

State one disadvantage of using a pressure greater than 200 atmospheres.

*4 (a) Nitric acid oxidises aqueous iron(II) ions.

(i) Use the *Data Tables* at the back of the book to write a possible equation for this reaction.

(ii) State the standard e.m.f. of this reaction.

(b) Nitrate in food and water can poison people.

(i) Briefly outline one harmful effect of nitrate on people.

(ii) Suggest how the nitrate gets into the water.

(c) A mixture of concentrated nitric and sulphuric acids is used in the nitration of benzene. Write the formula of the particles produced by the acid mixture that reacts with the benzene molecules.

5. (a) (i) Write down the electronic structure of nitrogen.
   (ii) Explain why the first ionization energy of oxygen is lower than that of nitrogen.

(b) Nitrogen is the most abundant gas found in the atmosphere.
   (i) Explain why nitrogen is found in large amount in the atmosphere.
   (ii) Describe briefly how nitrogen can be extracted form purified air.

(c) One of the most important uses of nitrogen is in the manufacture of ammonia by the Haber's process.
   (i) Describe the Haber's process, making particular reference to the conditions used to carry out the reaction.
   (ii) State why the temperature used to carry out the Haber's process is often referred to as an 'optimum temperature'.
   (iii) Draw a scheme to show the steps involved in the manufacture of ammonia.

(d) State three uses of ammonia.

6. (a) Ammonia is a gas which is very soluble in water.
   (i) Draw the shape of the ammonia molecule.
   (ii) Explain why ammonia is expected to be very soluble in water.

(b) When ammonia dissolves in water, it forms aqueous ammonia, which is a weak base.
   (i) What is a weak base?
   (ii) Why do you think that aqueous ammonia is a weak base.
   (iii) State why ammonia acts as a strong base when it dissolves in ethanoic acid.

(c) One of the main use of ammonia is in the manufacture of fertilizer, such as ammonium sulphate.
   (i) Name the other reagent required to manufacture ammonium sulphate.
   (ii) State why ammonium sulphate is potentially dangerous for the environment.

(d) A derivative of ammonia is hydrazine, N_2H_4.
   (i) Draw a dot and cross diagram for hydrazine.
   (ii) Hence draw the shape of the hydrazine molecule.

(e) Hydrazine reacts readily with hydrogen peroxide. One of the product of the reaction is nitrogen.
   (i) Write an equation for the reaction between hydrazine and hydrogen peroxide.
   (ii) State the type of reaction that has taken place.
   (iii) 3.20g of hydrazine was made to react with an excess of hydrogen peroxide. Calculate the volume of nitrogen gas, measured at r.t.p. produced during the reaction.

7. Some of the common oxides of nitrogen are listed below:

Oxides of nitrogen	Oxidation number of nitrogen
N_2O	
NO	
NO_2	
N_2O_4	
N_2O_5	

(a) Calculate the oxidation number of nitrogen in each of the oxides listed above.

(b) (i) What is the main source of nitrogen dioxide in the atmosphere?
   (ii) State two reasons why nitrogen dioxide and nitrogen monoxide are pollutants.
   (iii) How can the emission of oxides of nitrogen in the environment be limited?
   (iv) Suggest one substance which is present in the car exhaust that may limit the emission of oxides of nitrogen in the atmosphere.

(c) Draw the shape of the oxides of nitrogen tabulated above.

(d) (i) Nitrogen dioxide dissolves in water, in the presence of oxygen to produce nitric acid. Write a balanced equation for the reaction.
   (iii) State two uses of nitric acid.

8. (a) Explain the following:-
    (i) The nitrogen molecule is isoelectronic with the carbon monoxide molecule. However the bond energy of nitrogen is 944 KJmol-1 whereas that of carbon monoxide is 1074 KJmol-1.
    (ii) The dinitogentetroxide molecule, N_2O_4, is isoelectronic with the ethanedioate ion, $C_2O_4^{2-}$. However the N_2O_4 molecule decomposes on heating whereas the $C_2O_4^{2-}$ ion is thermally stable.
    (iii) Silver chloride is soluble in aqueous ammonia but does not dissolve in water.
    (iv) When zinc is added to dilute nitric acid, hydrogen gas is not produced.
    (v) Nitrogen has the formula N_2 whereas the formula of phosphorous is P_4.
(b) (i) When ammonium dichromate is heated, a redox reaction is started. One of the products of the reaction is chromium(III) oxide. Use the oxidation number method to identify the oxidation number of nitrogen in the product of the reaction and hence write a balanced equation for the reaction.
    (iii) Ammonium chloride reacts with sodium nitrite on heating. One of the products of the reaction is nitrogen. Write a balanced equation for the reaction .

Descriptive Questions

1. (a) Describe the steps involved in the Contact process used to manufacture sulphuric acid.
(b) Pure sulphuric acid is a covalent molecule. Draw a dot and cross diagram for sulphuric acid.
(c) Concentrated sulphuric acid can act as an acid, an oxidizing agent or as a dehydrating agent. Write balanced equations to show how concentrated sulphuric acid acts
    (i) as acid
    (ii) an oxidizing agent
    (iii) as a dehydrating agent
(d) The two main oxides of sulphur are sulphur dioxide, SO_2 and sulphur trioxide, SO_3.
    (i) Write down the dot and cross diagrams and draw the shapes of sulphur dioxide, SO_2 and of sulphur trioxide, SO_3.
    (ii) Both SO_2 and SO_3 are acidic oxides.Write equations for the reactions of these oxides with sodium hydroxide solution.
(e) Sulphur dioxide is one of the major pollutants in industrial zones.
    (i) State a natural source of SO_2.
    (ii) State an industrial source of SO_2.
    (iii) Why is sulphur dioxide considered to be a pollutant?
    (iv) State how the emission of sulphur dioxide in the environment can be limited.
    (v) Comment on two uses of sulphur dioxide in the industry.

2. (a) Write down the electronic structure of sulphur.
(b) Explain why the melting point of sulphur is higher than that of chlorine.
(c) When sulphur reacts with sodium sulphite, Na_2SO_3, sodium thiosulphate, $Na_2S_2O_3$ is formed.
    (i) Write an equation for the reaction.
    (ii) Calculate the maximum mass of sulphur that can dissolve in 50 cm^3 of 0.1 $moldm^{-3}$ solution of sodium sulphite.
(d) Write the equation for the reaction of sodium thiosulphate with:-
    (i) iodine
    (ii) chlorine

CHAPTER

16

TRANSITION ELEMENTS

SYLLABUS OBJECTIVES

In this chapter you should be able to:

- describe the general physical and characteristic properties of the first row transition elements, titanium to copper, including the colour of complexes
- explain what is meant by a transition element, in terms of *d*-block elements forming one or more stable ions with incomplete *d* orbitals
- state the electronic configuration of the first row transition elements and of their ions
- state that the following properties of the transition elements show little variation
  - atomic radii
  - ionic radii
  - first ionisation energies
- contrast qualitatively the following properties of the transition elements with those of calcium as a typical *s*-block element:
  - melting point
  - density
  - atomic radius
  - ionic radius
  - first ionisation energy
  - electrical conductivity
- describe the tendency of the transition elements to have variable oxidation states
- predict, given the electronic configuration, the likely oxidation states of a transition element
- describe and explain the use of Fe^{3+}/Fe^{2+}, MnO_4^-/Mn^{2+} and $Cr_2O_7^{2-}/Cr^{3+}$ as examples of redox systems
- predict using E values, the likelihood of redox reactions and
- describe and explain the reactions of transition elements with ligands to form complexes, including the complexes of copper(II) with water and ammonia and their colours
- explain qualitatively that ligand exchange may occur, (including CO/O_2 in haemoglobin) in terms of stability constants equilibria, including the dissolving of insoluble compounds and the effect of ligand exchange in E values
- explain the colours of transition metal complexes in term of *d*-orbital splitting and changes in colour as a result of ligand exchange
- state examples of catalysis by transition metals and/or their compounds

Definition

Characteristic Properties

Comparison with *s*-Block Elements

Electronic Configurations

Physical Properties

Variable Oxidation States

Oxidation States in Compounds

Transition Element Complexes

Shape of d-orbitals and colour of complexes

Uses of Transition Element ions in Redox Reactions

Transition Element Catalysts

16.1 Definition

- Transition elements form one or more stable ions with an incomplete d subshell of electrons. This is unique for the transition elements. For example, Fe^{3+} has the electronic structure

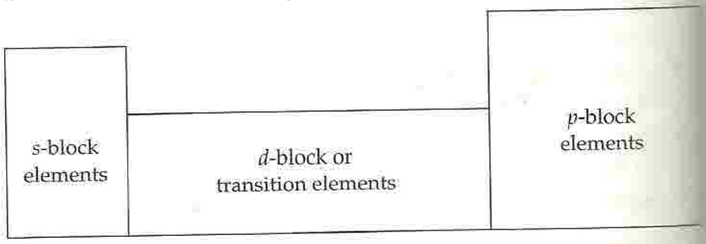
$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$$

The $3d$ subshell is incomplete — it has only 5 electrons.

- The position of the d-block or **transition elements** in the Periodic Table is shown in Fig 16.1. These elements have very similar physical and chemical properties. The *first transition series* or row of elements are the ten elements scandium (Sc) to zinc (Zn). However, scandium and zinc do not have most of the characteristic properties of the transition elements and thus are often excluded from the first transition series. The electronic structure of scandium ($_{21}$Sc) is $1s^22s^22p^63s^23p^63d^14s^2$. Scandium can form only one stable ion, namely Sc3+, by losing the electrons in the 4s and 3d- subshell. The resulting ion will not have any electron in the d-subshell. Therefore although scandium is a d-block element, it is not a transition element.
  The electronic structure of zinc ($_{30}$Zn) is $1s^22s^22p^63s^23p^63d^{10}4s^2$. Zinc can form only one stable ion, namely Zn2+, by losing the two electrons in the 4s subshell. The resulting ion will have a completely filled d-subshell($1s^22s^22p^63s^23p^63d^{10}$). Therefore although zinc is a d-block element, it is not a transition element. It does not show certain characteristic properties of transition elements. Thus :-

(i) it does not have variable oxidation states
(ii) it does not formed coloured compounds or solutions. All solutions of zinc salt are colourless
(iii) it cannot be used as catalyst

Hence in practice, the first transition series consists of the elements titanium (Ti) to copper (Cu).



▸ Fig 16.1 Position of s, p and d-block elements

16.2 Characteristic Properties

- Transition elements:
  (a) are *metals* with *high melting* and *boiling points;*
  (b) have *high densities* (compared with non-transition metals);

(c) have *variable oxidation numbers* in compounds (non-transition elements usually form one ion in compounds);
(d) form *coloured ions* in water;
(e) form a large number of *complexes* and *complex ions;*
(f) are often good catalysts (so are their compounds);
(g) can use orbitals from two different shells for bonding (eg 4*s* and 3*d*).

16.3 Comparison with *s*-Block Elements

- The properties of transition elements are compared with those of calcium, a typical *s*-block element, in Table 16.1.

property	transition elements	calcium
melting point	very high (over 1000°C)	lower than transition elements (850°C for calcium)
density	very high	low
atomic radius	smaller than calcium	larger than transition elements
ionic radius (M^{2+} ion)	smaller than calcium	larger than transition elements
first ionisation energy	larger than that of calcium	smaller than that of transition elements
electrical conductivity	good, but poorer than that of calcium	very good — better than that of most transition elements

▲ Table 16.1 Comparison of physical properties of typical transition elements with those of calcium

16.4 Electronic Configurations

- The electronic configurations of the first transition series are given in Table 16.2.
- Chromium has electronic configuration $3d^5\,4s^1$ because an exactly half-filled 3*d* subshell is particularly stable.
- Copper has electronic configuration $3d^{10}\,4s^1$ because a completely filled 3*d* subshell is particularly stable.
- For the elements titanium (Ti) to copper (Cu), the 4*s* subshell has more energy than the 3*d* subshell. However the energy difference between the 3*d* and the 4*s* is small.

- Transition metals can use orbitals from *two* different shells for bonding. For example, iron loses electrons from the 4*s* subshell (of the 4th shell) and the 3*d* subshell (of the 3rd shell) to form Fe^{3+} in iron(III) compounds.

▶ Table 16.2 Outer electronic configurations of the first transition series (the 3*s* and 3*p* subshells are completely filled for all the elements

element			**electronic configuration**					
			3*d*					4*s*
scandium	Sc	[Ar]	↑					↑↓
titanium	Ti	[Ar]	↑	↑				↑↓
vanadium	V	[Ar]	↑	↑	↑			↑↓
chromium	Cr	[Ar]	↑	↑	↑	↑	↑	↑
manganese	Mn	[Ar]	↑	↑	↑	↑	↑	↑↓
iron	Fe	[Ar]	↑↓	↑	↑	↑	↑	↑↓
cobalt	Co	[Ar]	↑↓	↑↓	↑	↑	↑	↑↓
nickel	Ni	[Ar]	↑↓	↑↓	↑↓	↑	↑	↑↓
copper	Cu	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑
zinc*	Zn	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

▶ Table 16.3 Simple ions of transition elements

element	**ion**	**outer electronic configuration**
chromium	Cr^{3+}	$3s^2\ 3p^6\ 3d^3\ 4s^0$
manganese	Mn^{2+}	$3s^2\ 3p^6\ 3d^5\ 4s^0$
iron	Fe^{2+}	$3s^2\ 3p^6\ 3d^6\ 4s^0$
	Fe^{3+}	$3s^2\ 3p^6\ 3d^5\ 4s^0$
cobalt	Co^{2+}	$3s^2\ 3p^6\ 3d^7\ 4s^0$
nickel	Ni^{2+}	$3s^2\ 3p^6\ 3d^8\ 4s^0$
copper	Cu^{2+}	$3s^2\ 3p^6\ 3d^9\ 4s^0$

3*d* subshell incomplete

16.5 Physical Properties

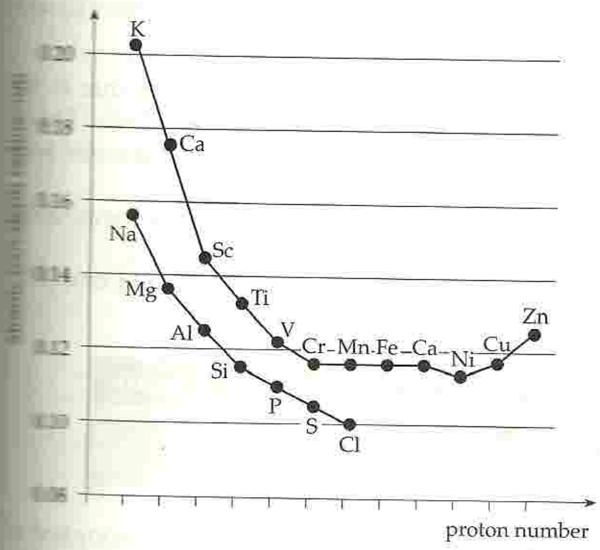
- The transition elements have very similar physical properties. Some of these properties are shown in Table 16.4. Note that there is very little change in atomic (metallic) radius, ionic radius and first ionisation energy.

element	proton number	atomic (metallic) radius/nm	ionic radius (M^{2+} ion)/nm	ionisation energy/kJ mol^{-1}	melting point/°C	density g cm^{-3}
titanium	22	0.145	0.090	660	1675	4.5
vanadium	23	0.132	0.088	650	1900	6.1
chromium	24	0.137	0.080	650	1890	7.2
manganese	25	0.137	0.088	720	1240	7.4
iron	26	0.124	0.076	760	1535	7.9
cobalt	27	0.125	0.074	760	1492	8.9
nickel	28	0.125	0.072	740	1453	8.9
copper	29	0.128	0.069	750	1083	8.9

▲ Table 16.4 Some physical properties of the first transition series

Melting Points

- Transition elements are all metals. They have higher melting and boiling points, compared to non-transition metals such as magnesium and sodium, because of the strong metallic bonds. The metallic bonds are strong because the transition elements have a lot of electrons (from the 3*d* and 4*s* subshells) which can be used for metallic bonding.



▲ Fig 16.2 Atomic (covalent) radii of the elements in the third Period and in the first row transition elements (covalent radii are used for all elements to make a valid comparison)

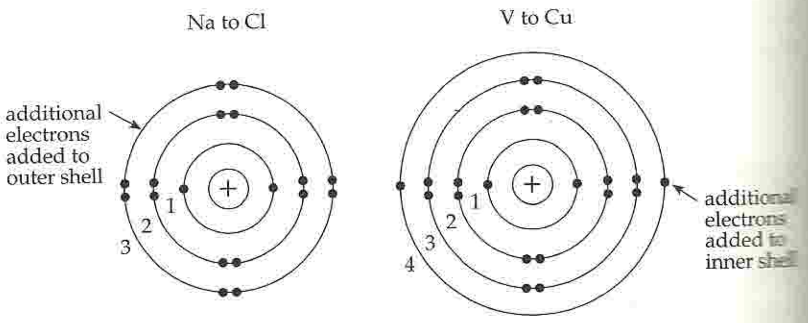
Atomic Radii

- The transition metals show little variation in their atomic (covalent) radii.

  Compare the atomic (covalent) radii of the elements V to Cu with those of the elements in the third Period, Na to Cl (Fig 16.2). The atomic (covalent) radii of the elements from V to Cu remain almost the same.

  As the proton number increases across the period Na to Cl, electrons are added to the *outer* shell (the 4*s* subshell). As the nuclear force increases, these outer electrons are pulled closer towards the centre, resulting in a decrease in the atomic radii across the period.

  In the case of the transition metals, from scandium to zinc, the nuclear force also increases. However the electrons are added to an *inner* shell (the 3*d* subshell) as shown in Fig 16.3. These inner electrons are between the nucleus and the outer 4*s* subshell are able to shield the outer electrons from the nuclear force, therefore cancelling the effect of the increasing nuclear force across the period. Thus the atomic radii remain almost constant from vanadium to copper.



▶ Fig 16.3 Addition of electrons with increasing nuclear charge

Ionisation Energy

- There is little change in the first ionisation energy of the transition elements from Ti to Cu. This is because:
  - (a) the atomic radii remain almost constant from Ti to Cu;
  - (b) the attractive forces on the outer electrons remain almost constant from Ti to Cu.

16.6 Variable Oxidation States

- Transition elements have variable oxidation states in their compounds. For example, iron commonly forms iron(II) and iron(III) compounds.
- The variable oxidation states in transition metals is due to the small energy difference between the 4*s* and 3*d* subshells. This is explained for iron, comparing it with magnesium (a metal with oxidation number of +2 in compounds).
  - (a) Iron has oxidation states I, II, III, IV, V and VI in compounds, although only II and III are common.
  - (b) The first four successive ionisation energies (in kJ mol^{-1}) for iron and magnesium are as follows:

element	first	second	third	fourth
magnesium	736	1450	7740	10500
iron	762	1560	2960	5400

  - (c) When compounds are formed, energy must be supplied to remove electrons from the atoms of the elements. The energy for this ionisation is supplied by the energy given out when the new bonds are formed.

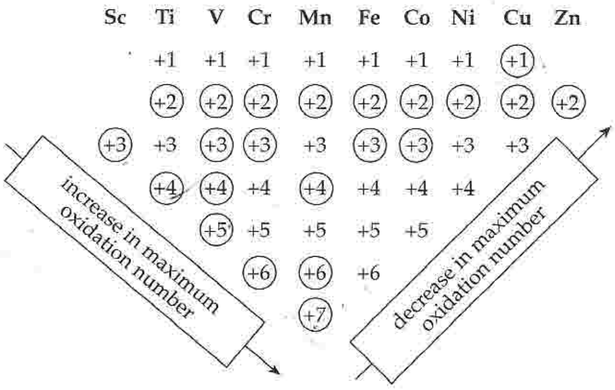
(i) When magnesium forms compounds, Mg^{2+} ions are easily formed. For example, the energy liberated when the Mg^{2+} and O^{2-} ions, come together to form electrovalent bonds is enough to supply the ionisation energy (736 + 1450 kJ mol^{-1}) to form Mg^{2+} ions. However this reaction will not supply the much larger amount of energy (7740 kJ) needed to remove the third electron from an inner shell. Hence magnesium only forms Mg^{2+} ions and not Mg^{3+} or Mg^{4+} etc.

(ii) When iron forms compounds, Fe^{2+} ions are easily formed, like Mg^{2+} in magnesium. However there is no big increase in the amount of energy required to remove the third electron (from the 3*d* subshell) because of the small energy difference between the 4*s* and 3*d*. As long as enough energy is released in the formation of an iron(III) compound, then the third electron can be removed to form Fe^{3+} ions.

The same applies to the loss of more electrons to form higher oxidation state compounds of iron. There is no big jump in ionisation energy, so more electrons can be lost as long as sufficient energy is liberated in the formation of the compound, though this is rare in the case of iron.

16.7 Oxidation States in Compounds

- The oxidation states of the transition elements in their compounds are shown in Fig 16.4. Scandium (Sc) and zinc (Zn) have been included.



Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+1	+1	+1	+1	+1	+1	+1	(+1)	
	(+2)	(+2)	(+2)	(+2)	(+2)	(+2)	(+2)	(+2)	(+2)
(+3)	+3	(+3)	(+3)	+3	(+3)	(+3)	+3	+3	
	(+4)	(+4)	+4	(+4)	+4	+4	+4		
		(+5)	+5	+5	+5	+5			
			(+6)	(+6)	+6				
				(+7)					

Fig 16.4 Oxidation states of Transition Elements

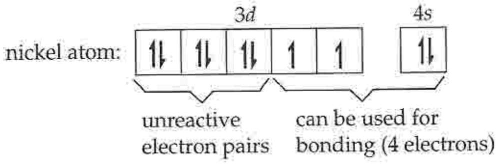
- The +2 oxidation state is generally due to the loss of two 4*s* electrons from the outer shell to form an M^{2+} ion.

- The maximum oxidation number of an element corresponds to the maximum number of electrons available for bonding. For example, the maximum oxidation state for chromium VI, is due to the use of all the $3d^5$ and $4s^1$ electrons for bonding. It is not possible to obtain a chromium(VII) compound, as there are only 6 electrons available for bonding.

  There is an increase in the maximum oxidation number from Sc to Mn as electrons from the 3*d* and 4*s* subshells are used for chemical bonds.

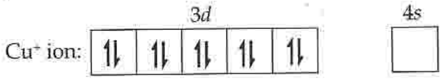
- The decrease in maximum oxidation number from Mn to Zn corresponds to the decrease in the number of single electrons in the 3*d* subshell and the 4*s* electrons.

  From Mn to Zn, some of the electrons in the 3*d* subshell are paired. These paired electrons are unreactive and are not used for bonding. An example is nickel:

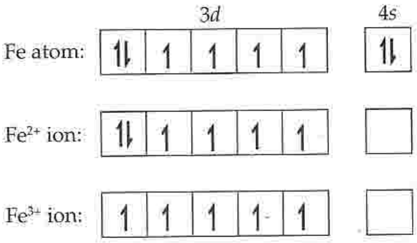


  Nickel can only use the two single electrons in the 3*d* subshell and the two 4*s* electrons for bonding. Hence the maximum oxidation number of nickel in nickel compounds is +4.

- The +1 oxidation state of copper is quite stable; the atom has lost the one 4*s* electron to leave a completely-filled 3*d* subshell, which is particularly stable:



- The common oxidation states of iron can be explained simply as follows:



  The iron(II), Fe^{2+}, is due to the loss of the two 4*s* electrons from the outer shell. These are less strongly held by the nucleus than the 3*d* electrons (although the energy difference is small).

  The iron(III), Fe^{3+}, is due to the loss of the two 4*s* electrons and one 3*d* electron. The 3*d* electron is one of an electron pair. There is considerable repulsion between electrons in a pair allowing easy removal of one of the pair.

16.8 Transition Element Complexes

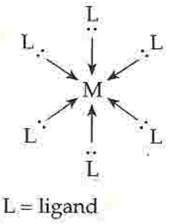


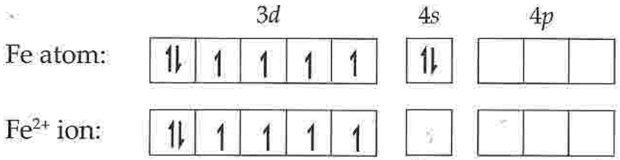
Fig 16.5 Co-ordinate bond

- A transition element **complex** consists of a transition metal atom surrounded by **ligand** particles. The ligand particles are molecules or anions that have *lone pairs of electrons*. The ligands form *co-ordinate (dative) bonds* with the empty orbitals of the transition metal atom (Fig 16.5).

  The transition metal atom is often a positive ion. Such complexes are called **complex ions.**

- The number of co-ordinate (dative) bonds formed by ligands with a transition metal in a complex is called the **coordination number** of the transition metal. The coordination number is usually 4 or 6 in complexes.

- An example of the bonding in complex ions, is shown below for the $[FeCl_4]^{2-}$ ion.
  (a) The Fe^{2+} ion uses the empty 4*s* and 4*p* orbitals for co-ordinate bonds:



orbitals used to form four co-ordinate bonds with lone pairs from four Cl^- ions

  (b) The structure of the $[FeCl_4]^{2-}$ ion is shown in Fig 16.6. The ion has a tetrahedral shape.

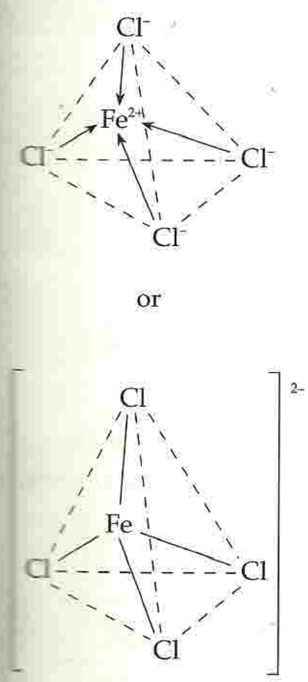
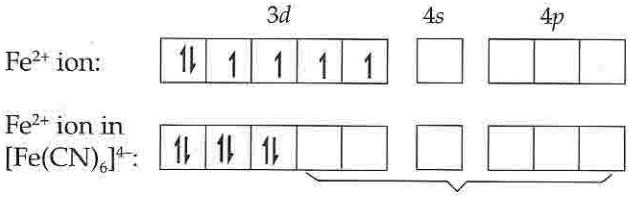


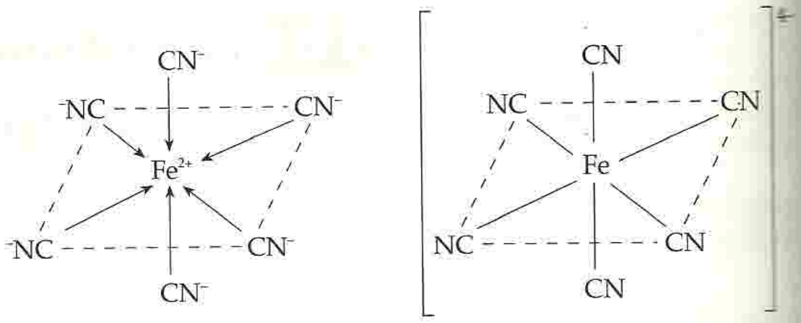
Fig 16.6 Structure of $[FeCl_4]^{2-}$

- In some complex ions, the single electrons in the 3*d* subshell pair up to help produce empty orbitals for forming co-ordinate bonds. An example is the $[Fe(CN)_6]^{4-}$ ion.
  (a) The $[Fe(CN)_6]^{4-}$ consists of six CN^- ions joined to a Fe^{2+} ion by dative bonds.
  (b) The electrons in the 3*d* orbitals pair up to produce two empty orbitals:



orbitals used to form six dative bonds with lone pairs from six CN^- ions

  (c) The structure of the $[FeCN)_6]^{4-}$ ion is shown in Fig 16.7. The iron has a coordination number of 6.



▸ Fig 16.7 Structure of $[Fe(CN)_6]^{4-}$

- Common ligands in transition metal complex ions are:

  neutral molecule: eg H_2O, NH_3 and anions: eg Cl^-, F^-, CN^-, SCN^-
- All the common transition metal cations form a complex ion of the type $[M(H_2O)_6]^{z+}$ in water. For example, $[Fe(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{3+}$.
- Some important transition metal complexes in A-level chemistry are summarised in Table 16.5. Many of these appear in experiments including the A-level Practical Examination.

Table 16.5 Important complex ions of Cr, Mn, Fe, Co and Cu

element	oxidation state	formula	colour	notes
chromium	III	$[Cr(H_2O)_6]^{3+}$	green	Cr^{3+} in water
	III	$[Cr(H_2O)_6]^{3-}$	green	formed when $Cr(OH)_3$ dissolves in excess NaOH
	VI	$Cr_2O_4^{2-}$	yellow	oxidising agent
	VI	$Cr_2O_7^{2-}$	orange	oxidising agent
manganese	II	$[Mn(H_2O)_6]^{2+}$	pale pink	Mn^{2+} in water
	VII	MnO_4^-	purple	oxidising agent
iron	II	$[Fe(H_2O)_6]^{2+}$	green	Fe^{2+} in water reducing agent
	II	$[Fe(CN)_6]^{4-}$	yellow	gives dark blue precipitate with Fe^{3+} ions
	III	$[Fe(H_2O)_6]^{3+}$	violet*	Fe^{3+} in water
	III	$[Fe(SCN)(H_2O)_5]^{2+}$	blood-red	sensitive test for Fe^{3+} ions
	III	$[Fe(CN)_6]^{3-}$	yellow	gives dark blue precipitate with Fe^{2+} ions
cobalt	II	$[Co(H_2O)_6]^{2+}$	pink	
	II	$[CoCl_4]^{2-}$	blue	
copper	II	$[Cu(H_2O)_6]^{2+}$	blue	Cu^{2+} in water
	II	$[CuCl_4]^{2-}$	yellow	Cu^{2+} & conc. HCl
	II	$[Cu(NH_3)_4(H_2O)_2]^{2+}$	dark blue	formed when $Cu(OH)_2$ dissolves in excess NH_3

*Cr^{3+}(aq) often appears green and Fe^{3+}(aq) often appears yellow because of the presence of other ligands, such as Cl^-.

Question A complex ion consists of six CN^- ions joined by dative bonds to a Mn^{3+} ion. What is the formula of the complex ion?

Answer The charge on the complex ion = +3 + 6(−1) = −3
Hence the formula of the complex ion is $[Mn(CN)_6]^{3-}$.

Question A complex ion has the formula $[Cr(NH_3)_4(Cl)_2]^+$. What is the oxidation state of the chromium ion?

Answer The ligands in the complex ion are NH_3 molecules and Cl^- ions.
Let x be the charge on Cr.
Then $x + 4(0) + 2(-1) = +1$.
Hence $x = +3$.
The charge on chromium is +3.
Hence the oxidation state of chromium ion is III (or +3).

- The ligands in a complex can be exchanged with other ligands to make a new complex. For example, when excess ammonia is added to $[Cu(H_2O)_6]^{2+}$ ions, four of the H_2O ligands are replaced with NH_3 to make $[Cu(NH_3)_4(H_2O)_2]^{2+}$ (Fig. 16.8). The colour of the complex changes from blue to dark blue.

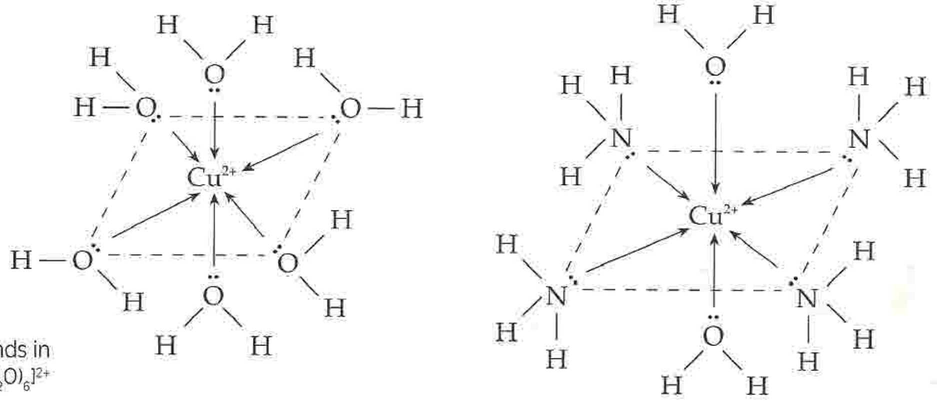


Fig 16.8 Exchange of ligands in $[Cu(H_2O)_6]^{2+}$

$$[Cu(H_2O_6]^{2+} \quad + \quad 4NH_3 \quad \longrightarrow \quad [Cu(NH_3)_4(H_2O)_2]^{2+}$$

A similar exchange of ligands takes place when excess concentrated hydrochloric acid is added to a solution of $[Cu(H_2O_6]^{2+}$ and $[Co(H_2O)_6]^{2+}$. In each case there is a colour change as the ligands are exchanged.

$$\underset{\text{blue}}{[Cu(H_2O)_6]^{2+}} + 4Cl^- \longrightarrow \underset{\text{yellow}}{[CuCl_4]^{2-}} + 6H_2O$$

$$\underset{\text{pink}}{[Co(H_2O)_6]^{2+}} + 4Cl^- \longrightarrow \underset{\text{blue}}{[CoCl_4]^{2-}} + 6H_2O$$

Stability Constants of Complexes, K_{stab}

- When concentrated hydrochloric acid is added to aqueous $Cu^{2+}(aq)$, the solution turns yellow due to the formation of $[CuCl_4]^{2-}$ complex ions:

$$[Cu(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CuCl_4]^{2-} + 6H_2O$$

The water molecule ligands of the $[Cu(H_2O)_6]^{2+}$ are displaced by Cl^- ions.

The equilibrium constant for this reaction is called the **stability constant**, K_{stab}, of the complex ion $[CuCl_4]^{2-}$.

$$K_{stab} = \frac{[CuCl_4^{2-}]}{[Cu^{2+}].\ [Cl^-]^4}$$

Note that the square brackets, [ ], represent concentrations. The $[Cu(H_2O)_6]^{2+}$ is represented simply as Cu^{2+} in the expression for the stability constant. The water displaced in the reaction is ignored in the expression for K_{stab}.

Stability constants for other complexes are written similarly.

- The stability constant for a complex is a measure of the stability of the complex. The larger the K_{stab}, the more stable the complex is.
- Some stability constants for complexes of copper(II) are given in Table 16.6.

▸ Table 16.6 Stability constants of copper(II) complexes

ligand	formula of complex	stability constant, K_{stab}
Cl^-	$[CuCl_4]^{2-}$	$4 \quad 10^5$
NH_3	$[Cu(NH_3)_4(H_2O)_2]^{2+}$	$1 \quad 10^{13}$

The table shows that the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex is about 20 000 000 times more stable than the $[CuCl_4]^{2-}$ complex.

- If a transition metal atom or ion has a choice of ligands, it will react with the ligands that forms the most stable complex (ie the one with the largest K_{stab}).

Question

Explain what will happen when
(a) KSCN(aq) is added to a solution of $Fe^{3+}(aq)$;
(b) KCN(aq) is then added to the product in (a).
[stability constants for Fe^{3+} complexes: SCN^- ligand = $13 \quad 10^6$; CN^- ligand = 10^{30}]

Answer

(a) The blood-red complex $[Fe(SCN)(H_2O)_5]^{2+}$ is formed when one of the water molecules in the $[Fe(H_2O)_6]^{3+}$ complex ion is replaced by an SCN^- ligand:

$$[Fe(H_2O)_6]^{3+} + SCN^- \rightleftharpoons [Fe(SCN)(H_2O)_5]^{2+} + H_2O$$

(b) The blood-red colour disappears as the CN^- ions displace all the ligands of the $[Fe(SCN)(H_2O)_5]^{2+}$ to form $[Fe(CN)_6]^{3-}$. The stability constant for $[Fe(CN)_6]^{3-}$ complex is much greater so it is more stable.

- Metal hydroxide precipitates dissolving in excess alkalis can be explained by competing equilibrium constants.
  For example, $Cr^{3+}(aq)$ gives a green precipitate with a little dilute NaOH:

$$Cr^{3+}(aq) + 3OH^{-}(aq) \rightleftharpoons Cr(OH)_3(s) \qquad \text{reaction 1}$$

When excess NaOH is added, the precipitate dissolves because of the reaction:

$$Cr^{3+}(aq) + 6OH^{-}(aq) \rightleftharpoons [Cr(OH_6)]^{3-}(aq) \qquad \text{reaction 2}$$

The equilibrium constant for reaction 2 is much larger than that for reaction 1, so, as the equilibrium in 2 shifts to the right, the equilibrium in 1 shifts to the left as the Cr^{3+} ions are removed, dissolving the $Cr(OH)_3$ precipitate.

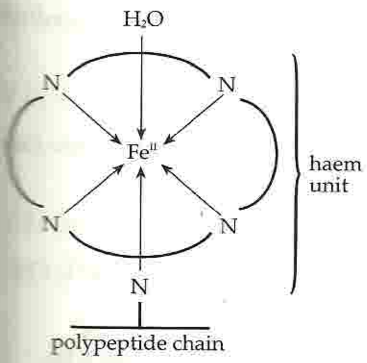


Fig 16.9 Structure of haemoglobin

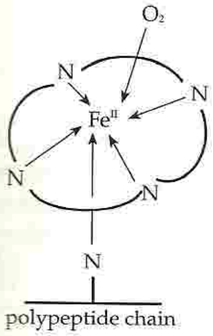


Fig 16.10 Structure of oxyhaemoglobin

Haemoglobin

- A haemoglobin molecule is made up of a *haem unit* attached to a polypeptide chain (protein). Fig 16.9 shows the simplified structure of a haemoglobin molecule.
- In the haemoglobin molecule, the iron atom
  (a) has an oxidation state of +2;
  (b) is attached to five nitrogen atoms and one oxygen atom (in the water molecule);
  (c) has a coordination number of 6.
- The haemoglobin absorbs oxygen from the lungs by forming oxyhaemoglobin (Fig 16.10). The oxygen molecule displaces the water molecule and forms a dative bond with the iron atom. The oxyhaemoglobin carries the oxygen through the blood.
- The reaction between oxygen and haemoglobin is reversible:

$$\text{oxygen} + \text{haemoglobin} \rightleftharpoons \text{oxyhaemoglobin}$$

At high altitudes, the concentration of oxygen in the atmosphere is lower than at sea level (because of the decrease in atmospheric pressure). By Le Chatelier's principle, the concentration of oxyhaemoglobin is decreased therefore less oxygen is transported in the blood for the combustion of food. Hence people become weak at high altitudes. People who *live* at high altitudes become acclimatized by increasing the concentration of haemoglobin in their blood. In this way they can form more oxyhaemoglobin and thus obtain their correct energy needs.

- The iron atom in haemoglobin also forms dative bonds with CO molecules and CN^{-} ions. These bonds are irreversible. As the bonds are much stronger than $Fe–O_2$ dative bonds, they are more readily formed, thus reducing the oxygen-carrying ability of the haemoglobin. This can lead to death.

Effect of Ligand on E$^{\ominus}$ Values

- The standard redox potentials for the interconversion of +2 and +3 oxidation states of iron with H_2O and CN^- as ligands are:

  $$[Fe(H_2O)_6]^{3+} + e^- \rightleftharpoons [Fe(H_2O)_6]^{2+}; \qquad E^{\ominus} = +0.77\ V$$
  $$[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}; \qquad E^{\ominus} = +0.36\ V$$

  The two standard redox potentials show that when the ligand is changed, the standard electrode potential is also changed.

- Iodide ions, I^-, can be oxidised to iodine:

  $$I^- \rightarrow \frac{1}{2} I_2 + e^-; \qquad E^{\ominus} = -0.54\ V$$

  When $I^-(aq)$ is added to $[Fe(H_2O)_6]^{3+}(aq)$, the I^- is able to reduce iron(III) to iron(II):

  $$[Fe(H_2O)_6]^{3+} + I^- \rightarrow [Fe(H_2O)_6]^{2+} + \frac{1}{2} I_2; \qquad E^{\ominus} = +0.23\ V$$

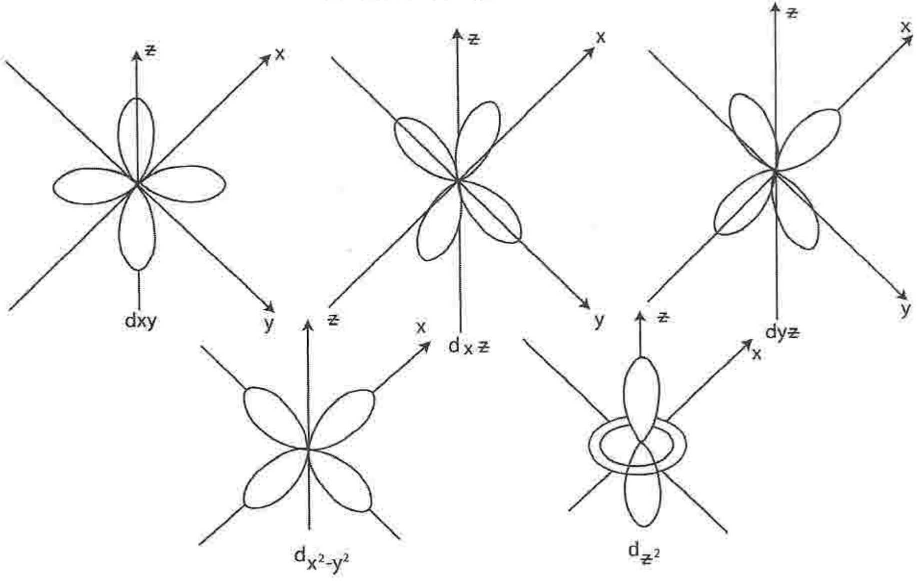
  When $I^-(aq)$ is added to $[Fe(CN)_6]^{3-}(aq)$, the I^- is *not* able to reduce iron(III) to iron(II):

  $$[Fe(CN)_6]^{3-} + I^- \rightarrow [Fe(CN)_6]^{4-} + \frac{1}{2} I_2; \qquad E^{\ominus} = -0.18\ V$$

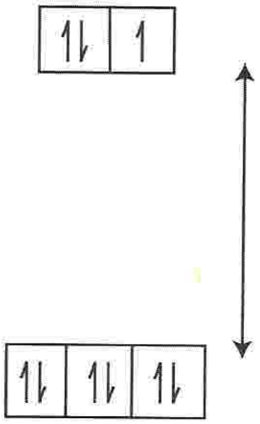
  Hence, iron(III) is more stable than iron(II) when the ligand is CN^-

16.9 Shape of d-orbitals and colour of complexes

- The d-subshell contains 5d orbitals. They are the d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$ and the d_{z2}. The d_{xy}, d_{yz} and d_{xz}, orbitals are oriented between the corresponding axes. For example in the d_{xy} the orbitals are oriented between the x and y axes. The d_{x2-y2} and the d_{z2} are oriented along the axes.



- In the gaseous state all the five d-orbitals possess the same energy. They are said to be degenerate orbitals.
  But during the formation of an octahedral complex, the ligands approach the d-subshell in the direction of the axes. As a result the electrons in the d_{x2-y2} and the d_{z2} orbitals are under a greater repulsive force than the electrons found in the d_{xy}, d_{yz} and d_{xz} orbitals.
  As a result the d-subshell splits into two parts having different energies. The d-orbitals are no more degenerate orbitals- the d_{x2-y2} and the d_{z2} orbitals will be more energetic than the d_{xy}, d_{yz} and d_{xz} orbitals.
  The difference in energy between the splitted d-subshell corresponds to a given energy found in the region of visible light in the electromagnetic spectrum.



$$\Delta E = hf = h\frac{c}{\lambda}$$

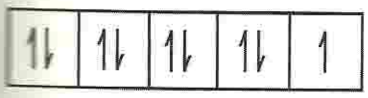
ΔE – difference in energy

h – planck's constant

f – frequency of light

c – velocity of light

λ – wavelength of light



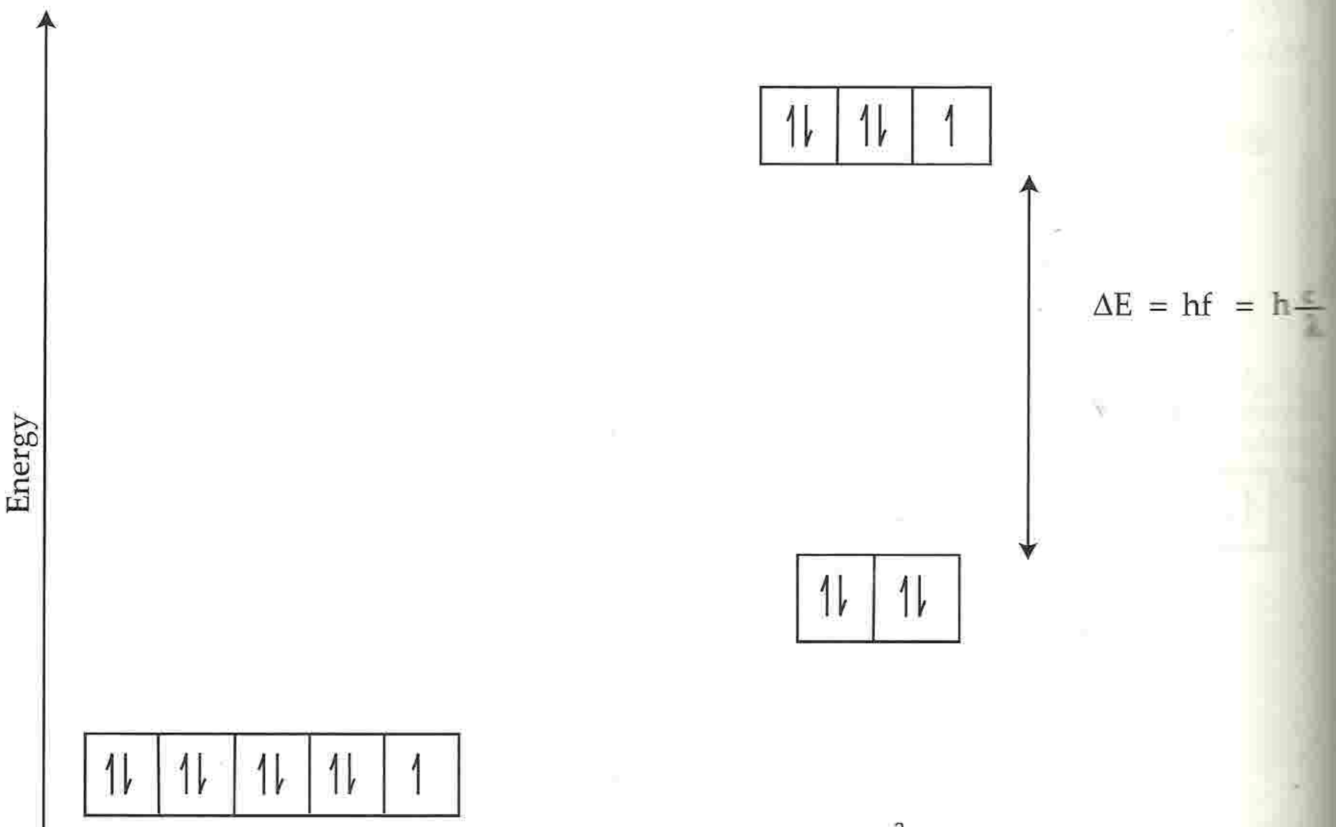
Cu^{2+} (g)

$[Cu(H_2O)_6]^{2+}$(aq)
octahedral complex

When white light comes into contact with the transition metal ions, electrons in the low energy 3d-subshell absorb photons which have exactly the same energy as the difference in energy between the splitted subshell and they are promoted to the higher d-orbitals.

The energy absorbed by the electron in the low d-orbitals corresponds to a colour (wavelength or frequency) of visible light. The colour of the solution will be the difference between white light and the colour absorbed by the metal ion. It will be called the complementary colour of the solution.

Note: In tetrahedral complexes the ligands approach the d-subshell in the direction between the axes. As a result the electrons in the d_{YZ}, d_{XY}, and d_{XZ}, orbitals are under a greater repulsion force than the electrons found in the d_{x2-y2} and d_{Z^2} orbitals. The splitted orbitals will be as shown below:-



Cu $^{2+}$ (g)

$[CuCl_4]^{2-}$
Tetrahedral complex

- An example is a solution of $[Cu(H_2O)_6]^{2+}$ which is blue in colour. When white light passes through the solution, the low energy 3*d* electrons absorb *red* light and move up into the high energy 3*d* Fig 16.11. The solution appears *blue* as this is *white light minus the red.*

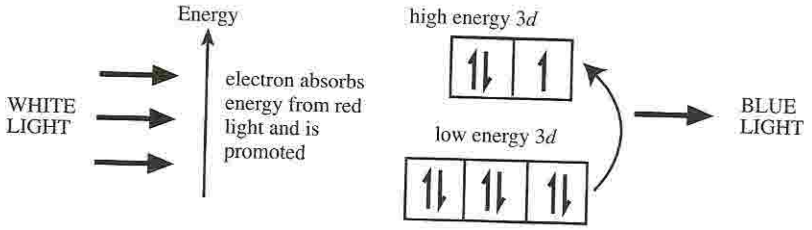


Fig 16.11 How Cu^{2+}(aq) appears blue

- A few transition element complex ions are colourless. This is usually found in complexes where the 3*d* subshell is
  (i) *completely full* of electrons, such as in copper(I), or
  (ii) *completely empty* of electrons, such as in titanium(IV).
  When the 3*d* subshell is completely full, there is no space for an electron to move between the two 3*d* energy levels. When it is completely empty, there are no 3*d* electrons available to absorb visible light.
- The actual colour of a transition element complex depends on the energy difference between the split 3*d* orbitals. This depends on
  (i) the oxidation state of the transition element;
  (ii) the ligands in the complex ion.
  Hence when the ligands are changed in a complex, the colour also changes. For example, when the H_2O ligands of $[Cu(H_2O)_6]^{2+}$ are replaced with Cl^- ligands in $[CuCl_4]^{2-}$, the colour changes from blue to yellow.

16.10 Uses of Transition Element Ions in Redox Reactions

- Iron commonly forms compounds with oxidation states of II and III. Solutions of Fe^{2+}(aq) are readily oxidised to Fe^{3+} by many oxidising agents, including acidified potassium dichromate(VI) and atmospheric oxygen. The reaction with oxygen in air is summarised in the following equations:

$$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O \qquad E^\ominus = +1.23\text{ V}$$

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^- \qquad E^\ominus = -0.77\text{ V}$$

Therefore, $O_2 + 2H^+ + 2Fe^{2+} \rightarrow H_2O + 2Fe^{3+}$ $\qquad E^\ominus = +0.46$ V

- Solutions of Fe^{3+}(aq) are readily reduced by many reducing agents, including aqueous potassium iodide. This reaction is summarised below.

$$\mathrm{Fe^{3+} + e^- \rightleftharpoons Fe^{2+}} \qquad E^\ominus = +0.77\ \mathrm{V}$$

$$\mathrm{2I^- \rightleftharpoons I_2 + 2e^-} \qquad E^\ominus = -0.54\ \mathrm{V}$$

$$\text{Therefore, } \mathrm{2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2} \qquad E^\ominus = +0.23\ \mathrm{V}$$

- Solutions of chromium(VI), such as dichromate(VI) [$Cr_2O_7^{2-}$], are oxidising agents. For example, a solution of potassium iodide is oxidised by acidified dichromate(VI) to iodine. This reaction is summarised below.

$$\mathrm{Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O} \qquad E^\ominus = +1.33\ \mathrm{V}$$

$$\mathrm{2I^- \rightleftharpoons I_2 + 2e^-} \qquad E^\ominus = -0.54\ \mathrm{V}$$

$$\text{Therefore, } \mathrm{Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 7H_2O + 3I_2} \qquad E^\ominus = +0.79\ \mathrm{V}$$

This reaction is used in redox titrations (see Chapter 3).

Although chromium also forms $Cr^{2+}(aq)$ ions, such ions are readily oxidised to $Cr^{3+}(aq)$ by air:

$$\tfrac{1}{2}\mathrm{O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O} \qquad E^\ominus = +1.23\ \mathrm{V}$$

$$\mathrm{Cr^{2+} \rightleftharpoons Cr^{3+} + e^-} \qquad E^\ominus = +0.41\ \mathrm{V}$$

$$\text{Therefore, } \tfrac{1}{2}\mathrm{O_2 + 2H^+ + 2Cr^{2+} \rightarrow H_2O + 2Cr^{3+}} \qquad E^\ominus = +1.64\ \mathrm{V}$$

Hence, when the chromium(VI) is reduced, the usual product is green $Cr^{3+}(aq)$.

- Solutions of manganese(VII), such as manganate(VII) [MnO_4^-], are oxidising agents. For example, a solution of iron(II) sulphate is oxidised to iron(III) by acidified manganate(VII) ions. The reaction is summarised below:

$$\mathrm{Fe^{2+} \rightleftharpoons Fe^{3+} + e^-}; \qquad E^\ominus = -0.77\ \mathrm{V}$$

$$\mathrm{MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O} \qquad E^\ominus = +1.52\ \mathrm{V}$$

$$\text{Therefore, } \mathrm{MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O} \qquad E^\ominus = +0.75\ \mathrm{V}$$

This reaction is used in redox titrations (see Chapter 3).

16.11 Transition Element Catalysts

- Many transition metals and their compounds of transition metals are good catalysts. The good catalytic powers of transition elements are due to
  - (a) the ability of transition elements to vary their oxidation states;
  - (b) the presence of suitable empty orbitals and lone pairs of electrons in the 3*d*, 4*s* and 4*p* subshells to form co-ordinate bonds with reactants.

(See Chapter 10 for further explanation of transition elements as catalysts.)

- Some examples of transition elements as catalysts in industry are given in Table 16.7.

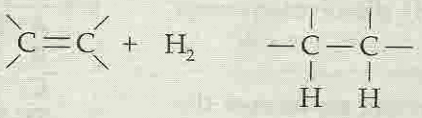
process	reaction	catalyst
Haber Process	$N_2 + 3H_2 \rightleftharpoons 2NH_3$	iron
Contact Process (manufacture of sulfuric acid)	$2SO_2 + O_2 \rightleftharpoons 2SO_3$	vanadium(V) compounds
oxidation of ammonia to nitric acid	$4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O$	platinum
hydrogenation of alkenes (eg manufacture of margarine)		nickel

Table 16.7 Transition element catalysts

Iron as a Catalyst

- Iron and its compounds are catalysts for several chemical reactions.
- Iron metal is a *heterogeneous* catalyst in the Haber Process for the manufacture of ammonia (see Chapter 15). Iron does this by using its empty orbitals, single electrons and lone pairs of electrons in the 3*d*, 4*s* and 4*p* subshells to form co-ordinate and other bonds with the reactants, adsorbing them onto the surface of the iron. When this happens, the bonds in the reactant molecules become weaker, lowering the activation energy so that the reactants can form the products more easily (see Chapter 10).
- Fe^{3+} is a *homogeneous* catalyst for the reaction between I^- ions and $S_2O_8^{2-}$ ions. The overall equation for the reaction is:

$$\underbrace{S_2O_8^{2-} + 2I^-}_{\text{electrons}} \rightarrow 2SO_4^{2-} + I_2$$

Iron catalyses this reaction by varying its oxidation state between +3 and +2. By doing this, it helps to transfer the electrons from $S_2O_8^{2-}$ to I^-.
In the first step, electrons are transferred from I^- to Fe^{3+}:

$$2I^- + 2Fe^{3+} \rightarrow I_2 + 2Fe^{2+}$$

The Fe^{2+} then transfers the electrons to $S_2O_8^{2-}$ and is itself oxidised back to Fe^{3+}.

$$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$$

The solid iron catalyst in the Haber Process is *heterogeneous* because it is in a *different* physical state from the gaseous H_2 and N_2 reactants.

The Fe^{3+}(aq) catalyst is *homogeneous* as the Fe^{3+}(aq) and $S_2O_8^{2-}$(aq)/I^-(aq) are all in the *same* physical state.

EXERCISE 16

Multiple Choice Questions

Section I

1 Element X forms the X^{2+} ion. Which feature of the ion shows X to be a transition element?

A An oxide containing X^{2+} is a catalyst.
B X^{2+} has a partially filled *d*-subshell.
C Some compounds containing X^{2+} are coloured.
D The precipitate $X(OH)_2$ dissolves in excess sodium hydroxide.

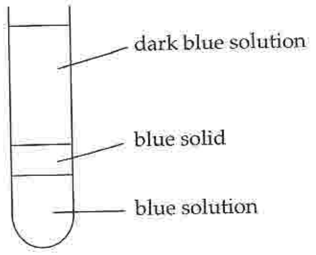
2 Which one of the following represents the electronic configuration of a transition element in the ground state?

A $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$
B $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^5$
C $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$
D $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

3 A transition metal, with symbol M, forms a complex ion with the formula $[M(CN)_6]^{4-}$. The *same metal*, in the *same oxidation state*, forms a complex ion with the formula $[M(NH_3)_4]^x$. What is the value of x?

A 4– **C** 2+
B 2– **D** 4+

4 A student added excess ammonia to copper(II) sulphate solution in a test tube, without shaking. The tube appeared as in the diagram.



What is the formula of the solid?

A $(NH_4)_2SO_4$ **C** $(NH_4)_2Cu(OH)_6$
B $Cu(OH)_2$ **D** $Cu(NH_3)_4SO_4$

5 Which one of the following elements is most likely to be a transition element?

	m.p./°C	b.p./°C	density /g cm^{-3}
A	1900	3400	6.1
B	157	2000	7.3
C	1280	2970	1.9
D	3730	4200	2.2

6 Five pairs of complex ions of a transition element are given below. In which pair is there the largest difference in the oxidation number of the transition element?

A $[CuCl_4]^{2-}$, $[Cu(NH_3)_4(H_2O)_2]^{2+}$
B $[MnCl_4]^{2-}$, $[MnCl_6]^{2-}$
C $[Fe(H_2O)_6]^{3+}$, $[Fe(CN)_6]^{4-}$
D $[Ni(SCN)_6]^{4-}$, $[NiF_6]^{3-}$

7 Manganese (Mn) has proton number 25. Which one of the following represents the electronic configuration of the Mn^{3+} ion in the ground state? [Ar] = electron configuration of argon atom.

		3*d*					4*s*
A	[Ar]	↑	↑	↑	↑	↑	↑↓
B	[Ar]	↑	↑	↑	↑		
C	[Ar]	↑↓	↑↓	↑↓			
D	[Ar]	↑↓	↑↓	↑↓	↑	↑	↑↓

8 Titanium has the electronic structure

$$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2\ 4s^2$$

Which one of the following compounds is not likely to exist?

A TiO_2 **C** Ti_2O_3
B K_2TiCl_4 **D** Na_2TiO_4

9 What are the oxidation and coordination numbers of nickel in the compound $K_3[Ni(CN)_5]$?

	oxidation number	*coordination number*
A	+3	5
B	+2	5
C	+3	8
D	+2	8

10 The electronic configuration of vanadium in the ground state is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3\ 4s^2$. What is the maximum oxidation number of vanadium in its compounds?

A +2 C +4
B +3 D +5

11 Iron is a typical transition element and calcium is a typical *s*-block element. Data for four properties of these elements is given below. For which property is the data placed under the *wrong* elements?

A	property	iron	calcium
B	melting point	1535°C	850°C
C	ionic radius (M^{2+} ion)	0.099 nm	0.076 nm
D	ionisation energy	762 kJ mol^{-1}	590 kJ mol^{-1}
	density	7.86 g cm^{-3}	1.54 g cm^{-3}

12 Which of the following are the correct colours for the complexes of copper(II)?

$[CuCl_4]^{2-}$	$[Cu(H_2O)_6]^{2+}$	$[Cu(NH_3)_4(H_2O)_2]^{2+}$
A yellow	blue	deep blue
B blue	yellow	deep blue
C yellow	green	blue
D deep blue	blue	yellow

Section II

Summary of directions

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

13 Which statement(s) about the iron atom in haemoglobin is(are) true?

1 The iron has an oxidation state of II.
2 The iron atom is bonded to nitrogen atoms in the haem unit.
3 The iron atom is oxidised to the III oxidation state when haemoglobin absorbs oxygen.

14 Which is/are true for *all* ligands in complexes?

1 Ligands have a lone pair of electrons.
2 Ligands form dative bonds.
3 Ligands are negative ions.

15 Which oxidation state(s) is/are not true for chromium ion (atomic number = 24) in its compounds?

1 +7 2 +6 3 +3

16 Which particles *can* be a ligand in a complex?

1 NH_4^+
2 CH_3NH_2
3 OH^-

17 When a reagent **X** was added to an aqueous solution of a transition metal ion **Y**, there was a colour change in the solution. Which of the following explains the change?

1 The oxidation state of **Y** was increased.
2 The oxidation state of **Y** was decreased.
3 **X** reacted with **Y** to form a complex ion.

18 The element molybdenum (symbol Mo) is below chromium in the Periodic Table. Which properties of molybdenum resemble those of chromium?

1 Molybdate ions, MoO_4^{2+}, are colourless.
2 The maximum oxidation state of molybdenum in compounds is VI.
3 Molybdenum forms the ion $Mo_2O_7^{2-}$.

Structured Questions

1 Copper is a typical transition element.

(a) A complex is formed when excess ammonia is added to $CuSO_4(aq)$.
  (i) What is the formula of the complex?
  (ii) What is its colour?
(b) State qualitatively how the following properties of copper compare with those of calcium:
  (i) first ionisation energy;
  (ii) density;
  (iii) melting point;
  (iv) ionic radius of the M^{2+} ion.
(c) Copper forms the chlorides CuCl and $CuCl_2$. What property of copper does this show?

2 Titanium (symbol Ti) has proton number 22.

(a) Write the full electronic configuration of vanadium in the ground state;

(b) Predict the *maximum* oxidation state of titanium in its compounds.

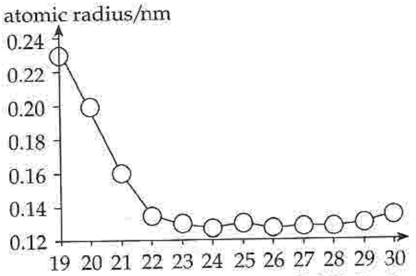
(c) Titanium(III) forms a complex ion containing one titanium atom and six chloride ions as ligands.
- (i) What electronic feature does a chloride ion have that enables it to bond with the titanium?
- (ii) Write the formula of the complex ion.

(d) (i) A solution of $[Ti(H_2O_6)]^{3+}$ is violet in colour. What causes the colour?
- (ii) Suggest a reason why titanium(IV) complexes are usually colourless.

3 (a)

The outer electronic configuration of a transition element, in the ground state, is shown above.
- (i) Identify the element and state its proton number.
- (ii) Write similar diagrams to show the outer electronic configurations of the Fe^{2+} and Fe^{3+} ions.

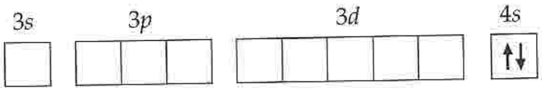
(b) Fig 16.12 shows the atomic radius of the elements potassium (K) to zinc (Zn).



▲ Fig 16.12

Explain why the atomic radii of the elements vanadium (V) to copper (Cu)
- (i) are smaller than the atomic radius of potassium;
- (ii) are almost constant.

4 (a) The outer electronic configuration of vanadium, in the ground state, is



Draw the electronic configuration of the V^{3+} ion.

this reaction takes place?
- (iii) State one condition for this reaction.

5 A simple reaction scheme is shown below.

$$\begin{tikzcd}
\mathrm{Cr^{3+}(aq)} \arrow[r, "\mathbf{A}"] & \mathrm{Cr(OH)_3(s)} \arrow[r, "\mathbf{B}"] & {\mathrm{[Cr(OH)_6]^{3-}(aq)}} \arrow[d, "\mathbf{C}"] \\
 & \mathrm{Cr_2O_7^{2-}(aq)} \arrow[ul, "\mathbf{E}"] & \mathrm{CrO_4^{2-}(aq)} \arrow[l, "\mathbf{D}"']
\end{tikzcd}$$

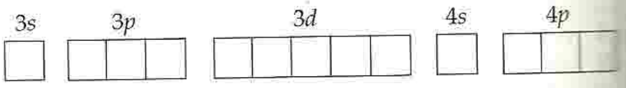
(a) In which reaction is the chromium
- (i) reduced;
- (ii) oxidised?

(b) For reaction **B**,
- (i) name a suitable reagent;
- (ii) in terms of equilibrium constants, explain why this reaction takes place.

(c) If the reagent in reaction **D** is dilute acid;
- (i) state the colour change that is observed;
- (ii) write an ionic equation for the reaction.

(d) Suggest a suitable reagent and conditions for reaction **E**.

6 (a) The outer electronic configuration of a cobalt atom is



Give the outer electronic configurations of Co^{2+} and Co^{3+} ions.

(b) $[Co(H_2O)_6]^{2+} + 4Cl^- \rightleftharpoons [CoCl_4]^{2-} + 6H_2O$

Aqueous Co^{2+} ions react with concentrated hydrochloric acid according to the equation above.
- (i) What is the colour of aqueous Co^{2+} ions?
- (ii) What is the colour of $[CoCl_4]^{2-}$ ions?
- (iii) When a mixture of concentrated hydrochloric acid and aqueous Co^{2+} ions is boiled, the mixture turns blue. When it is cooled with ice, the mixture turns red. What deduction can be made about H for the equation above?

(c) $[Co(CN)_6]^{3-} + e^- \rightleftharpoons [Co(CN)_6]^{4-}$ $E^{\ominus} = -0.8\,V$

$[Co(NH_3)_6]^{3+} + e^- \rightleftharpoons [Co(NH_3)_6]^{2+}$ $E^{\ominus} = +0.1\,V$

$[Co(H_2O)_6]^{3+} + e^- \rightleftharpoons [Co(H_2O)_6]^{2+}$ $E^{\ominus} = +1.8\,V$

$I_2 + e^- \rightleftharpoons I^-$ $E^{\ominus} = +0.54\,V$

$$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O \quad E^{-} = +0.85\ V$$

Use the electrode potentials above to answer the following questions.

(i) Which cobalt(II) ion(s) will reduce a solution of iodine, I_2?

(ii) What will happen to an aqueous solution of $[Co(H_2O)_6]^{3+}$ ions?

(a) Acidic solutions of manganate(VI), MnO_4^{2-} (aq), undergo the reaction shown by the equation:

$$3MnO_4^{2-}(aq) + 4H^+ \rightarrow 2MnO_4^-(aq) + MnO_2(s) + 2H_2O(l)$$

(i) Use the *Data Tables* at the end of this book to find the standard e.m.f. ($E^{\ominus}$) for this reaction.

(ii) What change would you expect to observe when this reaction takes place?

(iii) Describe the oxidation and reduction that take place in this reaction in terms of oxidation number.

(iv) Write an equation to show an aqueous ion of another transition metal undergoing a similar redox reaction.

(b) Account for the fact that hydrochloric acid is less suitable than sulphuric acid for titrations of reducing agents such as iron(II) salts.

Descriptive Questions

1 (a) Outline briefly why the ionisation energies of the transition elements show little change from titanium to copper.

(b) The most common oxidation states of iron are II and III. Explain this fact by referring to the electronic configurations of the Fe^{2+} and Fe^{3+} ions.

(c) Sketch a diagram to show the structure of the substance formed when haemoglobin absorbs oxygen.

Use your diagram to explain the harmful effect of breathing in carbon monoxide.

Explain how hospital patients suffering from carbon monoxide poisoning can be cured by breathing pure oxygen gas.

2 (a) Explain with one example, how ligands cause the colour of most transition metal complex ions.

(b) Suggest why a solution of $[CuCl_4]^{2-}$ is yellow in colour but a solution of $[CuCl_4]^{3-}$ is colourless.

(c) Treatment of iron with molten potassium nitrate under certain conditions yields a compound with the following composition by mass:

potassium 39.4%; iron 28.3%;

oxygen 32.3%

This compound forms an intense red solution in water and is a powerful oxidising agent. Deduce the empirical formula of the compound and the oxidation number of the iron in the compound.

3 (a) (i) What is a transition element?

(ii) Explain why although zinc is a d-block element, it is not considered to be a transition element.

(b) Draw the electronic structure of

(i) vanadium (ii) chromium (iii) manganese (iv) copper

(c) Explain why transition elements form coloured compounds whereas non-transition elements usually form white solids.

(d) By quoting and using relevant standard electrode potential values from the data booklet, explain the following observations:-

(i) when zinc is added to acidified potassium dichromate , effervescence occurs and the solution turns blue.

(ii) When sodium hydroxide is added to a solution of iron(II)sulphate, a green precipitate is formed which slowly turns brown on standing.

4. (a) What do you understand by the terms ligand and complex ion?

(b) The ethane-1,2-diaminetetraacetate ion($EDTA^{4-}$) is a polydentate ligand.

(i) Draw the structure of $EDTA^{4-}$ and indicate all the centers of dative bond formation in the ion.

(ii) Draw the strucure of the complex formed between copper ion and $EDTA^{4-}$.

(c) What do you understand by the stability constant of a complex ion?

(d) Describe and explain what will be observed in the following experiments:

(i) Aqueous ammonia is added to a solution containing Cu2+ ion, until it is in excess. Afterwards solution of EDTA4- is added.

(ii) Ammonium thiocyanate solution is added to a solution of Fe3+. Afterwards solution EDTA4- is added.

You may use the following data to answer the questions.

Complex	K_{stab}
$[Cu(NH_3)_4]^{2+}$	1.40×10^{13}
$[Cu(EDTA)]^{2-}$	6.30×10^{18}
$[Fe(H_2O)_5SCN)]^{2+}$	1.40×10^{2}
$[Fe(EDTA)]^{-}$	1.25×10^{25}

5 (a) Give three characteristic chemical properties of the d-block elements , giving suitable example for each property.

(b) Explain the following:-

(i) the atomic radii of the 3d-elements do not vary considerably while moving from scandium to zinc

(ii) the density of the 3d-elements generally increases from scandium to zinc

(iii) the first ionization energies of 3d elements are almost constant

(c) (i) Draw the electronic structure of chromium.

(ii) Complete the table below:-

Compound	Oxidation number of chromium	Colour of solution
$CrCl_2$		
$CrCl_3$		
K_2CrO_4		
$K_2Cr_2O_7$		

(iv) State and explain what will be observed when dilute sulphuric acid is added to potassium chromate(VI) solution.

(v) The Cr^{3+} ions can be oxidized to the dichromate ions using hydrogen peroxide in acidic medium. Use the Data Booklet to construct an equation for the reaction and calculate the cell potential of the reaction.

6. The properties of d-block elements differ considerably from those of non-transition metals such as calcium. Thus:-

(i) transition elements usually have very high melting points, densities and electrical conductivities as compared to non-transition metals

(ii) transition elements show variable oxidation numbers in their compounds whereas non-transition metals usually have fixed oxidation numbers in their compounds.

(iii) Transition elements usually form coloured compounds whereas non transition elements usually form white solids.

(iv) Transition elements and their compounds may be used as catalyst whereas non-transition metals are not used as catalyst.

Explain each of the above statements using iron and calcium as examples of transition and non-transition metals.

7. (a) Outline the structural requirements for the formation of a complex ion between a transition metal ion and ligands.

(b) Explain the following:-

(i) Fe^{3+} ion will be able to oxidize iodide ion in aqueous medium. However , in the presence of the cyanide ion, Fe^{3+} will not react with the iodide ion.

(ii) When a solution of Fe^{2+} is added to an acidified solution of potassium manganate(VII) , the purple solution turns almost colourless.

(c) Describe the biochemical importance of iron(II)ions in the body.

CHAPTER

17

STRUCTURE OF ORGANIC COMPOUNDS

Classification

Physical Properties

Homologous Series

Shapes and Formulae

Isomerism

SYLLABUS OBJECTIVES

This chapter provides an introduction to the following syllabus objectives. A fuller understanding will be achieved after studying later chapters where these ideas are applied.

In this chapter you should be able to:

- interpret and use the chemical names, general formulae and displayed formulae of the following classes of compound:
  (i) alkanes, alkenes and arenes
  (ii) halogenoalkanes and halogenoarenes
  (iii) alcohols and phenols
  (iv) aldehydes and ketones
  (v) carboxylic acids, acyl chlorides and esters
  (vi) amines (primary)
  (vii) amides
  (viii) amino acids
  (ix) nitriles
- understand use of a functional group
- describe the shapes of the ethane, ethene and benzene molecules and predict the shapes of related molecules
- explain the shapes of the ethane and ethene molecules
- describe structural isomerism
- describe *cis-trans* isomerism in alkenes and explain its origin in terms of restricted rotation of the C=C bond due to the presence of π bonds
- explain what is meant by a chiral centre and how it gives rise to optical isomerism
- determine the possible isomers for an organic molecule of known formula
- identify chiral centres and/or *cis-trans* isomerism in a molecule of given structural formula

Most of the ideas in this chapter apply to other chapters, mainly in organic topics.

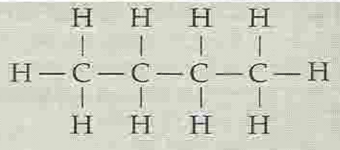
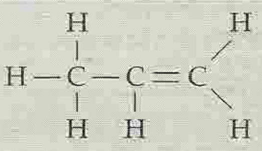
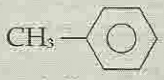
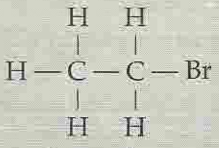
A few problems are given at the end of this chapter. Other problems, eg on isomerism, are incorporated into other chapters.

17.1 Classification

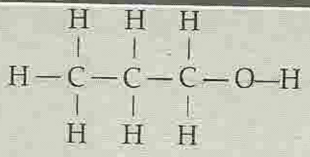
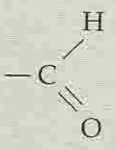
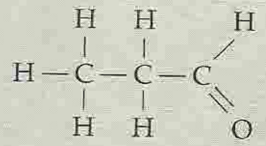
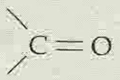
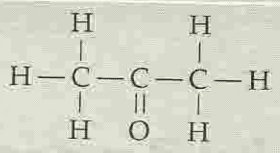
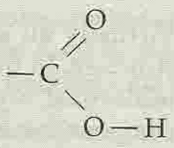
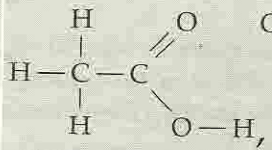
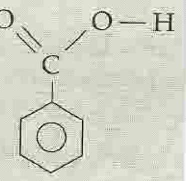
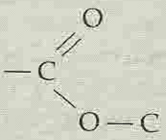
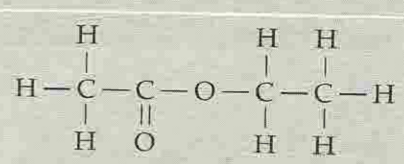
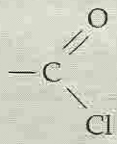
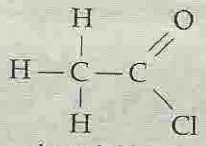
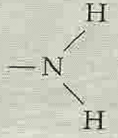
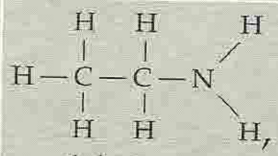
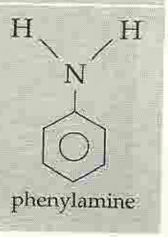
- Organic compounds are classified into different homologous series, such as alkenes, alcohols, amines, carboxylic acids, etc.
- The number of each organic homologous series contains the same reactive group of atoms. This reactive group of atoms is called a **functional group**. For example, all alcohols contain the —OH functional group; all carboxylic acids contain the —COOH functional group.
- Some organic compounds have two or more functional groups. For example, phenylamine has two functional groups: the —NH_2 group and the benzene ring.
- The functional groups studied at A-level are summarised in Table 17.1.

Note: Organic compounds containing a benzene ring, , are described as being **aromatic**.

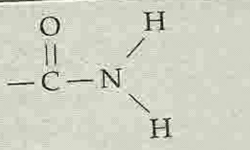
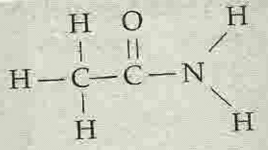
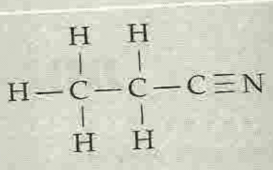
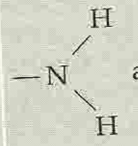
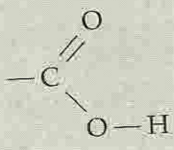
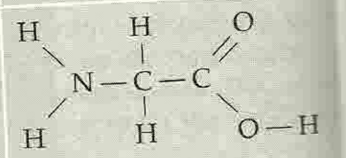
▸ Table 17.1 Classification of organic compounds

type of compound	functional group	examples
alkane	C—C	 butane
alkene	C=C	 propene
arene		 methylbenzene
halogenoalkane	C—X (where X = Cl, Br, I)	 bromoethane

(continued)

type of compound	functional group	examples
alcohol	—O—H (not attached to benzene ring)	 propan-1-ol
phenol	—O—H (attached to benzene ring)	
aldehyde		 propanal
ketone		 propanone
carboxylic acid		 ethanoic acid  benzoic acid
ester		 ethyl ethanoate
acyl chloride		 ethanoyl chloride
amine (primary)		 ethylamine  phenylamine

(continued)

type of compound	functional group	examples
amide	 (there are other types of amides)	 ethanamide
nitrile	$-C\equiv N$	 propanonitrile
amino acid	 and 	 aminoethanoic acid

17.2 Physical Properties

- Virtually all simple organic compounds have a molecular structure. In the liquid and solid states, the forces between the molecules are weak Van der Waals forces. Thus organic compounds have low melting and boiling points and are usually gases or liquids at room conditions. Most organic compounds are insoluble in water.
- Some organic compounds form hydrogen bonds between their molecules. These compounds have higher boiling points than expected for their molecular size. Alcohols, carboxylic acids and amines are examples of such compounds. These compounds are also fairly soluble in water, by forming hydrogen bonds with the water.

Question

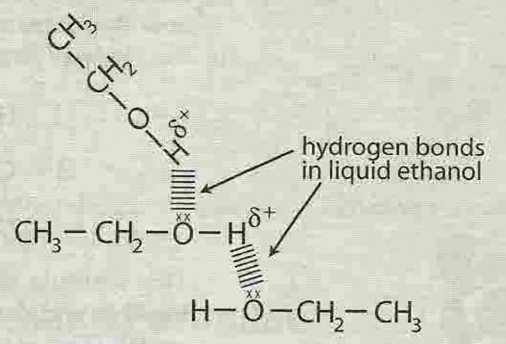
The relative molecular mass and boiling point of ethanol and of propane are given below.

compound	formula	M_r	b.p./°C
ethanol	CH_3CH_2OH	46	78
propane	$CH_3CH_2CH_3$	44	–42

Explain the difference in boiling point between these two compounds.

Answer In liquid propane, the forces between the molecules are weak Van der Waals forces.

Ethanol has a similar relative molecular mass, so its molecules are similar in size to those of propane. Hence the Van der Waals forces should be similar and we should expect a similar boiling point.
However ethanol has a much higher boiling point. This is due to hydrogen bonding between the molecules (Fig 17.1). The hydrogen bonds are stronger than the Van der Waals forces, so the boiling point is higher as more energy is required to break the bonds.



▶ Fig 17.1

17.3 Homologous Series

- A **homologous series** is a set of organic compounds all of which have the same functional group, and in which one compound differs from the next by an extra —CH_2 group of atoms.
- The set of alkenes shown in Table 17.2 is a homologous series.

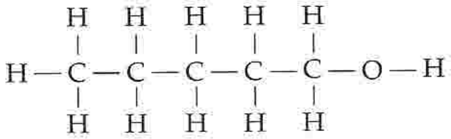
▶ Table 17.2 Homologous series of alkenes

formula	name	b.p./°C
$CH_2=CH_2$	ethene	–102
$CH_3-CH=CH_2$	propene	–48
$CH_3-CH_2-CH=CH_2$	but-1-ene	–6.5
$CH_3-CH_2-CH_2-CH=CH_2$	pent-1-ene	30
$CH_3-CH_2-CH_2-CH_2-CH=CH_2$	hex-1-ene	63

- Compounds in a homologous series usually have the same chemical reactions as they all have the same functional group.
- Compounds in a homologous series have small differences in physical properties. For example, as the molecules become larger there is only a gradual increase in boiling point, melting point and density.

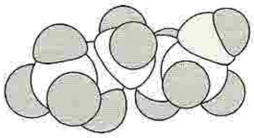
17.4 Shapes and Formulae

- The formula of an organic compound can be expressed in severa ways.
  For example, for pentan-1-ol:
  (a) the *molecular formula* is $C_5H_{12}O$. This formula does not sho how the atoms are connected;
  (b) the *displayed formula* is



$$\begin{array}{ccccccccccccc} & & H & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & C & - & O-H \\ & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & H & & \end{array}$$

  This formula shows clearly how all the atoms are joine together and also shows all the bonds. The angles shown he are 90°. This is not real but is drawn this way for clarity. Th real shape of a molecule of pentan-1-ol is shown in Fig 17.2

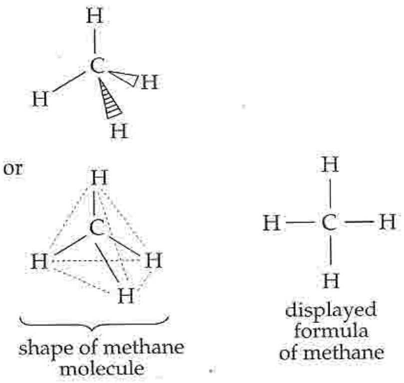


▲ Fig 17.2 Model of a molecule of pentan-1-ol

  (c) The *structural formula* is $CH_3—CH_2—CH_2—CH_2—CH_2—OH$ or $CH_3CH_2CH_2CH_2CH_2OH$. The structural formula is a abbreviated displayed formula. The displayed formula ca be deduced from the structural formula. The structura formula is usually the most useful formula to use for organi compounds.

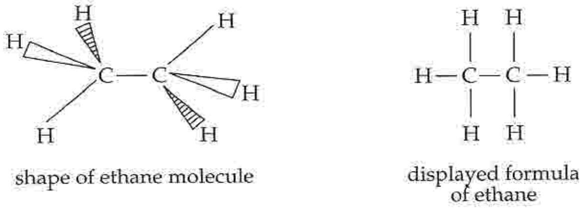
Shapes of Some Hydrocarbon Molecules

- The electron pairs in the four covalent bonds around a carbo atom have a tetrahedral arrangement so that they are as far apa as possible. Hence in methane, CH_4, the four hydrogen atoms ar arranged tetrahedrally. Two ways of drawing this are shown i Fig 17.3. The displayed formula shows clearly how the atoms ar joined together but does not show the correct bond angles.



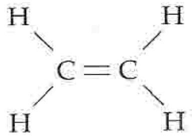
▲ Fig 17.3 Shape of methane molecule

- The shape of the ethane molecule, C_2H_6, is shown in Fig 17.4.



▶ Fig 17.4 Shape of ethane molecule

- The displayed formula of the ethene (C_2H_4) molecule is show below. This is also its shape. The molecule is planar.



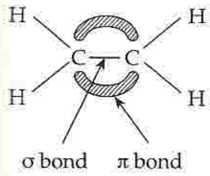
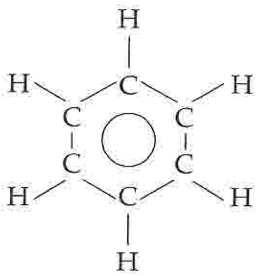


Fig 17.5 The bonds in ethene molecule

The C=C bond in ethene consists of an ordinary covalent bond and a π bond (in two parts) as shown in Fig 17.5.

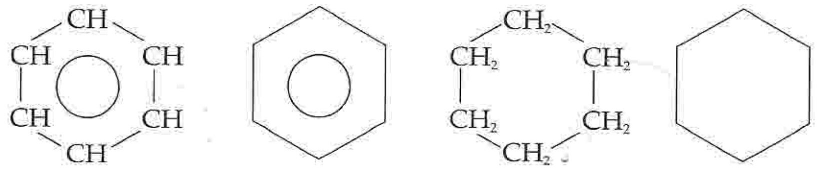
- The benzene molecule (C_6H_6) is planar. All the carbon—carbon bonds are identical. The shape and displayed formula of the benzene molecule is shown below.



The bonding and structure of benzene are considered in detail in Chapter 18.

Shorthand Formulae

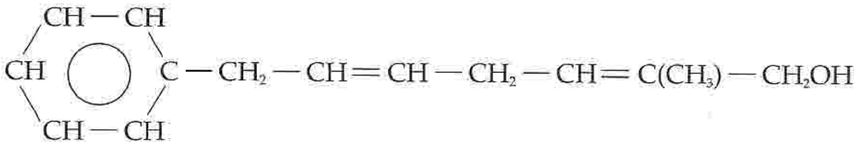
- The structural formulae of organic compounds can be shown as a 'shorthand' formula. The shorthand formulae for benzene and cyclohexane are shown below.



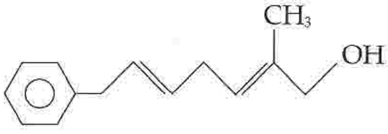
structural formula shorthand formula structural formula shorthand formula

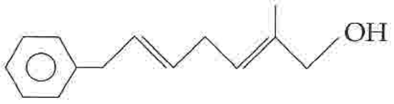
benzene (C_6H_6) cyclohexane (C_6H_{12})

- Big organic formulae can be written coveniently in a shorthand form. An example is shown below:



The shorthand form is



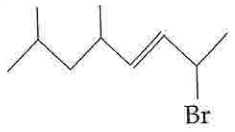


- In shorthand formulae,
  - (a) there is a carbon atom at every bend;
  - (b) there is a carbon atom at the end of every line (if no other atom is shown);
  - (c) all non-carbon and non-hydrogen atoms are shown;
  - (d) to produce the full formula, add hydrogen atoms to every carbon atom to produce 4 bonds.

- Another example of a shorthand formula is shown below:

$(CH_3)_2CH—CH_2—CH(CH_3)—CH=CH—CHBr—CH_3$

or



shorthand formula

17.5 Isomerism

- Different compounds with the same molecular formula are said to be **isomers**.
- There are three main types of isomerism: **structural isomerism**; **cis-trans isomerism** (this is part of geometrical isomerism); and **optical isomerism**.

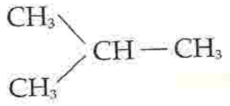
Structural Isomerism

- Structural isomerism occurs when isomers have different structural formulae (ie at least one atom is bonded to different atoms in the isomers).
- There are several different ways in which structural isomers can be obtained.
  (a) **Different arrangements of a carbon chain**

  eg: structural isomers of C_4H_{10}

$CH_3—CH_2—CH_2—CH_3$

butane (b.p. –0.5°C)



$$(CH_3)_2CH—CH_3$$

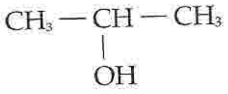
2-methylpropane (b.p. –12°C)

  (b) **Different positions of a functional group on a carbon chain or ring**

  eg: structural isomers of C_3H_7OH

$CH_3—CH_2—CH_2—OH$

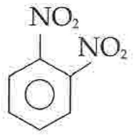
propan-1-ol (b.p. 97°C)

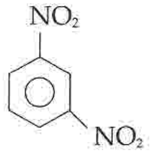


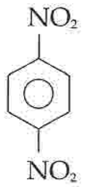
$$CH_3—CH(OH)—CH_3$$

propan-2-ol (b.p. 82°C)

eg: structural isomers of $C_6H_4N_2O_4$

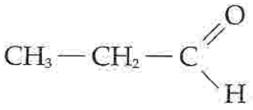

1,2-dinitrobenzene
(b.p. 319°C)

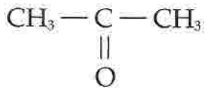

1,3-dinitrobenzene
(b.p. 303°C)


1,4-dinitrobenzene
(b.p. 299°C)

(c) **Different functional groups**

eg: structural isomers of C_3H_6O


propanal (an aldehyde) (b.p. 49°C)



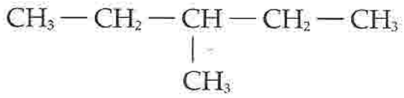
$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3$$

propanone (a ketone) (b.p. 56°C)

- An isomer in which all the carbon atoms are in a line is called **straight chain**. An isomer with carbon groups (eg methyl) attached along the main chain of carbon atoms is called **branched chain**. For example, hexane is a straight chain isomer and 3-methylpentane is a branched chain isomer.

$$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$$

hexane (straight chain)



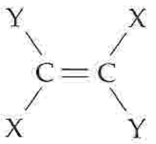
$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3$$

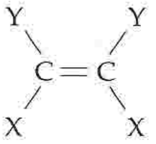
3-methylpentane (branched chain)

- Structural isomers have different melting and boiling points.

Cis-trans Isomerism (geometrical isomerism)

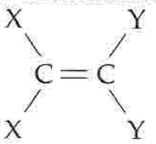
- Cis-trans isomerism can occur in compounds with a carbon-carbon double bond, C=C. The general case of cis-trans isomerism is the two isomers:


trans isomer


cis isomer

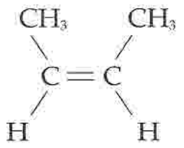
These two isomers have the same structural formula (each carbon atom is attached to an atom of X and an atom of Y).

Note that a third isomer with molecular formula $C_2X_2Y_2$ is

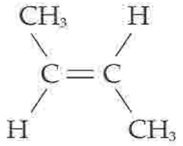


This third compound is *not* a cis-trans isomer of the other two as it has a different structural formula (eg both X groups are attached to the same carbon atom).

- Cis-trans isomerism occurs *because the C=C bond cannot be rotated* as this would break the π bond.
- Examples of two cis-trans isomers are the two but-2-ene compounds:

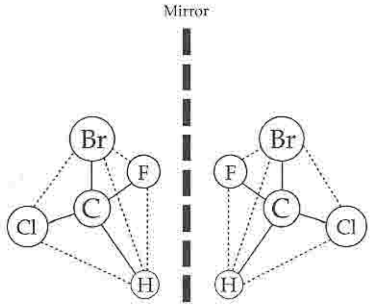


cis-but-2-ene
(b.p. 3.7°C)



trans-but-2-ene
(b.p. 0.8°C)

- Cis-trans isomers have different melting and boiling points.

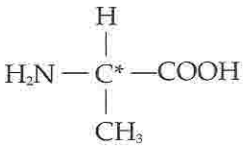


▲ Fig 17.6 Optical isomers of CHFClBr

Optical Isomerism

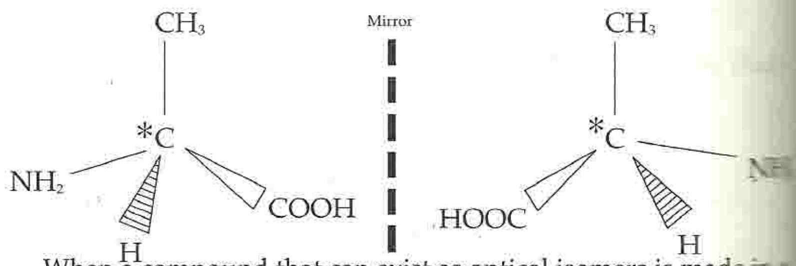
- Optical isomers are two compounds with the same structural formula, but *one isomer is the mirror image of the other*.
- Optical isomerism occurs when four different groups of atoms are joined to a carbon atom by four single covalent bonds. There are two possible arrangements (mirror images).

  An example of two optical isomers is CHFClBr. The two optical isomers are shown in Fig 17.6. If a mirror is placed between the two compounds, then each will appear as the mirror image of the other but are non-superimposable.
- Optical isomerism occurs because of the tetrahedral bonding around a carbon atom. If the molecule was flat with 90° angles, then two different isomers would not be obtained.
- Structures that can exist as two optical isomers are said to be **optically active** and possess a **chiral centre**. A chiral centre is a carbon atom with four different groups of atoms, which is the reason for the existence of the two different structures. The chiral centre is often marked an asterisk (*). An example is the amino acid $H_2N—CH(CH_3)—COOH$. This compound has a chiral centre, which is shown in Fig 17.7. The structures of its two optical isomers are shown in Fig 17.8.



$$H_2N — \underset{\displaystyle CH_3}{\overset{\displaystyle H}{C^*}} — COOH$$

▲ Fig 17.7 Chiral centre in $H_2N—CH(CH_3)—COOH$



▶ Fig 17.8 Optical isomers of $H_2N—CH(CH_3)—COOH$

- When a compound that can exist as optical isomers is made in a chemical reaction, an equal mixture of both isomers is usually obtained. Then the sample is non-optically active.

  One optical isomer is often produced in a biochemical reaction in living cells. Biochemical reactions in cells often only use one optical isomer. Optical isomerism is important in biochemical reactions. For example, nicotine, which is the chemical stimulant in cigarettes, is an optical isomer. The other optical isomer does not have the same effect on people who smoke.

Question

Five amino acids are given below. Which amino acid does *not* form optical isomers? Explain your answer.

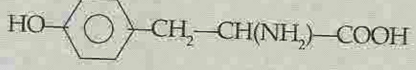
A $HOCH_2—CH_2—CH(NH_2)—COOH$

B $H_2N—OC—CH(NH_2)—COOH$

C $CH_3—CH(NH_2)—COOH$

D $H_2N—CH_2—COOH$

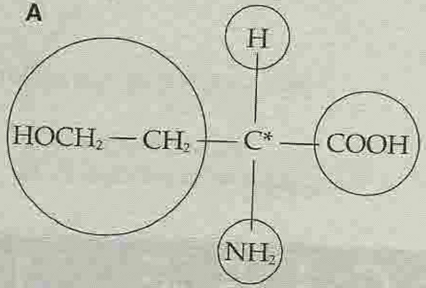
E



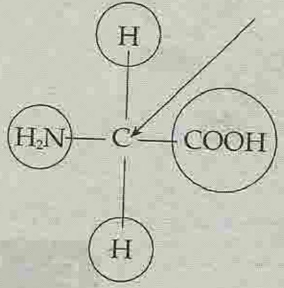
Answer

The structural formulae of the five amino acids are shown below. In A, B, C and E, there is a carbon atom (marked with an asterisk *) attached to four different groups of atoms (ie a chiral centre). The four different groups of atoms are circled. These four compounds form optical isomers.

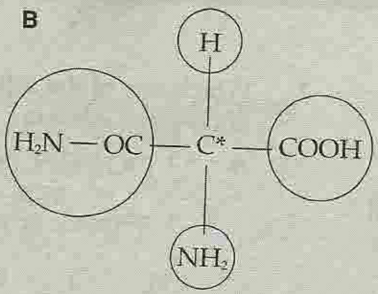
A



D

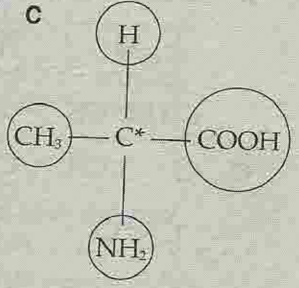


B

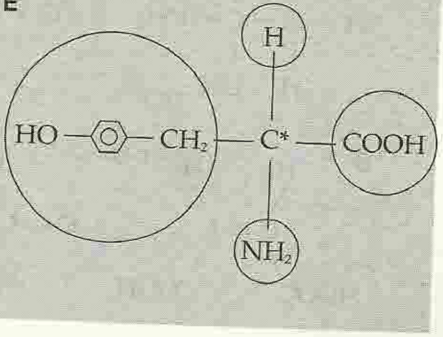


In compound, D, the carbon atom (arrowed) is only attached to three different groups (not four). Hence this compound does not form optical isomers.

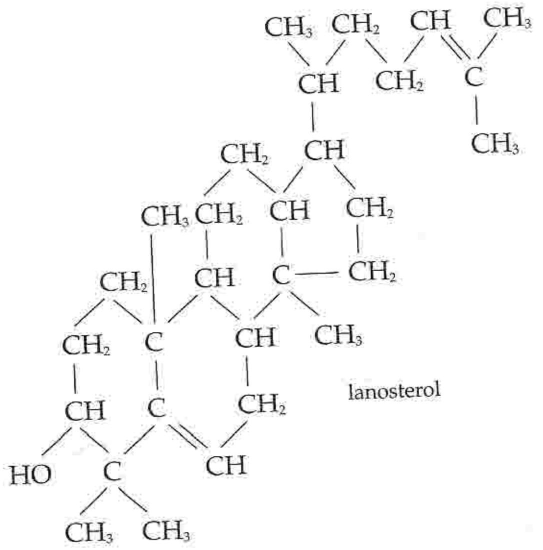
C



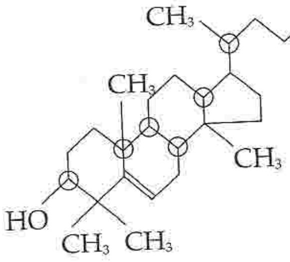
E



- Chiral centres are also found in cyclic compounds. A carbon at in a ring is a chiral centre if it is attached to four different grou An example is shown below for the compound lanosterol. The chiral centres are ringed in the shorthand formula.



lanosterol



Shorthand formula of lanosterol

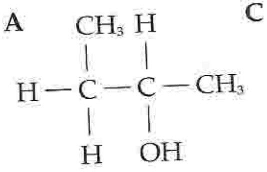
EXERCISE 17

Multiple Choice Questions

Section I

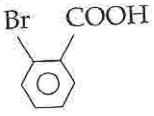
1 Which one of the following can exist as two optical isomers?

A

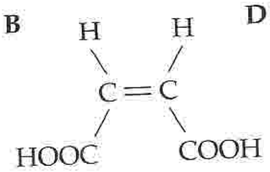


$\mathrm{H-C(CH_3)(H)-C(H)(OH)-CH_3}$

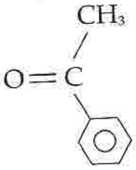
C



B

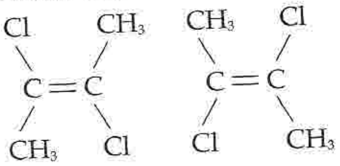


D

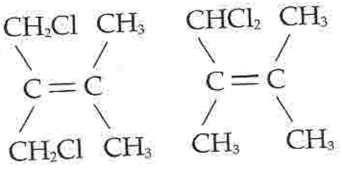


2 Which one of the following consists of a pa of cis-trans isomers?

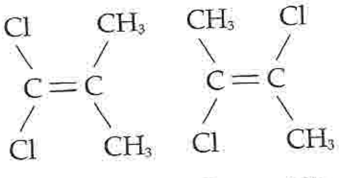
A



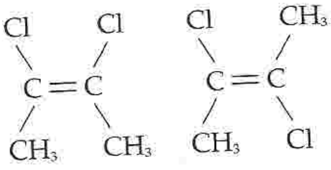
B



C



D



3 What is the minimum number of carbon atoms required in one molecule for an alkane to have a chiral centre?

A 4 C 6
B 5 D 7

4 Which one of the following compounds can form cis-trans isomers?

A $(CH_3)_2C{=}CH_2$
B $CH_3{-}CH{=}CH_2$
C $CH_3{-}CH{=}CH{-}CH_3$
D $CH_3{-}CH{=}C(CH_3)_2$

5 How many dinitrobenzene, $C_6H_4(NO_2)_2$, compounds exist?

A 1 C 3
B 2 D 4

6 Which one of the following molecules is *not* planar?

A ethene C methylbenzene
B chloroethene D 1,4-dichlorobenzene

How many different structural isomers exist with the molecular formula $C_nH_{(2n+2)}$, where $n = 6$?

A 4 C 6
B 5 D 8

Which one of the following has a chiral centre?

A $CH_3{-}CH(OH){-}CH_2{-}COOH$
B $CH_2OH{-}CH_2{-}CH_2{-}COCl$
C $CH_3{-}CH(OH){-}CH_3$
D $HOOC{-}CH_2{-}CH_2{-}NH_2$

Section II

Summary of directions

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

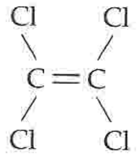
Two optical isomers have the *same*

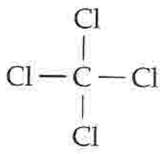
1 empirical formula.
2 structural formula.
3 boiling point.

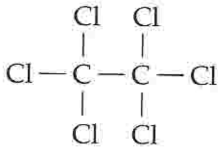
Two cis-trans isomers have *different*

1 boiling points.
2 empirical formulae.
3 molecular formulae.

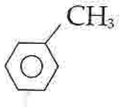
11 Which one of the following molecules are planar?

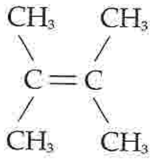
1


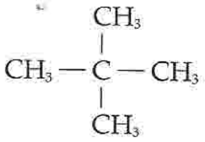
2


3


12 In which one of the following organic structures do all the *carbon* atoms lie in one plane?

1


2


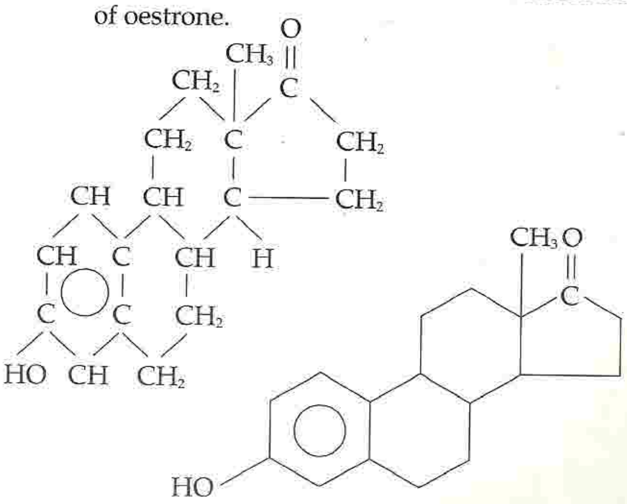
3


13 What type(s) of isomers can be obtained from a molecule with the molecular formula C_4H_8?

1 cis-trans isomers
2 structural isomers
3 optical isomers

Structured Questions

1 The structure of the hormone oestrone is shown in two ways below. Draw circles around the *three* chiral centres in the shorthand structure of oestrone.



2 But-2-ene can exist in two isomeric forms.
- (a) Give the displayed formula and chemical names of these two isomers.
- (b) What structural feature of but-2-ene explains how this type of isomerism is produced?
- (c) Write the chemical name and displayed formula of an isomer of but-2-ene that does not exhibit this type of isomerism.
- (d) State one physical property that would distinguish the three compounds with the formulae you have drawn above.

3 (a)

Write the structural formulae of *three* structural isomers of the compound above.

(b) 1,1,1-trichloroethane, $CH_3—CCl_3$, is an important organic solvent.
- (i) How many other structural isomers of this compound exist?
- (ii) Write the displayed formula and chemical name of one of these isomers.
- (iii) How would you attempt to separate a mixture of the isomer in (ii) and 1,1,1-trichloroethane?

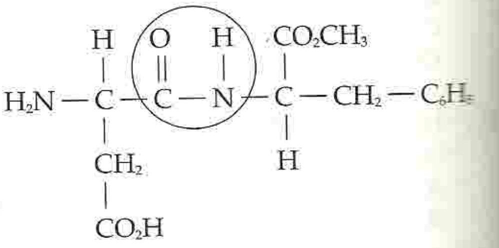
4 **A** $CH_3CH_2CO_2H$
B $CH_3CH(OH)CH_2CH_3$
C $CH_3CO_2CH_3$
D $CH_3CH_2COCH_2CH_3$
E $CH_3CH_2CONH_2$
F $H_2NCH_2CH_2CH_3$
G C_6H_5CHO

A list of seven organic compounds is given above.
- (a) Which compound is
  - (i) an ester;
  - (ii) an aldehyde;
  - (iii) an alcohol;
  - (iv) an amide;
  - (v) an aromatic compound and
  - (vi) an acid?
- (b) Which two compounds are structural isomers?
- (c) Which compound has a chiral centre?

Descriptive Questions

1 (a) What do you understand by the ter *structural isomerism*?
Write displayed formulae for all the structural isomers of $C_4H_{10}O$ that are alcohols.

(b) Aspartame is used as an artificial sweetener in food, in place of sugar. Aspartame has the structural formula shown below.



- (i) Aspartame contains an amide gro (also called a peptide bond), circle State the other functional groups th are present in aspartame.
- (ii) What type of isomerism is present i aspartame?

2 (a) What do you understand by the ter *optical isomerism* and *cis-trans isomeris*
(b) What type(s) of isomerism, if any, a shown in the following compounds?

(i)

(ii) $CH_2(OH)CH_2CH(CH_3)CH=$
$CHCH(CH_3)CH_2CH_2OH$

(iii) $(CH_3CH_2)_2C=CHCH_2CH(OH)CH$
$CH=C(CH_2CH_3)_2$

*3 An aromatic hydrocarbon has composi 90.0% carbon and 10.0% hydrogen. 0.2 g of vaporised hydrocarbon has a volume of 5 cm^3 at 400 K and at 100 kPa.
- (a) Deduce the empirical and molec formulae of the hydrocarbon.
- (b) (i) Write one structural formula for t hydrocarbon in which all the car *atoms* lie in the same plane.
  - (ii) Write one structural formula for t hydrocarbon in which the car atoms are *not* planar.

CHAPTER 18

HYDROCARBONS

SYLLABUS OBJECTIVES

In this chapter you should be able to:

- interpret and use the chemical names, general formulae and displayed formulae of alkanes, alkenes and arenes
- recognise the general unreactivity of alkanes
- describe the following reactions of alkanes:
  - combustion of alkanes; substitution reactions with chlorine and bromine
- describe the mechanism for free radical substitution of methyl groups with reference to initiation, propagation and termination reactions
- describe the following reactions of alkenes:
  - addition of H_2, H_2O, HCl, HBr, Cl_2, Br_2; oxidation by cold dilute manganate(VII) to form a diol and by hot concentrated manganate(VII) leading to the breaking of the C=C (polymerisation)
- for poly(alkenes), suggest the repeat unit of the polymer from a given monomer
- given a section of a poly(alkene), state that it was formed by addition polymerisation and identify the monomer
- describe the mechanism for electrophilic addition in alkenes
- explain the use of crude oil as a source of both aliphatic and aromatic hydrocarbons
- explain how 'cracking' can be used to obtain more useful alkanes and alkenes of lower M_r from larger hydrocarbon molecules
- recognise pollution problems caused by disposing plastics
- explain the shape of the benzene molecule in terms of σ and π C=C bonds
- describe the following reactions of arenes:
  - substitution reactions with chlorine and bromine; nitration and oxidation of side chain to give a carboxylic acid
- describe the mechanism for electrophilic substitution in arenes
- predict whether substitution by chlorine/bromine takes place in the side chain or in the benzene ring in compounds such as methylbenzene, depending on the conditions
- apply knowledge of positions of substitution of the benzene ring in electrophilic substitution
- know some of the environmental effects of carbon monoxide, oxides of nitrogen and unburnt hydrocarbons from internal combustion engines (eg car engines) and their catalytic removal (ie catalytic converters in car exhausts)

Alkanes

Mechanism for Free Radical Substitution of Alkanes

Alkenes

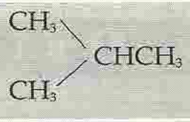
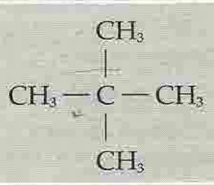
Mechanism for Electrophilic Addition in Alkenes

Arenes (Aromatic Hydrocarbons)

Mechanism for Nitration of Benzene

18.1 Alkanes

- Alkanes are hydrocarbons with the general formula C_nH_{2n+2}. Some examples of alkanes are given in Table 18.1.

alkane	formula	m.p./°C	b.p./°C
methane	CH_4	–183	–162
ethane	CH_3CH_3	–172	–89
propane	$CH_3CH_2CH_3$	–188	–42
butane	$CH_3CH_2CH_2CH_3$	–135	–0.5
2-methylpropane		–159	–12
2,2-dimethylpropane	 $C(CH_3)_4$	–16	9.5
decane	$CH_3(CH_2)_8CH_3$	–30	174

▸ Table 18.1 Examples of alkanes

Chemical Reactions

- Alkanes do not react with polar molecules such as H_2O and aqueous NaOH because:
  - (a) all the electrons and orbitals of carbon (ie 2*s* and 2*p*) are used in bonding in alkanes, thus there are no empty orbitals available to form dative bonds with molecules and ions like H_2O and OH^-, which have lone pairs of electrons (see *Distinctive Chemistry of Carbon* in Chapter 13);
  - (b) the electronegativities of carbon and hydrogen are similar, thus the C—H bond is hardly polarised. Also, carbon is in fact more electronegative than hydrogen, so carbon is slightly negative in the C—H bond and will repel the negative oxygen in H_2O and OH^-.

Cracking of Alkanes

- Large alkane molecules can be broken into smaller molecules by passing the vaporised alkane over a catalyst at about 500° C. An example is the cracking of $C_{22}H_{46}$:

	$C_{22}H_{46}$ big alkane molecule	$\rightarrow$	$C_{10}H_{22}$ small alkane molecule	$+$	$C_{12}H_{24}$ small alkene molecule
or	$C_{22}H_{46}$	$\rightarrow$	$C_{12}H_{26}$ small alkane molecule	$+$	$5C_2H_4$ small alkene (ethene) molecules

- Cracking produces more small alkane molecules for use as fuel for motor cars.
- Large amounts of ethene are produced from cracking reactions, as shown in the second equation above. This ethene is used to manufacture many chemicals such as ethanol, ethanoic acid and poly(ethene), (see further on in this section).

Combustion of Alkanes

- Alkanes burn in air and oxygen. Carbon dioxide and water are produced when combustion is complete. An example is the complete combustion of ethane:

$$C_2H_6 + 3\tfrac{1}{2}O_2 \rightarrow 2CO_2 + 3H_2O$$

- The main use of alkanes is in combustion to produce energy. Examples of this include the combustion of petrol in motor cars, bottled gas (butane) for cooking food, and oil in electricity-generating stations.

Combustion of Petrol on Motor car Engines

- Petrol is a mixture of C_5 to C_{10} alkanes. A typical petrol molecule is octane, C_8H_{18}.
- Energy is obtained by igniting a gaseous mixture of air and petrol with an electric spark.
- The exhaust fumes from a motor car engine contain the following pollutants:
  - (a) carbon monoxide, CO, from incomplete combustion. Carbon monoxide is absorbed by haemoglobin in the blood (see *Haemoglobin* in Chapter 16);
  - (b) unburnt hydrocarbon fuel;
  - (c) nitrogen oxides, from the reaction of N_2 and O_2 (both from the air) in the engine. These oxides cause 'acid rain';
- In many countries, pollution from motor cars is being reduced by fitting a platinum catalyst converter onto motor car exhausts. The exhaust gases (nitrogen oxides, carbon monoxide and unburnt fuel) react together on the surface of the platinum and are converted into harmless nitrogen, carbon dioxide and steam. One reaction is:

$$\underset{\text{harmful pollutants}}{2CO \;+\; 2NO} \rightarrow \underset{\substack{\text{harmless except for}\\ \text{greenhouse effect of } CO_2}}{N_2 \;+\; 2CO_2}$$

Substitution with Halogens

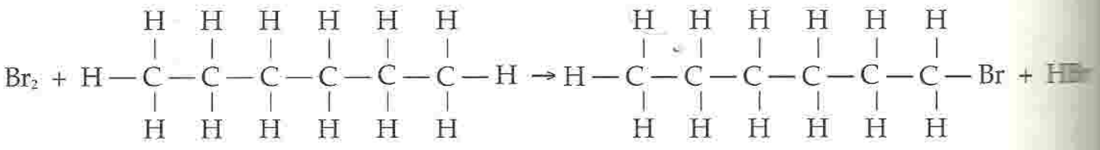
- Alkanes react with chlorine in the presence of sunlight. The reaction is *slow*. A *substitution* reaction takes place. The hydrogen atoms of the alkane are substituted with chlorine atoms, one by one. The amount of substitution depends on the amount of chlorine.

For example, when methane reacts with chlorine, the hydrogen atoms are substituted with chlorine in a chain of reactions until CCl_4 is obtained:

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$
$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$$
$$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$$
$$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$$

In practice a mixture of CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 is obtained. This mixture can be separated by fractional distillation. The mechanism of this reaction is free radical. See the following section.

- Alkanes also react with bromine in the presence of sunlight. The reaction is *slow*. A *substitution* reaction takes place (similar to the reaction with chlorine). For example, hexane reacts with bromine according to the equation:



$$Br_2 + H{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}H \rightarrow H{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}Br + HBr$$

C_6H_{14}

$C_6H_{13}Br$
1-bromohexane

In the reaction,
(a) the bromine is decolourised;
(b) fumes of hydrogen bromide gas are produced;
(c) substitution of any of the hydrogen atoms can occur, so that a mixture of isomers is obtained;
(d) with more bromine, more hydrogen atoms can be substituted by bromine to produce dibromohexane molecules, etc.

18.2 Mechanism for Free Radical Substitution of Alkanes

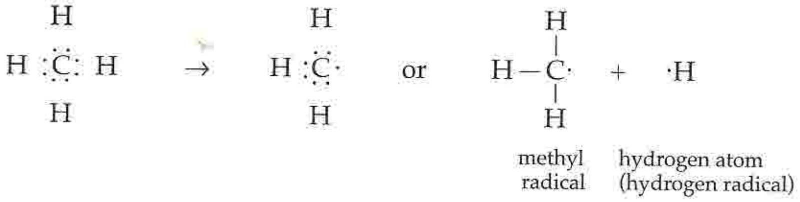
- The mechanism of an organic reaction describes how the particles react together in the reaction.

Free Radicals

- A **free radical** is a particle in which one atom has an unpaired electron. A hydrogen atom, by itself, is a radical. It has a single unpaired electron in its 1*s* orbital. A hydrogen radical is written as H·. The dot represents the unpaired electron.

  A chlorine atom, Cl· is also a radical as it also has an unpaired electron in its outer 3*p* orbital.

Radicals are produced when a covalent bond in a molecule is broken so that each atom receives *one* electron. This type of bond breaking is called **homolytic fission**. Hence a methyl radical is produced by breaking a C—H bond in methane:



$$\mathrm{H{:}\overset{H}{\underset{H}{\ddot{C}}}{:}H} \rightarrow \mathrm{H{:}\overset{H}{\underset{H}{\ddot{C}}}\cdot} \text{ or } \mathrm{H{-}\overset{H}{\underset{H}{C}}\cdot} + \cdot\mathrm{H}$$

Two radicals are produced in homolytic fission, as shown in the example above.

- Free radicals are usually very reactive, as an unpaired electron joins up with another electron to form an electron pair as quickly as possible.
- Homolytic fission should be compared with **heterolytic fission**. In heterolytic fission, one atom receives *both* electrons when a covalent bond is broken. This produces positive and negative ions, as shown simply below for the heterolytic fission of a C—Br bond:

$$\geqslant\mathrm{C} : \mathrm{Br} \rightarrow \geqslant\mathrm{C}^+ + :\mathrm{Br}^-$$

Free Radical Reaction of Methane with Chlorine

- A **substitution reaction** is an organic reaction where one or more atoms of an organic molecule are replaced with one or more other atoms.
- Alkanes react with chlorine by a **free radical substitution reaction**. For example, methane reacts with chlorine according to the equation

$$Cl_2 + CH_4 \rightarrow CH_3Cl + HCl$$

One of the hydrogen atoms of the methane is substituted by a chlorine atom. The CH_3Cl can undergo further substitution with chlorine, to produce CH_2Cl_2, $CHCl_3$ and finally CCl_4.

- The experimental facts about the reaction of chlorine with methane are as follows.
  (a) The reaction requires light energy. In the presence of sunlight, the reaction is very rapid. In darkness at room temperature, there is no reaction.
  (b) For each photon of light absorbed by the reaction mixture, thousands of HCl and CH_3Cl molecules are produced.
  (c) The reaction can also be started by adding a few methyl radicals, $CH_3\cdot$, from the decomposition of tetramethyl lead, $Pb(CH_3)_4$.
- The mechanism for the reaction of methane and chlorine involves a number of steps.
  (a) A photon of light breaks up a chlorine molecule into chlorine atoms or radicals:

$$Cl_2 \rightarrow Cl^\bullet + Cl^\bullet \qquad \text{step 1}$$

This step (which starts the reaction) is called **initiation**.

(b) A chlorine atom reacts with a methane molecule to give a methyl radical:

$$Cl^\bullet + CH_4 \rightarrow HCl + CH_3^\bullet \qquad \text{step 2}$$

(c) The methyl radical then reacts with another Cl_2 molecule:

$$CH_3^\bullet + Cl_2 \rightarrow CH_3Cl + Cl^\bullet \qquad \text{step 3}$$

These two steps (2 and 3) by which the reaction is continued are called **propagation**.

(d) Steps 2 and 3 are repeated until all the Cl_2 and CH_4 are used up, or until the radicals are destroyed by a reaction such as

$$Cl^\bullet + CH_3^\bullet \rightarrow CH_3Cl$$

This step by which the radicals are destroyed and the reaction stopped, is called **termination**. Other termination steps are:

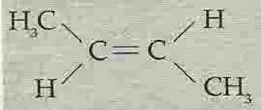
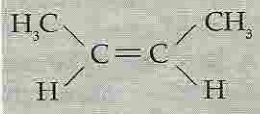
$$CH_3^\bullet + CH_3^\bullet \longrightarrow \underset{\text{ethane}}{CH_3CH_3}$$

$$Cl^\bullet + Cl^\bullet \longrightarrow Cl_2$$

- The reaction can be started by adding a few methyl radicals. This enables step 3 to take place, producing $Cl^\bullet$ atoms. Step 2 can then take place and so on.
- Methane reacts with bromine similarly.

18.3 Alkenes

- Alkenes are hydrocarbons with the general formula C_nH_{2n}. Alkenes contain a C=C bond. Some examples of alkenes are given in Table 18.2.

alkene	formula	m.p./°C	b.p./°C
ethene	$CH_2{=}CH_2$	–169	–102
propene	$CH_3{-}CH{=}CH_2$	–185	–48
but-1-ene	$CH_3{-}CH_2{-}CH{=}CH_2$	–185	–4.5
trans-but-2-ene		–105.5	1
cis-but-2-ene		–139	4
pent-1-ene	$CH_3{-}CH_2{-}CH_2{-}CH{=}CH_2$	–138	30

▶ Table 18.2 Examples of alkenes

- Alkenes are obtained from alkanes during cracking of petroleum. Large amounts of ethene are produced for industry this way. Alkenes can be produced in the laboratory by dehydrating alcohol (see Chapter 21).

- The C=C bond in alkenes cannot be rotated because the π bond would have to be broken. Because of this, many alkenes form cis-trans isomers (see *Cis-trans Isomerism* in Chapter 17).

Chemical Reactions

- Alkenes undergo *electrophilic addition* reactions with several reagents. In the addition reaction, the C=C bond reacts. The C=C bond is the *functional group* of alkenes.

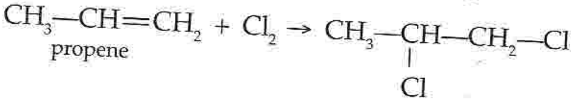
(a) **Addition of HX** (where X = Cl, Br or I)

$$\underset{\text{ethene}}{CH_2{=}CH_2} + HI \rightarrow \underset{\text{iodoethane}}{CH_3{-}CH_2I}$$

$$\underset{\text{but-2-ene}}{CH_3{-}CH{=}CH{-}CH_3} + HCl \rightarrow \underset{\text{2-chlorobutane}}{CH_3CH_2{-}CHCl{-}CH_3}$$

(b) **Addition of X_2** (where X = Cl or Br)

$$\underset{\text{ethene}}{CH_2{=}CH_2} + Br_2 \rightarrow \underset{\text{1,2-dibromoethene}}{Br{-}CH_2{-}CH_2{-}Br}$$



$$\underset{\text{propene}}{CH_3{-}CH{=}CH_2} + Cl_2 \rightarrow CH_3{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}CH_2{-}Cl$$

1,2-dichloropropane

These addition reactions are very rapid. Hence, when an alkene is mixed with bromine, the bromine is *rapidly decolourised.*

(c) **Addition of hydrogen**

Alkenes react with hydrogen over a nickel or palladium catalyst, producing an alkane.

$$\underset{\text{ethene}}{CH_2 = CH_2} + H_2 \xrightarrow{\boxed{\begin{matrix}\text{Ni catalyst}\\ 150°\text{ C}\end{matrix}}} \underset{\text{ethane}}{CH_3 - CH_3}$$

$$\underset{\text{but-1-ene}}{CH_3 - CH_2 - CH = CH_2} + H_2 \xrightarrow{\boxed{\begin{matrix}\text{Ni catalyst}\\ 150°\text{ C}\end{matrix}}} \underset{\text{butane}}{CH_3 - CH_2 - CH_2 - CH_3}$$

This reaction is used to convert alkenes, obtained from cracking, into alkanes for use as fuel in cars and aircraft. Alkenes are not used as fuel in vehicles because (i) they produce more soot and (ii) they react with air and water to form solids that can block fuel pipes.

(d) **Oxidation of diol**

(i) In the laboratory, alkenes react with cold alkaline or acidic $KMnO_4$ to produce a diol.

$$CH_2 = CH_2 + \underset{(kMnO_4/OH^-)}{[O]} + H_2O \longrightarrow \underset{\text{ethane 1,2 diol}}{CH_2OHCH_2OH}$$

$$CH_2 - CH = CH_2 + \underset{(kMnO_4/OH^-)}{[O]} + H_2O \longrightarrow \underset{\text{propane 1,2 diol}}{CH_3\,CH\,(OH)\,CH_2OH}$$

In this reaction, the purple $KMnO_4$ turns green. Note that this is *not* an industrial method of making a diol such as ethane-1,2-diol. Note that if more powerful oxidising conditions are used, such as hot acidified $KMnO_4$, the C=C is broken.

$$CH_3-CH=CH-CH_3 + \underset{\substack{\text{Hot}\\(KMnO_4/H_3O^+)}}{4[O]} \longrightarrow 2CH_3COOH$$

This reaction can be used to find the position of a C=C bond in an organic compound.

Note that C–C bonds are **not** broken during reaction

Question When an alkene is refluxed with hot acidic $KMnO_4$, a mixture of the following two acids is produced:

$CH_3—COOH$ and $CH_3—CH_2—CH_2—COOH$

What is the name and structural formula of the alkene?

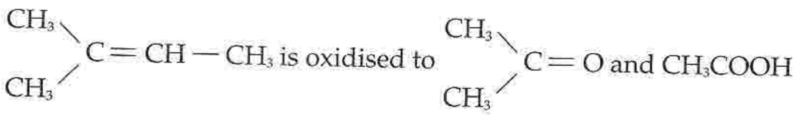
Answer The alkene is hex-2-ene, $CH_3—CH \quad CH=CH_2—CH_2—CH_3$.

Note that some alkenes can give other products:

- A single carbon atom on the end of a C=C bond is usually oxidised to carbon dioxide, rather than an acid:

  $CH_3—CH=CH_2$ is oxidised to CH_3COOH and CO_2

- Branched carbon chains on the end of a C=C bond are usually only oxidised to C=O:



(e) **Addition of water**

In industry, alkenes are reacted with steam on a hot solid catalyst containing phosphoric acid at 300°C to produce alcohols:

$$\underset{\text{ethene}}{CH_2=CH_2} + H_2O \xrightarrow{\boxed{\begin{array}{c}H_3PO_4/SiO_2\\ \text{catalyst; }300^\circ C\end{array}}} \underset{\text{ethanol}}{CH_3-CH_2OH}$$

Polymers from Alkenes

- When several identical molecules are joined together to form a single molecule, the product is called a **polymer**. The initial (small) molecules are called **monomers**, and the reaction is known as **polymerisation**.

$$\underset{\text{monomer}}{n\,A} \rightarrow \underset{\text{polymer}}{-A-A-A-A-A-A-A-A-A-A-A-} \quad \text{or} \quad [\,A\,]_n$$

The section (–A–) is called the **repeat unit** of the polymer.

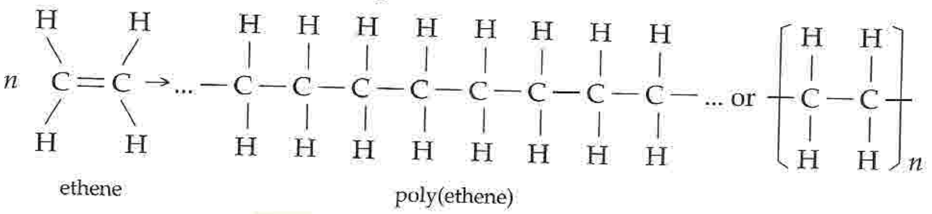
- If two types of monomers are used, a **copolymer** is produced:

$$nA + nB \rightarrow -A-B-A-B-A-B-A-B-A-B-A-B- \quad \text{or} \quad [\,A-B\,]_n$$

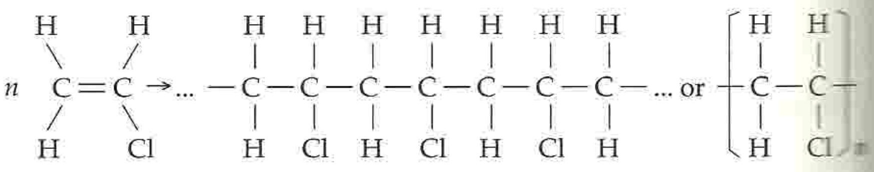
- The section (–A–B–) is the repeat unit of the copolymer.
- The number of monomers, n, in a polymer molecule is variable. It is usually a big number (> 1000). In practice, a sample of a polymer consists of a mixture of molecules with different values of n.
- There are two main types of polymerisation:
  (i) addition polymerisation (of monomers containing C=C bonds);
  (ii) condensation polymerisation (of monomers which are alcohols and acids or amines and acids). See *Polyesters* in Chapter 22 and *Nylons* in Chapter 23.

Addition Polymerisation

- Addition polymerisation occurs when the monomer molecules join together to form *one* product molecule.
- Most addition polymers are obtained by the polymerisation of compounds containing a C=C bond. In the polymerisation, the C=C bonds open so that the monomer molecules can join together.
- Examples of addition polymers
  (a) **poly(ethene)**, also known as *polythene*
  Use: plastic bags

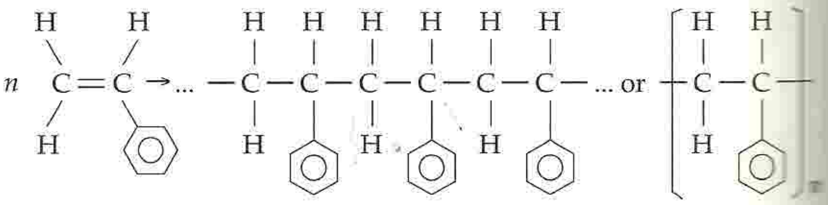


(b) **poly(chloroethene)**, also called *PVC*
Use: waterproof plastic sheet, electrical insulation tape



chloroethene poly(chloroethene)

(c) **poly(phenylethene)**, also known as *polystyrene*
Use: expanded polystyrene for packaging and heat insulati



phenylethene poly(phenylethene)

- An addition polymer has the *same empirical formula* as the monomer.

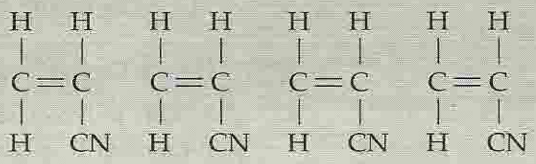
NOTE : You will learn more about polymer in Chapter 26

Question

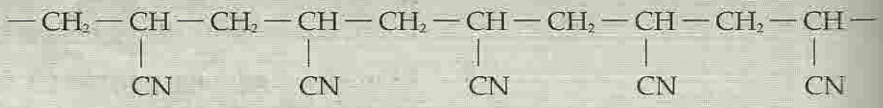
Write down the polymer formed by addition polymerisation of $CH_2{=}CH{-}CN$. What is the repeat unit of this polymer?

Answer

Write down several monomer molecules, as shown below:

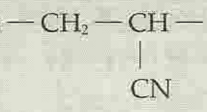


Then open the double bonds to join the monomer molecules together:



$$-CH_2-\underset{\underset{CN}{|}}{CH}-CH_2-\underset{\underset{CN}{|}}{CH}-CH_2-\underset{\underset{CN}{|}}{CH}-CH_2-\underset{\underset{CN}{|}}{CH}-CH_2-\underset{\underset{CN}{|}}{CH}-$$

The repeat unit is



$$-CH_2-\underset{\underset{CN}{|}}{CH}-$$

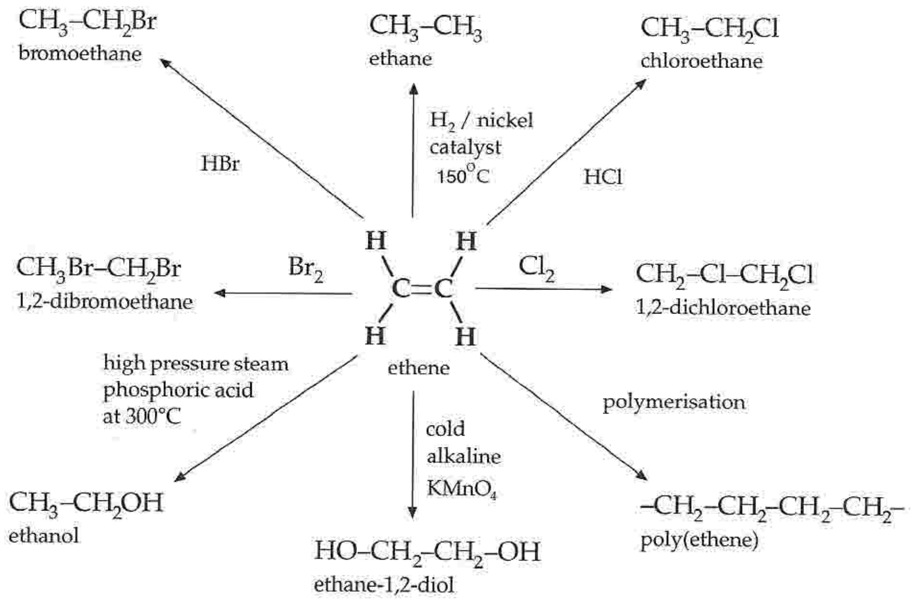
Pollution problems of poly(alkenes)

- Poly(alkenes) such as polythene plastic bags are **non-biodegradable**. This means they are not decomposed by bacteria in the ground. Hence, discarded plastic materials pollute the ground and water.
- Poly(alkenes) can be destroyed by burning. For example, poly(ethene) burns to form carbon dioxide and water — if combustion is complete.
- Combustion of some poly(alkenes) can cause pollution of the air. Some examples are:
  (a) Incomplete combustion can produce poisonous carbon monoxide, CO.
  (b) Poly(phenylethene) produces large amounts of soot and poisonous hydrocarbons such as benzene when the combustion is incomplete.
  (c) Poly(chloroalkanes) such as PVC produce hydrogen chloride gas, HCl. HCl is poisonous and adds acidity to the soil.
  (d) Some plastics containing the —CN group produce deadly poisonous hydrogen cyanide gas, HCN. HCN, like CO, poisons people by reacting with haemoglobin in the blood.

Tests for Alkenes

- Shake the compound with a solution of bromine in CCl_4. Alkenes rapidly decolourise the bromine.
- Shake the compound with a cold and dilute alkaline or acidified solution of potassium manganate(VII), $KMnO_4$. The purple colour of the $KMnO_4$ disappears (the $KMnO_4$ may turn green and then brown).

Summary of Reactions of Ethene



Cyclohexane and Cyclohexene

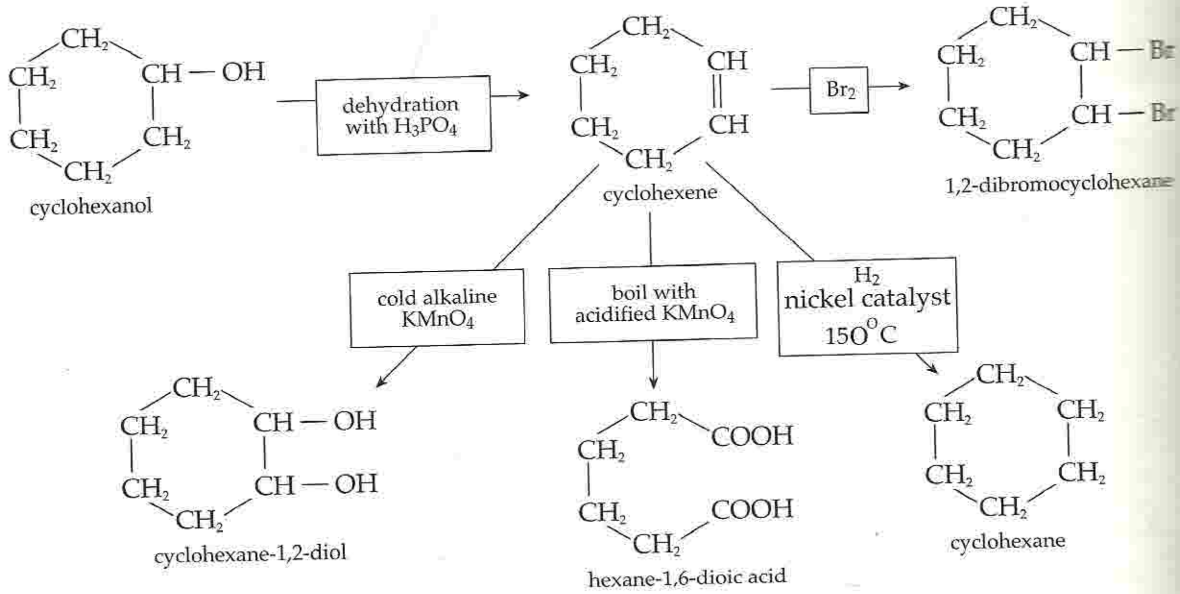
- Cyclohexane has the molecular formula C_6H_{12}. The structural formula of cyclohexane is

Although cyclohexane does not have the formula of an alkane, it behaves chemically like alkanes. For example, it reacts slowly with bromine in the presence of sunlight, in a substitution reaction:

$$C_6H_{12} + Br_2 \rightarrow C_6H_{11}Br + HBr$$

- Cyclohexene has the molecular formula C_6H_{10}. The structural formula of cyclohexene is

Cyclohexene undergoes the chemical reactions of alkenes — because of the C=C bond. Fig 18.1 shows some reactions of cyclohexene.

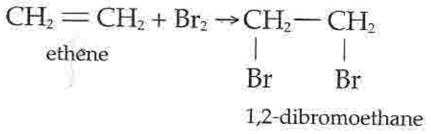


▲ Fig 18.1 Reactions of cyclohexene

$HOOC + CH_2 +_4 COOH$

18.4 Mechanism for Electrophilic Addition in Alkenes

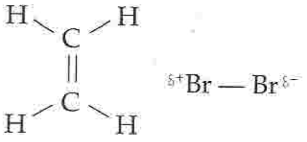
- An **addition reaction** is an organic reaction in which two or more molecules combine together to form a *single* molecule as the only product.
- Ethene reacts with bromine by an addition reaction. The equation for the reaction is



$$CH_2 = CH_2 + Br_2 \rightarrow \underset{Br}{CH_2} - \underset{Br}{CH_2}$$

- This reaction is an example of an **electrophilic addition**. The Br_2 molecule is an **electrophile**.

  An electrophile is a particle that is attracted to electrons. In ethene, the electrons in the double bond attract the electrophile. In this reaction, the electrophile is the Br_2 molecule.
- The electrons in the C=C bond repel electrons in the Br_2 molecule. The Br_2 molecule becomes polarised:

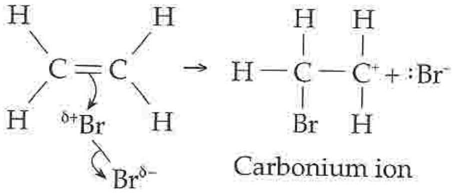


The δ+ end of the Br_2 molecule is attracted to the C=C bond electrons.

Important note:

The arrows drawn in reaction mechanisms show the *movement of electrons* and not the physical movement of atoms, molecules or ions.

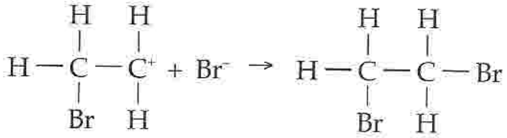
- A two-step reaction takes place.
  (a) The Br_2 molecule becomes polarised and the $^{\delta+}Br$ atom attaches itself onto one of the C atoms:



step 1

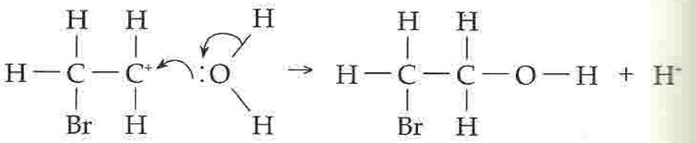
In this step, the covalent Br—Br bond undergoes heterolytic fission.

(b) The $CH_2Br—CH_2^+$ then reacts with the Br^- ion:



step 2

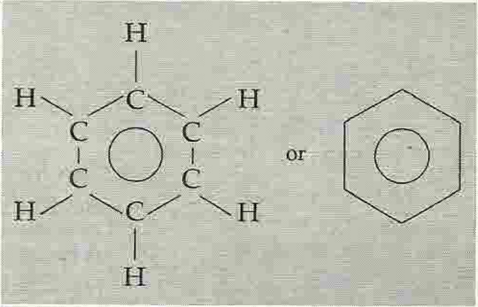
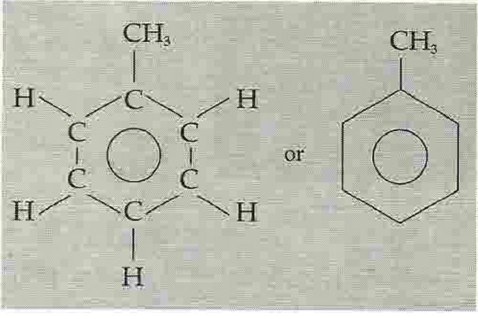
- If ethene is mixed with an aqueous solution of bromine, Br_2(a the main product is $CH_2Br—CH_2OH$. In this case, the $CH_2Br—CH_2^+$ reacts with H_2O:



This shows that the $CH_2Br—CH_2^+$ ion is first formed in the addition reaction.

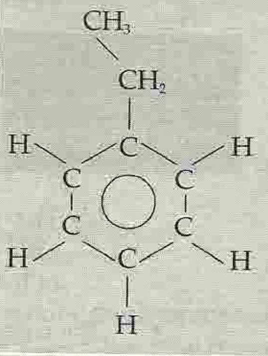
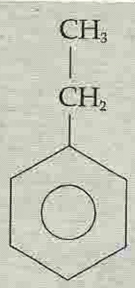
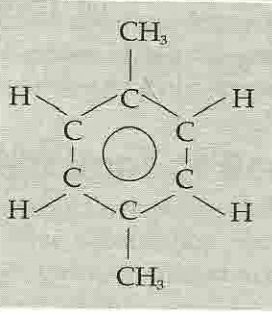
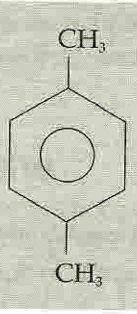
18.5 Arenes (Aromatic Hydrocarbons)

- Arenes are hydrocarbons containing a benzene ring. Some examples of arenes are shown in Table 18.3.

compound	molecular formula	structural formula	b.p./°C
benzene	C_6H_6		80
methylbenzene	$C_6H_5—CH_3$		111

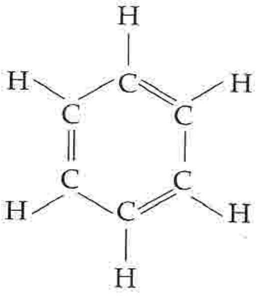
▲ Table 18.3 Examples of arenes

(conti

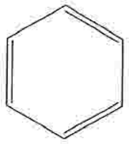
compound	molecular formula	structural formula	b.p./°C
ethylbenzene	$C_6H_5-C_2H_5$	 or 	136
1,4-dimethylbenzene	$CH_3-C_6H_4-CH_3$	 or 	138

Structure of Benzene

- Benzene is a liquid hydrocarbon with the molecular formula C_6H_6.
- From its molecular formula, benzene would be expected to have several C=C bonds. One possible structural formula for benzene is



or written simply as



This formula is known as the **Kekule structure of benzene**.

- The Kekule formula of benzene is not correct for the following reasons.
  - (a) Benzene does not react with $KMnO_4$ (hence it cannot contain C=C bonds).
  - (b) Benzene does not react directly with bromine (hence it cannot contain C=C bonds).

    Benzene only reacts with bromine in the presence of a catalyst such as iron. In this reaction benzene undergoes substitution (not addition):

$$C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$$

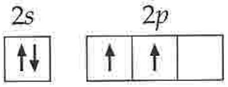
(c) The bond lengths for C—C and C=C are different. However, all the carbon—carbon bond lengths in benzene are the same, and half-way between the length of a single bond and the length of a double bond:

type of bond	C—C	C=C	carbon-carbon bond in benzene
bond length/nm	0.154	0.134	0.139

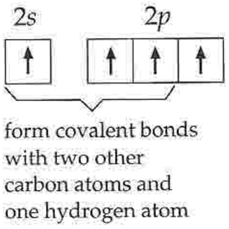
(d) The enthalpy change of hydrogenation of benzene is -207 kJ mol^{-1}. If benzene had three C=C, the enthalpy change of hydrogenation should be about -360 kJ mol^{-1}.

- The correct structure of benzene is as follows:

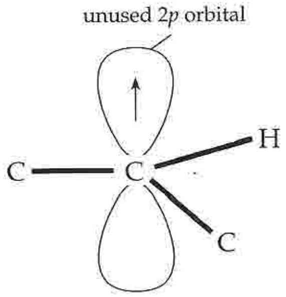
(a) The outer electronic configuration of each carbon atom is



One electron from the 2s orbital is promoted into the empty 2p orbital:

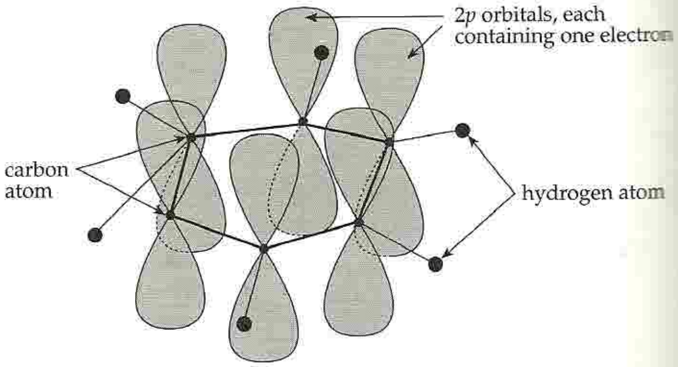


(b) Three of the orbitals and electrons of each carbon atom form covalent bonds with two other carbon atoms and one hydrogen atom, leaving one 2p orbital unused (Fig 18.2).



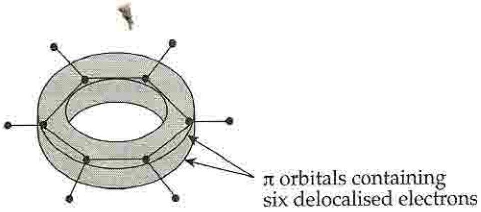
▲ Fig 18.2

(c) Six carbon atoms are joined in a ring, as shown in Fig 18.3.



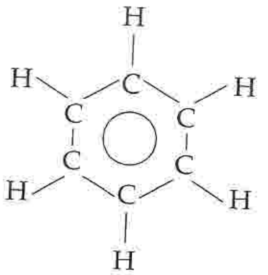
▶ Fig 18.3

(d) The six unused 2p orbitals (one from each carbon atom) overlap to form one large orbital. This orbital consists of two rings, above and below the carbon atoms, and contains six electrons (Fig 18.4). The six electrons are free to move throughout the rings and are thus delocalised. This orbital is called a π orbital.



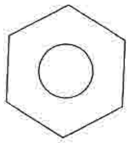
▲ Fig 18.4

(e) The structural formula of benzene is drawn as



full structural formula of benzene

or



shorthand structure of benzene

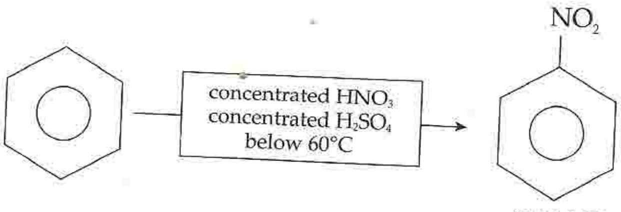
- The delocalised ring of electrons makes benzene very stable. For this reason, although benzene is unsaturated, it does not readily undergo addition reactions. Instead, benzene mainly undergoes substitution reactions of its hydrogen atoms because this does not affect the delocalised ring of electrons.

Chemical Reactions of Benzene

- Benzene undergoes *electrophilic substitution* reactions with several reagents. In these substitution reactions, one of the hydrogen atoms is replaced with another atom or group of atoms (see Section 18.6 for the mechanism).

  After substitution of one hydrogen atom, other hydrogen atoms can be replaced — though this is more difficult.

  (a) **Nitration of benzene** (reaction with nitric acid)
  Benzene reacts with a mixture of concentrated nitric and sulphuric acids to produce nitrobenzene. The temperature of the reaction mixture must be kept below 60°C (at higher temperatures, large amounts of dinitrobenzene are produced).



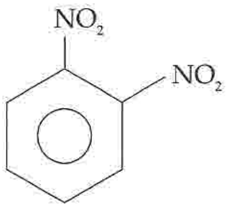
$C_6H_5NO_2$
nitrobenzene

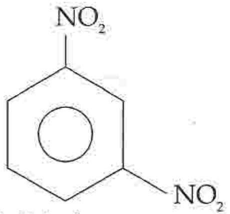
The balanced equation for this reaction is

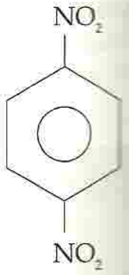
$$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$$

The mechanism of this reaction is described in the next section.

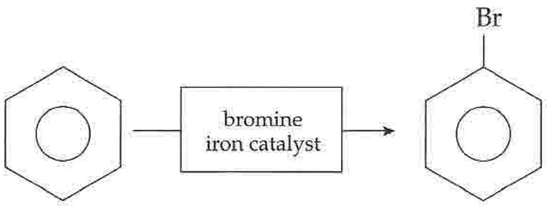
Above 60°C, nitrobenzene reacts with more concentrated nitric acid to produce dinitrobenzene, $C_6H_4(NO_2)_2$. A mixture of three isomers is produced (the mixture is mainly 1,3-dinitrobenzene):


1,2-dinitrobenzene


1,3-dinitrobenzene
(main product)


1,4-dinitrobenzene

(b) **Reaction with bromine**
Benzene reacts with bromine in the presence of a catalyst. The catalyst can be iron powder or anhydrous aluminium bromine, $AlBr_3$:

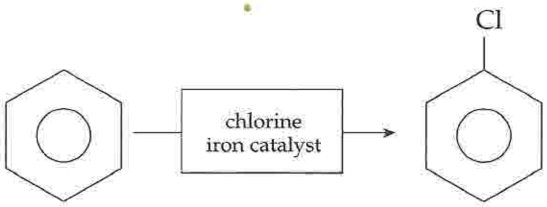


C_6H_5Br
bromobenzene

The balanced equation for the reaction is

$$C_6H_6 + Br_2 \rightarrow C_6H_5Br + HBr$$

(c) **Reaction with chlorine**
Benzene reacts with chlorine in the presence of a catalyst. The catalyst can be iron powder, iron(III) chloride or anhydrous aluminium chloride, $AlCl_3$:



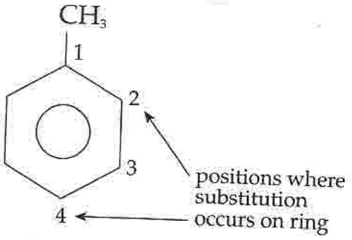
C_6H_5Cl
chlorobenzene

The balanced equation for the reaction is

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$$

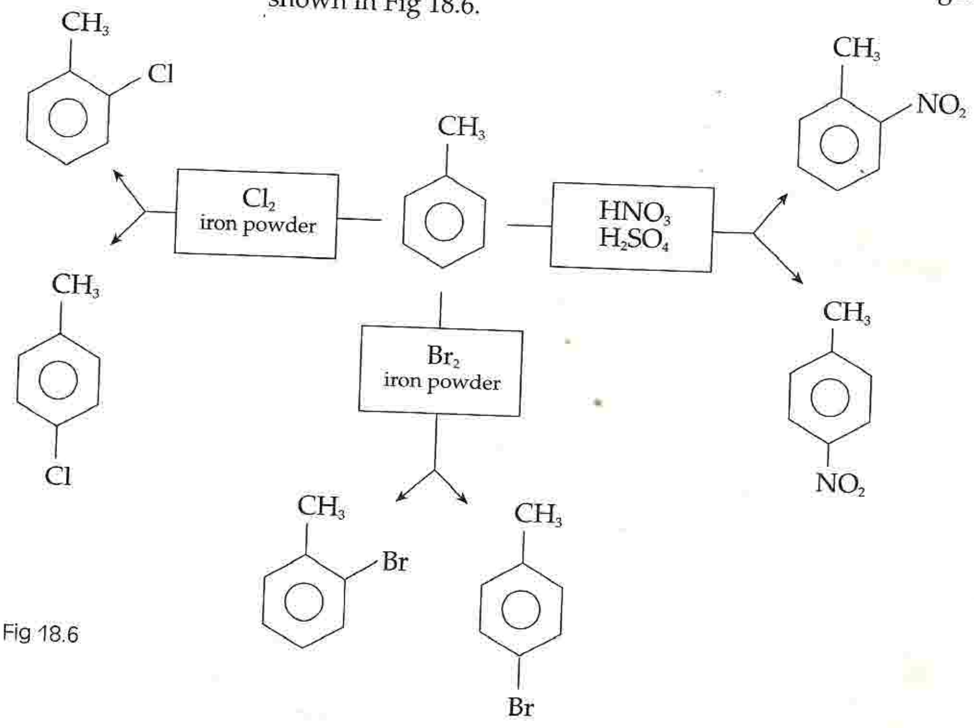
- Under the right conditions, benzene reacts with hydrogen and nickel catalyst to produce cyclohexane. This is an *addition* reaction.

Reactions of Methylbenzene



▶ Fig 18.5

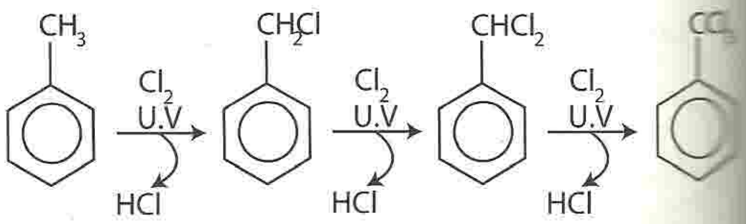
- Methylbenzene has two sets of reactions:
  (i) substitution reactions of the benzene ring (like the reactions of benzene);
  (ii) reactions of the —CH$_3$ group.
  (a) **Reactions of the benzene ring**
  The benzene ring undergoes substitution reactions. Methylbenzene is more reactive than benzene because the —CH$_3$ group is electron repelling. Thus the π electrons is intensified. The —CH$_3$ group makes the substitution take place at the '2' and '4' positions on the benzene ring (Fig 18.5), so that approximately equal quantities of two isomers are produced. A summary of the reactions of the benzene ring is shown in Fig 18.6.



▶ Fig 18.6

(b) **Reactions of the —CH$_3$ group**

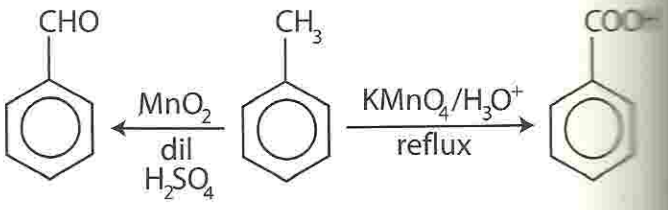
(i) Chlorine reacts with the —CH$_3$ group in the presence of ultraviolet light. A substitution reaction occurs by a free radical mechanism. The actual product depends on how long the chlorine is bubbled through the liquid methylbenzene.



▶ Fig 18.7

Note that the reaction of methylbenzene with chlori depends on the conditions. In the presence of iro substitution takes place in the benzene ring; in th presence of light, substitution takes place in the meth group.

(ii) The —CH_3 group can be *oxidised* to —COOH by reflux the methylbenzene with acidified $KMnO_4$ for sever hours.

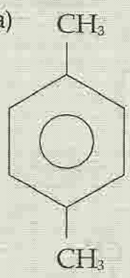


Any carbon group on a benzene ring is oxidised —COOH by refluxing with acidified .

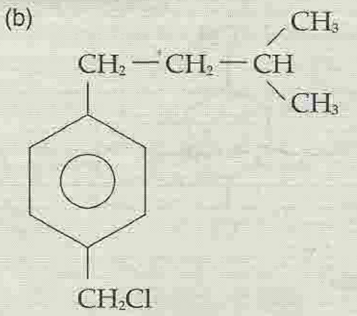
Question

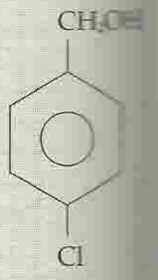
Write down the formulae of the organic products when the following compounds are boiled with potassium manganate(VII) for some time:

(a)



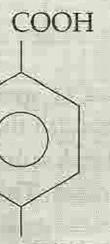
(b)



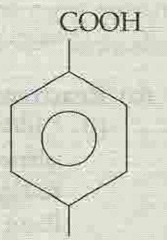


Answer

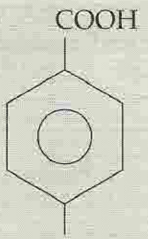
(a)



(b)



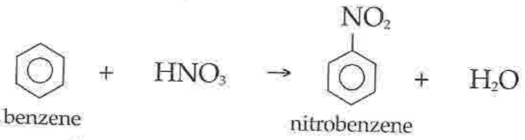
(c)



(chlorine atom on ring does not react)

18.6 Mechanism for Nitration of Benzene

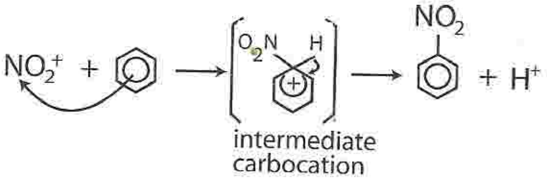
- Benzene undergoes many **electrophilic substitution** reactions. The six delocalised electrons of the benzene ring attract electrophiles.
- Benzene reacts with nitric acid to produce nitrobenzene. The equation for the reaction is



- To make nitrobenzene, the benzene is reacted with a mixture of concentrated sulphuric acid and concentrated nitric acid. The two acids react together to produce NO_2^+:

$$2H_2SO_4 + HNO_3 \rightarrow 2HSO_4^- + H_3O^+ + NO_2^+$$

- The NO_2^+ is the electrophile. It is attracted to the benzene ring by the ring of delocalised electrons. The NO_2^+ displaces a hydrogen atom:



EXERCISE 18

Multiple Choice Questions

Section I

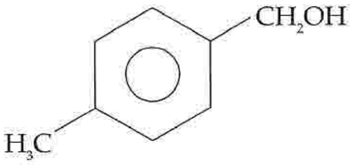
1 What is the electrophile in the nitration of benzene?

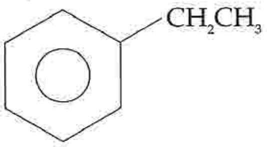
A NO_3^- C NO_2^-
B NO_3^+ D NO_2^+

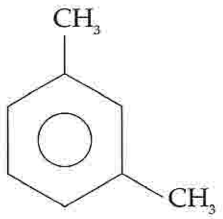
2 What is the *initiation* step in the reaction of chlorine with methane in the presence of light?

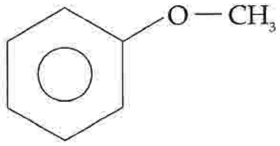
A $CH_4 \rightarrow CH_3\cdot + H\cdot$
B $CH_4 \rightarrow CH_3^- + H\cdot$
C $Cl_2 \rightarrow Cl^+ + Cl^-$
D $Cl_2 \rightarrow 2Cl\cdot$

3 Which one of the following compounds will react with potassium manganate(VII) to produce benzoic acid?

A


B


C


D


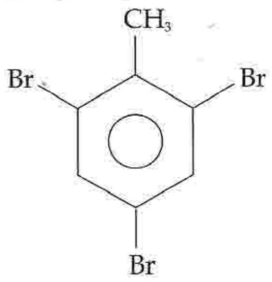
4 Which one of the following statements about the length of the carbon—carbon bonds in benzene is true?

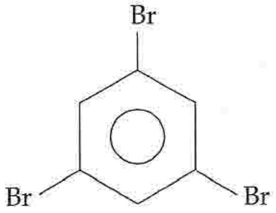
A The bond length is longer than the length of the carbon—carbon bond in ethane.
B The bond length is longer than the length of the carbon—carbon bond in ethene.
C The bond length is longer than the length of the carbon—carbon bond in diamond.
D Three of the bonds have the same length as the C—C bond in ethane, and the other three have the same length as the C=C bond in ethene.

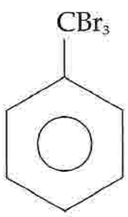
5 How many dichlorobenzene, $C_6H_4Cl_2$, isomers exist?

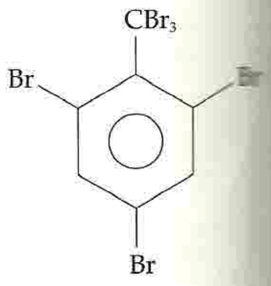
A 2 C 4
B 3 D 5

6 Methylbenzene and excess bromine were heated together in complete darkness, in the presence of a little iron powder. Which one of the following compounds is likely to be the final organic product?

A


B


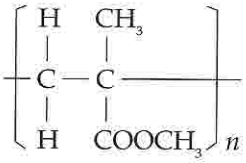
C


D


What is produced in the polymerisation of propene, C_3H_6?

A a fuel **C** a plastic
B a solvent **D** an explosive

Perspex has the formula



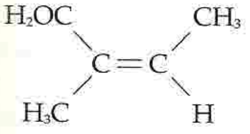
$$\left[\begin{array}{cc} H & CH_3 \\ | & | \\ -C- & C- \\ | & | \\ H & COOCH_3 \end{array}\right]_n$$

What is the monomer?

A $CH_2{=}C(CH_3)CO_2CH_3$
B $CH_2{=}CH{-}CO_2CH_3$
C

$CH_3{-}\underset{\displaystyle CO_2CH_3}{\underset{|}{CH}}{-}CH_3$

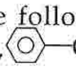
D



Section II

Summary of directions

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

Which of the following statements about phenylethene, —$CH{=}CH_2$ are likely to be true?

1 Phenylethene will undergo an addition reaction with bromine.
2 Phenylethene can be oxidised to benzoic acid, C_6H_5COOH, by potassium manganate(VII).
3 Phenylethene will undergo a substitution reaction with chlorine in the presence of iron(III) chloride.

Which of the following hydrocarbons can undergo a substitution reaction with chlorine under suitable conditions?

1 methylbenzene
2 benzene
3 hexane

11 Which statements about the benzene molecule are true?

1 The benzene molecule contains six delocalised electrons.
2 All the carbon—carbon bonds in a benzene molecule are identical.
3 The benzene molecule is planar in shape.

12 Which of the following pollutants in motor car exhaust gases are the products of incomplete combustion of fuel?

1 carbon monoxide
2 nitrogen oxides
3 lead(II) bromide

13 The effect of sunlight on chlorine molecules in the reaction of chlorine with methane is

1 an example of homolytic fission.
2 an example of radical formation.
3 an initiation reaction.

14 Which of the following are the same for ethene and polyethene?

1 empirical formula
2 relative molecular mass
3 chemical reactivity

Structured Questions

1 Show clearly in an equation *one* example of *each* of the following processes. Choose a different example for each case.

(a) heterolytic fission
(b) free radical formation
(c) electrophilic substitution
(d) homolytic fission

*2 The mechanism for the reaction of bromine with ethane to make bromoethane, is shown below.

$Br_2 \rightarrow 2Br$ step 1
$Br + C_2H_6 \rightarrow C_2H_5 + HBr$ step 2
$C_2H_5 + Br_2 \rightarrow C_2H_5Br + Br$ step 3

(a) Write a balanced equation for the overall reaction.
(b) (i) What do you mean by *free radical*?
 (ii) Write 'dot cross' diagrams for the radicals shown in the equations above.
(c) How might step 1 in the mechanism be brought about?
(d) Write an equation for a possible termination step in the reaction.

(e) What is the formula of the *final* organic product, if ethane reacts with a very large excess of bromine?

(f) The products of the reaction include two isomers each containing 89.89% bromine. Write the chemical names and displayed formulae of the isomers.

3 1,3-dinitrobenzene is made by reacting benzene with a mixture of concentrated nitric and sulphuric acids.

(a) (i) Write a balanced equation for the reaction of benzene with nitric acid.
  (ii) What are the conditions for this reaction?
  (iii) What *type* of mechanism is involved in this reaction?

(b) (i) Write an equation to show the purpose of the sulphuric acid.
  (ii) What particle reacts with the benzene ring? What *type* of particle is it?

(c) Write the structural formulae of two isomers of 1,3-dinitrobenzene.

4 Petrol for motor cars consists mainly of a $C_7 - C_{10}$ mixture of alkanes.

(a) (i) Write the molecular formula of a C_8 hydrocarbon in petrol.
  (ii) Write the full structural formula of a branched chain isomer of the hydrocarbon in (i) above.
  (iii) Write a balanced equation for the complete combustion of this isomer in air.
  (iv) Write the formula of a radical produced from the lead tetraethyl.

(b) The typical composition of the exhaust gases from a motor car is given below.

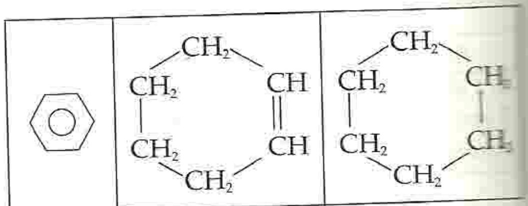
substance	*percentage*
argon	0.5
carbon dioxide	8
carbon monoxide	5
hydrocarbons	0.3
hydrogen	2
lead(II) bromide	0.001
nitrogen oxides	0.2
oxygen	4.5
water vapour	9

  (i) The total percentage of the exhaust gases does not equal 100%. What is the main component of the exhaust gas?
  (ii) Which three gases in the table are the products of incomplete combustion of petrol?
  (iii) Suggest an explanation for the incomplete combustion, despite the presence of unreacted oxygen.
  (iv) Name *two* of the most serious air pollutants in the exhaust gases and briefly outline the harmful effects of each one.

5 (a) Draw the repeat units of (i) poly(propene) and (ii) poly(chloroethene) or PVC.

(b) (i) Explain briefly why there is a problem in the waste disposal of polymers such as poly(propene) and poly(chloroethene).
  (ii) Write a word equation for a chemical reaction that shows one way of disposing of poly(propene).
  (iii) Suggest *one* problem that could be caused by disposing of poly(chloroethene) by the same method.

6

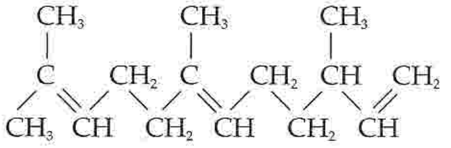


(a) Each of the three compounds above reacts with bromine in one of the following types of reaction:
  (i) electrophilic addition;
  (ii) electrophilic substitution;
  (iii) nucleophilic substitution and
  (iv) free radical chain reaction.

Name the type of reaction for each of the compounds.

(b) (i) Which one of the three compounds above reacts most rapidly with bromine?
  (ii) Each of the other two compounds requires one important condition or additional substance for the reaction to take place. State what these conditions/additional substances are.

*7 Apple skins produce farnesene which attracts the larva of the moth, *Laspeyresia pomenella*. The structure of farnesene is



(a) (i) Write the structural formula of the product when farnesene is reacted with excess bromine.

(ii) Circle the chiral centres in this product.

(b) 0.2 mole of farnesene was reacted with excess hydrogen gas in the presence of finely divided nickel.

(i) What is the increase in mass of the farnesene?

(ii) What volume of hydrogen, measured at s.t.p. is absorbed by the farnesene?

A gaseous mixture of 20.0 cm^3 of a hydrocarbon and 100.0 cm^3 of oxygen, an excess, is exploded. When the gaseous mixture is brought to room temperature, it occupies 70.0 cm^3. The mixture is then passed through aqueous sodium hydroxide and its volume is reduced by 60.0 cm^3.

(a) Calculate the formula of the hydrocarbons.

(b) Draw the display formula of the hydrocarbon.

(c) How can this hydrocarbon be prepared in the laboratory ?

(d) (i) What type of polymerisation it undergoes ?

(ii) Draw the polymer with three repeated units.

(iii) Give one use of the polymer.

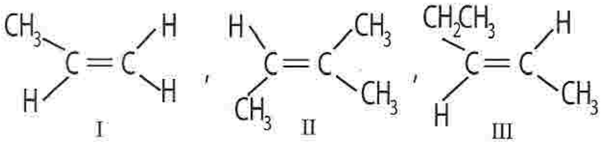
When ethene is passed into aqueous chlorine containing sodium bromide dissolved in, the productions are 1,.2-dichlroethane, 2-chloroethanol and 1-bromo, 2-chloroethane but never 1,2-dibromoethane.

(a) Write a balanced equations to show the formation of the products.

(b) What is the mechanism of the reaction ?

(c) Use the mechanism to account why 1,2 dibromoethane is not formed.

10. (a) Consider the following alkenes.



Which structure(s) show geometrical isomerism. Where the full structures of the isomers.

b. Give the names, the structural formulae of their products and write balanced equation for each of the following reaction of the above alkenes with :

(i) steam

(ii) hydrogen bromide

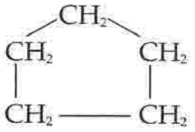
(iii) cold dilute acidified $KMnO_4$

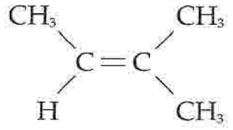
(iv) hot concentrated acidified $KMnO_4$

Descriptive Questions

1 Four isomeric alkenes have the molecular formula C_5H_{10}.

The structural formulae of two of these isomers, **W** and **X**, are





(a) The other two isomers, **Y** and **Z**, are cis-trans isomers. Identify these isomers and draw their structural formulae. Explain the feature of their molecules that results in this type of isomerism.

(b) Isomers **W** and **X** both react with bromine. The reaction of **W** is slow and that of **X** is rapid. For each reaction, give

(i) the type of mechanism involved;

(ii) the formula of the initial intermediate particle formed by **W** and **X** in the mechanism;

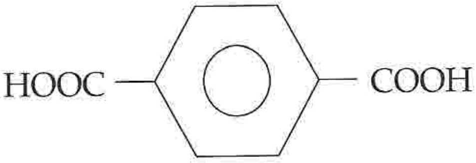
(iii) the structural formula of one product of the reaction.

(c) Isomers **Y** and **Z** react with bromine to give the same product. Draw the structural formula of this product and label any chiral centres with an asterisk (*).

2 Show how the following reactions could be carried out in the laboratory by naming the reagents and important conditions required in each case.

reaction

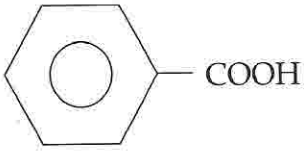
(a) propene into propane-1,2-diol
(b) benzene into nitrobenzene
(c) cyclohexane into chlorocyclohexane
(d) methylbenzene into $C_6H_5CCl_3$
(e) 1,4-dimethylbenzene into



*3 Liquid hydrocarbon **P** contains 90.91% carbon by mass. At 450 K and 100 kPa, 1.0g of vapourised **P** has a volume of 283 cm^3.

(a) Calculate the relative molecular mass of **P** and find its molecular formula.

(b) When **P** is refluxed with acidified potassium manganate(VII), a mixture of two carboxylic acids is obtained. One acid has the structural formula



Find the formula of the other acid and write the structural formula of **P**.

(c) Write the structural formula of a hydrocarbon isomeric with **P**, which has a chiral centre. Label the chiral centre with an asterisk (*).

4. The main source of hydrocarbon is crude oil.

(a) What is the origin of crude oil ?

(b) How do the constituents of crude oil show that "like dissolves" ?

(c) (i) Why is it not possible to use crude oil directly ?
(ii) What is the process used to separate the constituents of crude oil ?

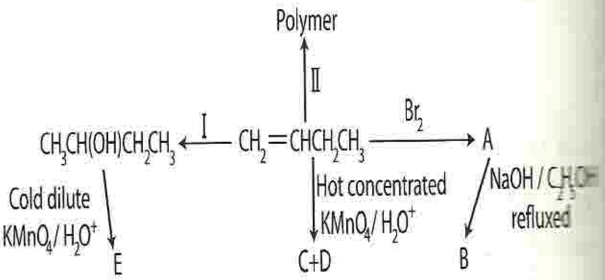
(d) (i) What is the process used to manufacture smaller molecules from the fractions of crude oil. Give the conditions of the process.
(ii) Write an equation to show three products obtained by the cracking of $C_{13}H_{28}$.
(i) Which product will immediately decolorise bromine ?
(ii) Describe using equations, the mechanism of the reaction.

5. (a) The enthalpy change of hydrogenation of cyclohexene, $\Delta H^{\ominus}$ = - 120 kJ mol-1.

(i) What is the enthalpy change of a cyclic triene, $\Delta H^{\ominus}$?
(ii) The enthalpy change of hydrogenation of benzene is -208 KJ mol^{-1}. Explain this discrepancy though both cyclic triene and benzene have the same formula, C_6H_6.

(b) (i) Give reagents conditions to convert benzene to methylbenzene.
(ii) Name the mechanism of the reaction.
(iii) Describe, with equations, essential reagents and conditions, the mechanism of the nitration of benzene.

6. Some reactions of butene are shown in the scheme below.



(a) (i) Name the type of reaction involved in I and II.
(ii) What type of mechanism occurs to produce B from A ?

(b) (i) Write the display formulae for the following compounds :
A, B, C, D and E.

(ii) Write the formula of the polymer showing two repeated units.

(c) When butene reacts with hydrogen-chloride, two products are formed.

(i) What are the two products ?
Give their structural formulae.

(ii) Describe the mechanism to show the formation of the two products.

CHAPTER 19

ORGANIC HALOGEN COMPOUNDS

Halogenoalkanes

Mechanism for Nucleophilic Substitution of Halogenoalkanes

Halogenoarenes

SYLLABUS OBJECTIVES

In this chapter you should be able to:

- interpret and use the chemical names, general formulae and displayed formulae of halogenoalkanes and halogenoarenes
- recall the chemistry of halogenoalkanes, exemplified by the following nucleophilic substitution reactions of bromoethane:
  - hydrolysis
  - formation of nitriles
  - formation of primary amines by reaction with ammonia
- recall the elimination of hydrogen bromide from halogenoalkanes
- describe the mechanism of S_N1 and S_N2 nucleophilic substitution in halogenoalkanes
- explain the different reactivities of halogenoalkanes and chlorobenzene with reference to hydrolysis and the relative strengths of the carbon-halogen bonds
- explain the uses of fluoroalkanes and fluorohalogenoalkanes in terms of their relative inertness
- have knowledge about the possible effect of chlorofluoroalkanes (CFCs) on the ozone layer

19.1 Halogenoalkanes

There are three types of organic halogen compounds:

(a) **halogenoalkanes** (an alkane with one or more hydrogen atoms replaced with halogen atoms), eg bromoethane CH_3—CH_2—Br;

(b) **halogenoarenes** with a halogen atom on the benzene ring, eg chlorobenzene C_6H_5—Cl;

(c) **acyl chlorides**, containing the —CO—Cl group of atoms, eg ethanoyl chloride CH_3—CO—Cl.
(See Chapter 22 for properties of acyl chlorides)

Each of these compounds have the formula of an alkane with one or more hydrogen atoms substituted with a halogen atom. Some examples of these compounds are given in Table 19.1.

compound	formula	b.p./°C
chloromethane	CH_3Cl	–24
chloroethane	CH_3CH_2Cl	12
bromoethane	CH_3CH_2Br	38
iodoethane	CH_3CH_2I	72
1-bromobutane	$CH_3CH_2CH_2CH_2Br$	102
trichloromethane	$CHCl_3$	61
tetrachloromethane	CCl_4	77

▶ Table 19.1 Examples of halogenoalkanes

Chemical Reactions

- Halogenoalkanes undergo *nucleophilic substitution* reactions with several reagents (see section 19.2 for the mechanism). In the reactions, the halogen atom is replaced with some other group of atoms.

  These reactions apply to chloro-, bromo- or iodo-compounds. They do not apply to fluoro-compounds. The order of reactivity is:

  iodo > bromo > chloro

  This is due to the size of the halogen atom. The bigger the atom, the weaker the halogen—carbon bond. Hence it is easier to break the bond making the compound more reactive (Table 19.2).

bond	bond energy /kJ mol^{-1}
C—Cl	338
C—Br	276
C—I	238

Table 19.2 Bond energies of carbon—halogen bonds

- Halogenoalkanes with *all* the hydrogen atoms replaced with halogen atoms (eg CCl_4) are chemically unreactive.

  (a) **Hydrolysis**

  Hydrolysis is the reaction with water. Some halogen compounds react rapidly with water. However, hydrolysis is usually carried out by boiling the halogen compound with aqueous sodium hydroxide. In the reaction, the halogen atom is replaced with —OH, producing an alcohol.

eg: $$\underset{\text{chloroethane}}{CH_3—CH_2—Cl} + NaOH \rightarrow \underset{\text{ethanol}}{CH_3—CH_2—OH} + NaCl$$

eg: $$\underset{\text{1-bromobutane}}{CH_3—CH_2—CH_2—CH_2—Br} + NaOH \rightarrow$$
$$\underset{\text{butan-1-ol}}{CH_3—CH_2—CH_2—CH_2—OH} + NaBr$$

The nucleophile in this reaction is the OH^- ion. The two mechanisms for this reaction are described later in this chapter.

(b) **Reaction with potassium cyanide in alcohol**

When a halogenoalkane is refluxed with potassium cyanide in alcohol, the halogen atom is replaced with a —CN group to produce a nitrile.

eg: $$\underset{\text{iodoethane}}{CH_3—CH_2—I} + KCN \rightarrow \underset{\text{ethane nitrile}}{CH_3—CH_2—CN} + KI$$

eg: $$\underset{\text{1-bromobutane}}{CH_3—CH_2—CH_2—CH_2—Br} + KCN \rightarrow$$

$$\underset{\text{butanenitrile}}{CH_3—CH_2—CH_2—CH_2—CN} + KBr$$

The nucleophile in this reaction is the cyanide ion, CN^-.

This reaction is important because the number of carbon atoms in the product is *increased by one*. The nitrile can then be converted into a carboxylic acid or an amine.

(i) Hydrolysis with boiling dilute acid (H_2SO_4 or HCl) or alkali produces an acid.

eg:
$$CH_3—CH_2—CN + 2H_2O \rightarrow \underset{\text{propanoic acid}}{CH_3—CH_2—COOH} + NH_3$$

If alkali is used, the sodium salt of the acid is obtained. If acid is used, an ammonium salt is obtained instead of NH_3 gas. (See *Carboxylic Acids* in Chapter 22)

(ii) Reduction with lithium aluminium hydride ($LiAlH_4$) produces an amine.

eg:
$$CH_3—CH_2—CH_2—CN—\boxed{LiAlH_4} \rightarrow \underset{\text{butylamine}}{CH_3—CH_2—CH_2—CH_2—NH_2}$$

(See *Amines* in Chapter 23)

(c) **Reaction with ammonia**

When a halogenoalkane is heated with excess concentrated ammonia in a sealed tube, the halogen atom is replaced with an $—NH_2$ group to form an amine.

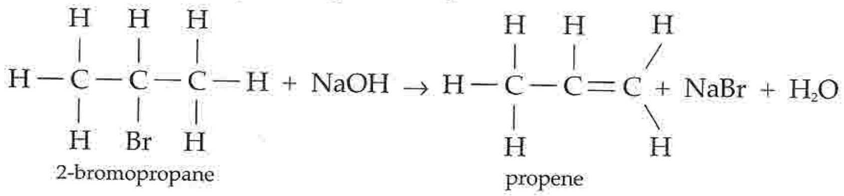
eg: $$\underset{\text{iodoethane}}{CH_3—CH_2—I} + \underset{\text{(excess)}}{NH_3} \rightarrow \underset{\text{ethylamine}}{CH_3—CH_2—NH_2} + HI$$

(reacts with more NH_3 to become NH_4I)

$$\underset{\text{bromopropane}}{CH_3—CH_2—CH_2—Br} + \underset{\text{(excess)}}{NH_3} \rightarrow \underset{\text{propylamine}}{CH_3—CH_2—CH_2—NH_2} + HBr$$

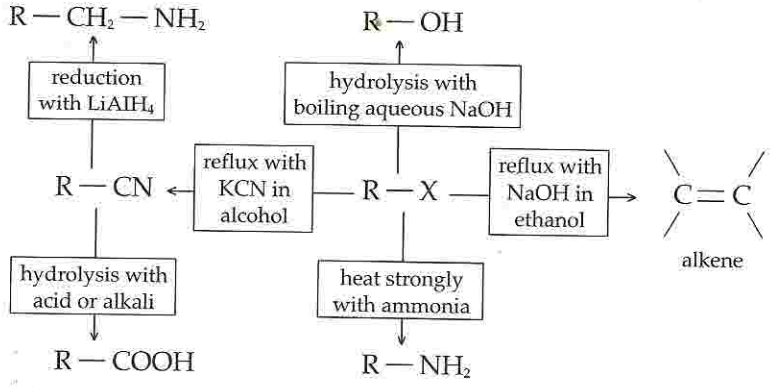
The nucleophile in this reaction is the NH_3 molecule.

- Halogenoalkanes undergo an *elimination* reaction with a boiling solution of sodium hydroxide in ethanol (known as 'ethanolic sodium hydroxide'). In this reaction a HX molecule is removed from the halogen compound to produce a C= C bond.



The reaction gives a very poor yield if the halogen atom is at the end of a carbon chain. For example, 1-bromoethane only gives 1% ethene (other organic compounds are formed instead).

- An elimination is an organic reaction in which a small molecule is removed from an organic compound.
- A summary of the reactions of halogenoalkanes is given in Fig 19.1. (R = alkye group; X = halogen atom, Cl, Br or I)



▶ Fig 19.1

Chloroethene

- Chloroethene has the formula $CH_2=CH—Cl$. It is used as a monomer to produce poly(chloroethene) or *PVC* (see Chapter 18).
- Chloroethene is produced by the elimination of HCl from 1,2-dichloroethane:

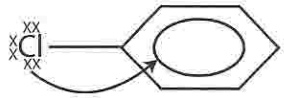
$$Cl—CH_2—CH_2—Cl \rightarrow CH_2=CH—Cl + HCl$$

This reaction is carried out in industry by passing 1,2-dichloroethane vapour over a catalyst at a high temperature. The reaction can be produced in the laboratory by heating the 1,2-dichloroethane with NaOH in alcohol.

Note: The $CH_2=CH—Cl$ product does not react with NaOH.

Tests for Halogen Compounds

- Boil a little of the compound with aqueous sodium hydroxide for a few minutes. Then cool the products. Acidify the products with nitric acid to neutralise any unreacted alkali. Then add silver nitrate solution. A precipitate shows the presence of halogen in the organic compound.



$$R-X \xrightarrow{\boxed{\text{aqueous NaOH}}} R-OH + NaX$$

$$X^-(aq) + Ag^+(aq) \rightarrow AgX(s) \qquad \text{i.e.} \quad \begin{cases} \text{AgCl is white} \\ \text{AgBr is pale yellow} \\ \text{AgI is yellow} \end{cases}$$

This test will *not* work for chlorobenzene because the C-Cl bond is strengthened by delocalisation of a lone pair on the chlorine atom on the π system.

▲ Fig 19.2 Formulae of two CFC's

$$CFCl_3 \quad CF_2Cl_2$$

Uses of Fluoroalkanes and Chlorofluoroalkanes

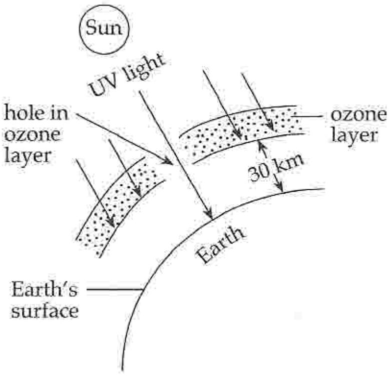
- Fluoroalkanes and chlorofluoroalkanes (commonly called CFCs) have low chemical reactivity and do not burn. One reason for their lack of reactivity is the relatively high strength of the C—F bond (Table 19.3).

▶ Table 19.3 Relative strengths of covalent bonds

bond	bond energy /kJ mol^{-1}
C—F	484
C—H	410
C—C	350
C—Cl	340

- Because of their low reactivity, these compounds are used as coolants in air-conditioners and refrigerators, fire extinguishers, solvents, making foam plastic (such as expanded polystyrene packaging) and as propellants in aerosol spray cans.
- The uses of some of these compounds have been greatly reduced for environmental reasons (see below).

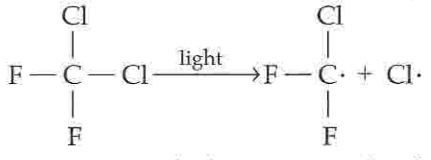
Pollution Problems of Chlorofluoroalkanes (CFCs)



▲ Fig 19.3 The ozone hole over Antarctica

- CFC molecules are chemically inert. They do not react with air or water and are not biodegradable. The molecules rise up high into the atmosphere where they are decomposed by ultraviolet light to produce chlorine atoms.

  A typical reaction is



$$F-\underset{F}{\overset{Cl}{C}}-Cl \xrightarrow{\text{light}} F-\underset{F}{\overset{Cl}{C}}\cdot + Cl\cdot$$

The chlorine atoms react with the ozone molecules (O_3) in the *ozone layer* about 30 kilometres above the Earth's surface. In the reaction, the ozone molecules (O_3) are destroyed:

$$Cl\cdot + O_3 \rightarrow ClO\cdot + O_2$$

- Ozone absorbs harmful ultraviolet radiation from the sun. As a result of the 'ozone hole', dangerous ultraviolet radiation now reaches the surface of Antarctica. There is great concern that the destruction of the ozone layer could spread to other inhabited areas of the world. If this happens, the ultraviolet radiation could cause skin cancer in people and damage vegetation, including crops.

- To protect the ozone layer, many countries have agreed to adopt the following measures:
  (a) to greatly reduce the use of CFCs;
  (b) to find substitutes for CFCs which do not damage the ozone layer. These substitutes either contain no chlorine atoms (eg they are hydrocarbons or are fluorocarbons) or contain hydrogen atoms which make the compound more reactive so that it is naturally destroyed by atmospheric oxygen and water.

19.2 Mechanism for Nucleophilic Substitution of Halogenalkanes

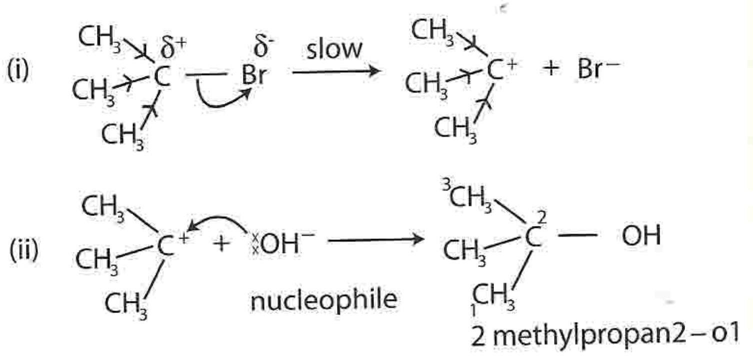
- A **nucleophile** is a particle that is attracted to the positive site of a substance.
  A *nucleophile* has the following properties:
  (a) It has a lone pair of electrons. This lone pair of electrons is used to form a dative bond with the atom that attracts the nucleophile.
  (b) It is a negative ion or a neutral molecule. Nucleophiles cannot be positive particles; they would be repelled by the positive site.
  Some common nucleophiles are OH^-, CN^-, H_2O and NH_3.

- An example of nucleophilic substitution is the reaction of halogenoalkanes with aqueous sodium hydroxide. There are two distinct mechanisms for nucleophilic substitution.

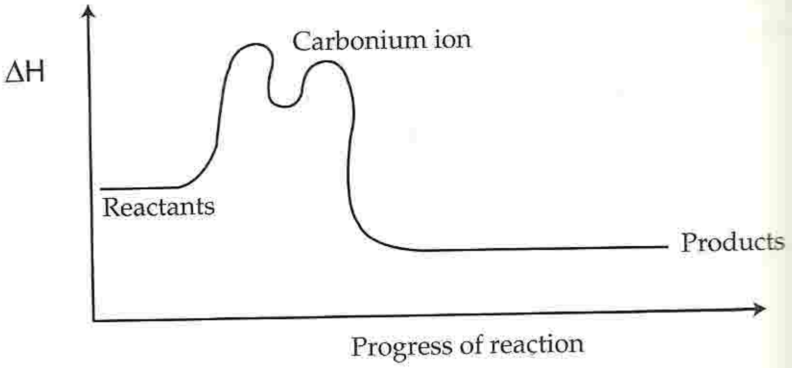
- The first is known as S_N1 (S stands for substitution, N for nucleophilic and 1 for first order / unimolecular. Here the slow rate determining step consists of one molecule only. Tertiary halogenoalkanes react via S_N1 mechanism. A stable tertiary carbocation is formed as the intermediate by heterolytic fission of the carbon – halogen bond. It then combines with the nucleophile to form the product 2-bromo, 2 methylpropan reacts with sodium hydroxide to give 2 methylpropan -2-ol.

$$(CH_3)_3CBr + NaOH \longrightarrow (CH_3)_3COH + NaBr$$

- Mechanism



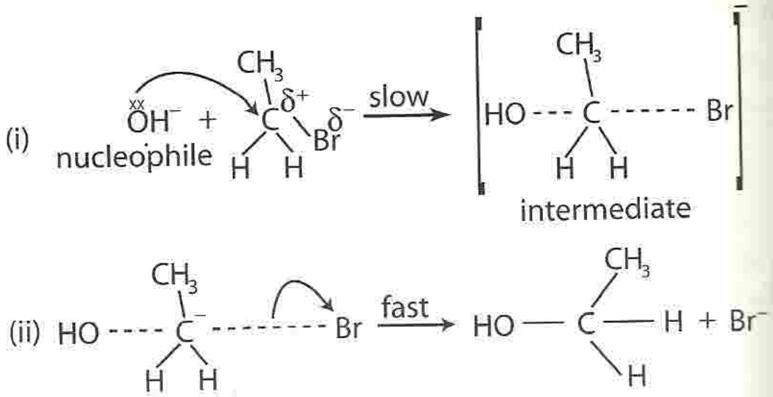
- Energy Profile Diagram



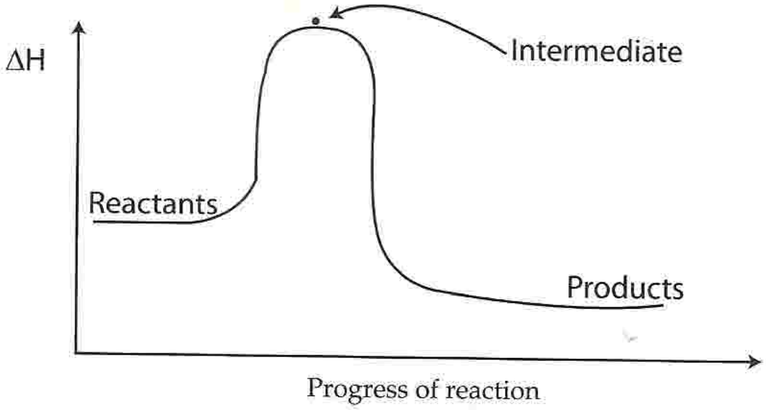
- The second mechanism is S_N2, the 2 means second order / bimolecular. The slow rate determining step consists of two molecules. Primary halogenalkanes react via this type of mechanism. This is because the primary carbocation is relatively unstable such that the intermediate has a partially broken carbon-halogen bond and a partially formed carbon – nucleophile bond. Bromoethane reacts with sodium hydroxide to form ethanol.

$$CH_3CH_2Br + NaOH \longrightarrow CH_3CH_2OH + NaBr$$

- Mechanism



- **Energy Profile Diagram.**

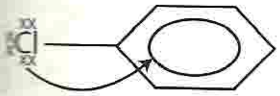


- S_N1 reactions are generally faster than S_N2. Thus, the rate of hydrolysis of halogenoalkanes is tertiary secondary primary.

- Note that secondary halogenoalkanes undergo hydrolysis partly by S_N1 and partly by S_N2 mechanism.

19.3 Halogenoarenes

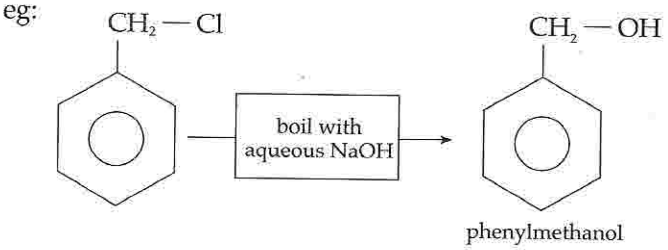
- Halogenoarenes have a halogen atom attached directly to a benzene ring. An example is chlorobenzene (Fig 19.4).
- When the halogen atom is on the benzene ring, it is chemically unreactive because the C—Cl bond is exceptionally strong. This is caused by one of the chlorine lone pairs being drawn into benzene's delocalised ring of electrons.
- The halogen atoms does **not** undergo the usual nucleophilic substitution reactions of halogenalkanes. For example, there is no reaction when chlorobenzene is refluxed with aqueous sodium hydroxide in the laboratory.



▲ Fig 19.4

- The compound $-CH_2CL$ is unlike chlorobenzene. The chlorine atom is not directly attached to the benzene ring. Hence this compound undergoes all the usual nucleophilic substitutions of halogenoalkanes.

eg:



EXERCISE 19

Multiple Choice Questions

Section I

1 Organic compound **X** undergone the following successive reactions:

I reaction with hydrogen chloride
II boiling with aqueous sodium hydroxide
III reaction with hot concentrated phosphoric acid

The final organic product was ethene. Which of the following was most likely to be compound **X**?

A ethene **C** chloroethane
B ethanol **D** ethanoic acid

2 Organic compound **Y** undergone the following successive reactions:

I boiling with potassium cyanide in alcohol
II boiling with dilute sulphuric acid

The final organic product was $CH_3CH_2CH_2COOH$. Which of the following was most likely to be compound **Y**?

A $CH_3CH_2CH_2CH_2I$
B $CH_3CH_2CH_2Br$
C $CH_3CH_2CH{=}CH_2$
D $CH_3CH_2CH_2OH$

3 Organic compound **Z** undergone the following reactions:

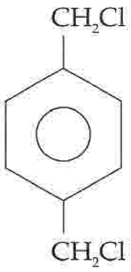
I reaction with bromine
II boiling with potassium cyanide in alcohol
III boiling with sodium hydroxide in water

The final product was $NaOOC—CH_2—CH_2—COONa$. Which of the following was most likely to be compound **Z**?

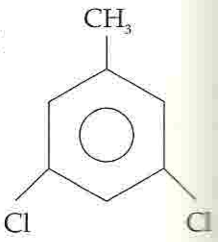
A $CH_3—CH{=}CH—CH_3$
B $CH_2{=}CH—CH_2—CH_3$
C $CH_2{=}CH—CH{=}CH_2$
D $CH_2{=}CH_2$

4 Which of the following compounds is least likely to react least *easily* with sodium hydroxide?

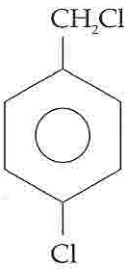
A



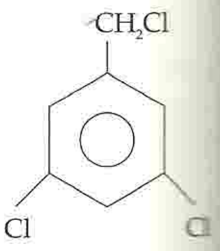
C



B

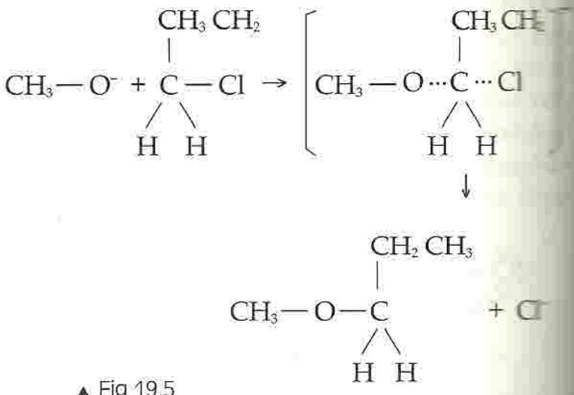


D



5 The mechanism of a reaction is shown in Fig 19.5. This reaction is

A an addition reaction .
B a nucleophilic substitution reaction.
C an electrophilic substitution reaction.
D an elimination reaction.



▲ Fig 19.5

6 Which one of the following explanations best explains why 1-iodobutane reacts more rapidly than 1-chlorobutane with aqueous sodium hydroxide?

A The iodine atom is larger than the chlorine atom.
B The 1-iodobutane is more soluble in water than 1-chlorobutane.
C The iodine atom is more easily oxidised than the chlorine atom.
D The C—I bond is weaker than the C—Cl bond.

Section II

Summary of directions

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

7 Which of the following can react with halogenoalkanes in a nucleophilic substitution reaction?

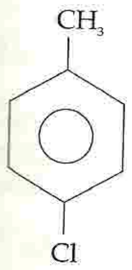
1 NH_3 2 CN^- 3 OH^-

8 An organic compound was boiled with aqueous sodium hydroxide for some time. The products were then cooled and acidified wth nitric acid.

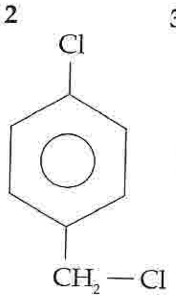
When silver nitrate solution was added, no precipitate was observed.

Which of the following could be the organic compound?

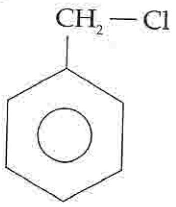
1



2



3



$CH_3CH_2CH_2Br$ was reacted with potassium cyanide in alcohol, and the product boiled with dilute sulphuric acid. In this process,

1 an organic acid was produced.
2 a compound with four carbon atoms was produced.
3 ammonium ions were produced.

A set of halogen compounds has the molecular formula CH_3CH_2X, where X = Cl, Br or I. For this set of compounds, as the proton number of X increases,

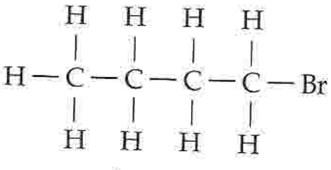
1 the boiling point increases.
2 the C—X bond energy increases.
3 the compounds become less reactive with aqueous NaOH.

Structured Questions

1 An organic compound **X** has the composition by mass: C, 35.04%; H, 6.57% and Br, 58.39%.

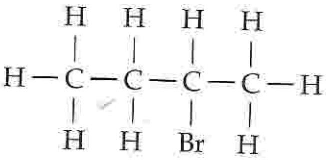
(a) Show that the empirical formula of **X** is C_4H_9Br.

(b) The molecular formula of **X** is C_4H_9Br. Two possible isomers of **X** are shown below.



$CH_3CH_2CH_2CH_2Br$

isomer I



$CH_3CH_2CHBrCH_3$

isomer II

Draw the structure of *another* possible isomer of **X** and give its chemical name.

(c) **X** reacts with hot aqueous sodium hydroxide.

(i) How would the rates of this reaction change if X were C_4H_9Cl?

(ii) Give a reason for your answer in (i).

(d) Isomer I reacts with potassium cyanide in ethanol to produce organic compound **Y**.

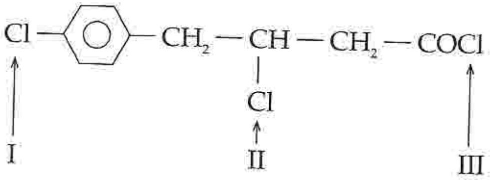
(i) Write the equation for the reaction.

(ii) State the *type* of mechanism for the reaction.

(iii) Write the formula of the organic product when **Y** is refluxed with dilute sulphuric acid.

(e) Write the formula of the product when Y is refluxed with dilute sulphuric acid.

2 Fig 19.6 shows the structure of compound **X**. The three chlorine atoms are labelled I, II and III.



▲ Fig 19.6

(a) Which chlorine atom would react

(i) least readily with aqueous alkali?

(ii) most readily with aqueous alkali?

(b) Give the structural formula of the organic product you would expect if compound **X** is

(i) shaken with cold water;
(ii) refluxed with aqueous NaOH for a short time;
(iii) refluxed with acidified $KMnO_4$ for some hours.

3 Ozone (O_3) is produced in the upper atmosphere by sunlight. The reactions are

$$O_2 \xrightarrow{\text{light}} O\cdot + O\cdot$$
$$O\cdot + O_2 \rightarrow O_3$$

Large amounts of the compound $CFCl_3$ have been used in industry and the industrial products have been released into the atmosphere. The compound remains unchanged in the environment for approximately 75 years. It is believed to be destroying atmospheric ozone by the following mechanism:

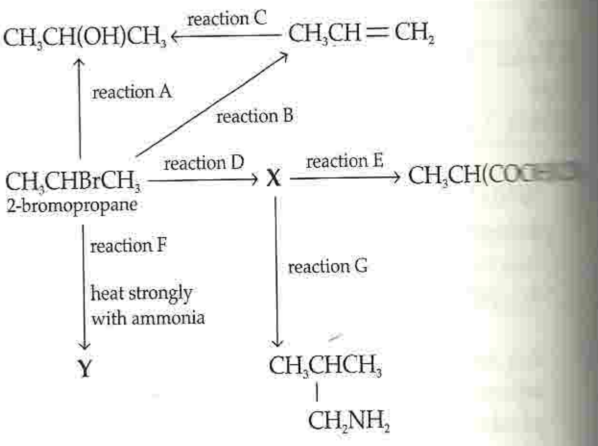
$$CFCl_3 \rightarrow Cl\cdot + \cdot CFCl_2 \qquad \text{step 1}$$
$$Cl\cdot + O_3 \rightarrow ClO\cdot + O_2 \qquad \text{step 2}$$

The chlorine atoms are then regenerated by the reaction

$$ClO\cdot + O\cdot \rightarrow Cl\cdot + O_2 \qquad \text{step 3}$$

(a) Suggest one large-scale former use of $CFCl_3$.
(b) Explain why $CFCl_3$ remains unchanged in the environment for 75 years.
(c) (i) Suggest how the reaction in step 1 is brought about.
  (ii) Suggest why the C—Cl bond breaks rather than the C—F bond.
  (iii) What type of particles are produced in this reaction?
(d) Steps 2 and 3 are propagation steps in this reaction. Suggest a possible termination reaction.
(e) Where does the oxygen radical ($O\cdot$) in step 3 come from?
(f) State the potential harm that could be caused by the effect of $CFCl_3$ on atmospheric ozone.

4 Some reactions of 2-bromopropane are
in the reaction scheme below.



(a) Write the full structural formulae of
  (i) compound **X**;
  (ii) compound **Y**.
(b) What type of reaction is
  (i) reaction A?
  (ii) reaction B?
  (iii) reaction C?
(c) (i) What is the significance of reacti
  D?
  (ii) State the nucleophile in this reac
(d) Name a suitable reagent for reaction C
(e) (i) Name the reagents and conditio
  reaction E.
  (ii) Write a balanced equation for reaction E.

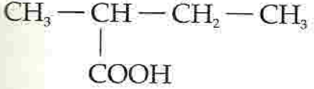
5. 2-Bromo, 2-methyl propane reacts
aqueous sodium hydroxide via an
mechanism.
(a) What do you understand by the
mechanism ?
(b) Why does 2-bromo, 2-methyl prop
reacts via S_N1 not S_N2 mechanism ?
(c) Name an isomer of 2-bromo, 2-meth
propane that reacts via S_N2 mechanis
(d) Describe, with equations, the mechan
of S_N1 and S_N2 mechanism.
(e) Identify the rate determining step in ea
mechanism.
(f) Give the energy profile diagram for the
and S_N2 mechanisms.

Descriptive Questions

Outline how 2-bromobutane, $CH_3—CHBr—CH_2—CH_3$, can be converted into the following compounds:

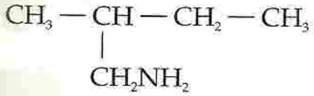
(a) butan-2-ol, $CH_3—CHOH—CH_2—CH_3$

(b)



$CH_3-\underset{\displaystyle COOH}{\underset{|}{CH}}-CH_2-CH_3$

(c)



$CH_3-\underset{\displaystyle CH_2NH_2}{\underset{|}{CH}}-CH_2-CH_3$

(d) 2,3-dibromobutane, $CH_3—CHBr—CHBr—CH_3$

Compound **X** has composition 12.8% carbon, 85.1% bromine, 2.1% hydrogen and a relative molecular mass of 188.

Compound **X** reacts with sodium hydroxide to produce an organic compound **Y**. Compound **Y** reacts with sodium metal to give a flammable gas.

Compound **Y** can also be made by oxidising an alkene to a diol.

(a) Deduce the molecular formula of compound **X**.

(b) Write full structural formulae for compounds **X** and **Y** and explain all the reactions described above.

(a) Describe giving essential reagents, conditions and balanced equation, the formation of propanoyl chloride from propanoic acid.

(b) How and under what conditions will propanoyl chloride react with

(i) ammonia

(ii) phenol

(c) Give (i) balanced equation for each reaction.

(ii) name the products and give their structural formulae.

CHAPTER 20

ORGANIC HYDROXY COMPOUNDS

Alcohols

Phenols

SYLLABUS OBJECTIVES

In this chapter you should be able to:

- interpret and use the chemical names, displayed formulae of the three types of alcohols
- classify alcohols into primary, secondary and tertiary
- describe and explain the production of ethanol by fermentation
- recall the chemistry of alcohols in the following reactions:
  - combustion; substitution to give halogenoalkanes; reaction with sodium; oxidation to aldehydes, ketones and carboxylic acids; dehydration to alkenes; esterification and acylation
- suggest characteristic distinguishing reactions for the three types of alcohols
- describe the reactions of $CH_3CH(OH)$— compounds which give triiodomethane with alkaline aqueous iodine
- recall the chemistry of phenol in the following reactions:
  - with bases
  - with sodium
  - nitration and halogenation of the aromatic ring
- explain the relative acidities of water, phenol and ethanol

Organic hydroxy compounds contain the —OH group of atoms. There are two types of hydroxy compounds:

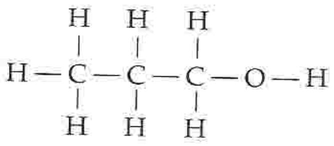
(a) **alcohols** (an alkane with a hydrogen atom replaced with an —OH group), eg ethanol CH_3—CH_2—OH;

(b) **phenols** (the —OH group is directly attached to the benzene ring), eg phenol C_6H_5—OH.

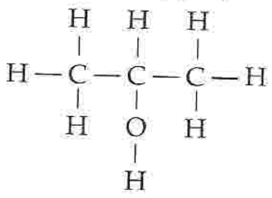
20.1 Alcohols

- An alcohol has the formula of an alkane plus an oxygen atom.
- Alcohols are classified into primary, secondary and tertiary.

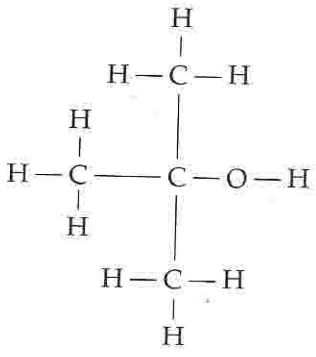
Primary: —OH group attached to a carbon atom with *two* hydrogen atoms, eg propan-1-ol



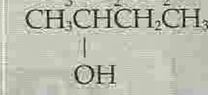
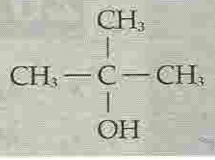
Secondary: —OH group attached to a carbon atom with *one* hydrogen atom, eg propan-2-ol



Tertiary: —OH group attached to a carbon atom with *no* hydrogen atoms, eg 2-methylpropan-2-ol



- Some examples of alcohols are given in Table 20.1.

compound	formula	type	b.p./°C
methanol	CH_3OH	primary	64
ethanol	CH_3CH_2OH	primary	78
propan-1-ol	$CH_3CH_2CH_2OH$	primary	98
butan-1-ol	$CH_3CH_2CH_2CH_2OH$	primary	118
butan-2-ol	 $CH_3\underset{\overset{\vert}{OH}}{C}HCH_2CH_3$	secondary	100
2-methylpropan-2-ol	 $CH_3-\overset{\overset{CH_3}{\vert}}{\underset{\underset{OH}{\vert}}{C}}-CH_3$	tertiary	83

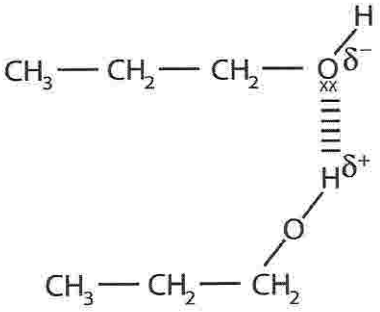
▶ Table 20.1 Examples of alcohols

Physical Properties

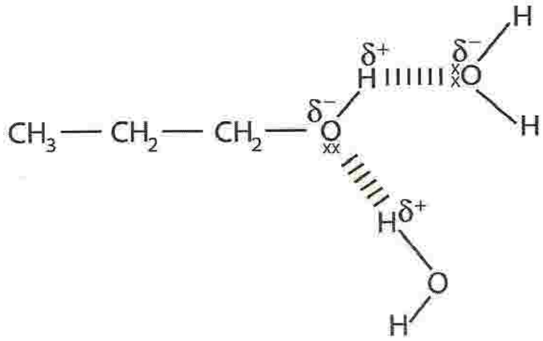
- Alcohols have molecular structures. In the solid or liquid state, the forces between the molecules are *hydrogen bonds*.
- Alcohols have low melting and boiling points. However their boiling points are higher than those of alkanes of similar mass and size.

  eg: butane $CH_3CH_2CH_2CH_3$ $M_r = 58$, b.p. = –0.5°C
  propan-1-ol $CH_3CH_2CH_2OH$ $M_r = 60$, b.p. = 98°C

  The alcohol has a higher boiling point than the alkane because of hydrogen bonds between the molecules (Fig 20.1).
- Alcohols are soluble in water, because they form hydrogen bonds with the water molecules (Fig 20.2).



▶ Fig 20.2 Hydrogen bond in liquid propan-1-ol



▶ Fig 20.3 Propan-1-ol in water

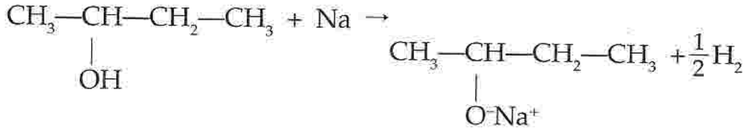
Chemical Reactions

- **Combustion**
  Alcohols burn in air or oxygen. Carbon dioxide and water are produced when the combustion is complete.

  eg: $CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

- **Reaction with sodium metal**
  Alcohols react with sodium metal. In the reaction, the hydrogen of the OH group is displaced by Na and hydrogen gas is produced.

  eg: $\underset{\text{ethanol}}{CH_3—CH_2—OH} + Na \rightarrow \underset{\text{sodium ethoxide}}{CH_3—CH_2—O^-Na^+} + \frac{1}{2}H_2$



$$CH_3—\underset{\underset{\displaystyle OH}{|}}{CH}—CH_2—CH_3 + Na \rightarrow CH_3—\underset{\underset{\displaystyle O^-Na^+}{|}}{CH}—CH_2—CH_3 + \frac{1}{2}H_2$$

The sodium compounds are white solids. Each of these compounds reacts with water to produce a solution of alcohol and NaOH.

eg: $CH_3—CH_2—O^-Na^+ + H_2O \rightarrow CH_3—CH_2—OH + NaOH$

Question 1.6 g of an alcohol was found to react with excess sodium metal, producing 0.56 dm^3 of hydrogen gas (measured at s.t.p.). Deduce the relative molecular mass and formula of the alcohol.
(1 mole of gas occupies 22.4 dm^3 at s.t.p.)

Answer 0.5 mole of H_2 gas is produced from 1 mole of alcohol
ie 11.2 dm^3 of H_2 gas is produced from 1 mole of alcohol.
From the experiment, 0.56 dm^3 of H_2 gas was produced from 1.6 g of alcohol.
Hence 11.2 dm^3 of gas would be produced from $\frac{11.2 \times 1.6}{0.56}$ = 32 g of alcohol.
Therefore the relative molecular mass of the alcohol = 32.
The formula of the alcohol is CH_3OH (methanol).

- **Substitution of —OH with halogen atom**
  The —OH group of an alcohol can be substituted with a halogen atom by two main methods.
  (a) **Reaction with HX (HCl, HBr, HI)**
  The HX is usually prepared by mixing NaX or KX with concentrated sulphuric or phosphoric acid. This is done in the presence of the alcohol, so that the HX produced reacts immediately with the alcohol. For example, ethanol is converted into bromoethane by reacting the ethanol with NaBr and concentrated sulphuric acid.

  eg: $NaBr + H_2SO_4 \rightarrow HBr + NaHSO_4$
  $CH_3—CH_2—OH + HBr \rightarrow CH_3—CH_2Br + H_2O$

Concentrated sulphuric acid cannot be used to prep iodocompounds because the sulphuric acid oxidises HI iodine. To make an iodocompound, phosphoric acid be used.

$$CH_3CH_2CH_2OH \xrightarrow{\boxed{\text{NaI and } H_3PO_4\text{, heat}}} CH_3CH_2CH_2I$$

propan-1-ol 1-iodopropane

(b) **Reaction with phosphorus halides, PX_3 or PX_5**

eg: $3CH_3CH_2OH + PI_3 \rightarrow 3CH_3CH_2I + H_3PO_3$

ethanol iodoethane

$CH_3CH_2CH_2OH + PCl_5 \rightarrow CH_3CH_2CH_2Cl + POCl_3 + HCl$

propan-1-ol 1-chloropropane

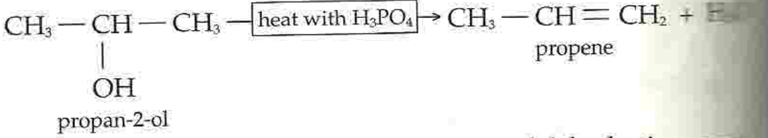
To make iodocompounds, it is normal to add iodine mixture of the alcohol and red phosphorus. The iodine rea with the red phosphorus to make PI_3 which rea immediately with the alcohol.

- **Dehydration of alcohols**
  Alcohols can be dehydrated to alkenes by eliminating a mole of water. There are two ways of doing this:
  (a) by heating the alcohol with a dehydrating agent such phosphoric acid or *excess* concentrated sulphuric acid; or
  (b) by passing alcohol vapour over hot aluminium oxide, wh catalyses the reaction.

eg:

$$CH_3-CH_2-OH \xrightarrow{\boxed{\text{heat with excess concentrated } H_2SO_4 \text{ at } 170°C}} CH_2=CH_2 + H$$

ethanol ethene



$$\underset{\substack{|\\OH}}{CH_3-CH-CH_3} \xrightarrow{\boxed{\text{heat with } H_3PO_4}} CH_3-CH=CH_2 + H$$

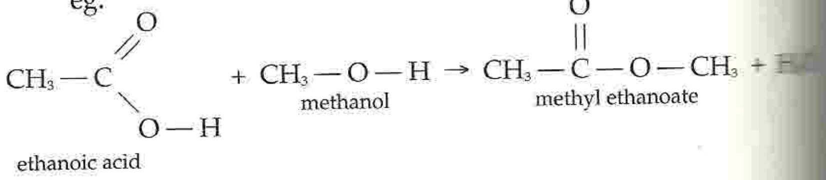
propene

propan-2-ol

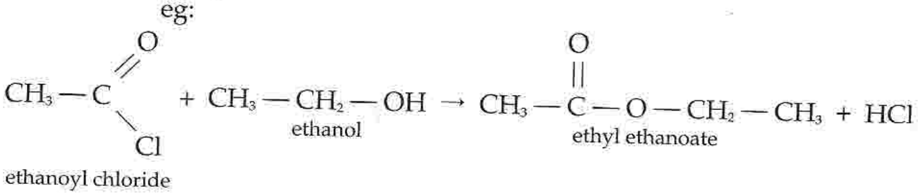
Concentrated sulphuric acid is not a very good dehydrating ag as it is also an oxidising agent. It oxidises alcohols and is its reduced to SO_2.

- **Esterification**
  (a) An alcohol reacts with a carboxylic acid to produce an es and water.
  (b) The alcohol/carboxylic acid mixture is heated with a concentrated sulphuric acid.
  (c) The sulphuric acid serves two purposes:
  — it supplies H^+ ions to catalyse the reaction;
  — it absorbs the water produced in the reaction: increases the yield of the ester.

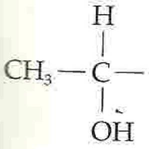
eg:



- **Reaction with acyl chlorides**
  Acyl chlorides react with alcohols to produce esters. No heating is required.
  eg:



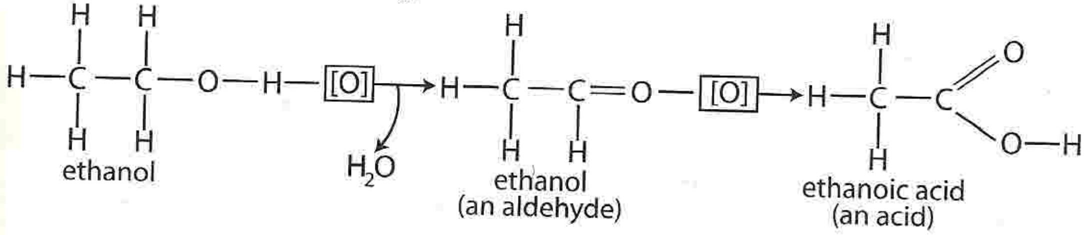
This reaction is an example of **acylation**. Acylation is the substitution of the R—CO— group into another compound.



▲ Fig 20.4

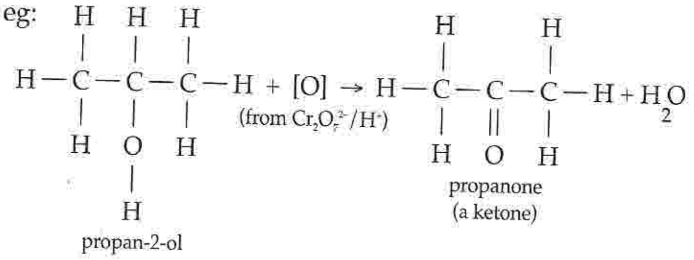
- **Triiodomethane reaction**
  (a) Alcohols which contain the group shown in Fig 20.4 react with iodine and aqueous sodium hydroxide to produce triiodomethane, CHI_3. The reaction often takes place at room temperature, but sometimes it is necessary to warm the reactants.
  (b) The CHI_3 is seen as a yellow precipitate. This reaction is used as a test for the presence of CH_3—CH(OH)— in organic compounds.
  (c) The alcohols which give a positive triiodomethane reaction are:
  primary alcohols: ethanol *only*
  secondary alcohols: all secondary methyl alcohols
  (eg propan-2-ol; butan-2-ol)
  tertiary alcohols: none
  (d) Some aldehydes and ketones also give a positive triiodomethane reaction (see Chapter 21).

- **Oxidation of alcohols**
  (a) Primary and secondary alcohols can be oxidised by a hot mixture of potassium dichromate(VI) solution and sulphuric acid. In the reaction, the *orange* dichromate ions turn *green*.
  (b) Primary alcohols are oxidised to aldehydes and then to acids.
  eg:



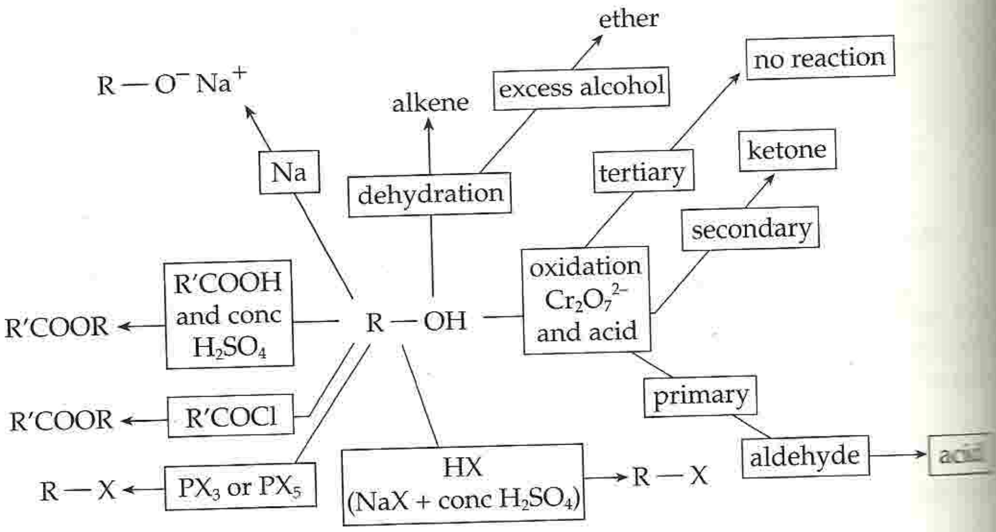
  (c) Secondary alcohols are oxidised to ketones.

eg:



(d) Tertiary alcohols are *not* oxidised by acidified potassium dichromate(VI).

- A summary of the reactions of alcohols is shown in Fig 20.5.

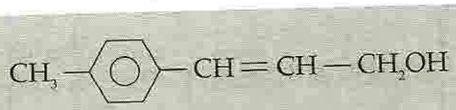


▶ Fig 20.5

Tests for Alcohols

- Add PCl_5 to the compound. Alcohols give white fumes of HCl gas. Carboxylic acids give the same result, but (unlike alcohols) they also give a pH less than 7 with universal indicator.
- Add ethanoic acid and a little concentrated sulphuric acid to the compound. Boil the mixture for a minute. Alcohols react to produce esters, which have a sweet smell.
- Boil the compound with a little potassium dichromate(VI) solution and dilute sulphuric acid. Primary and secondary alcohols are oxidised. The orange dichromate turns green. Other organic compounds (eg aldehydes) also give the same result.

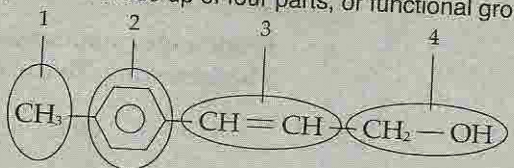
Question



How and under what conditions would you expect the compound above to react with

(a) bromine;
(b) potassium manganate(VII); and
(c) phosphorus pentachloride?

The organic compound is made up of four parts, or functional groups (Fig 20.6).



▸ Fig 20.6

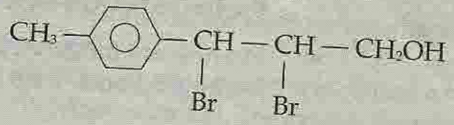
To answer this question,

- first decide the conditions for each reagent
- then decide how each group will react with the reagent, and finally, write down the formula of the product.

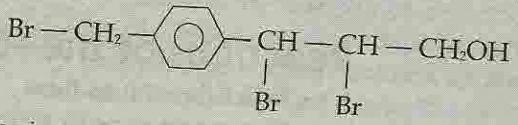
Answer

(a) Bromine can react under three conditions: bromine alone; bromine with light and bromine with iron catalyst.

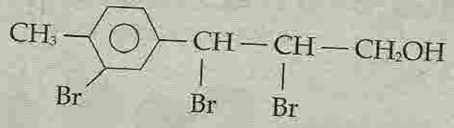
(i) With bromine alone, only the — C=C reacts. Hence the product is



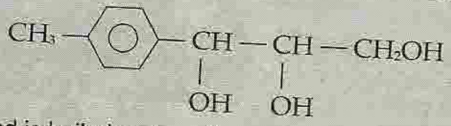
(ii) With bromine and light, the —C=C reacts *and* the $-CH_3$ undergoes substitution.
One possible product is



(iii) With bromine and iron catalyst, the —C=C reacts *and* the benzene ring undergoes substitution. One possible product is



(b) With cold, dilute alkaline $KMnO_4$, only the —C=C— reacts. The product is



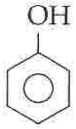
If the compound is boiled under reflux with acidified $KMnO_4$ for some hours, the carbon groups on the benzene ring become —COOH. The product is

Other products such as ketones and acids can be obtained from reaction with $KMnO_4$.

(c) Only the alcohol —OH group will react with the PCl_5. Hence the product is

20.2 Phenols

- Phenols are compounds with an —OH group attached directly to a benzene ring. Two examples of phenols are shown below.



phenol (b.p. 181°C)

4-methylphenol (b.p. 201°C)

Physical Properties

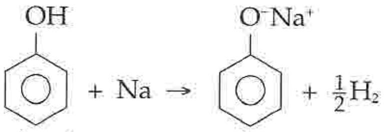
- Phenols have relatively high melting and boiling points, because the forces between the molecules are hydrogen bonds.
- Phenols are moderately soluble in water, because they can form hydrogen bonds with the water molecules.

Chemical Properties

Phenols have two reactive groups: the —OH group and the benzene ring.

Reactions of the –OH Group

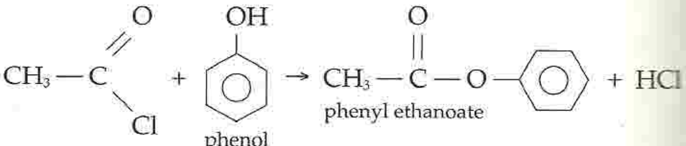
- **Reaction with sodium**
  Phenols react with sodium metal. The hydrogen of the —OH group is replaced with Na, and hydrogen gas is produced.
  eg:



phenol

sodium phenoxide

- **Reaction with acyl chlorides**
  Phenols react with acyl chlorides to produce esters.
  eg: reaction of phenol with ethanoyl chloride

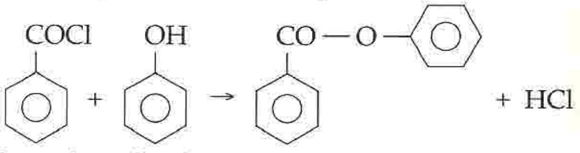


ethanoyl chloride

phenol

phenyl ethanoate

  This is an example of acylation of phenol.
  eg: reaction of phenol with benzoyl chloride

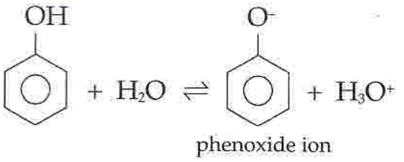


benzoyl chloride

phenol

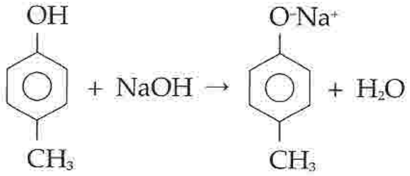
phenyl benzoate

- **Acidity of phenols**
  (a) Phenol is a weak acid. Phenol reacts with water according to the following equation:



Hence, aqueous solutions of phenol have a pH < 7.

  (b) Phenols dissolve in aqueous sodium hydroxide.
  eg:

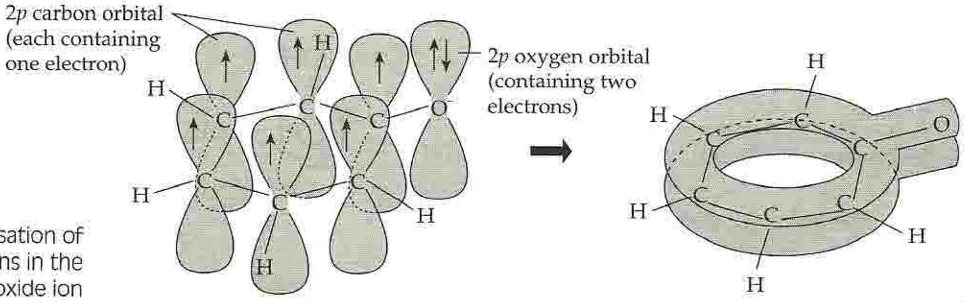


  (c) Phenols do *not* react with sodium carbonate to produce CO_2 gas.

  (d) The acidity of phenol is caused by the relative stability of the phenoxide ion. The oxygen atom in the phenoxide ion has lone pairs of electrons. One of the lone pairs (in a 2*p* orbital) overlaps with the 2*p* orbitals of the carbon atoms to form a delocalised ring over the six carbon atoms and the oxygen atom (Fig 20.7).

  Because the lone pair of electrons of the oxygen are now partly delocalised around the benzene ring, the oxygen atom has partly lost some electrons. So the oxygen takes electrons from the O—H bond. Hence the hydrogen atom of the O—H readily becomes H^+.

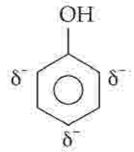
  Ethanol is not acidic because there is no benzene ring to stabilize the $CH_3—CH_2—O^-$ ion. Hence, aqueous solutions of ethanol are neutral.



▸ Fig 20.7 Delocalisation of electrons in the phenoxide ion

- Phenols do *not* have similar reactions as alcohols.
  (a) No reaction with phosphorus halides such as PCl_3 or PCl_5.
  (b) No dehydration.
  (c) No oxidation with acidified dichromate(VI).
  (d) No reaction with carboxylic acids to produce esters.

Reactions of the Benzene Ring

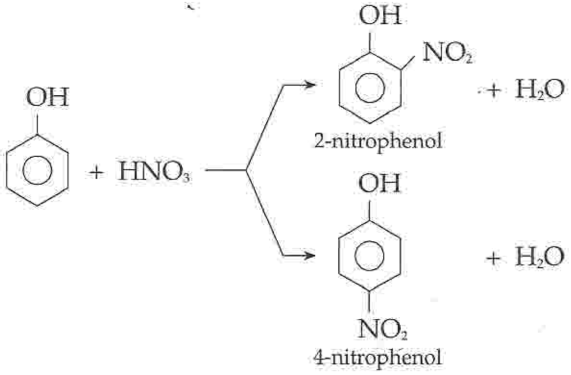


▲ Fig 20.8 2,4 positions on the benzene ring that attract electrophiles

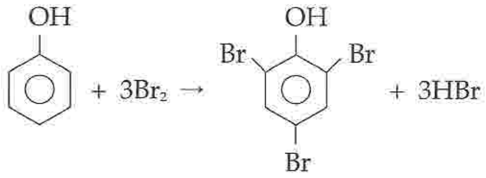
- Because the lone pair of electrons from the oxygen atom is partly delocalised with the π electrons of the benzene ring, the carbon atoms of the benzene ring become slightly negative and so readily attract electrophiles. Thus phenol undergoes electrophilic substitution more easily than benzene itself.

  When phenol undergoes electrophilic substitution, the substitution occurs at the '2' and '4' positions of the benzene ring as those carbon atoms are slightly negative (Fig 20.8), to give a mixture of isomers (see reaction with nitric acid).

- **Reaction with nitric acid**
  Phenol reacts with dilute nitric acid to produce a mixture of 2-nitrophenol and 4-nitrophenol. No sulphuric acid is required.



- **Reaction with bromine**
  An aqueous solution of bromine reacts with an aqueous solution of phenol to produce a white precipitate of 2,4,6-tribromophenol. The bromine is immediately decolourised. No iron catalyst is required for the reaction.



Question Excess aqueous bromine was added to 1.00 dm^3 of 0.01 mol dm^{-3} phenol. Calculate the mass of precipitate formed.
[H = 1.00; C= 12.00; O = 16.0; Br = 80.0]

Answer Number of moles of phenol used in the reaction = 1.00 × 0.01
= 0.01 mole

$$C_6H_5OH + 3Br_2 \rightarrow \underset{\text{precipitate}}{C_6H_2Br_3OH} + 3HBr$$

From the equation,
number of moles of $C_6H_2Br_3OH$ = number of moles of phenol
= 0.01 mole
mass of $C_6H_2Br_3OH$ = 0.01 × relative formula mass
= 0.01 × 331 = 3.31 g

Test for Phenol

- An aqueous solution of phenol reacts with an aqueous solution of bromine. The following are observed:
  (a) immediate decolourisation of the bromine;
  (b) a white precipitate of 2,4,6-tribromophenol.

EXERCISE 20

Multiple Choice Questions

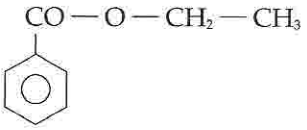
Section I

Which one of the following compounds is a tertiary alcohol?
A $CH_3CH_2C(CH_3)_2OH$
B $CH_3CH_2CH(CH_2OH)CH_2CH_3$
C $CH_3CH_2CH(OH)C(CH_3)_3$
D $(CH_3CH_2)_3CCH_2OH$

What type of reaction takes place when ethanol reacts with hydrogen bromide?
A addition C oxidation
B elimination D substitution

What type of reaction mechanism takes place when phenol reacts with dilute nitric acid?
A electrophilic addition
B electrophilic substitution
C nucleophilic substitution
D free radical substitution

4 What type of reaction takes place when propan-2-ol reacts with hot phosphoric acid?
A elimination C oxidation
B substitution D addition

5 

Which substances react together to produce the compound above?
A ethanoic acid and benzoyl chloride
B ethanol and benzoyl chloride
C phenol and ethanoic anhydride
D ethanoic acid and phenol

6 A sample of propan-1-ol was reacted with sodium metal. The organic product was then added to excess water. What was the final organic product?
A propene
B sodium propoxide
C propanoic acid
D propan-1-ol

7 Which reagent gives a yellow precipitate with propan-2-ol?

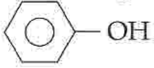
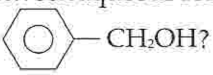
A sulphuric acid and potassium dichromate(VI)
B sodium hydroxide and potassium manganate(VII)
C sodium hydroxide and iodine
D sulphuric acid and ethanoic acid

8 Why is phenol more acidic than ethanol?

A The benzene ring gives electrons to the —OH group.
B Hydrogen bonding makes phenol soluble in water.
C The benzene ring undergoes electrophilic substitution.
D The benzene ring stabilises the $C_6H_5O^-$ ion.

9 An organic compound reacts with sodium metal to produce a gas, but does not react with acidified potassium dichromate(VI) solution. Which one of the following could be the organic compound?

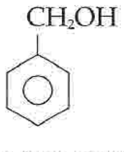
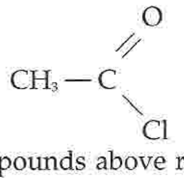
A $(CH_3)_3COH$
B $CH_3CH(CH_3)OH$
C $CH_3CH_2CH_2CH_2OH$
D $HOCH_2CH_2CH_2OH$

10 Which one of the following reagents could be used to distinguish between aqueous solutions of  and ?

A ethanoyl chloride
B phosphorus pentachloride
C concentrated sulphuric acid
D aqueous bromine

11 Which one of the following compounds gives a positive triiodomethane test?

A $CH_3CH(OH)CH_2CH_3$
B $CH_3CH_2CH(OH)CH_2CH_3$
C $CH_3CH_2CH_2CH_2OH$
D $(CH_3)_3CCH_2CH_2OH$

12  

The two compounds above reacted together. Which one of the following could be one of the products?

A $C_6H_5COCH_3$ **C** $C_6H_5CH_2OOCCH_3$
B $C_6H_5OCOCH_3$ **D** $C_6H_5CH_2COCl$

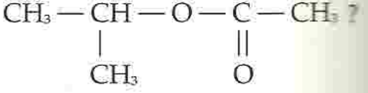
Section II

Summary of directions

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

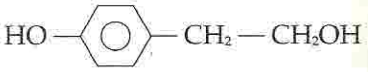
13 Propan-2-ol reacts with the following reagents. In which reactions does the relative molecular mass, M_r, of the organic compound increase?

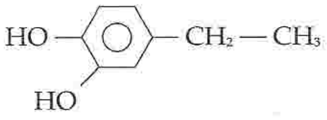
1 sodium bromide and concentrated sulphuric acid
2 acidified potassium dichromate solution
3 excess hot phosphoric acid

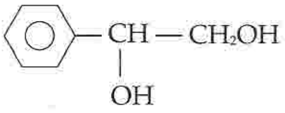
14 Which reagent reacts with propan-2-ol to produce  $CH_3-\underset{\underset{CH_3}{|}}{CH}-O-\underset{\underset{O}{||}}{C}-CH_3$?

1 a little concentrated sulphuric acid
2 ethanoyl chloride
3 ethanoic acid

15 Organic compound **X** produces an aqueous solution with pH less than 7 and gives 1 mole of H_2 gas per mole of **X** when reacted with excess sodium. Which of the following could be **X**?

1 

2 

3 

16 What changes are seen when an aqueous solution of bromine is added to a dilute aqueous solution of phenol?

1 A white precipitate is produced.
2 The bromine is rapidly decolourised.
3 Dense fumes of hydrogen bromide gas are produced.

Structured Questions

1 Compound **X** has composition by mass, C, 64.9%; H, 13.5% and O, 21.6%.

(a) Show that the empirical formula **X** is $C_4H_{10}O$.

(b) **X** has the following properties or reactions. Say what can be deduced about **X** from each of these.

(i) **X** is optically active.

(ii) **X** gives a yellow precipitate when warmed with alkaline aqueous iodine.

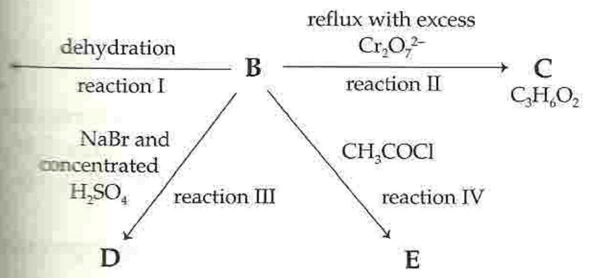
(iii) When refluxed with excess acidified potassium dichromate(VI), **X** produces the compound C_4H_8O as the only final product.

(c) (i) Suggest the name of **X** and draw its displayed formula.

(ii) Draw the displayed formula of the C_4H_8O produced when **X** reacts with acidified potassium dichromate(VI).

(iii) Give the formula of an isomer of **X** which will *not* react with acidified potassium dichromate(VI).

2 The flow chart shows some reactions of organic compounds **A–E**.



(a) Name compounds

(i) **A** (ii) **B** (iii) **C** (iv) **D** (v) **E**

(b) Suggest suitable reagents and conditions for reaction I.

(c) What is the name of reaction II?

(d) (i) Write an equation for reaction IV.

(ii) Name suitable reagents and conditions that can be used in place of CH_3COCl in reaction IV.

*3 Compound **P** has composition 38.7% carbon, 51.6% oxygen and 9.7% hydrogen.

(a) Calculate the empirical formula of **P**.

In an experiment, 0.10 g of compound **P** was vaporised at 400 K. The vapour was found to have a volume of 53.6 cm^3 at 100 kPa pressure.

(b) Calculate the relative molecular mass, M_r, of **P**.

(c) (i) Find the molecular formula of **P**.

(ii) Write the full structural formula of **P**.

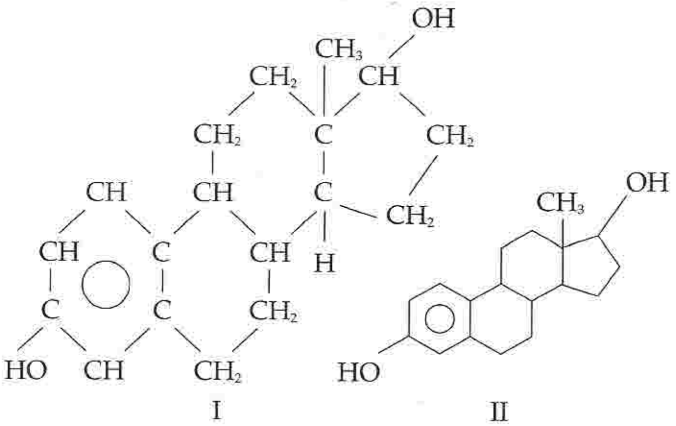
(d) Calculate the volume of gas produced, measured at s.t.p., when 0.200 mole of compound **P** is reacted with excess sodium. Write a balanced equation for the reaction.

(e) How and under what conditions would you expect compound **P** to react with

(i) potassium dichromate(VI) and

(ii) hydrogen bromide?

4 The sex hormone, oestradiol, can be represented by either of the structures in Fig 20.8. All the atoms are shown in structure I while structure II is an abbreviated formula.

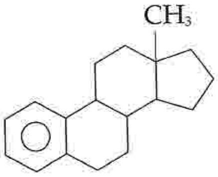


▲ Fig 20.8

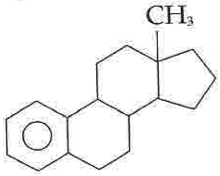
(a) In the full structural formula I, place a circle around each of the four carbon atoms that are chiral centres.

(b) Complete the outline structures below to show the structural formulae of the substances which are formed when oestradiol reacts with each of the named reagents:

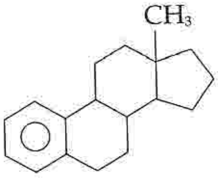
(i) sodium metal



(ii) aqueous sodium hydroxide



(iii) aqueous bromine



(iv) ethanoic acid and a little sulphuric acid

5. Consider the scheme below.

$$CH_3CH_2OH \underset{C}{\overset{A}{\rightleftharpoons}} CH_3CHO \xrightarrow{B} CH_3COOH$$

(a) Briefly describe how you would bring about react A so as to obtain ethanal only.

(b) How would you bring about reaction B and C. Name the reagents and essential conditions.

(c) (i) Describe two industrial processes for the manufacture of ethanol. Give details of the starting materials, reagents and conditions.

(ii) Explain which method is preferred to manufacture ethanol for use as a solvent.

Descriptive Questions

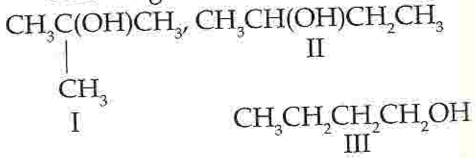
1 For the following pairs of compounds, outline how the first compound could be converted into the second compound.

(a) ethanol into ethene
(b) propan-1-ol into 1,2-dibromopropane
(c) butan-1-ol into butyl ethanoate
(d) ethanol into ethanoic acid
(e) 2-bromopropane into propanone

2 Outline a simple test, in each case, to distinguish between the following pairs of organic compounds. In each case,
— briefly outline the test;
— state what you would observe;
— give balanced equations for the reactions if possible.

(a) $CH_3—CH_2—CH_2—CH_2—OH$ and $(CH_3)_3C—OH$
(b) $CH_3—CH_2—CH_2—CH(OH)—CH_3$ and $CH_3—CH_2—CH(OH)—CH_2—CH_3$

3. (a) How would you differentiate between the following alcohols.



Give : $CH_3\underset{\displaystyle CH_3}{\underset{|}{C}}(OH)CH_3$, $CH_3CH(OH)CH_2CH_3$

I II

$CH_3CH_2CH_2CH_2OH$

III

(i) reagents and conditions
(ii) observation
(iii) write balanced equations
(iv) write the display formula of the organic products.

(b) (i) Give the three structural formulae of the isomers of molecular formula $C_4H_{10}O$.
(ii) Give simple chemical tests to distinguish between them.

Write balanced equations where appropriate.

4. How and under what conditions would you expect the compound below :

to react with :

(i) sodium metal
(ii) aqueous sodium hydroxide at room temperature
(iii) refluxed with aqueous NaOH.
(iv) Phosphorous pentachloride
(v) Acidified potassium dichromate (VI)
(vi) Lithium aluminium hydride in dry ether. In each case give the structural formula of the organic product.

5. (a) Give a concise description of the preparation of phenol starting from benzene.
Give details of reagents and conditions.
Write balanced equations.

(b) Arrange the following substances in decreasing acidity and give concise comments on your reasoning:
Phenol, methanol, ethanoic acid.

CHAPTER

21

ORGANIC CARBONYL COMPOUNDS

SYLLABUS OBJECTIVES

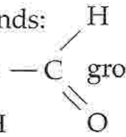
In this chapter you should be able to:

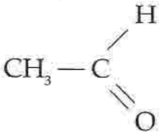
- interpret and use the chemical names, general formulae and displayed formulae of aldehydes and ketones
- describe the formation of aldehydes and ketones from primary and secondary alcohols respectively [eg by oxidation with acidified dichromate(VI)]
- describe the reduction of aldehydes and ketones to primary and secondary alcohols respectively (eg by sodium borohydride $NaBH_4$)
- describe the mechanism of the nucleophilic addition reactions of hydrogen cyanide with aldehydes and ketones
- describe the use of 2,4-dinitrophenylhydrazine (2,4-DNPH) to detect the presence of aldehydes and ketones
- distinguish between aldehydes and ketones from the results of simple tests [ie Fehling's and Tollen's reagents, ease of oxidation by acidified dichromate(VI)]
- describe the reaction of CH_3CO— compounds with alkaline aqueous iodine to give triiodomethane

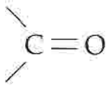
Aldehydes and Ketones

Mechanism for Nucleophilic Addition of Hydrogen Cyanide to Carbonyl Compounds

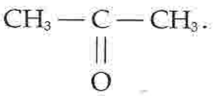
21.1 Aldehydes and Ketones

- Organic carbonyl compounds contain the C=O group of atoms. They have a molecular formula equal to that of an alkene plus an oxygen atom, $C_nH_{2n}O$.
- There are two types of carbonyl compounds:
  (a) Aldehydes: containing a —CHO or  group of atoms.

  An example is ethanal,  or $CH_3—CHO$

  (b) Ketones: containing a  or  group of atoms,

  but with *no hydrogen atom on the carbon of the CO group.*
  An example is propanone,

  $CH_3—CO—CH_3$ or 

  $$CH_3-\underset{\underset{O}{\parallel}}{C}-CH_3.$$

Preparation of carbonyl compounds.

1. **By oxidation of primary or secondary alcohols using acidified potassium dichromate as oxidizing agent.**

Primary alcohols will produce the corresponding aldehydes. For example:

$$CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$$

However the aldehyde formed must be distilled out as soon as it is formed otherwise it may be further oxidized to an organic acid. Alternatively a weaker oxidizing agent such as pyridinium dichromate dissolved in dry dichloromethane can be used.In this case the aldehyde will not be further oxidized.
Secondary alcohols will be converted to ketones . As ketones do not undergo further oxidation, no special precaution has to be used in its preparation. For example:

$$CH_3CH(OH)CH_3 + [O] \longrightarrow CH_3COCH_3 + H_2O$$

2. **By catalytic dehydrogenation of alcohols.**

When primary alcohol vapour is passed over copper at a temperature of about 300°C, dehydrogenation takes place and an aldehyde is produced.

$$CH_3CH_2OH_{(g)} \xrightarrow[300^{\circ}C]{Cu} CH_3CHO_{(l)} + H_{2(g)}$$

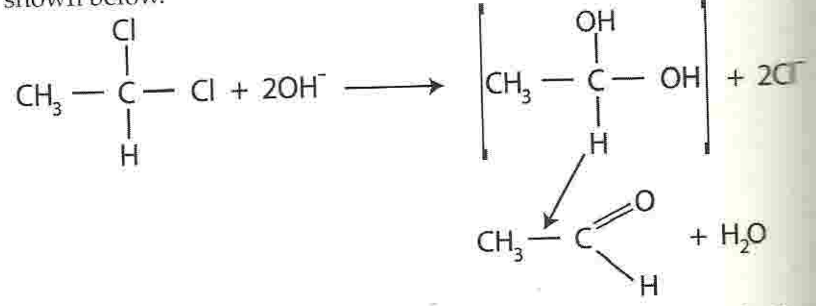
If secondary alcohols are used , ketones will be produced

$$CH_3CH_2OH_{(g)} \xrightarrow[300^{\circ}C]{Cu} CH_3CHO_{(l)} + H_{2(g)}$$

3. **By hydrolysis of dihalides.**

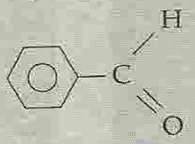
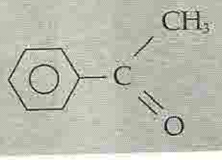
When a dihalide is heated under reflux with aqueous sodium hydroxide hydrolysis (or a nucleophilic substitution reaction) takes place. At first two –OH group substitute the halogens in the molecule. There will be two –OH group on one carbon atom. This arrangement is very unstable. As a result, a water molecule is lost leaving behind the carbonyl compound.

This method can be used to prepare aldehydes as well as ketones as shown below.



- The chemical reactions of aldehydes and ketones are very similar. The main difference is in oxidation. Aldehydes can be oxidised easily but not ketones.

  Some examples of aldehydes and ketones are given in Table 21.1.

compound	formula	b.p./°C
aldehyde		
methanal	HCHO	–21 (gas)
ethanal	CH_3CHO	21
propanal	CH_3CH_2CHO	49
butanal	$CH_3CH_2CH_2CHO$	75
benzaldehyde		179
ketone		
propanone	CH_3COCH_3	56
butanone	$CH_3COCH_2CH_3$	80
pentan-2-one	$CH_3COCH_2CH_2CH_3$	102
pentan-3-one	$CH_3CH_2COCH_2CH_3$	102
phenylethanone		202

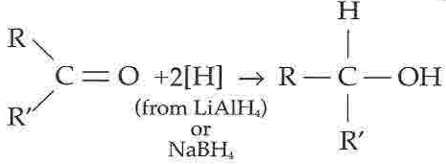
▶ Table 21.1 Examples of aldehydes and ketones

Chemical Reactions

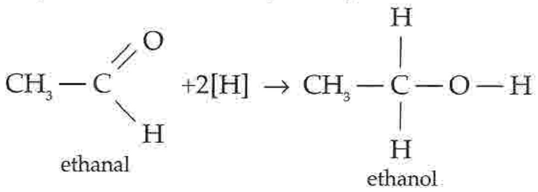
- Reduction by lithium aluminium hydride, $LiAlH_4$, dissolved in dry ether or by using sodium borohydride dissolved in methanol, $NaBH_4$.

  Aldehydes and ketones are reduced to alcohols by lithium aluminium hydride.

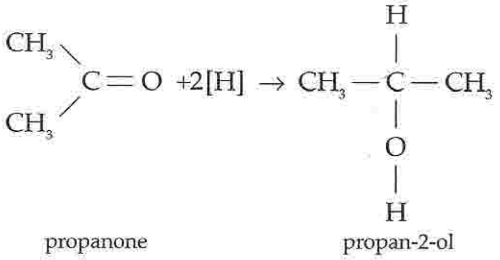
  The equation for the reaction can be written simply as:

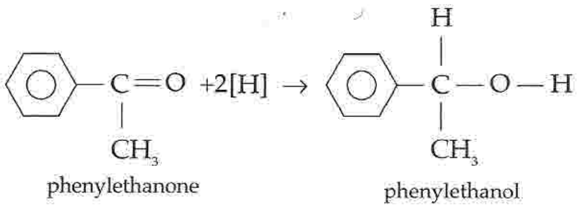


An aldehyde is reduced to a primary alcohol.

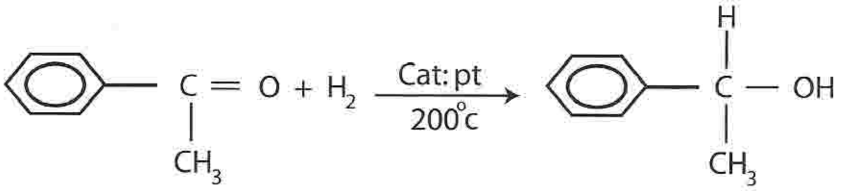


A ketone is reduced to a secondary alcohol.

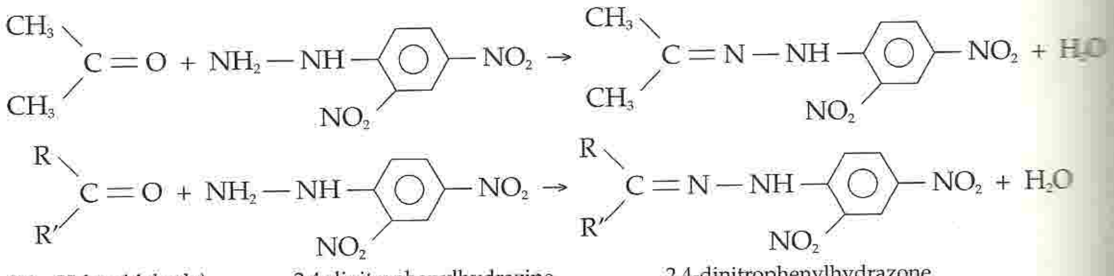




- Reduction also takes place if hydrogen is used in the presence of a catalyst such as finely divided nickel , platinum or palladium.



- **Reaction with 2,4-dinitrophenylhydrazine**
  Aldehydes and ketones react with 2,4-dinitrophenylhydrazine to produce 2,4-dinitrophenylhydrazones in a condensation reaction. A water molecule is eliminated in the reaction. A little acid is required as catalyst.

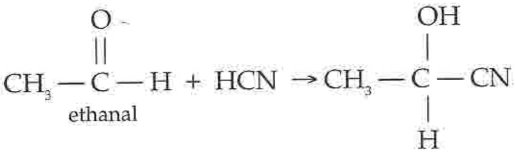


(R′ = H for aldehyde) 2,4-dinitrophenylhydrazine 2,4-dinitrophenylhydrazone

2,4-dinitrophenylhydrazones are orange or yellow crystalline solids. They are used:
(a) as a test for aldehydes and ketones;
(b) to identify aldehydes and ketones from the melting points of the respective 2,4-dinitrophenylhydrazones.

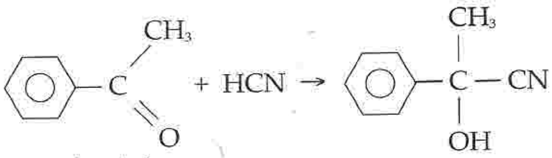
- **Addition of hydrogen cyanide**
  Aldehydes and ketones react with hydrogen cyanide, HCN, to form cyanohydrins. In this reaction hydrogen cyanide, HCN, adds to the carbonyl group.

eg:



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-H + HCN \rightarrow CH_3-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-CN$$

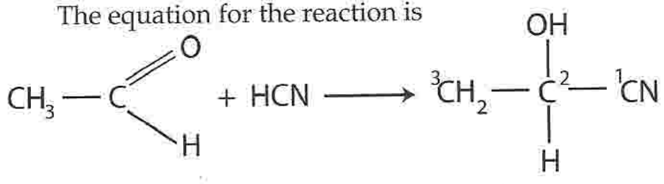
ethanal



phenylethanone

21.2 Mechanism for Nucleophilic Addition of Hydrogen Cyanide to Carbonyl Compounds

- An example is the addition of hydrogen cyanide, HCN, to ethanal. The equation for the reaction is



2 - hydroxy propane nitrile

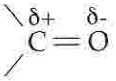
- The hydrogen cyanide is too weak an acid to provide enough cyanide ion for the reaction to occur at a reasonable rate. Therefore a catalyst must be used. The reaction can be catalysed using either an alkali, OH^- or a solution of sodium cyanide.

Consider the reaction of ethanal with hydrogen cyanide using a trace of base, for example aqueous sodium hydroxide.

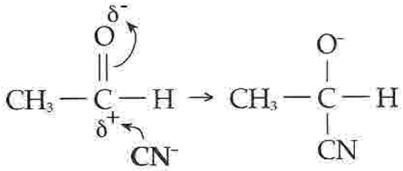
- The hydroxide ion generates cyanide ion from the hydrogen cyanide

$$HCN + OH^- \longrightarrow CN^- + H_2O$$

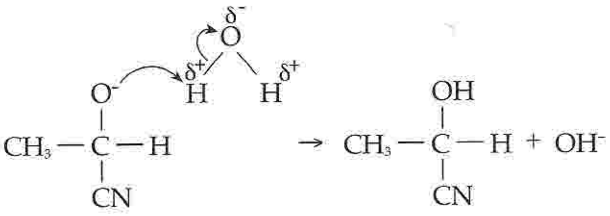
- The nucleophile in the reaction is the cyanide ion, CN^-.
- The C=O bond in ethanal is polarised as the oxygen atom is more electronegative:



- The negative CN^- is attracted to the positive carbon atom:



- The $\overset{\delta^-}{O}$ then reacts with a water molecule:



The hydroxide ion is regenerated back, showing that it is acting as a catalyst.

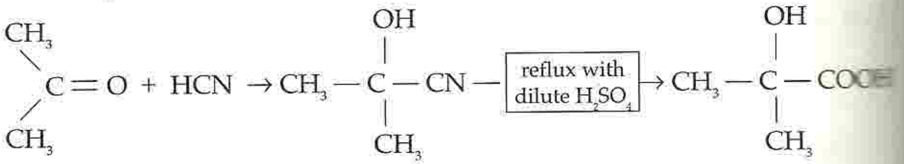
Note the following points:

(a) This reaction is an example of *nucleophilic addition*. The cyanide ion, CN^-, is the nucleophile.The reaction must be carried out in *slightly* alkaline conditions to make sure there is a large concentration of CN^- ions from the HCN.

(b) Benzaldehyde does not give this reaction; a different reaction takes place.

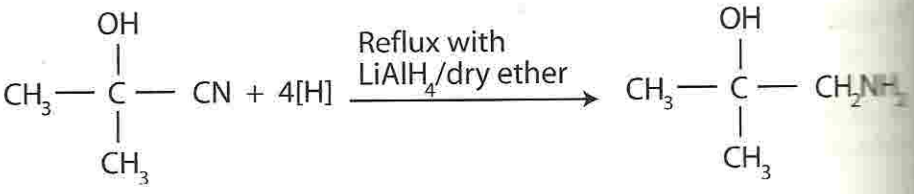
(c) This reaction is an important method of increasing the number of carbon atoms in a molecule and producing a group of compounds called 2-hydroxyacids by hydrolysis of the —CN group:

eg:

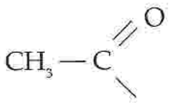


$$\begin{matrix}CH_3\\ \diagdown\\ C=O\\ \diagup\\ CH_3\end{matrix} + HCN \rightarrow CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle OH}{C}}-CN-\boxed{\begin{matrix}\text{reflux with}\\ \text{dilute }H_2SO_4\end{matrix}}\rightarrow CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle OH}{C}}-\text{COO}$$

- The –CN group can also be reduced using either lithi aluminium hydride dissolved in dry ether or using hydrogen i presence of nickel, platinum or palladium as catalyst.



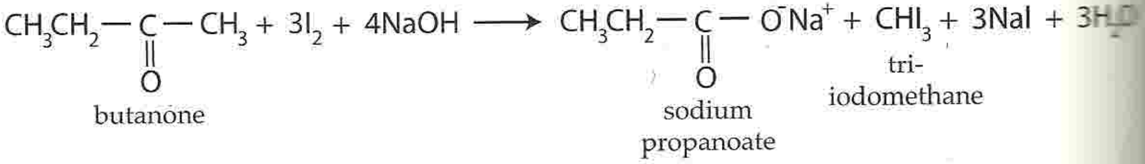
$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle OH}{C}}-CN + 4[H] \xrightarrow[]{\text{Reflux with } LiAlH_4\text{/dry ether}} CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle OH}{C}}-CH_2NH$$



▲ Fig 21.1

- **Triiodomethane reaction**
  (a) Aldehydes and ketones which contain the group shown in F 21.1 react with iodine and aqueous sodium hydroxide t produce triiodomethane, CHI_3. The reaction often takes pla at room temperature, but sometimes it is necessary to warm i

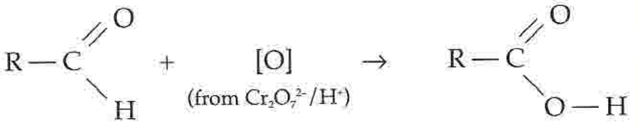
eg:



$$CH_3CH_2-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3 + 3I_2 + 4NaOH \longrightarrow CH_3CH_2-\underset{\displaystyle O}{\underset{\|}{C}}-O^-Na^+ + CHI_3 + 3NaI + 3H$$

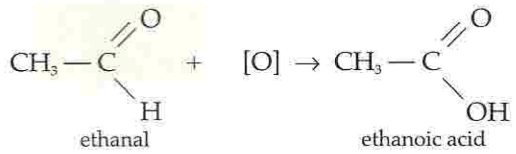
  (b) The CHI_3 is seen as a yellow precipitate. The reaction is use as a test for the presence of the CH_3—CO— group in orga compounds.
  (c) The aldehydes and ketones which give a positi triiodomethane reaction are
    — for aldehydes: ethanal *only*
    — for ketones: all methyl ketones (eg propanone, butano phenylethanone)
  (d) Some alcohols also give a positive triiodomethane reacti (see Chapter 20).

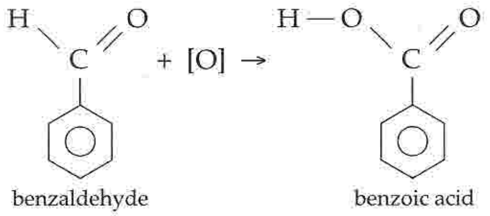
- **Oxidation**
  Aldehydes are oxidised to carboxylic acids. The usual oxidis agent is a mixture of sulphuric acid and sodium or potassi dichromate(VI).



$$R-C\begin{matrix}\diagup\!\!\diagup O\\ \diagdown H\end{matrix} + \underset{(\text{from } Cr_2O_7^{2-}/H^+)}{[O]} \rightarrow R-C\begin{matrix}\diagup\!\!\diagup O\\ \diagdown O-H\end{matrix}$$

eg:





Ketones are not easily oxidised. They do not react with acidified potassium dichromate(VI).

- **Reaction with $[Ag(NH_3)_2]^+$**- the silver mirror test
  Aldehydes react with $[Ag(NH_3)_2]^+$ to produce silver metal and a carboxylic acid.

$$RCHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow RCO_2^- + \underset{\substack{\downarrow\\ \text{Silver}\\ \text{mirror}}}{2Ag} + 4NH_3 + 2H_2O$$

The $[Ag(NH_3)_2]^+$ is obtained by adding ammonia to silver nitrate solution. This is called **Tollen's reagent**. When a few drops of aldehyde are added and the mixture heated, a shiny layer of silver metal or a grey/black precipitate is seen. This reaction is known as the 'silver mirror test for aldehydes'.

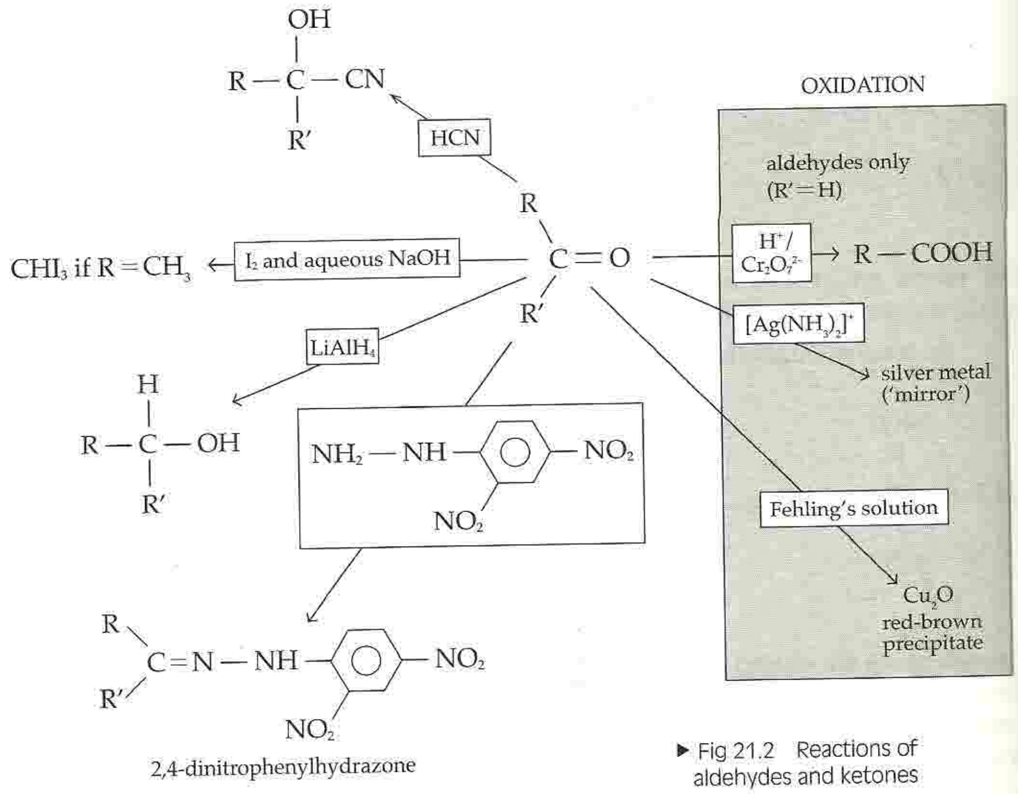
Ketones give a *negative* reaction with Tollen's reagent.

- **Reaction with Fehling's solution**
  When an aldehyde is boiled with Fehling's solution (an alkaline solution of complex Cu^{2+} ions), a red-brown precipitate of copper(I) oxide, Cu_2O, is obtained.

$$RCHO + 2Cu^{2+} + 5OH^- \longrightarrow RCO_2^- + \underset{\substack{\downarrow\\ \text{Copper(I)oxide}\\ \text{brick red precipitate}}}{Cu_2O} + 3H_2O$$

Ketones , **as well as aromatic aldehydes**, do not react with Fehling's solution.

- A summary of the reactions of aldehydes and ketones is shown in Fig 21.2.



▸ Fig 21.2 Reactions of aldehydes and ketones

Tests for Aldehydes and Ketones

- For aldehydes *and* ketones:
  Add 2,4-dinitrophenylhydrazine solution and a little acid to the organic compound. Warm. Aldehydes and ketones give orange crystalline precipitates of 2,4-dinitrophenylhydrazones.

- For aldehydes *only:*
  (a) Silver mirror test: Add Tollen's reagent to a little of the organic compound. Heat the mixture and leave it to stand. Aldehydes produce a silver precipitate (usually seen as a shiny silvery deposit on the test tube).
  Ketones do not give this reaction.
  (b) Add Fehling's solution to a little of the organic compound. Boil the mixture. Aldehydes produce a red-brown precipitate of copper(I) oxide.
  Ketones and benzaldehyde do not give this reaction.
  (c) Boil the compound with a little potassium dichromate(VI) and dilute sulphuric acid. Aldehydes are oxidised and turn the orange dichromate to green Cr^{3+}.
  This is also a positive test for alcohols, but ketones do not give this reaction.

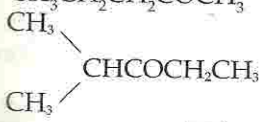
EXERCISE 21

Multiple Choice Questions

Section I

1 What type of reaction takes place when ethanal reacts with hydrogen cyanide?
A electrophilic addition
B nucleophilic substitution
C nucleophilic addition
D electrophilic substitution

2 Solvents used to remove nail varnish often contain propanone. Which reagent could be used to show the presence of propanone in such a solvent?
A Fehling's solution
B acidified aqueous potassium dichromate(VI)
C aqueous silver nitrate and ammonia
D aqueous sodium hydroxide and iodine

3 Which compound gives a yellow precipitate when warmed with alkaline aqueous iodine?
A $CH_3CH_2COCH_2CH_3$
B $CH_3CH_2CH_2COCH_3$
C


D


4 A sample of propanal was first treated with acidified potassium dichromate(VI). The product of this reaction was then treated with aqueous sodium hydroxide. What could be the final organic product?
A CH_3CH_2COOH
B CH_3CH_2COONa
C CH_3COCH_3
D $CH_3CH_2CH_2ONa$

5 Which one of the following reagents could be used to distinguish between the two compounds $CH_3—CO—CH_2—CH_2—CH_3$ and $CH_3—CH_2—CO—CH_2—CH_3$?
A Fehling's solution
B solution of silver nitrate and ammonia
C 2,4-dinitrophenylhydrazine solution
D solution of iodine and aqueous sodium hydroxide

6 Which one of the following compounds produces $(CH_3)_2CHCOCH_3$ on oxidation?
A 2-methylpropan-1-ol
B 2,3-dimethylbutan-2-ol
C 2,2-dimethylpropan-1-ol
D 3-methylbutan-2-ol

7 An organic compound gave a yellow precipitate with iodine and aqueous sodium hydroxide, but gave *no reaction* with $[Ag(NH_3)_2]^+$ (Tollen's reagent). Which one of the following could be the organic compound?
A $CH_3CH_2CH_2COCH_3$
B $CH_3CH_2COCH_2CH_3$
C $CH_3CH_2CH_2CH_2CHO$
D $HOCH_2CH_2CH_2CHO$

8 An organic compound gave a yellow precipitate with iodine and aqueous sodium hydroxide, and a red-brown precipitate with Fehling's solution. Which one of the following could be the compound?
A $CH_3COCH_2CH_3$
B CH_3CH_2CHO
C CH_3COCH_3
D CH_3CHO

9 Why does propanone react with hydrogen cyanide but propene does not?
A Propanone is more susceptible to nucleophilic attack than propene.
B Propanone is more susceptible to electrophilic attack than propene.
C The C$=$O bond in propanone is stronger than the C$=$C bond in propene.
D The addition product formed with propene would be unstable.

Section II

Summary of directions

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

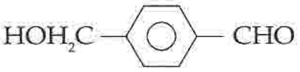
10 Which of the following reagents can be used to distinguish between propanal and propanone?

1 Tollen's reagent, $[Ag(NH_3)_2]^+$
2 Fehling's solution
3 acidified potassium dichromate(VI)

11 Which of the following statements about the reaction of ethanal with Fehling's solution is/are true?

1 Ethanoic acid is a product of the reaction.
2 The ethanal is an oxidising agent.
3 The copper in the Fehling's solution is oxidised.

12



Which properties would you expect for the compound above?

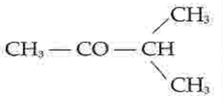
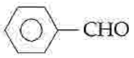
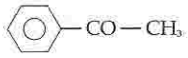
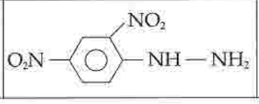
1 It would produce a silver mirror with $[Ag(NH_3)_2]^+$.
2 It would turn acidified $Cr_2O_7^{2-}$ green.
3 It would give a yellow precipitate with $I_2(aq)$ and NaOH(aq).

13 Which statement is true for the reaction of ethanal with hydrogen cyanide?

1 The nucleophile in the reaction is the CN^- ion.
2 An addition reaction takes place.
3 The number of carbon atoms in the organic molecule increases.

Structured Questions

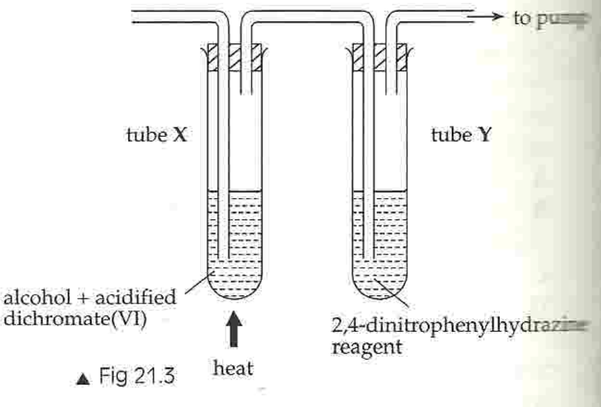
1 The following table shows some reactions of aldehydes and ketones. Complete the table.

starting compound	reagent	important conditions	organic product
	hydrogen cyanide		
	$K_2Cr_2O_7$ and H_2SO_4		
CH_3-CH_2-CHO	Fehling's solution		
			

2 Alcohols are classified as primary, secondary or tertiary.

(a) State the types of organic compounds produced (if any) when
(i) primary alcohols
(ii) secondary alcohols
(iii) tertiary alcohols are oxidised by acidified dichromate(VI).

(b) The experiment shown in Fig 21.3 was carried out to distinguish among the three types of alcohols. The pump was used to suck hot vapours from tube **X** into the solution in tube **Y**.

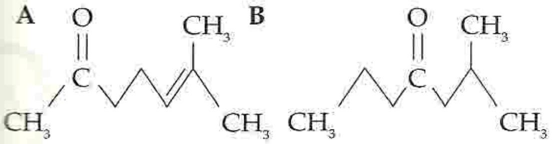


▲ Fig 21.3

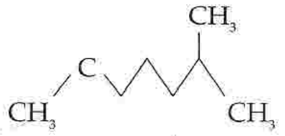
What would be *seen* in tubes **X** and **Y** for each of the three types of alcohol?

(c) The experiment was repeated, in order to distinguish between primary and secondary alcohols.
(i) Name a suitable reagent that would show different results for primary and secondary alcohols to replace 2,4-dinitrophenylhydrazine.
(ii) State what you would see in tube **Y** if a primary alcohol was used in tube **X**.
(iii) State what you would see in tube **Y** if a secondary alcohol was used in tube **X**.

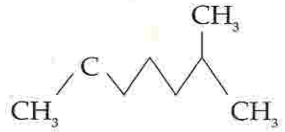
3 The structures of two compounds used as alarm pheromones by the ant *Tapinoma nigerrimum* are shown below.



(a) State what you would observe if each compound was treated separately with the following reagents:
    (i) aqueous bromine;
    (ii) aqueous iodine followed by aqueous sodium hydroxide.
(b) Would you expect compound **A** to form cis-trans isomers?
(c) Complete the structures below to show the organic product when compound **A** reacts with
    (i) hydrogen cyanide;



    (ii) 2,4-dinitrophenylhydrazine.



4 Compound **P** has a composition of 62.1% carbon, 27.6% oxygen and 10.3% hydrogen.
(a) Find the empirical formula of **P**.
(b) The relative molecular mass, M_r, of **P** is 58. Write down the molecular formula of **P**.
(c) Compound **P** reacts with iodine and aqueous sodium hydroxide to produce a yellow precipitate.
    (i) What is the formula of this precipitate?
    (ii) What structural feature or group of atoms must be present in compound **P**?
(d) Draw the full structural formula of compound **P**.
(e) Describe one chemical test you would carry out to confirm the functional group that is present in compound **P**.
(f) Outline how you would convert compound **P** into $(CH_3)_2C(OH)—COOH$.

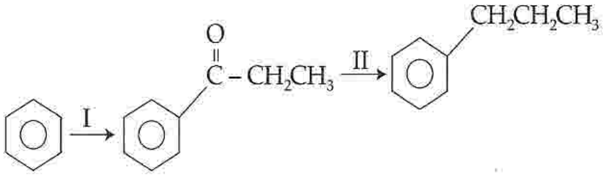
5 (a) How does propanone reacts with the following reagents ?
    (i) Hydrogen Cyanide
    (ii) Iodine and Sodium hydroxide
    (iii) Sodium brohydride

Give the equation for each reaction, the conditions and name the organic products.

(b) What type of mechanism is a (i) ?

Write equations to describe the mechanism.

6. The sequence below shows the two step synthesis of propyl benzene.



(a) (i) What reagent is needed for step I ?
    Describe:
    (ii) the mechanism of the reaction showing the intermediate.
    (iii) Name the reagent needed for step II. What type of reaction occurs ?
(b) Give two chemical tests to show that the product of Step I is a ketone.

Write balanced equations where appropriate.

Descriptive Questions

1 Five bottles contain aqueous solutions of the following organic compounds (a different compound in each bottle). The labels have been removed from the bottles so the contents cannot be identified.

phenol, $C_6H_5—OH$
propanal, CH_3CH_2CHO
propan-2-ol, $CH_3—CH(OH)CH_3$
pentan-3-one, $CH_3CH_2COCH_2CH_3$
phenylmethanol, $C_6H_5—CH_2OH$

Outline *one* chemical test you could carry out on *each* compound, to identify it. You must give a different test for each compound.

Explain how the results of the tests could be used to identify each compound. Write equations for the reactions.

2 Some information on three organic compounds, **A** – **F**, is given below. In each case, suggest one identity for the compound shown and write the full displayed formula and explain the reactions.

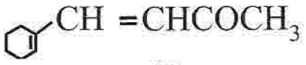
(a) Compound **A**, C_4H_8O:

A gives an orange precipitate with 2,4-dinitrophenylhydrazine, but has no effect on Fehling's solution.

(b) Compound **B**, C_7H_8O:
B is oxidised by acidified potassium dichromate(VI) to **C** which gives a silver mirror with Tollen's Reagent. **C** can be further oxidised to **D**, an acid with the formula $C_7H_6O_2$.

(c) Compound **E**, C_8H_8O:
E gives a yellow precipitate with aqueous alkaline iodine solution and an orange precipitate with 2,4-dinitrophenylhydrazine reagent.

(d) Compound **F**:
F gives a red-brown precipitate with Fehling's solution. 13.2 g of carbon dioxide is produced when 0.100 mol of **F** is completely burnt in oxygen.



X

3. (a) (i) What type of isomerism does X exhibit ?
(ii) Draw the structures of the isomers.

(b) Give the structure of the product formed when X reacts with each of the following reagent.

(i) Bromine dissolved in pentane.
(ii) 2, 4 - dinitrophenyl hydrazine
(iii) Sodium hydroxide and iodine
(iv) $NaBH_4$

4. Give simple chemical tests to distinguish between the members of each of the following pairs.
Give reagents, conditions and observations.
Name and draw structures of the organic products.

(a) $CH_3\,CO\,CH_3$ and $CH_3\,CH_2\,CHO$
(b) CH_3OH and $CH_3CH_2\,OH$
(c) CH_3OH and $CH_3\,CHO$
(d) $C_6\,H_5\,CHO$ and HCHO
(e) $C_6\,H_5\,Cl$ and $C_6\,H_5\,CH_2Cl$

CHAPTER

22

ORGANIC CARBOXYLIC ACIDS AND DERIVATIVES

Carboxylic Acids

Acyl Chlorides

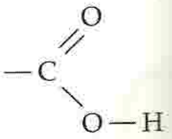
Esters

SYLLABUS OBJECTIVES

In this chapter you should be able to:

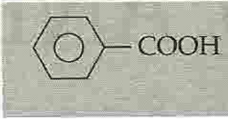
- interpret and use the chemical names, general formulae and displayed formulae of carboxylic acids, acyl chlorides and esters
- describe the formation of carboxylic acids:
  - from alcohols and aldehydes [eg by oxidation with acidified dichromate(VI)]
  - from nitriles (eg by hydrolysis with dilute acids)
- describe the reactions of carboxylic acids in the formation of:
  - salts (eg by reaction with bases)
  - esters (eg by reaction with alcohols)
  - acyl chlorides (eg by reaction with PCl_5)
- explain the acidity of carboxylic acids and chlorine-substituted ethanoic acids (eg $ClCH_2COOH$) in terms of their structures
- describe the hydrolysis of acyl chlorides
- describe the reactions of acyl chlorides with:
  - alcohols
  - phenols
  - primary amines
- explain the relative ease of hydrolysis of acyl chlorides, alkyl chlorides and aryl chlorides (eg CH_3COCl, CH_3CH_2Cl, C_6H_5Cl)
- describe the formation of esters from carboxylic acids or acyl chlorides, using ethyl ethanoate and phenyl benzoate as examples (eg conditions for making ethyl ethanoate from ethanoic acid and ethanol)
- describe the hydrolysis of esters by aqueous acids and aqueous alkalis
- describe the characteristics of condensation polymerisation in the formation of polyesters (eg *Terylene*)
- identify the monomer(s) present in a given section of a polyester (eg the acid and alcohol in *Terylene*)
- deduce the repeat unit of a polyester obtained from given monomer(s)

22.1 Carboxylic Acids

- Carboxylic acids contain the —COOH group, 

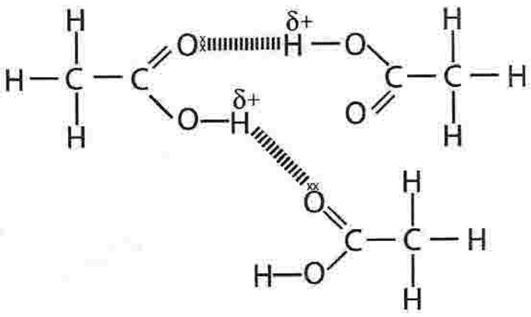
- Some examples of carboxylic acids are given in Table 22.1.

▶ Table 22.1 Examples of carboxylic acids

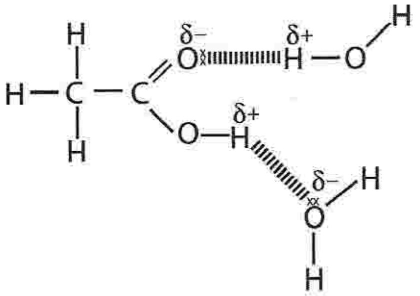
compound	formula	b.p./°C
methanoic acid	HCOOH	101
ethanoic acid	CH_3COOH	118
propanoic acid	CH_3CH_2COOH	141
butanoic acid	$CH_3CH_2CH_2COOH$	163
benzoic acid	 —COOH	(melts at 121°C and then decomposes)

Physical Properties

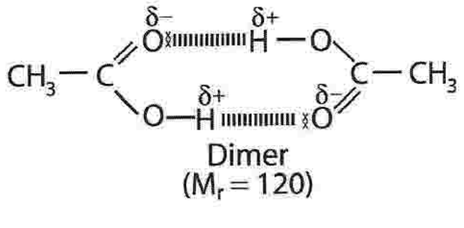
- Carboxylic acids have a molecular structure. In the solid or liquid state, the forces between the molecules are *hydrogen bonds* (Fig 22.1).
  - (a) Carboxylic acids have higher boiling points than other organic compounds of similar molecular size and mass, because of the strong hydrogen bonds.
  - (b) Carboxylic acids are soluble in water, because they form hydrogen bonds with the water molecules (Fig 22.2).
  - (c) In some non-aqueous solvents (liquid pentane), the molecules of carboxylic acids are in pairs. The molecules are joined together by hydrogen bonds (Fig 22.3).



▲ Fig 22.1 Hydrogen bonding in liquid ethanoic acid

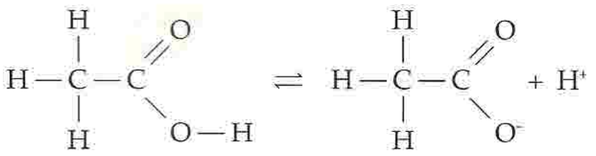


▶ Fig 22.2 Dissolving ethanoic acid in water



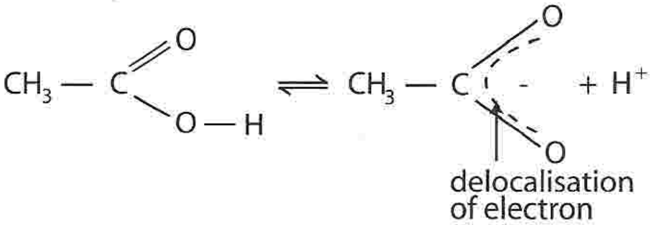
▶ Fig 22.3 Ethanoic acid dissolving in benzene

- Carboxylic acids are weak acids. In water, a small fraction of ethanoic acid molecules are ionised according to the equation



Strengths of Substituted Acids

- Carboxylic acids are the most acidic organic substances which contains atoms of carbon , hydrogen and oxygen only. They are stronger acids than aliphatic or aromatic alcohols.
- The relative acidity of organic acids compared to alcohols is due to the relative stabilization of the carboxylate ion by the delocalisation of electron. Such delocalisation and stabilization is not present in alkoxide ion.

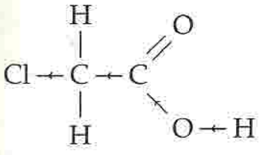


$$CH_3CH_2OH \rightleftharpoons CH_3CH_2\ddot{\underset{\cdot\cdot}{O}}{:}^- + H^+$$

No delocalisation

- While moving down the homologous series of the carboxylic acid, the length of the carbon chain increases. However the length of the carbon chain does not have much influence on the relative acidity of organic acids as indicated by the pKa values of some acids below:-

Acid	pKa
Methanoic acid	3.75
Ethanoic acid	4.76
Propanoic acid	4.87
Butanoic acid	4.86



chloroethanoic acid

Fig 22.4

- The relatively high pKa value for methanoic acid is due to the absence of alkyl group in this acid.
- The ionisation of ethanoic acid (CH_3COOH) requires the breaking of the O—H bond. When this bond is broken, the electrons of the bond go onto the oxygen atom and a H^+ ion is formed.

  Any process that helps pull electrons out of the O—H bond, onto the oxygen atom, will make it easier to form H$^+$(aq) and hence make the compound more acidic.

- When a hydrogen atom is replaced by a chlorine atom in a molecule of ethanoic acid, the chlorine atom (which is very electronegative) pulls electrons towards it (Fig 22.4).

  This process causes electrons to be pulled towards the oxygen atom in the O—H bond. Hence the hydrogen atom in the O—H bond liberates H$^+$(aq) more easily.

- Furthermore the carbon atom bonded to the halogen atom acquires a partial positive charge(! +). Due to the presence of this partial positive charge, the carbon atom will attract electrons from the negatively charged carboxylate ion. As a result the negative charge of the carboxylate ion is dispersed and the resulting anion is stabilized. Less H+ ions will recombine with the anion. The substituted halogenoacid will therefore be a stronger acid than the corresponding organic acid.
  Thus chloroethanoic acid is a stronger acid than ethanoic acid.

- When more hydrogen atoms are replaced with chlorine atoms, the acid becomes stronger. This is shown in Table 22.2.

acid	formula	pK_a	relative acid strength
ethanoic acid	CH_3—COOH	4.76	STRONGER ↓
chloroethanoic acid	ClH_2C—COOH	2.86	
dichloroethanoic acid	Cl_2HC—COOH	1.29	
trichloroethanoic acid	Cl_3C—COOH	0.65	

▶ Table 22.2

- See Chapter 20 for the acidity of alcohols and phenol.

- The same effect is found to occur with other halogen atoms. For example, bromoethanoic acid is stronger than ethanoic acid because bromine is an electronegative atom and therefore pulls electrons towards it. However, bromine is less electronegative than chlorine, so BrH_2C—COOH is not as strong as ClH_2C—COOH. This is shown in Table 22.3.

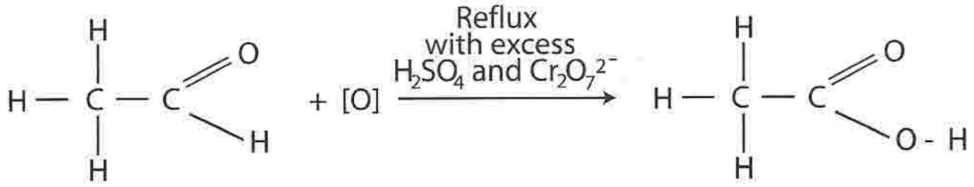
acid	formula	pK_a	relative acid strength
ethanoic acid	CH_3—COOH	4.76	STRONGER ↓
bromoethanoic acid	BrH_2C—COOH	2.90	
chloroethanoic acid	ClH_2C—COOH	2.86	
fluoroethanoic acid	FH_2C—COOH	2.66	

▶ Table 22.3

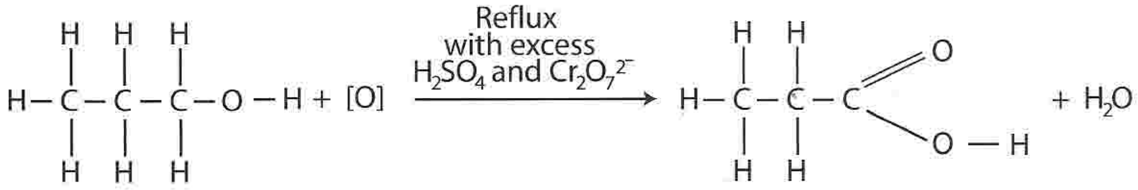
- Fluoroethanoic acid is stronger than chloroethanoic acid because fluorine is more electronegative than chlorine. Hence fluorine pulls electrons away from the hydrogen in the O—H more strongly than chlorine.

Preparation of Carboxylic Acids

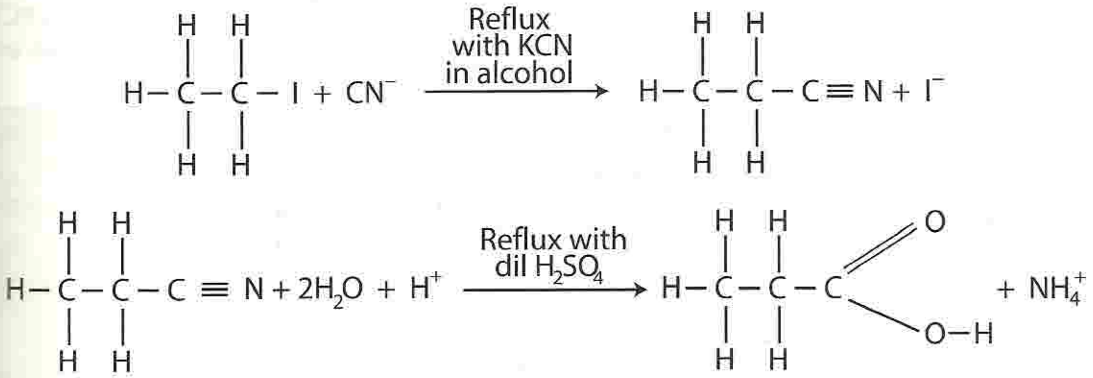
- Carboxylic acids are prepared by oxidation of aldehydes and primary alcohols. The acid is made by refluxing the *primary* alcohol or aldehyde with excess acidified potassium dichromate(VI).



In this reaction, the propan-1-ol is first oxidised to propanal. The oxidation continues, to produce the propanoic acid.



- Carboxylic acids can also be prepared by hydrolysis of nitriles. The nitriles are obtained from halogenoalkanes.



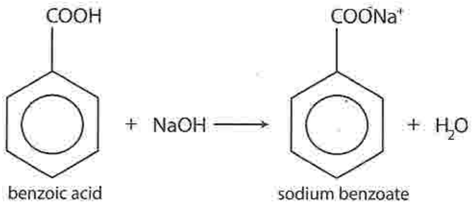
Chemical Reactions

- **Reaction with bases**

  Carboxylic acids react with bases to form salts.

  eg: $2\ CH_3\text{-}COOH + CuO \rightarrow Cu(CH_3COO)_2 + H_2O$

ethanoic acid	copper(II) oxide	copper(II) ethanoate

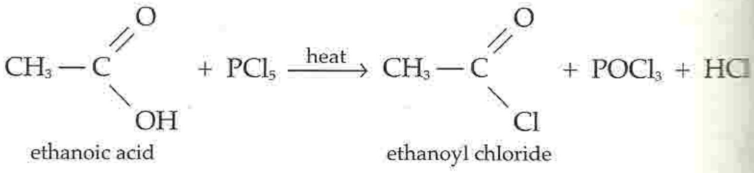


Carboxylic acids react with sodium carbonate to liberate carbon dioxide gas.

$$2CH_3COOH + Na_2CO_3 \longrightarrow 2CH_3COO^- \, Na^+ + H_2O + CO_2$$

This reaction may be used to distinguish between alcohols, phenols and organic acids.

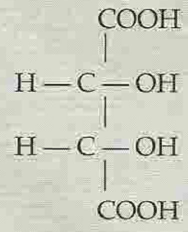
- **Reaction with PCl$_5$**
  Acids react with phosphorus pentachloride to form acyl chlorides.



Note that the —OH group in an alcohol also reacts with PCl$_5$ to produce HCl gas. So, one mole of HCl is obtained from every mole of acid (—COOH) or alcohol (—OH) that reacts.

Example

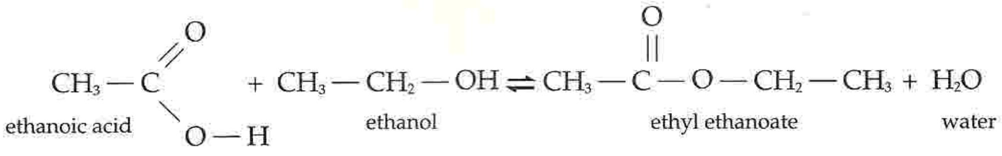
How many moles of HCl are obtained when excess PCl$_5$ reacts with the compound below?

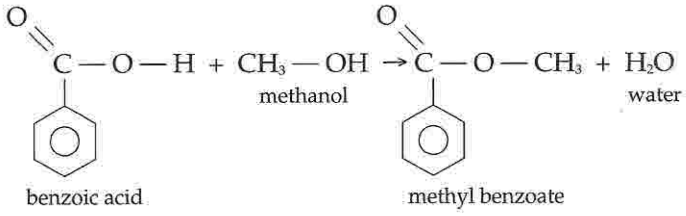


$$\begin{array}{c} COOH \\ | \\ H - C - OH \\ | \\ H - C - OH \\ | \\ COOH \end{array}$$

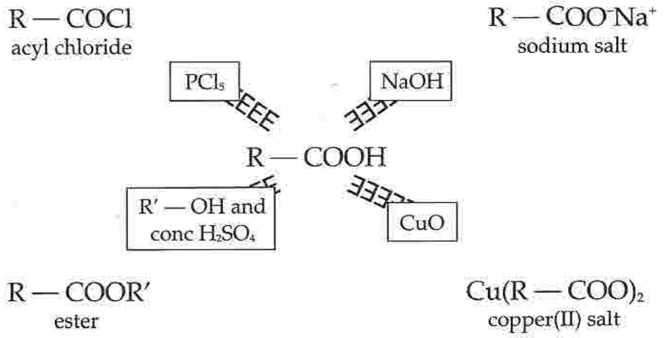
The compound contains two —COOH groups and two alcohol —OH groups. One mole of it has four reactive groups which will produce four moles of HCl.

- **Reaction with alcohols to form esters (esterification)**
  A carboxylic acid reacts with an alcohol in the presence of a little concentrated sulphuric acid, to produce an ester and water.





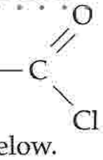
- A summary of the reactions of carboxylic acids is given in Fig 22.5.



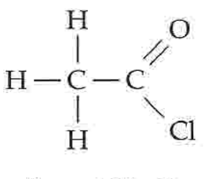
▶ Fig 22.5

22.2 Acyl Chlorides

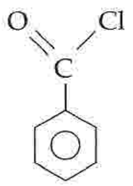
- Acyl chlorides contain the —COCl group,



- Two examples of acyl chlorides are given below.



ethanoyl chloride



benzoyl chloride

Chemical Reactions

- **Reaction with water**

  Acyl chlorides react *rapidly* with water to form a solution of two acids. For example, ethanoyl chloride forms a solution of ethanoic acid and hydrochloric acid:

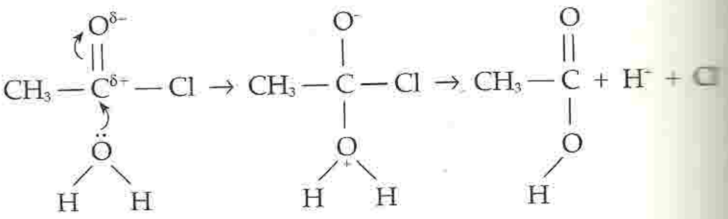
$$CH_3—COCl + H_2O \rightarrow CH_3—COOH + HCl$$

This reaction has three important features:

(a) the reaction is *rapid* and *vigorous* (heat is evolved);
(b) a solution of a *strong* acid is produced (HCl is a strong acid);
(c) a solution of the products gives an *immediate* precipitate of silver chloride, AgCl, with silver nitrate solution.

Thus, acyl chlorides are different from other organic halogen compounds in their reaction with silver nitrate. Only acyl chlorides react directly with silver nitrate solution to give an *immediate* precipitate of AgCl.

Acyl chlorides are rapidly hydrolysed by water because the chlorine atom is quite electronegative and pulls electrons away from the carbon atom of the C=O group. The oxygen atom also pulls electrons from this carbon atom, so it becomes quite positive. Hence a water molecule can easily form a dative bond with the carbon atom, as shown for ethanoyl chloride:

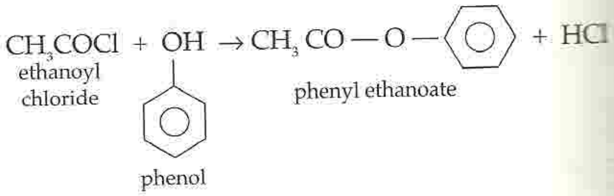


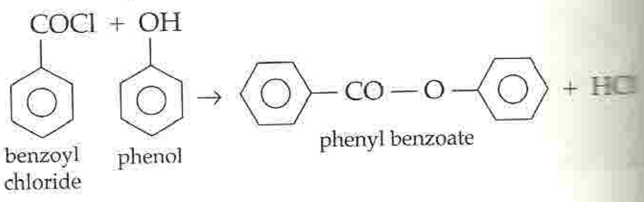
- **Reaction with alcohols and phenols**

  Acyl chlorides react with alcohols and phenols to produce esters. The reaction is rapid and does not require heating.

$$\underset{\text{ethanoyl chloride}}{CH_3COCl} + \underset{\text{butan-1-ol}}{CH_3CH_2CH_2CH_2OH} \rightarrow \underset{\text{butyl ethanoate}}{CH_3CO—O—CH_2CH_2CH_2CH_3} + HCl$$

When phenol is used, it must be dissolved in a base such as sodium hydroxide or pyridine.

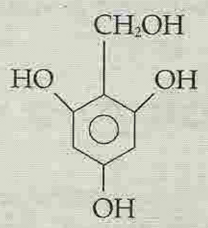




One mole of HCl is obtained from every mole of —OH in the compound that the acyl chloride reacts with.

Question

How many moles of HCl are obtained in the reaction of excess CH_3COCl with the compound below?



Answer

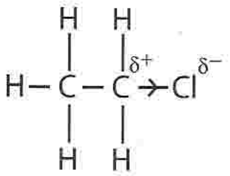
The compound contains one alcohol —OH group and three phenol —OH groups. So one mole of it has four reactive groups which will produce four moles of HCl.

- **Reaction with amines**
  Acyl chlorides with primary amines to produce amides.

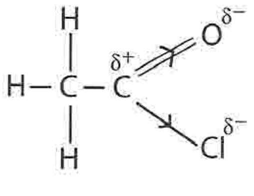
$$CH_3COCl + CH_3CH_2CH_2CH_2NH_2 \rightarrow CH_3CONHCH_2CH_2CH_2CH_3 + HCl$$

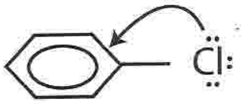
Ease of hydrolysis of halogenocompounds

The relative ease of hydrolysis of halogenocompounds depends on the degree of electron deficiency of the carbon atom to which the halogen is bonded.
In chloroalkane, the carbon atom to which is bonded the chlorine atom is electron-deficient as the chlorine atom is more electronegative than carbon[fig 1].



In acyl chloride the carbon atom bonded to the chlorine atom is also bonded to an oxygen atom(fig2). Therefore electrons are being pulled from the carbon atom both by the chlorine atom as well as by the oxygen atom. Hence the carbon atom in acyl chloride will be more electron deficient than the carbon atom in halogenoalkane, that is the partial positive charge on the carbon atom in acyl chloride is greater than that in halogenoalkane.Hence the acylchloride will attract nucleophile more readily than halogenoalkane.The acyl chloride will be more reactive than the halogenoalkane.



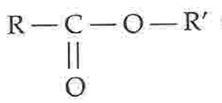


In chlorobenzene, the orbital of one lone pair of electron on the [illegible] atom interacts with the benzene ring and enters into resonance [illegible] the ring(fig 2). As a result a cloud of delocalised electron cloud is [illegible] which:
(i)decreases the polarity of the C—Cl bond
(ii)increases the strength of the C—Cl bond
Therefore the chlorine atom in chlorobenzene cannot be removed [illegible] as a result of which chlorobenzene is almost unreactive.
Hence the ease of hydrolysis increases in the order shown below

$$\xrightarrow[\text{increase in ease of hydrolysis}]{\text{Chlorobenzene} < \text{chloroalkane} < \text{acyl chloride}}$$

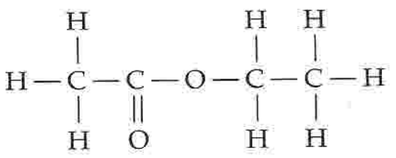
22.3 Esters

- Esters have the general formula



$$R-\underset{\underset{O}{\|}}{C}-O-R' \quad \text{or} \quad R-COO-R'$$

An example of an ester is ethyl ethanoate, $CH_3COOCH_2CH_3$. [illegible] full structural formula of ethyl ethanoate is shown in Fig 22.[illegible]

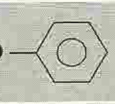
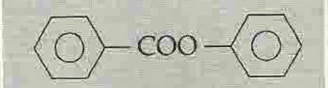
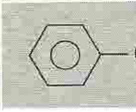


$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-H$$

▲ Fig 22.6

- Esters have the same molecular formulae as carboxylic [illegible] are *neutral compounds.*
- Some examples of esters are shown in Table 22.4.

▶ Table 22.4 Examples of esters

compound	formula	b.p./°C
methyl methanoate	$HCOOCH_3$	32
ethyl ethanoate	$CH_3COOCH_2CH_3$	56
phenyl ethanoate	CH_3COO 	196
phenyl benzoate	 COO	(melts at [illegible]
methyl benzoate	 $COOCH_3$	200

Preparation of esters

- By the reaction between an organic acid or the salt of an organic acid and an aliphatic alcohol, using concentrated sulphuric acid in catalytical amount. The mixture is heated under reflux.A reversible reaction takes place.

$$CH_3CO_2H + CH_3CH_2OH \rightleftharpoons CH_3CO_2CH_2CH_3 + H_2O$$

Note: phenols do not react with organic acids.

- By the reaction between an acyl chloride and an aliphatic or phenols. The phenols is usually dissolved in a suitable base, such as sodium hydroxide, before carrying out the reaction.

$$CH_3COCl + CH_3CH_2OH \longrightarrow CH_3CO_2CH_2CH_3 + HCl$$

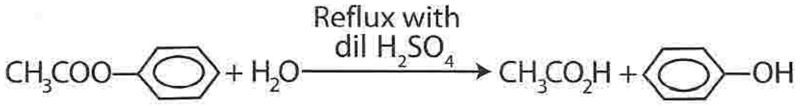
$$R-COO-R^1 + H_2O \xrightarrow{\text{Reflux with dil } H_2SO_4} RCOOH + R^1-OH$$

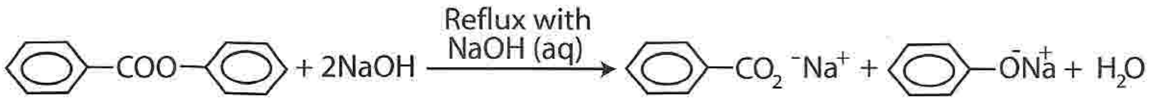
$$CH_3COOCH_2CH_3 + H_2O \overset{\text{Reflux with dil } H_2SO_4}{\rightleftharpoons} CH_3COOH + CH_3CH_2OH$$

$$CH_3CH_2COOCH(CH_3)_2 + OH^- \xrightarrow{\text{Reflux with NaOH (aq)}} CH_3CH_2COO^- + CH_3CH(OH)CH_3$$

Note that *two organic products* are obtained from the hydrolysis of an ester. This is a distinctive characteristic of esters.

An ester made from a phenol instead of an alcohol, is hydrolysed to an acid and a phenol. If dilute sulphuric acid is used for the hydrolysis, two *acidic organic products* are obtained. If sodium hydroxide is used for the hydrolysis, two sodium salts are obtained.



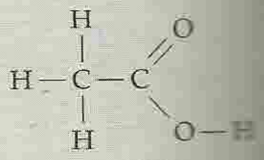


Uses of Esters

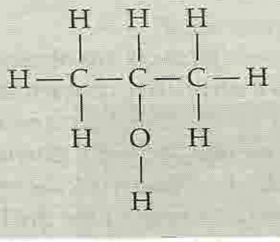
- Esters are used as solvents for paints and varnishes.
- Most esters are sweet-smelling and are used as artificial flavourings for food.
- Esters are used in perfumes

Question A neutral organic compound **P** has the molecular formula $C_5H_{10}O_2$. When **P** is refluxed with dilute sulphuric acid, two organic compounds **Q** and **R** are produced. **Q** has the molecular formula $C_2H_4O_2$. **R** is a neutral compound that gives a yellow precipitate when heated with iodine and aqueous sodium hydroxide. Deduce the structural formulae of **P**, **Q** and **R**. Explain your reasoning.

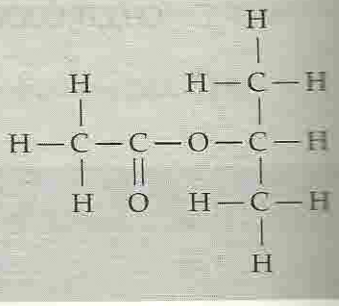
Answer **P** must be an ester because
(a) it is neutral, and
(b) it produces *two* organic products when refluxed with dilute sulphuric acid.
An ester produces an acid and an alcohol when hydrolysed. Hence **R** must be the alcohol, since it is neutral, and **Q** is an acid, ethanoic acid,



R gives a positive triiodomethane reaction, so **R** must contain the $CH_3-CH(OH)-$ group of atoms, ie **R** must be a secondary methyl alcohol. Hence **R** is propan-2-ol (as it must contain three carbon atoms):
[*Note:* other answers are possible]



The formula of **P** is

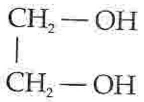


Polyesters

- Condensation polymerisation occurs when monomer molecules join together to produce a polymer molecule *and* other small molecules (which are eliminated). The other small molecules are usually H_2O or HCl molecules.
- The two main types of condensation polymers are
  (a) polyesters (made from alcohols and acids), and
  (b) nylons (made from amines and acids) (see *Nylons* in Chapter 26).

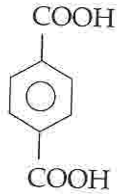
Terylene

- The most common polyester is *Terylene*. *Terylene* is made from the monomers ethane-1,2-diol and benzene-1,4-dicarboxylic acid:



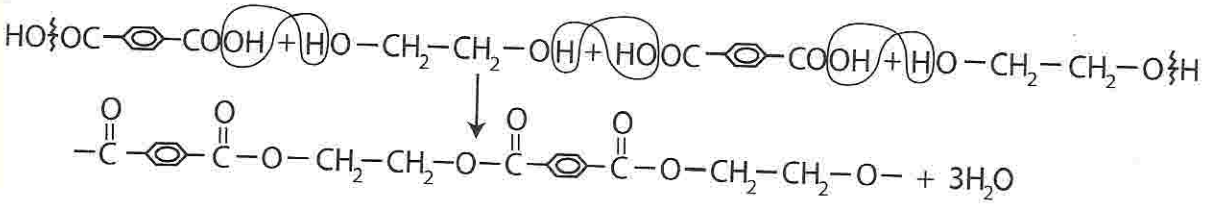
$$\begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array}$$

ethane-1,2-diol

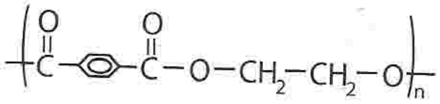


benzene-1,4-dicarboxylic acid

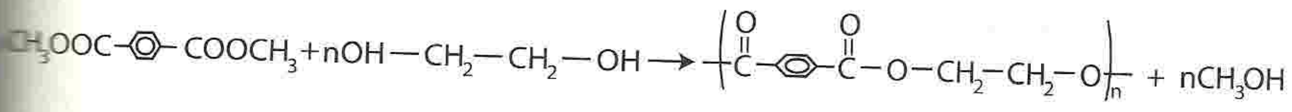
The two monomers react together in a condensation reaction, as shown below.



The simplified formula for *Terylene* is



In practice, *Terylene* is usually made by heating ethane-1,2-diol with the dimethyl ester of benzene-1,4-dicarboxylic acid. Methanol molecules are then eliminated (instead of water molecules) in the condensation reaction:



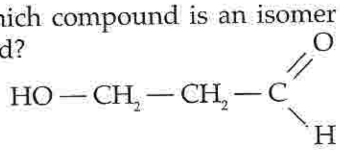
- Materials made of polyesters can be weakened by dilute acids and alkalis. These reagents catalyse hydrolysis of the ester bonds in the polymer chains, so the polyesters change back into their small monomer molecules.

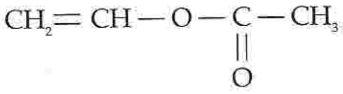
EXERCISE 22

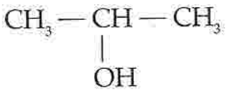
Multiple Choice Questions

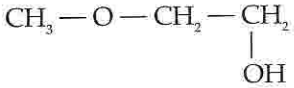
Section I

1 Which compound is an isomer of propanoic acid?

A 
$HO-CH_2-CH_2-CHO$

B 
$CH_2=CH-O-C(=O)-CH_3$

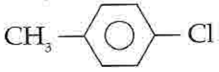
C 
$CH_3-CH(OH)-CH_3$

D 
$CH_3-O-CH_2-CH_2-OH$

2 Which one of the following compounds is a product of the reaction between ethanoyl chloride and phenyl methanol, $C_6H_5CH_2OH$?

A $C_6H_5OCOCH_3$
B $C_6H_5CH_2Cl$
C $C_6H_5CH_2COCl$
D $C_6H_5CH_2OCOCH_3$

3 Which one of the following compounds reacts vigorously with water to produce a strongly acidic solution?

A CH_3CH_2COCl
B CH_3CH_2COOH
C $CH_3CH_2CH_2Cl$
D 

4 Which materials are required to obtain a sample of ethyl ethanoate in the laboratory?

A CH_3COOH, CH_3OH, dilute sulphuric acid
B CH_3COOH, CH_3CH_2OH, concentrated H_2SO_4
C CH_3CH_2OH, CH_3COOH
D CH_3COOH, CH_3CH_2OH, concentrated NaOH

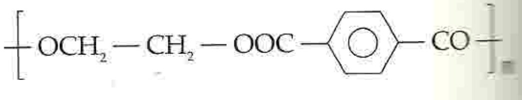
5 What is the organic product when phenol a benzoyl chloride are reacted together?

A $C_6H_5OOC_6H_5$
B $C_6H_5COOC_6H_5$
C $C_6H_5CH_2OCOC_6H_5$
D $C_6H_5COOCH_2C_6H_5$

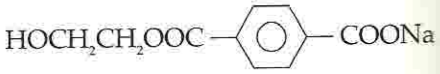
6 In which one of the following are the aci arranged in the order of decreasing pK_a valu

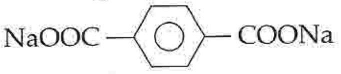
A phenol, ethanol, ethanoic acid, chloroethanoic acid
B ethanoic acid, chloroethanoic acid, phenol, ethanol
C chloroethanoic acid, ethanoic acid, phenol, ethanol
D ethanol, phenol, ethanoic acid, chloroethanoic acid

7 The formula of *Terylene* is



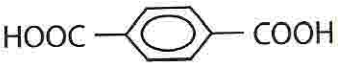
What are the products when *Terylene* completely hydrolysed with dilute sodi hydroxide?

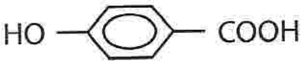
A 

B NaOCH₂CH₂ONa and


C $HOCH_2CH_2OH$ and


D $HOCH_2CH_2OH$, CO_2 and


B. 

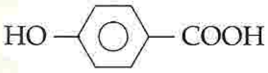
C. 

formula correctly for answers B&C

Which one of the following compounds reacts with ethane-1,2-diol to form a polymer?

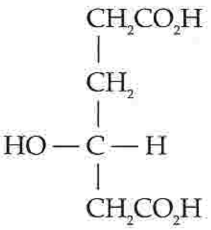
A $HOCH_2CH_2CH_2CH_2CH_2CH_2OH$

B 

C 

D $ClCH_2CH_2CH_2CH_2CH_2COOH$

How many moles of hydrogen chloride are produced when excess PCl_5 is added to one mole of the acid below?



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

What type of organic compounds are commonly used to provide artificial flavourings in sweets?

A ketones
B carboxylic acids
C acyl chlorides
D esters

The same carboxylic acid is obtained either by hydrolysis of a nitrile **X** or by oxidation of alcohol **Y**. Which pair could be **X** and **Y**?

	X	Y
A	CH_3CH_2CN	CH_3CH_2OH
B	$C_6H_5CH_2CN$	$C_6H_5CH_2CH_2OH$
C	$C_6H_5CH_2CN$	$C_6H_3CH_2OH$
D	$(CH_3)_2CHCN$	$(CH_3)_3COH$

Section II

Summary of directions

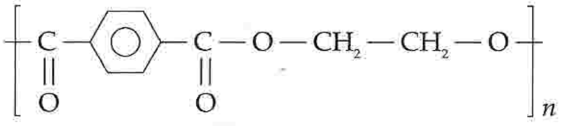
A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

12 Which of the following reactions gives ethanoic acid as one of the products?
1 addition of water to ethanoyl chloride
2 heating ethanal with acidified potassium dichromate(VI)
3 boiling ethyl ethanoate with dilute sulphuric acid

13 Which of the following reagents can react with an ester to produce *two* organic products?
1 aqueous sodium hydroxide
2 dilute sulphuric acid
3 aqueous potassium hydroxide

14 In the hydrolysis of ethanoyl chloride
1 the chlorine atom attracts electrons from the carbon atom of the carbonyl group.
2 the reacting water molecule is a nucleophile.
3 the oxygen atom makes the carbon atom of the carbonyl group slightly negative.

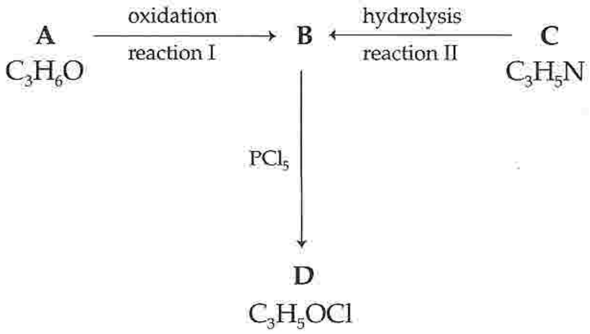
15 In the production of the polymer



from ethane-1,2-diol and benzene-1,4-dicarboxylic acid,
1 a condensation reaction occurs.
2 water is produced.
3 a polyester is produced.

Structured Questions

1 Some reactions of organic compounds **A**–**D** are shown in the flow chart.

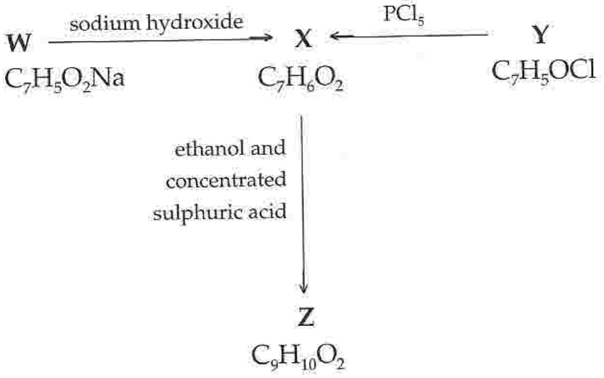


(a) Give the chemical name and structural formula of
  - (i) compound **A**
  - (ii) compound **B**
  - (iii) compound **C**
  - (iv) compound **D**

(b) State suitable reagents and conditions for
  - (i) reaction I
  - (ii) reaction II

(c) How could compound **D** be converted back into compound **B**?

2 Some reactions of organic compounds **W–Z** are shown in the flow chart below.



(a) Suggest the identities of **W–Z** by giving the name or structural formula:
  - (i) compound **W**
  - (ii) compound **X**
  - (iii) compound **Y**
  - (iv) compound **Z**

(b) What is the purpose of the sulpuric acid in the conversion of **X** into **Z**?

(c) Write the equation for the reaction of **Y** with phenol.

3 Compound **P** has composition by mass, C, 40.0%; O, 53.3% and H, 6.67%.

(a) Show that the empirical formula of **P** is CH_2O.

(b) **P** has the following properties or reactions. Say what can be deduced about **P** from each of these.
  - (i) **P** is optically active.
  - (ii) **P** gives a yellow precipitate when warmed with alkaline aqueous iodine.
  - (iii) **P** reacts with aqueous sodium carbonate, producing carbon dioxide gas.

(c) (i) Name two functional groups present in **P**.
  - (ii) Suggest a possible displayed formula for **P**.

(d) **P** reacts with acidified potassium dichromate(VI) to produce organic compound **Q**.
  - (i) Suggest a possible displayed formula for **Q**.
  - (ii) Outline a simple chemical test for the functional group which is present in **Q** but not in **P**.

4 Three organic compounds are isomers. They each have the molecular formula $C_3H_6O_2$. The three isomers react with aqueous sodium hydroxide in three different reactions according to the following equations:

Reaction A: $C_3H_6O_2 + NaOH \rightarrow C_3H_5O_2Na + H_2O$
Reaction B: $C_3H_6O_2 + NaOH \rightarrow CHO_2Na + C_2H_5O$
Reaction C: $C_3H_6O_2 + NaOH \rightarrow C_2H_3O_2Na + CH_3O$

(a) Name and write the full structural formula of the isomer in each reaction.

(b) Outline a simple chemical test to distinguish between the products of reaction A and the products of reaction B.

*5 A monobasic organic acid **X** has the composition 31.6% carbon, 5.3% hydrogen and 63.1% oxygen.

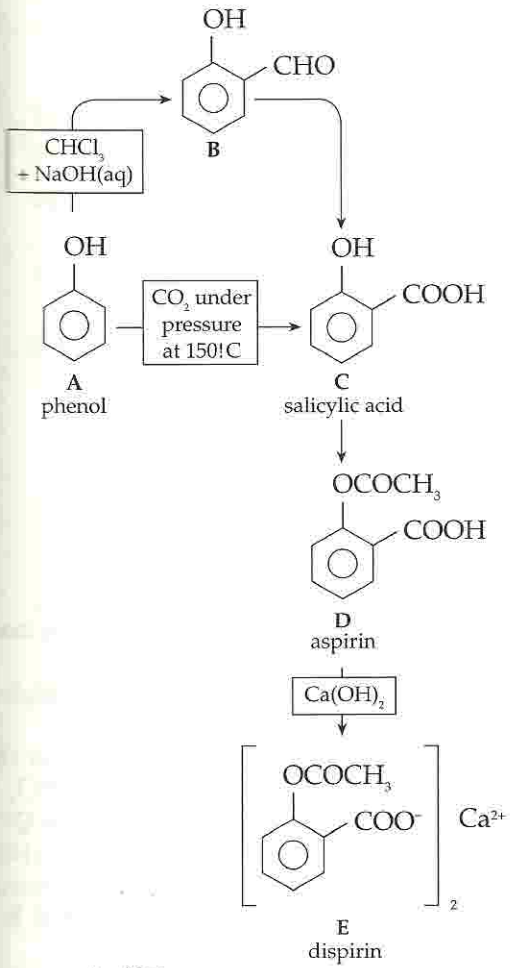
(a) What is the empirical formula of acid X?

(b) An aqueous solution contains 11.4 g of X per dm^3. 20 cm^3 of this solution required 30.0 cm^3 of 0.100 mol dm^{-3} NaOH for reaction in a titration.
  - (i) Calculate the relative molecular mass of the acid.
  - (ii) Deduce the full structural formula of **X**.

(c) Write the structural formulae of the organic products obtained from reacting **X** with

(i) aqueous sodium hydroxide;
(ii) phosphorus pentachloride, PCl_5.

6 The industrial manufacture of two drugs aspirin and dispirin from phenol, by two alternative methods, is shown in the reaction scheme (Fig 22.7).



▲ Fig 22.7

(a) Name the reagents that could be used to carry out the following stages in the laboratory:
   (i) compound **B** into compound **C**;
   (ii) compound **C** into compound **D**.

(b) What type of reaction occurs in the conversion of
   (i) compound **C** into compound **D**;
   (ii) compound **D** into compound **E**?

(c) Outline one test in each case, to show the presence of the
   (i) —OH group, and
   (ii) the —CHO group on the benzene ring in compound **B**.

(d) Dispirin is more effective than aspirin in relieving a headache, because it is more soluble in water. Why is the solubility of dispirin greater?

(e) Suggest which one of the two methods of manufacturing salicylic acid from phenol is cheaper. Give a reason for your answer.

*7 An organic compound **X** has the composition by mass: 38.7% carbon; 51.6% oxygen; 9.7% hydrogen.

(a) Calculate the empirical formula of compound **X**. In an experiment to determine the relative molecular mass of **X**, 0.500 g of vaporised **X** was found to have a volume of 268 cm^3 at a temperature of 400 K and a pressure of 100 kPa.

(b) (i) Calculate the relative molecular mass of compound **X**.
   (ii) What is the molecular formula of **X**?
   (iii) Write a full structural formula for **X**.

(c) When **X** is treated with excess hot acidified potassium dichromate, the final organic product is an acid **Z**. **Z** slowly decolourises warm acidified solution of potassium manganate(VII).
   (i) Write a full structural formula for compound **Z**.
   (ii) Write a balanced equation for the decolourisation of potassium manganate(VII) by compound **Z**.

8. (a) Consider the two reactions of ethanoic acid below.

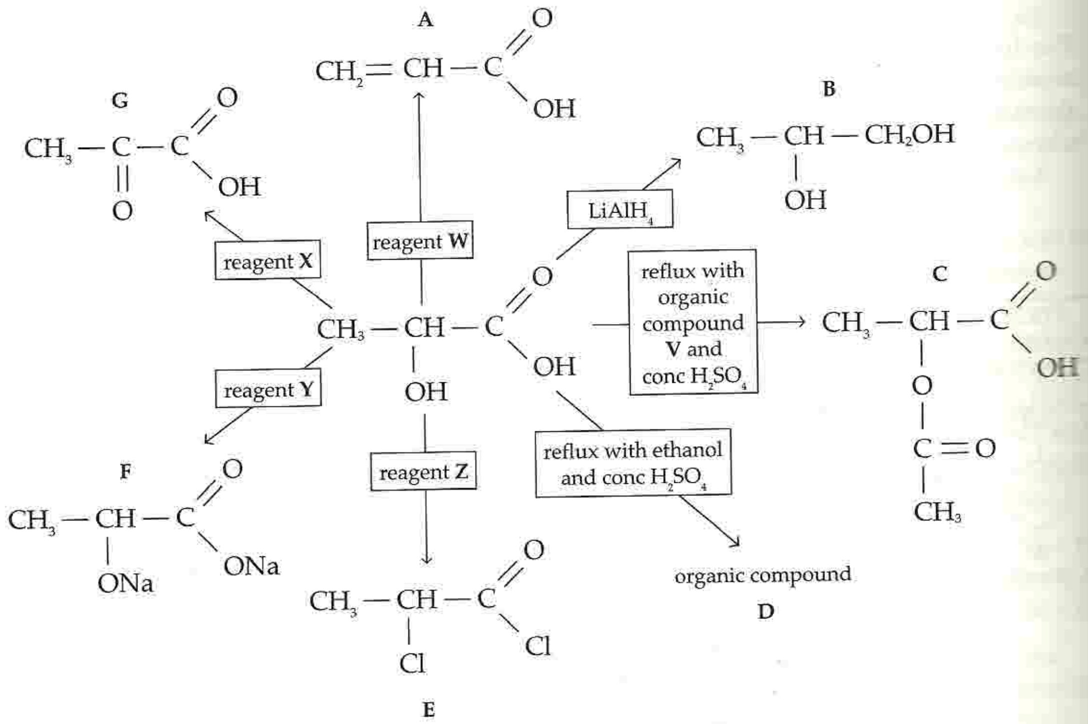
$$A \xleftarrow{PCl_5} CH_3COOH \xrightarrow[U.V]{Cl_2(g)} B$$

Write the display formula of A and B.

(b) What happens (if any) when :
A is added to water followed by aqueous silver nitrate.
Write the balanced equation of A with water.

(c) Briefly discuss the relative acidity of CH_3COOH, $CH_2ClCOOH$, $CHCl_2COOH$ and CCl_3COOH.

9 Some reactions of 2-hydroxypropanoic acid are shown in the reaction scheme in Fig 22.8.



▲ Fig 22.8

(a) Name suitable chemicals which could be the reagents **W**, **X**, **Y** and **Z**.
(b) Name organic compound **V**.
(c) Write the full structural formula of compound **D**.
(d) Which one of the compounds, **A** – **F**, has an ionic structure?
(e) Which of the compounds, **A** – **F**, can exist as optical isomers?
(f) Which one of the compounds, **A** – **F**,
  (i) decolourises a solution of bromine in CCl_4?
  (ii) gives an orange precipitate with 2,4-dinitrophenylhydrazine reagent?
  (iii) reacts with water to form a strongly acidic solution, which gives an immediate white precipitate with silver nitrate solution?
(g) Outline how 2-hydroxypropanoic acid is made from ethanal in the laboratory.

10* Compound **Q has the composition 78.7% carbon, 13.1% oxygen and 8.2% hydrogen.
(a) Find the empirical formula of **Q**.
In an experiment, 0.294 g of the vapour of **Q** at 100 kPa and 500 K, was found to have a volume of 100 cm^3.
(b) (i) Calculate the relative molecular mass M_r, of **Q**.
  (ii) Hence find the molecular formula of **Q**.

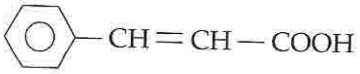
Compound **Q** is a neutral compound that produces hydrogen chloride gas with PCl_5.
(c) What functional group is present in **Q**?
When compound **Q** is boiled with a mixture of sulphuric acid and potassium dichromate(VI), an organic acid **R** is obtained.
When **Q** is heated with concentrated sulphuric acid, an organic compound **S** is obtained. **S** rapidly decolourises a solution of bromine in an inert solvent.
(d) Deduce structural formulae for
  (i) **Q**, (ii) **R** and (iii) **S**.
(e) Which one of the compounds, **Q**, **R** or **S** (if any), forms optical isomers? Explain your answer.

Descriptive Questions

1 Describe how you would distinguish between the following pairs of compounds in the laboratory, by a chemical test. In each case

— describe what you would do;
— state what is observed for each compound;
— write equations for any reactions that occur.
(a) $CH_3CH_2COCH_3$ and CH_3CH_2COOH
(b) CH_3COCl and $CH_3CH_2CH_2CH_2Cl$
(c) CH_3COCl and C_6H_5COCl
(d) $CH_3COCH_2CH_3$ and $CH_3CH_2COCH_2CH_3$

2



The formula of cinnamic acid is shown above.
(a) How and under what conditions would cinnamic acid react with
  (i) bromine;
  (ii) ethanol?
(b) Cinnamic acid shows *cis-trans isomerism*. Explain this statement.
(c) The main source of cinnamic acid is from an ester found in plant oils. The ester consists of cinnamic acid combined with phenylmethanol, $C_6H_5CH_2OH$.

Write a full structural formula for the ester and outline how the cinnamic acid could be obtained from this ester.

3 (a) State and explain the relative strengths of ethanoic acid, chloroethanoic acid and trichloroethanoic acid.
(b) Outline how the following compounds could be prepared from the starting chemical given.
  (i) $CH_3CH_2CH_2CO_2H$ from $CH_3CH_2CH_2CH_2I$
  (ii) $CH_3CH_2CH_2CO_2H$ from $CH_3CH_2CH_2Br$
  (iii) $CH_3CH(OH)CO_2H$ from CH_3CHO

4 Two neutral isomeric compounds, **P** and **Q**, have the molecular formula $C_{14}H_{12}O_2$.

When compound **P** is hydrolysed with boiling aqueous sodium hydroxide, compounds **X** and **Y** are obtained. Compound **X** is a sodium salt with the formula $C_7H_5O_2Na$. Compound **Y** is a neutral compound with the formula C_7H_8O.

When compound **Q** is hydrolysed with boiling aqueous sodium hydroxide, compounds **X** and **Z** are obtained. Compound **X** is the sodium salt with the formula $C_7H_5O_2Na$. Compound **Z** is also a sodium compound. When compound **Z** is treated with hydrochloric acid, a weakly acidic organic compound is obtained.

Write the full structural formulae for compounds **P**, **X** and **Y**. Write one possible full structural formula for compound **Q** and the *three* possible isomers for compound **Z**. Show your working.

*5 (a) Write balanced equations for the reaction of ethanoyl chloride with
  (i) water,
  (ii) ethanol,
  (iii) phenol, and
  (iv) phenylamine.
(b) A sample of ethanoyl chloride required 40.0 cm^3 of 0.2 mol dm^{-3} aqueous sodium hydroxide for complete reaction. Calculate the mass of ethanoyl chloride in the sample.

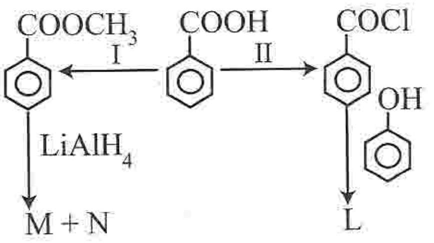
*6 Some information is given below on six organic compounds, **P** – **U**. In each case deduce a full structural formula for the compound and explain the chemical reactions.
(a) Compound **P**, molecular formula C_2H_3ClO, reacts vigorously with water, producing a strongly acidic solution and fumes of hydrogen chloride gas.
(b) Compound **Q**, molecular formula $C_8H_8O_2$, is a neutral liquid. When **Q** is boiled with aqueous sodium hydroxide for some time and the products acidified with dilute hydrochloric acid, a white precipitate of compound **R** is obtained. **R** has the molecular formula $C_7H_6O_2$.
(c) Compound **S**, molecular formula $C_3H_6O_2$, is a neutral liquid. When **S** is boiled with dilute hydrochloric acid for some time, a mixture of two organic products is obtained. One product, **T**, is an acid. The other organic product, **U**, is neutral. When **U** is vaporised, 0.100 g of the vapour is found to have a volume of 72.2 cm^3 at 100 kPa and at 400 K.

*7 A monocarboxylic acid **X** is found in animal milk. **X** has the composition by mass: 62.1% carbon; 27.6% oxygen; 10.3% hydrogen.
A 0.20 g of **X** required 17.2 cm^3 of 0.10 mol dm^{-3} sodium hydroxide for neutralisation.
(a) Calculate the empirical and molecular formula of **X**.
(b) **X** can be synthesised in the laboratory from 1-bromopentane by a two-stage reaction sequence:

$$CH_3(CH_2)_4Br \rightarrow Z \rightarrow X$$

(i) Suggest the reagents and conditions necessary for each step of the synthesis.
(ii) Predict the structural formulae of **X** and **Z**, explaining your reasoning.

8. Consider the following reactions of benzoic acid.



(a) Name the reagents and conditions for step I.
(b) Write the molecular formula of M and N.
(c) Name a reagent for step II.
(d) Write a balanced equation for the formation of L.
Draw the display formula of A.
(e) What is the function of the NaOH.
(f) When L is refluxed with aqueous NaOH and the mixture is refluxed , the distillate does not contain an organic product. But when dilute hydrochloric acid is added to the mixture then distilled, an organic product is the first distillate.

(i) Explain the type of reaction of L with NaOH.
(ii) Write the names and structural formulae of the products.
(iii) Why does an organic product appear in the distillate only after the addition of HCl ?

CHAPTER

23

ORGANIC NITROGEN COMPOUNDS

SYLLABUS OBJECTIVES

In this chapter you should be able to:

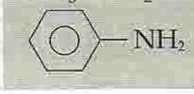
- interpret and use the chemical names, general formulae and displayed formulae of primary amines, amides and amino acids
- describe the formation of ethylamine (eg by reduction of a nitrile) and phenylamine (by reduction of nitrobenzene)
- explain the basicity of amines
- explain the relative basic strength of ammonia, ethylamine and phenylamine in terms of their structures
- describe the reactions of phenylamine with aqueous bromine
- describe the formation of amides from $RNH_2/RCOCl$ (eg primary amines with acyl chlorides)
- describe the hydrolysis of amides by aqueous alkali or acid
- diazonium ions and coupling reactions to form azodyes
- describe the acid/base properties of amino acids and the formation of zwitterions
- describe the characteristics of condensation polymerisation in polyamides such as peptides, proteins and nylons
- suggest the type of polymerisation reaction (ie addition or condensation) from a given monomer or type of monomer and hence deduce the repeat unit of the polymer obtained
- for polyamides, suggest the type of polymerisation reaction from a given section of the polymer obtained
- for polyamides, identify the monomer(s) present in a given section of a polymer (eg the amino acids in a section of a protein)
- describe the formation of peptide bonds between amino acids and hence explain protein formation

- There are three main types of organic nitrogen compounds.
  - (a) **Primary amines**: These compounds have the general fo R—NH_2.
  - (b) **Amides**: Simple amides have the general for R—CO—NH_2.
  - (c) **Amino acids:** Amino acids contain an acidic —COOH g and a basic —NH_2 group.

23.1 Amines

- Some examples of primary amines are given in Table 23.1.

▶ Table 23.1 Examples of primary amines

compound	formula	b.p./!C
methylamine	$CH_3—NH_2$	–7 (g
ethylamine	$CH_3—CH_2—NH_2$	17
propylamine	$CH_3—CH_2—CH_2—NH_2$	49
butylamine	$CH_3—CH_2—CH_2—CH_2—NH_2$	78
phenylamine		184

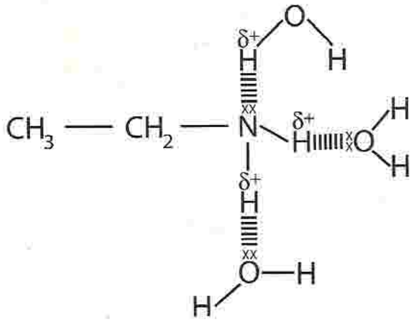
Physical Properties

- Amines have a molecular structure. In the solid or liquid state forces between the molecules are *hydrogen bonds*.
- Amines have low melting and boiling points, but the boiling p of an amine is higher than that of an alkane of similar mass size.

  propylamine $CH_3CH_2CH_2NH_2$, M_r = 59; b.p. = +78!C
  butane $CH_3CH_2CH_2CH_3$, M_r = 58; b.p. = –0.5!C

  The amine has the higher boiling point because of hydrogen b between the molecules.
- Amines are soluble in water because they form hydrogen b with water (Fig 23.1).

  The solubility of amines in water decreases as the relati molecular mass becomes larger.



▲ Fig 23.1 Ethylamine in water

Preparation

- Amines can be made by the reduction of nitriles (R—C compounds) with lithium aluminium hydride. The nitriles a obtained by boiling halogenoalkanes with potassium cyanide i alcohol.

$$R-X \xrightarrow{\boxed{\text{KCN in alcohol}}} R-CN \xrightarrow{\boxed{LiAlH_4}} R-CN_2-NH_2$$

$$CH_3CH_2I + CN^- \xrightarrow{\text{Reflux with alc.kCN}} CH_3CH_2CN + I^-$$

$$CH_3CH_2CN + 4[H] \xrightarrow[\text{in dry ether}]{\text{Reflux with } LiAlH_4} CH_3CH_2CH_2NH_2$$

The equation for the reduction of ethanonitrile can be written as:

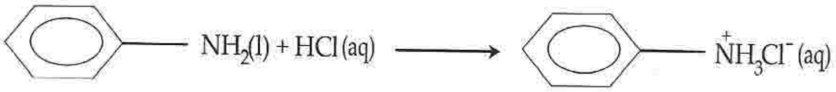
$$CH_3-CH_2-CN + 4[H] \rightarrow CH_3-CH_2-CH_2-NH_2$$

- Amines can also be made by heating halogenoalkanes with ammonia (see *Halogenoalkanes* in Chapter 19).
- Aromatic amines are made by the reduction of aromatic nitrocompounds. For example, phenylamine is made by reducing nitrobenzene with tin and concentrated hydrochloric acid:

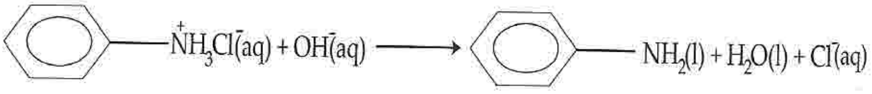
The equation for this reaction can be written as:

$$C_6H_5-NO_2 + 6[H] \rightarrow C_6H_5-NH_2 + 2H_2O$$

In practice, since phenylamine is a base, as soon as it is formed, it will react with the hydrochloric acid to produce phenylammonium chloride.

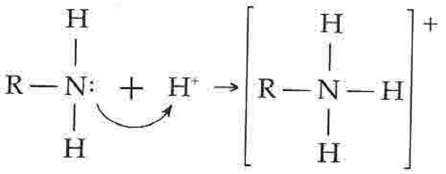


Sodium hydroxide is then added to the solution of phenylammonium chloride, as a result of which the phenylamine is liberated from the mixture as a separate layer.



Basic Properties of Amines

- Amines are weak bases. The nitrogen atom can use its lone pair of electrons to form a dative bond with a proton (H^+). The nitrogen atom is a proton acceptor.



$$R-\underset{H}{\overset{H}{N}}: + H^+ \rightarrow \left[R-\underset{H}{\overset{H}{N}}-H\right]^+$$

- Amines are weak alkalis in water.

  $$CH_3—CH_2—NH_2 + H_2O \rightleftharpoons CH_3—CH_2—NH_3^+ +$$

- Amines react with acids to form salts.

  $$CH_3—NH_2 + HCl \rightarrow CH_3—NH_3^+Cl^-$$

  $$2CH_3—CH_2—NH_2 + H_2SO_4 \rightarrow (CH_3—CH_2—NH$$

- The salts are analogous to ammonium salts. Like amm amines are produced again when the salts are rea aqueous sodium hydroxide.

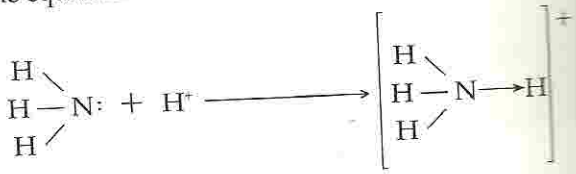
  $$CH_3—NH_3^+Cl^- + NaOH \rightarrow CH_3—NH_2 + NaCl + H$$

  $(CH_3—CH_2—NH_3^+)_2 SO_4^{2-}$ reacts with aqueous sodium to give the amine and sodium sulphate.

  $$(CH_3—CH_2—NH_3^+)_2SO_4^{2-} + 2NaOH \rightarrow 2CH_3—CH_2— \\ + Na_2SO$$

Relative Strength of Amines as Bases

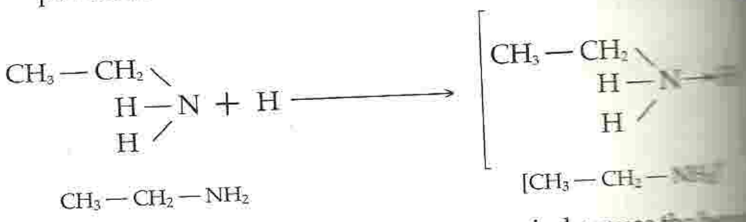
- Ammonia is a weak base. It reacts with hydrogen ions to the equation:

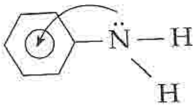


- In the reaction, the lone pair of electrons from the nitro forms a dative bond with the hydrogen ion.

  Any process that helps to push electrons from the form the dative bond, will make it easier for ammonia the proton to form NH_4^+ and hence make ammonia a base.

- When a hydrogen atom in ammonia is replaced $—CH_2—CH_3$ group, the compound ethylamine is $(CH_3—CH_2—NH_2)$. The $—CH_2—CH_3$ group pushes towards the nitrogen, so that the lone pair of electrons the dative bond with H$^+$ more easily. The ethylamine powerful base than ammonia, as it is a stronger proton





▲ Fig 23.2

- Phenylamine is a *weaker* base than ammonia, because the ring pulls electrons away from the nitrogen, towards the (Fig 23.2). The lone pair of electrons from the nitrogen partly delocalised around the benzene ring. Hence the atom is less able to use the lone pair of electrons to protons.

The relative basic strength of ammonia, ethylamine and phenylamine are in the order:

Strongest base $\xrightarrow{\hspace{6cm}}$ *Weakest base*

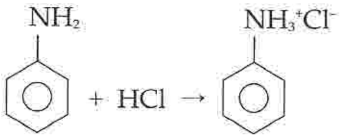
ethylamine, ammonia, phenylamine

Reactions of Phenylamine, $C_6H_5NH_2$

- Phenylamine has a —NH_2 group directly attached to the benzene ring. Thus phenylamine has the reactions of the —NH_2 amine group and the benzene ring.

Reactions of the —NH_2 group

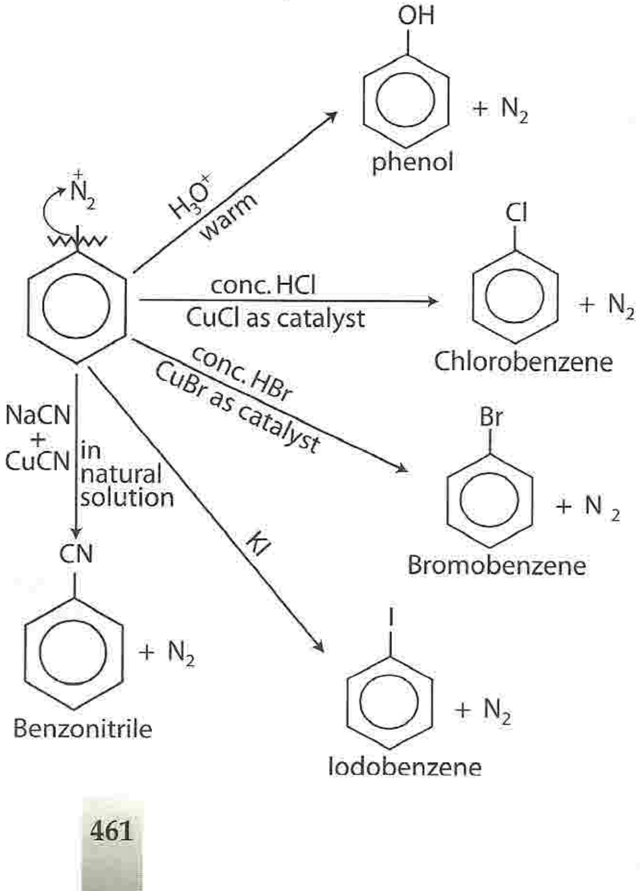
(a) Phenylamine reacts with acids to form salts.



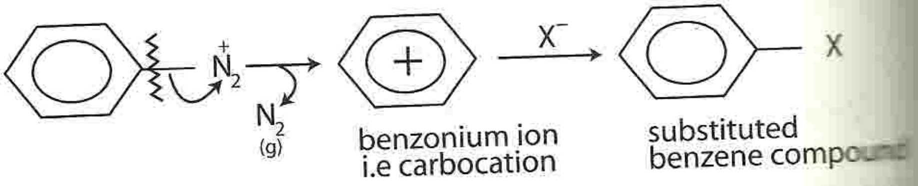
- Phenylamine reacts with nitrous acid, $(NaNO_2/ H_3O^+)$, below 5°C to form a solution of benzenediazonium ions.

$$C_6H_5NH_2+HNO_2(aq) + H+(aq) \rightarrow C_6H_5\overset{+}{N}_2(aq) + 2H_2O(l)$$

- Benzenediazonium salts are never isolated due to their explosive nature. In fact the diazonium ions is very reactive and is used as intermediate to prepare other aromatic compounds.
- When it reacts with nucleophiles, nitrogen gas evolves and substituted benzene compounds are formed as shown below.



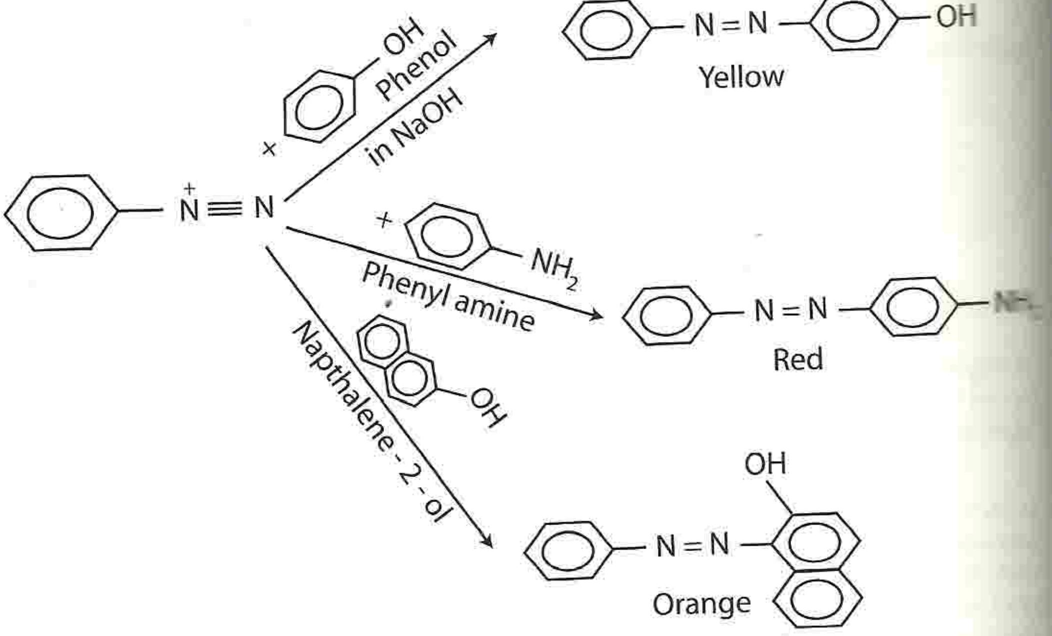
- All the above reactions pass through an intermediate, benz ion.



- Coupling reactions

  In such reactions the benzene diazonium can behaves as a electrophile due to the positive charge on the -N≡N

  It attacts the cloud of another benzene ring to form compou containing the -N∃N- bond between two aromatic rings. Such reactions are known as coupling reactions. Highly coloured dia compounds are formed. These are used as dyes.

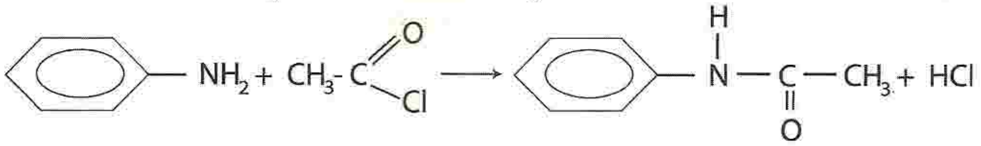


- The bezene diazonium ion bonds preferentically to position – on the other aromatic ring. If this position is occupied then the diazonium ion bonds to position -2 on the aromatic ring.

- The azo dyes are brightly coloured due to extensive electr delocalisation between the two aromatic rings via the -N=N group.

- Since the azo compounds are stable, azo dyes are fast, that is they do not lose their colour easily.

(b) Phenylamine reacts with acyl chlorides to form substituted amides.



Reaction of amines with nitrous acid.

- Nitrous acid ,HNO_2 is an unstable substance. Therefore it is usually prepared in situ by the reaction between sodium nitrite and hydrochloric acid at a low temperature(usually < 5^{0}C).

$$NaNO_2(s) + HCl(aq) \longrightarrow HNO_2(aq) + NaCl(aq)$$

- When nitrous acid reacts with a primary amine, effervescence occurs and nitrogen gas as well as a primary alcohol are produced.

For example consider the reaction between nitrous acid and ethylamine.

$$CH_3CH_2NH_2(aq) + HNO_2(aq) \longrightarrow CH_3CH_2OH(aq) + N_2(g) + H_2O(l)$$

- When nitrous acid reacts with a secondary amine,a yellow oil, referred to as a nitrosoamine is produced.

For example consider the reaction of dimethylamine with nitrous acid

$$(CH_3)_2HN(l) + NHO_2(aq) \longrightarrow (CH_3)_2N-N=O(l) + H_2O(l)$$

N-nitrosodimethylamine(yellow oil)

- When nitrous acid reacts with a tertiary amine,a trialkyl ammonium salt is produced which is soluble in water

For example consider the reaction between triethylamine and nitrous acid

$$(C_2H_5)_3N(l) + HNO_2(aq) \longrightarrow (C_2H_5)_3\overset{+}{N}HNO_2^-(aq)$$

- Therefore the reaction of aliphatic amines with nitrous acid can be used to distinguish between primary, secondary and tertiary amines as the three amines give different visible reactions.

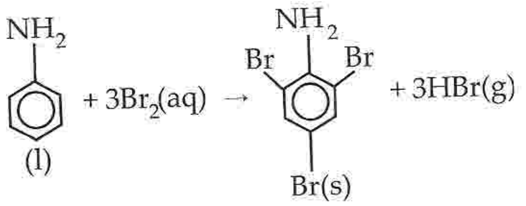
Aliphatic amine	Reaction with nitrous acid
Primary amine	Effervescence occurs and nitrogen gas is produced.
Secondary amine	A yellow oily layer is produced
Tertiary amine	No **visible** reaction occurs.

- The products of the reaction of aromatic amines with nitrous acid depends largely upon the temperature at which the reaction is carried out.

(i) If the reaction between nitrous acid and aromatic amine is carried out at a temperature higher than 10^{0}C, effervescence occurs and nitrogen gas is produced.

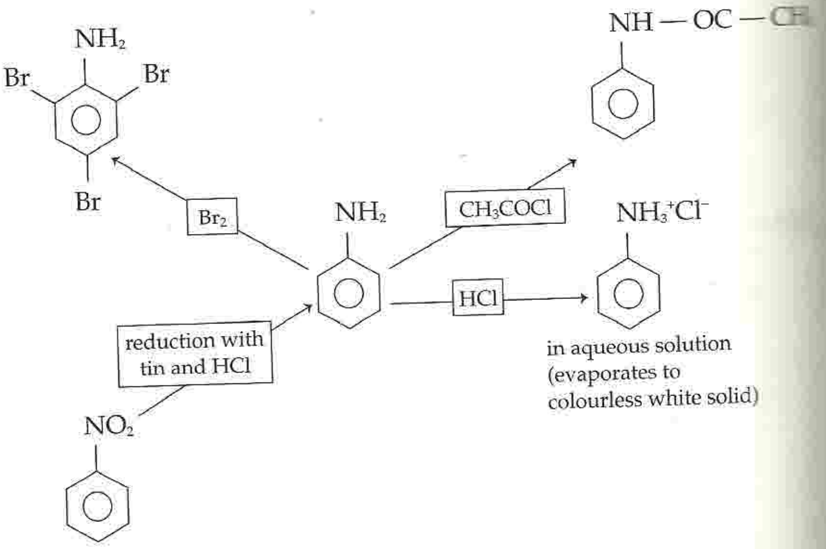
Reactions of the benzene ring

The —NH_2 group in phenylamine makes the benzene ring much more reactive than benzene itself. Thus phenylamine reacts with aqueous bromine to produce a white precipitate of 2,4,6-tribromophenylamine and fumes of hydrogen bromide evolve...



In the reaction, the bromine is decolourised.

In this reaction, phenylamine resembles phenol; both compounds in water give an immediate precipitate with aqueous bromine (and decolourise the bromine) (see *Phenols* in Chapter 20).



▶ Fig 23.3 Reactions of phenylamine

Test for Phenylamine

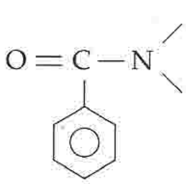
Add aqueous bromine to an aqueous solution of phenylamine. A white precipitate of tribromophenylamine is obtained and the bromine is decolourised.

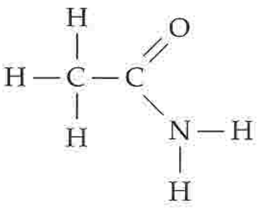
23.2 Amides

- Simple amides contain the —CO—NH_2 group of atoms.
- Substituted amides have the formula R—CO—NH—R′. An example of a substituted amide is CH_3—CO—NH—CH. Substituted amides contain the —CO—NH— group of atoms which is called the **peptide bond**.

- Amides are made by reacting acyl chlorides with ammonia or amines.

$$\underset{\text{ethanoyl chloride}}{CH_3\text{—}CO\text{—}Cl} + NH_3 \rightarrow \underset{\text{ethanamide}}{CH_3\text{—}CO\text{—}NH_2} + HCl$$


benzamide


or $CH_3\text{—}CO\text{—}NH_2$

ethanamide

- Amides are solids. They dissolve in water to form neutral solutions.
- Hydrolysis of amides
  Amides are hydrolysed by boiling with dilute acids (HCl or H_2SO_4) or with dilute alkalis (NaOH)

  The overal reactions are:

$$\underset{\text{amide}}{R\text{—}CONH_2} + H_2O \longrightarrow RCOOH + NH_3$$

$$\underset{\text{substituted amide}}{R\text{—}CONH-R' + H_2O} \longrightarrow RCOOH + R'NH_2$$

(a) If dilute sodium hydroxide is used, the sodium salt of the organic acid is obtained and ammonia gas evolves. The latter is used to distinguish an amide from an amine. Amines do not evolve ammonia gas.

$$\underset{\text{ethanamide}}{CH_3CONH_2(aq)} + NaOH \xrightarrow{\text{reflux}} CH_3CO\bar{O}\overset{+}{Na}(aq) + NH_3(g)$$

$$\underset{\text{N - phenylethanamide}}{CH_3CONHC_6H_5} + NaOH \xrightarrow{\text{reflux}} CH_3CO\bar{O}\overset{+}{Na} + \underset{\text{phenylamine}}{C_6H_5NH_2}$$

(b) If dilute acid is used, a carboxylic acis and an ammonium salt are obtained.

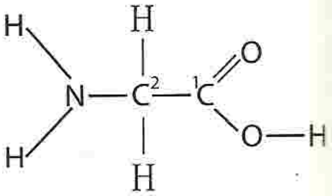
$$\underset{\text{ethanamide}}{CH_3CONH_2(aq)} + H_3\overset{+}{O}(aq) + C\bar{l}(aq) \longrightarrow \underset{\text{ethanoic acid}}{CH_3COOH(aq)} + \underset{\text{ammonium chloride}}{\overset{+}{N}H_4C\bar{l}(aq)}$$

$$CH_3CONHC_6H_5(l) + H_3\overset{+}{O}(aq) + C\bar{l}(aq) \longrightarrow CH_3COOH(aq) + \underset{\text{phenyl ammonium chloride}}{C_6H_5\overset{+}{N}H_3C\bar{l}(aq)}$$

23.3 Amino Acids

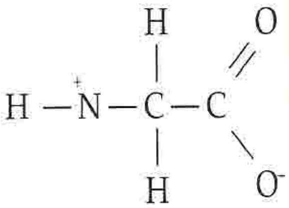
- An amino acid contains an acidic —COOH group *and* a basic —NH_2 group. Amino acids contain the -NH_2 group on the carbon atom adjacent to the -COOH group. They are known as 2-amino acids. An example of an amino acid is aminoethanoic acid:

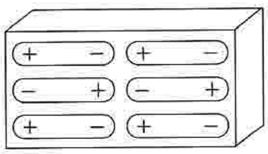
$H_2N—CH_2—COOH$ or



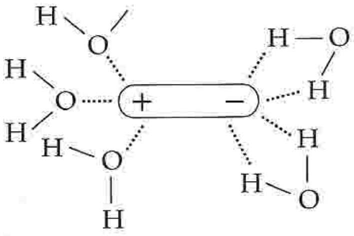
- Amino acids are crystalline solids. They are soluble in water.
  In the solid state and in neutral aqueous solution, the H^+ from the —COOH group goes to the basic —NH_2 group to form a **zwitterion**. A zwitterion is a particle containing both a positive ion and a negative ion. The zwitterion formed by aminoethanoic acid is shown below.

$^+H_3N—CH_2—COO^-$ or





▲ Fig 23.4 Simplified structure of solid aminoethanoic acid



▲ Fig 23.5 Zwitterion in water

In solid aminoethanoic acid, the lattice particles are zwitterions. The forces between the zwitterions are mainly electrovalent bonds (Fig 23.4).

Aminoethanoic acid dissolves in water because it is ionic (Fig 23.5). Amino acids can also form hydrogen bonds with the water molecules.

- In acidic solution (eg in dilute HCl), the amino acid molecules are positive ions. The —NH_2 group accepts a proton from the acid. For example, aminoethanoic acid particles in acidic solution (pH < 7) are $^+H_3N—CH_2—COOH$.
- In alkaline solution (eg in dilute NaOH), the amino acid molecules are negative ions. The OH^- of the alkali takes a proton from the —COOH group. For example, aminoethanoic acid particles in alkaline solution (pH > 7) are $H_2N—CH_2—COO^-$.

Chemical Reactions of Amino Acids

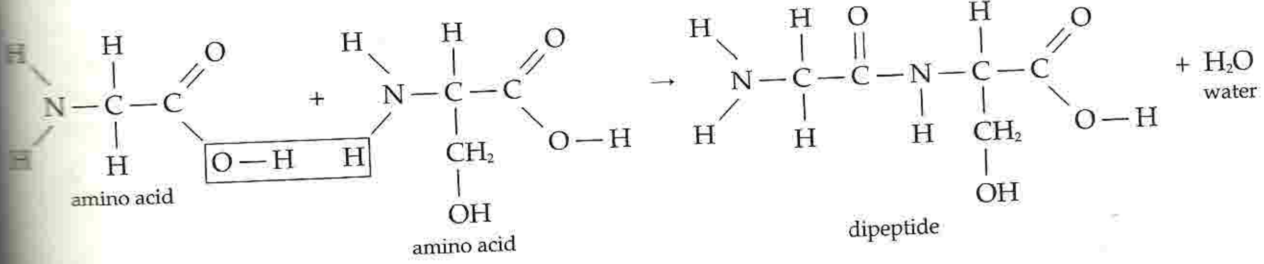
- Amino acids have the reactions of the —NH_2 group *and* the —COOH group.
- **Reaction with acids to form salts**
  Amino acids react with acids to form salts. This is a reaction of the —NH_2 group.

$$H_2N—CH_2—COOH + HCl \rightarrow {}^-Cl^+H_3N—CH_2—COOH$$

- **Reaction with alkalis to form salts**
  Amino acids react with alkalis to form salts. This is a reaction of the —COOH group.

  $$H_2N—CH_2—COOH + NaOH \rightarrow H_2N—CH_2—COO^-Na^+ + H_2O$$

- **Condensation of amino acids**
  Two or more amino acids can be joined together to form a **polypeptide**. If two amino acids are joined together, the organic product is called a **dipeptide**. Three amino acids join together to form a **tripeptide**, etc.
  When amino acids join together, a **peptide bond** is formed between the —COOH group of one molecule and the —NH_2 group of another molecule. The reaction is called **condensation**, because water is eliminated.
  When amino acids join together, a **peptide bond** is formed between the —COOH group of one molecule and the —NH_2 group of another molecule. The reaction is called **condensation**, because water is eliminated.



EXERCISE 23

Multiple Choice Questions

Section I

1 What type of reaction mechanism occurs when phenylamine reacts with aqueous bromine?
- A electrophilic substitution
- B nucleophilic substitution
- C nucleophilic addition
- D electrophilic addition

2 Which compound will react with aqueous sodium hydroxide to produce a gas that turns damp red litmus paper blue?
- A $NH_2—CH_2—COOH$
- B $C_6H_5—NH_2$
- C $CH_3—CO—NH_2$
- D $CH_3—CO—NH—C_6H_5$

3 Which one of the following shows the formula of aminoethanoic acid particles in a dilute aqueous solution?
- A $H_2N—CH_2—COOH$
- B $^+H_3N—CH_2—COOH$
- C $H_2N—CH_2—COO^-$
- D $^+H_3N—CH_2—COO^-$

4 In which of the following are the properties of phenol and phenylamine similar?
- A effect on Universal Indicator
- B reaction with aqueous sodium hydroxide
- C reaction with hydrochloric acid
- D reaction with aqueous bromine

5 The formula of nylon 6 is shown below.

$$[—NH—(CH_2)_5—CO—]_n$$

Which compound is obtained from the acid hydrolysis of nylon 6?
- A $^+NH_3—(CH_2)_5—OH$
- B $HO—(CH_2)_5—CO_2H$
- C $^+NH_3—(CH_2)_5—CO_2H$
- D $HO_2C—(CH_2)_4—CO_2H$

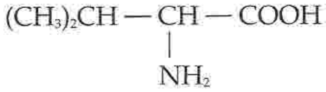
6 Which one of the following reagents does *not* react with phenylamine?
- A bromine
- B hydrochloric acid
- C ethanoyl chloride
- D ammonia

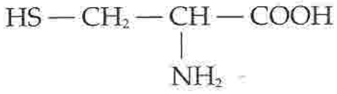
7 Why is phenylamine a weaker base than ethylamine in water?
- A Phenylamine is less soluble in water.
- B Phenylamine does not form hydrogen bonds with the water.
- C In phenylamine, the protons are attracted to the benzene ring rather than to the nitrogen atom.
- D In phenylamine, the lone pair of electrons on the nitrogen atom is delocalised.

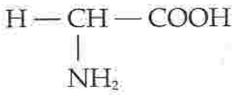
8 Which one of the following amino acids does *not* have a chiral centre?

A

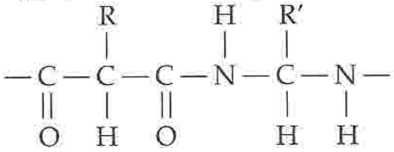
$H_2N-OC-\underset{NH_2}{\underset{|}{CH}}-COOH$

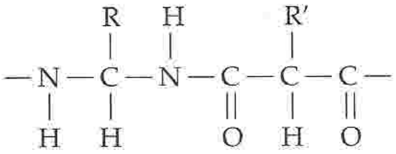
B

$(CH_3)_2CH-\underset{NH_2}{\underset{|}{CH}}-COOH$

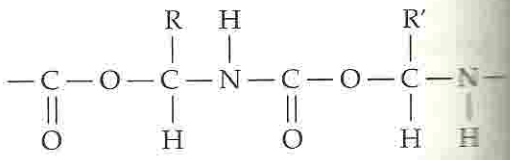
C

$HS-CH_2-\underset{NH_2}{\underset{|}{CH}}-COOH$

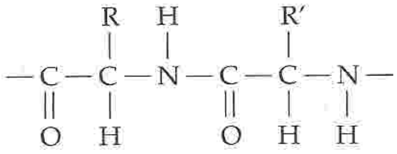
D

$H-\underset{NH_2}{\underset{|}{CH}}-COOH$

9 Which one of the following represents parts of a polypeptide chain in a protein?

A


B


C


D


The amino acid $NH_2CH_2CH_2CH_2CH_2COOH$ polymerises to form a polymer. What is the repeat unit of this polymer?

A $—NH—(CH_2)_4—CO—$

B $—NH—(CH_2)_4—COO—$

C $—NH—(CH_2)_4—COO—NH—$

D $—NH—(CH_2)_4—NH—CO—(CH_2)_4—CO—$

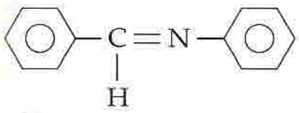
Reducing a nitrate **P** and reacting a bromo-compound **Q** with ammonia give the same product.

	P	Q
A	CH_3CH_2CN	CH_3CH_2Br
B	$(CH_3)_2CHCN$	$(CH_3)_3CBr$
C	$C_6H_5CH_2CN$	$C_6H_5CH_2CH_2Br$
D	C_6H_5CN	C_3H_3Br

What is the organic product when phenylamine, $C_6H_5NH_2$, reacts with benzoyl chloride, C_6H_5COCl?

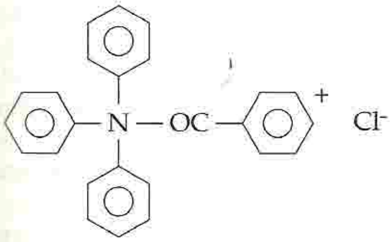
A

B



C

D



Which one of the following compounds can polymerise by itself to produce a condensation polymer?

A $HOOC—(CH_2)_6—COOH$

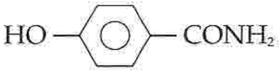
B $H_2N—(CH_2)_6—NH_2$

C $ClOC—(CH_2)_6—COCl$

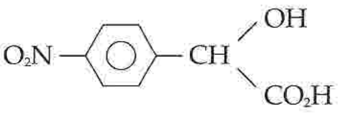
D $H_2N—(CH_2)_5—COOH$

14 Which one of the following nitrogen compounds possesses a chiral centre *and* forms a zwitterion?

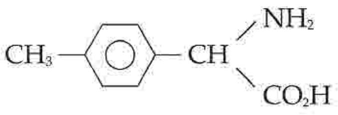
A



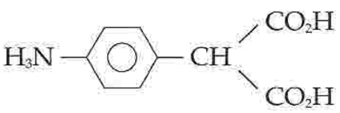
B



C



D



Section II

Summary of directions

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

15 A type of nylon has the repeat unit $—[CO—(CH_2)_4—CO—NH—(CH_2)_6—NH]—$ What takes place when the nylon is made from hexane-1,6-dioic acid and hexane-1,6-diamine?

1 Condensation polymerisation takes place.

2 Peptide bonds are formed.

3 Ammonia is eliminated.

16 Which of the following compounds react with ethanoyl chloride, producing hydrogen chloride as one of the products?

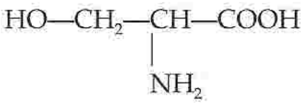
1 phenylamine

2 1-aminohexane

3 aminoethanoic acid

Structured Questions

1 The compound serine has the formula shown below.



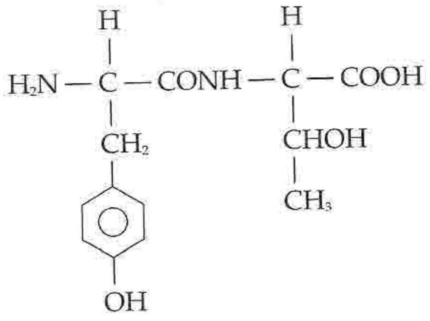
$$HO—CH_2—\underset{\displaystyle NH_2}{\underset{|}{CH}}—COOH$$

(a) Serine has a chiral centre. Draw a ring around part of the molecule to show where it is.

(b) Write the formulae of the particles of serine in aqueous solution
   (i) at pH = 7,
   (ii) at pH = 12, and
   (iii) at pH = 2.

(c) Two molecules of serine can combine together, eliminating a molecule of water.
   (i) Write the displayed formula of the organic product.
   (ii) What type of reaction is this?
   (iii) What type of substance is produced from joining together large numbers of serine molecules by a similar reaction?

2 The formula of a dipeptide is shown below. The dipeptide is made from two amino acids, **A** and **B**.



(a) Write the displayed formulae of amino acids **A** and **B**.

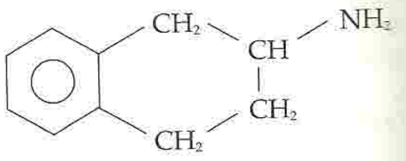
(b) (i) How can a mixture of amino acids **A** and **B** be obtained from the dipeptide?
   (ii) How could this mixture of amino acids be separated?

(c) One of the two amino acids, **A**, when warmed with a solution of iodine and aqueous sodium hydroxide, produced a yellow precipitate.
   (i) What is the yellow precipitate?
   (ii) What group of atoms in the amino acid produces this yellow precipitate?
   (iii) Draw the structural formula of amino acid **A**.

(d) Amino acid **B** reacts with aqueous bromine. Draw the formula of one possible organic product of this reaction.

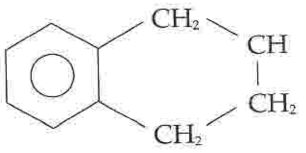
(e) Amino acids **A** and **B** can be condensed together to form a dipeptide *isomeric* with the dipeptide above. Write the structural formula of this dipeptide.

3 Benzedrine is a drug that can be used to keep people awake. Its structure is shown below.

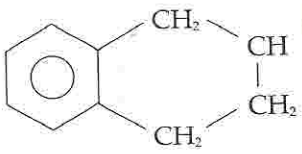


(a) Cirles any chiral centres in this molecule.

(b) Complete the structural formula below to show the organic product when benzedrine reacts with ethanoyl chloride.



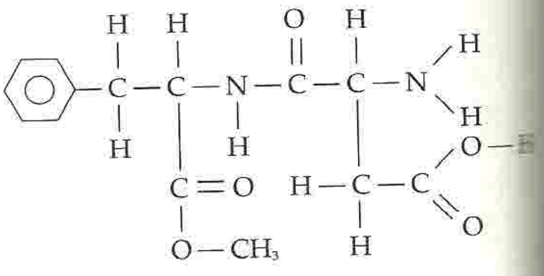
(c) Benzedrine is almost insoluble in water but is very soluble in hydrochloric acid.
   (i) Complete the structural formula below to show the organic product when benzedrine dissolves in hydrochloric acid.



   (ii) In this reaction, benzedrine is acting as a base. Briefly explain this fact, using the Bronsted-Lowry theory of acids and bases.

(d) Suggest the formula of the final organic product, containing a benzene ring, when benzedrine is refluxed with acidified concentrated potassium manganate(VII).

4 Aspartame is a common artificial sweetener used in sugar-free drinks. Aspartame is the methyl ester of a dipeptide. Its structural formula is shown below.



(a) Mark the two chiral centres in the structure above, with an asterisk (*) for each chiral centre.

(b) Draw a ring around the peptide link or bond in the structure above.

(c) Aspartame is hydrolysed in the body into its two component amino acids and a third organic compound.
   - (i) What does the term hydrolysis mean?
   - (ii) Suggest how hydrolysis of aspartame might be carried out in the laboratory.
   - (iii) What is the third organic product of the hydrolysis?

(d) Aspartame is commonly used in acidic soda drinks. Suggest how you would attempt to find out if the aspartame in a soda drink had been partly hydrolysed into its amino acids.

(e) One of the amino acids from which aspartame is made does *not* contain a benzene ring. Write the displayed formula of the zwitterion formed by this amino acid.

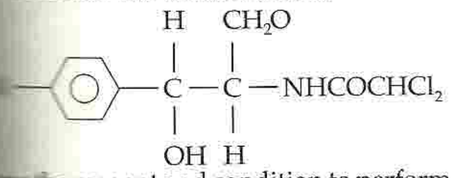
An organic nitrogen compound, A, has the following composition by mass :
61.01% of Carbon, 15.25% of hydrogen and 23.73% of nitrogen.
   - (i) Calculate the empirical formula of A.
   - (ii) Give the name and structural formula of A.

When A is treated with nitrous acid, effervescence occurs, nitrogen gas evolves and an alcohol B is formed.
   - (i) Write a balanced equation for the reaction.
   - (ii) Give the name and structural formula of B.

How and under what conditions does A react with
   - (i) hydrochloric acid.
   - (ii) Ethanoyl chloride

In each case write balanced equation. Give the name and display formula of the products.

Consider the scheme below.



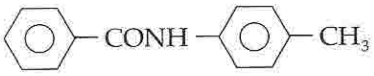
the reagent and condition to perform step
   - (i) I
   - (ii) II

(b) The amines are said to be basic.
Explain how the amines behave as bases.

(c) Arrange the following compounds in order of increasing basic strength
$NH_3C_6H_5\,NH_2$ $\quad$ $CH_3\,NH_2$
$(CH_3)_2\,NH$

Give a brief explanation of your reasoning.

7. Consider the structure below.



(a) Identify two functional groups in the above compound.

(b) When M is refluxed with dilute hydrochloric acid two organic products are formed. An acid N and another nitrogen compound K.
   - (i) Write a balanced equation for the reaction of M with dilute hydrochloric acid.
   - (ii) Write the structural formulae fo N and K.

(c) When K is treated with nitrous acid between 0°C to 5°C, a yellow liquid is formed.
   - (i) Write a balanced equation for the reaction.

Give the name and structural formula of k.

Descriptive Questions

*1 Some information is given on five organic compounds, **A** to **E**. For each compound, write its full structural formula and explain the reactions and properties described.

(a) Compound **A**, molecular formula C_2H_5NO, slowly produces an alkaline gas when boiled with aqueous sodium hydroxide.

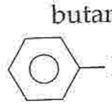
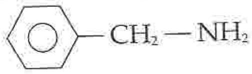
(b) Compound **B**, molecular formula C_7H_9N, reacts with cold nitrous acid to form a diazonium compound.

(c) Compound **C**, relative molecular mass =123, reacts with tin and hydrochloric acid to produce compound **E**. When an aqueous solution of compound **E** is shaken with aqueous bromine, the bromine is decolourised and a white precipitate is formed.

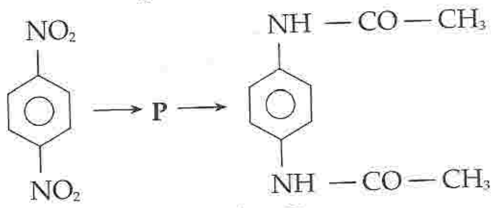
2 (a) Outline a simple chemical test in each case to distinguish between the following pairs of compounds. Write equations for the chemical reactions, where possible.

(i) phenol and phenylamine;

(ii) butan-1-ol and butylamine;

(iii)  and 

(b) Suggest how you would carry out the following conversion.



Identify intermediate **P**.

3. (a)(i) Explain the term zwitterion.

(ii) Draw the display formula of the zwitterion of 2-aminoethanoic acid.

(b) Explain what happens to the zwitterions when :

(i) a few cm^3 of an alkali is added. In each case draw the formula of the ion formed.

(c) How does the molecular 2-aminoethanoic acid react with :

(i) sodium hydroxide

(ii) hydrochloric acid

(iii) nitrous acid

(iv) ethanol

Give conditions, write balanced equations and name the organic products.

4. (a) Give the structural formula of the benzenediazonium chloride ?

(b) How and under what conditions does the benzenediazonium ion reacts with

(i) water

(ii) potassium iodide

(i) copper(1) chloride

Write balanced equation for each reaction, name the organic products formed and give their structural formulae.

(c) The benzenediazonium ion undergoes coupling reaction with other aromatic ring to form highly coloured compounds known as azodyes.

(i) What do you understand by coupling reaction.

(ii) Why are the azodyes highly coloured and are fast dyes ?

(d) Write the structural formula of the azo compound formed when the benzenedazonium ion reacts with

(i) phenol in an alkaline medium

(ii) napthalen – 2ol

(iii) N-dimethylphenylamine

CHAPTER

24

Peptides and Protein

Syllabus Objectives

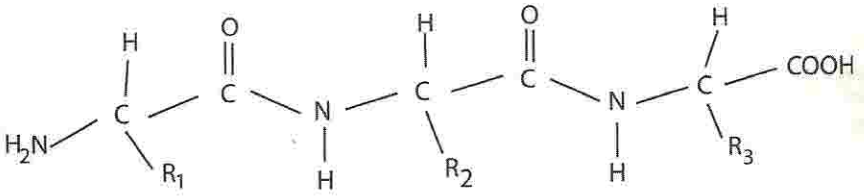
In this chapter you should be able to:

- Recall that protein are condensation polymers of amino acids. Distinguish between the structures of primary, secondary and tertiary proteins
- Describe and explain the characteristric of enzymes and their functions. What are enzymes inhibitors, cofactors and coenzymes.
- Competitive and non-competitive enzyme inhibitors
- The structure of the DNA. Replication of genetics information. The function of the RNA. DNA mutation and genetically based diseases.The DNA profiling.
- Hydrolysis of ATP to ATP+Pi with energy release.
- Why some metal ions are essential to life and recognise that others are toxic.

24.1 Proteins

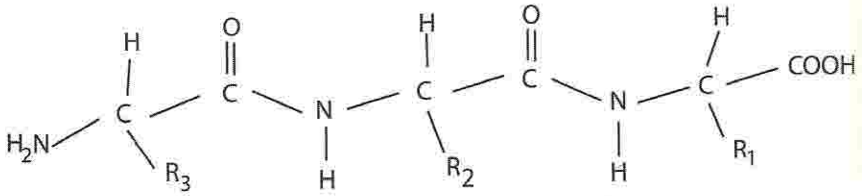
- Each protein contains a fixed number of amino acid residues bond to each other in a definite sequence. This sequence is known as the primary structure of the protein. The structure of a tripeptide is shown below.

▸ Fig 24.1



- By convention the terminal $-NH_2$ group of the first amino acid is on the left and the terminal –COOH group of the third amino acid is on the right.

Thus a different tripeptide with the same three amino acid can be constituted such as



$R_3 - R_2 - R_1$

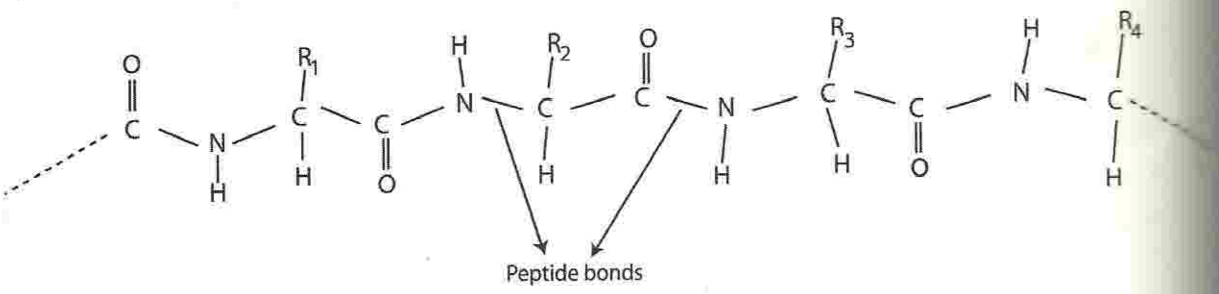
Where the $-NH_2$ group of R_3 is still on the left and the –COOH group of R_1 is still on the right.

- Each type of protein in a biological organism has its unique sequence of amino acids. It is this sequence that gives the protein its ability to accomplish its characteristic function.

- **Primary structure**

  The primary structure of a protein is the sequence of the amino acids which forms the protein. It shows how the atoms of the protein molecules are linked by covalent bonds to form the chains. It is the primary structure which determines what the protein is, how it folds and defines its functions.

▸ Fig 24.2 In a protein, there is a repeated unit of peptide linkages. For example

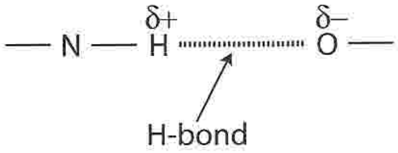


Here R_1 R_2 R_3 and R_4 represent different type of amino acids chains. There are indeed a very very large number of ways in which these amino acids can be arranged.

- The peptide structure of proteins can be obtained by different methods. For example by:
  (i) hydrolysis of the protein by acids, bases or enzymes. Peptides and eventually amino acids are formed.
  (ii) infrared spectra show bonds characteristic of the amino group.
  (iii) identification of the amino acids is done by electrophoresis.

- **Secondary structure**

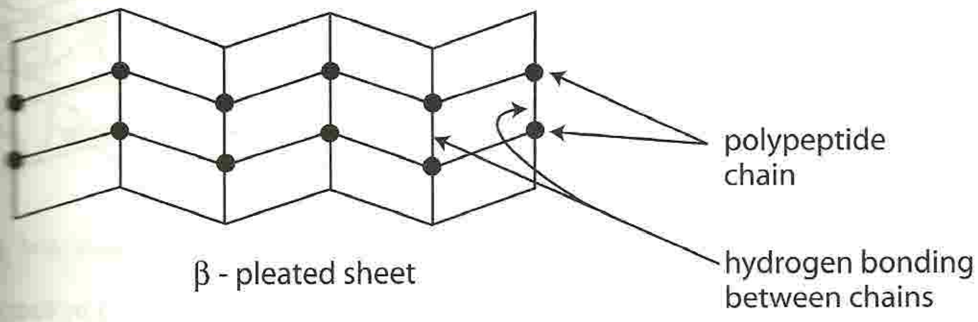
The structure of secondary proteins have been extensively studied by x-ray diffraction. It indicates that there are regular repeated structural units. The key importance has been the stabilising effect where a large number of hydrogen bonds between peptide chains hold the longer peptide chains.
The hydrogen bonds are formed between:



$$-N-\overset{\delta+}{H}\cdots\cdots\overset{\delta-}{O}-$$

One such arrangement gives a pleated sheet which is known as the beta sheet arrangement. The chains lie side by side and they are held by strong hydrogen bonds.

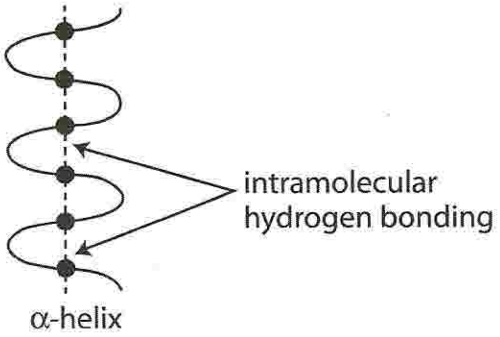
An example of the **β–pleated** sheet is in silk fibroin.



- However when the side chain (R) in the amino acid residues are quite large, they are better stabilised when the peptide chain coiles. A helix is formed.

The helix is stabilised by intra H-bonds between different parts of the same chain. The amino acid residues in a helix is of the same configuration, the L-configuration, then the helix is right-handed as shown below. This is known as the alpha-helix, L-helices occur in unstretched wool, hair, horn and nails.

Fig 24.4



- ## Tertiary structure

A tertiary structure is formed when each α-helix coils onto itself to form a superhelix. Every 35 turns of an α-helix makes another turn. Then six of these superhelices are woven about a seventh straight strand. Thus forming a seven strand cable. These occur via hydrogen bonding.

It is the tertiary structure that accounts for the three-dimensional shape of the globular protein. The unique twisted or folded form of the protein is a result of random coil of the pleated and helical secondary structure.

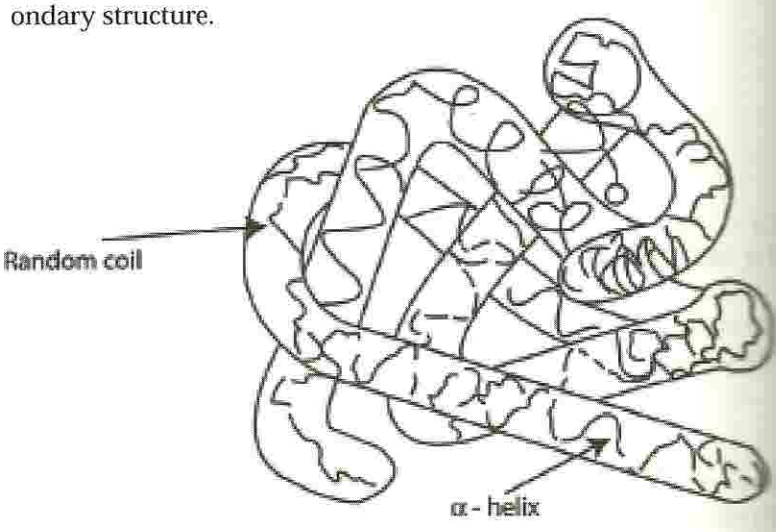


Fig 24.5

Examples are enzymes, antibodies, some hormones and globulin of blood serum.
The stabilisation of the tertiary structure is achieved by four ways.

These are:

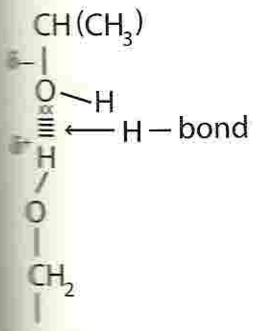
1. Covalent bonds

Here disulfide bridges occur between different parts of the protein when S – H group occurs on the amino acid residues.

$$\square - S - H + H - S - \square \xrightarrow{[O]} \square - S - S - \square + H_2O$$

$$R - S - H + H - S - R \xrightarrow{[O]} R - S - S - R + H_2O$$

24.6 Polypeptide Chain



Such bonding occurs in hair in its normal structure. During the curling of hair the – S – S bridges are reduced.

$$-S-S- + 2\,[H] \longrightarrow -S-H + H-S-$$

With curlers the – S – H groups are displaced. Then an oxidizing agent is used on the curled hair so as to form new linkages that retain the curls or waves.

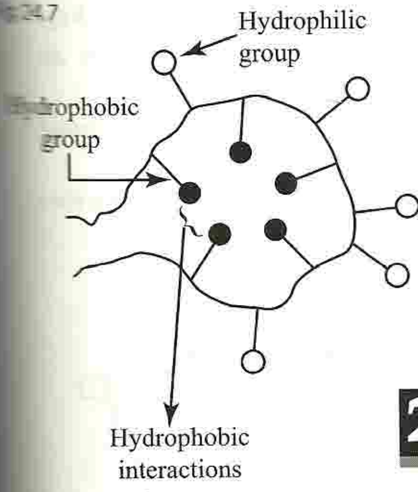
2. Hydrogen bonding

In this case there are polar groups on the side chain such that hydrogen bonding are formed between them.

3. Salt bridges

In these cases ionic bonds, that is electrostatic forces are formed between $-\overset{+}{N}H_3$ and $-COO^-$ groups.

24.7

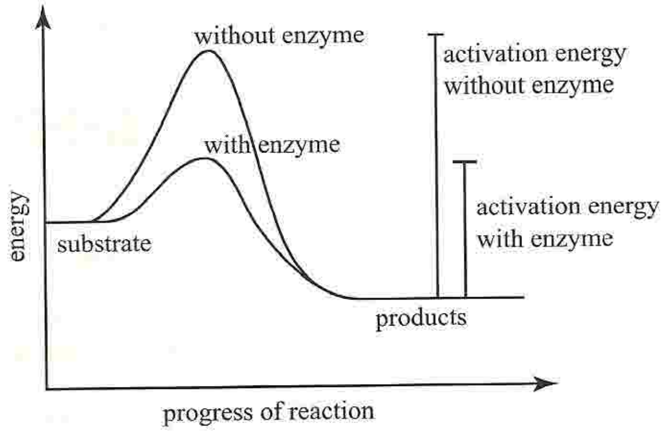


4. Hydrophobic interactions or Van der Waals' interaction

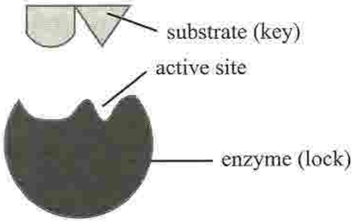
The non-polar, hydrophobic side group of the amino acid residues tend to lump together on the inside. This forces the protein chain to clump together into a tertiary shape. The polar parts of the molecules remain on the outside. This interaction excludes water from the non-polar interior of the protein. This is in fact an entropy induced process.
Then each polypeptide chain is called a subunit. The subunits are held together in a precise structural arrangement.

24.2 Enzyme

- The enzymes are usually water soluble globular proteins.
- They increase the rate of a biological reaction without being used up at the end of the reaction.
- They usually act by providing an alternative reaction pathway that has a lower activation energy than the uncatalysed reaction.



- Enzymes have 'grooves' or 'clefts' of specific three dimensional structure. These 'grooves' or 'clefts' are known as the active site of the enzyme.
- The substance upon which an enzyme acts is called a substrate.
- The substrate has a similar shape to the active site of the enzyme.



- Enzymes act through the 'Lock and Key' mechanism.

THE LOCK AND KEY MECHANISM

- The enzyme**(E)** acts as the lock and the substrate**(S)** acts as the key.
- The substrate binds reversibly with the enzyme to form an enzyme/substrate **(E/S)** complex.
- Bonds in the substrate weaken and are broken. An enzyme/product(s)**(E/P)** complex is formed.
- The enzyme releases the product(s)**(P)** and can be used for further enzymatic reactions.

$$E + S \rightleftharpoons E / S \longrightarrow E / P \longrightarrow E + P$$

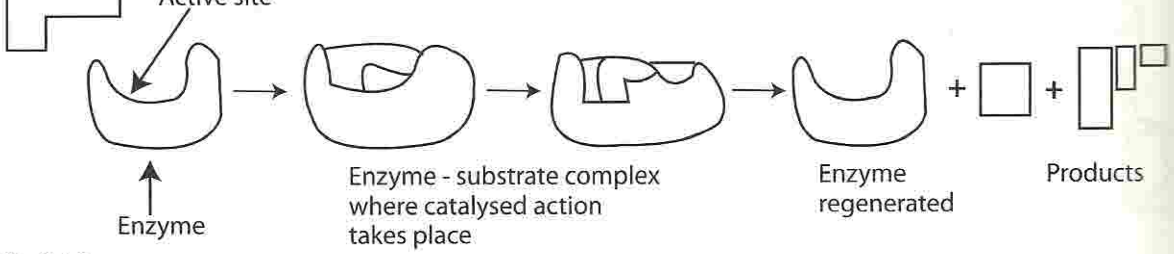


Fig 24.2

24.3 Competitive and Non-competitive Inhibitors

- An inhibitor is a substance that slows down the rate of the enzyme catalysed reaction.
  If the inhibitor forms covalent bonds with the enzyme, the inhibition is irreversible. Then the structure of the enzyme is either destroyed or permanently modified. But if weak forces of attractions bind the enzyme and the inhibitor, inactivity of the enzyme is reversible.
- Thus there are two main types of inhibition.
  These are:

(i) Competitive inhibition

Here the shapes of the inhibitor and the substrate are similar. They slow down the reaction because they occupy the active sites on the enzyme which become less accessible to the substrate. Yet no reaction occurs to form products.

When the inhibition is reversible, an increase in the concentration of the substrate reduces the impact of inhibition. This is according to le chatelier's principle, the excess substrates minimises the effect of the inhibitor.

Therefore the extent of competitive inhibition depends on:

— the concentration of the substrate
— the concentration of the inhibition

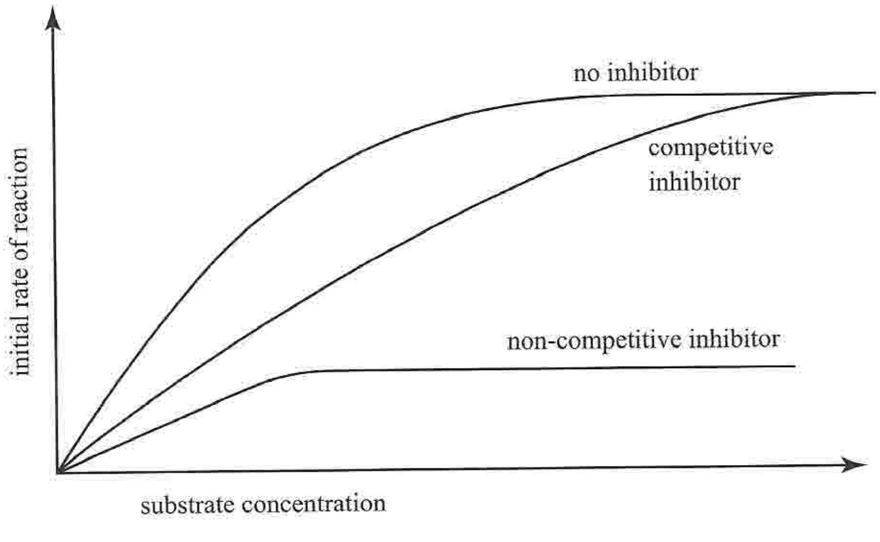
Fig 24.3

Here substrate is in the active site of enzyne

Here a competitive inhibition is in the enzyme active site

(ii) Non-competitive inhibitor

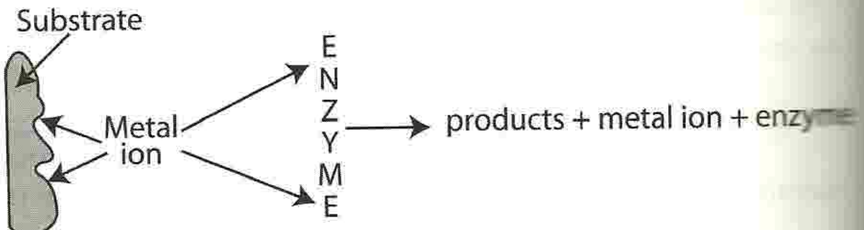
The non-competitive inhibitor binds on any site on the enzyme, but not on the active site. This causes the enzyme to change its shape so that the substrate cannot bind with the enzyme. Here the shape of the inhibitor is not similar to the substrate and there is no competition between substrate and inhibitor. With non-competitive inhibitors, increasing the concentration of the substrate has no effect since the enzyme's shape still remains altered.



24.4 Cofactors and co-enzymes

- Many enzymes require additional help from other substances so that they may function effectively. These additional substances are known as cofactors. These may be ions such as manganese, zinc, magnesium or iron or even small molecules such as hydrogen. It is believed that the cofactors temporary bind to the enzyme and substrate during the reaction.
  Also the cofactor may not act as a primary catalytic centre, it may simply stabilise the structure of the enzyme protein in its catalytically active form.

▸ Fig 24.3. For example a metal ion may act as a bridge initially linking the enzyme and the substrate.



- **Co-enzymes**

  An organic cofactor is a co-enzyme. The coenzyme forms covalent bond with the peptide portion of the enzyme. Thus the enzyme is activated to perform a specific task. For example in the biological oxidation of ethanol to ethanal. The reaction is catalysed by an enzyme, and an organic molecule, commonly known as NAD acts as co-enzyme. Here the enzyme brings together the ethanol and the co-enzyme and the latter does the actual oxidation by abstracting a hydride ion from the ethanol molecules.

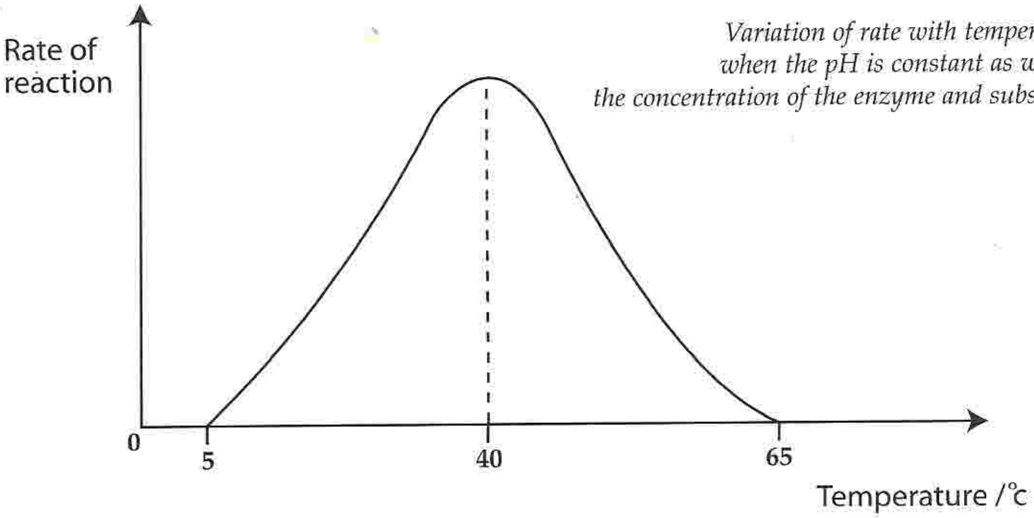
$$CH_3\,CH_2OH + \overset{+}{NAD} \longrightarrow CH_3CHO + \underset{\substack{\uparrow \\ \text{Reduced NAD}}}{NADH} + \overset{+}{H}$$

Co-enzymes are often derived from a vitamin. Vitamins are complex organic substances which are supplied in the diet for proper growth and maintenance of structure. They are, in fact, needed for their co-enzyme activity.

24.5 The effect of Temperature, pH changes and Heavy metal ions on Enzymes Activity

- The action of an enzyme is related to its specific shape. Increase in temperature increases enzymatic reaction rates as the substrates collide with the active sites on the enzyme more frequently with the necessary activation energy. However the rate of the reaction drops sharply when the temperature increases beyond a certain point. The thermal agitation of the enzyme disrupts the hydrogen bonding, ionic bonding or other non-covalent attractions that stabilise the active site and rate of reaction drops.
  Then the enzyme is said to be denatured. The optimum temperature for most enzymes is about 40°C.

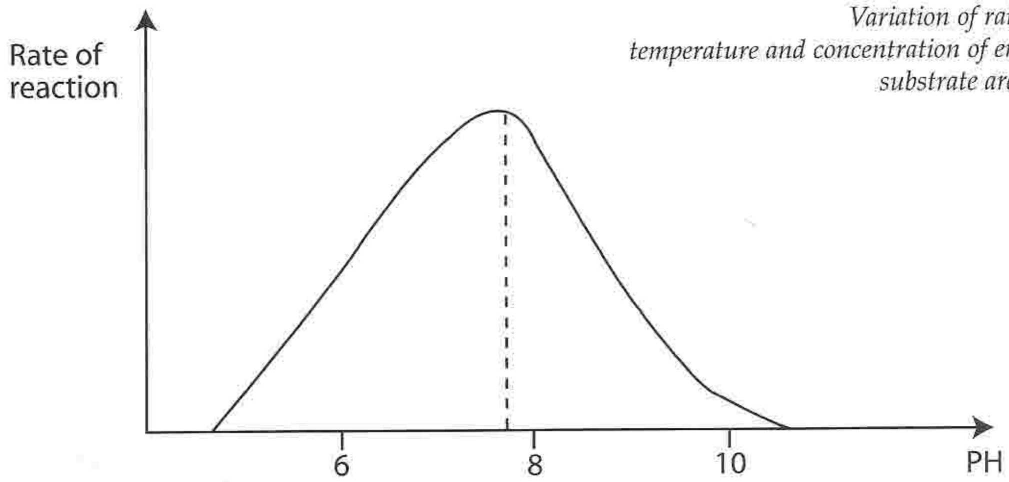
Fig 24.5



Variation of rate with temperature when the pH is constant as well as the concentration of the enzyme and substrate.

- Enzymes are proteins containing the $-NH_2$ and $-COOH$ groups which are affected by drastic pH changes. High and very low pH values bring charges on the amino acid residues. This affects the bonds between them such that the tertiary structure is altered. The enzyme is then said to be denatured and its catalytic activity drops.

▸ Fig 24.6



Variation of rate with pH
temperature and concentration of enzyme and
substrate are constant

Heavy metal ions such as Hg^+, Ag^+,As^+ can react with the sulfydryl group, with carboxylic group and can also break disulfide linkages.

For example:-

(i) $RSH + Ag^+ \rightarrow RSAg + H^+$

(ii) $-CH_2\text{-}S\text{-}S\text{-}CH_2\text{--} + 4Hg^+ \rightarrow 2\,-CH_2\text{-}S\text{–}Hg + 2Hg^{2+}$

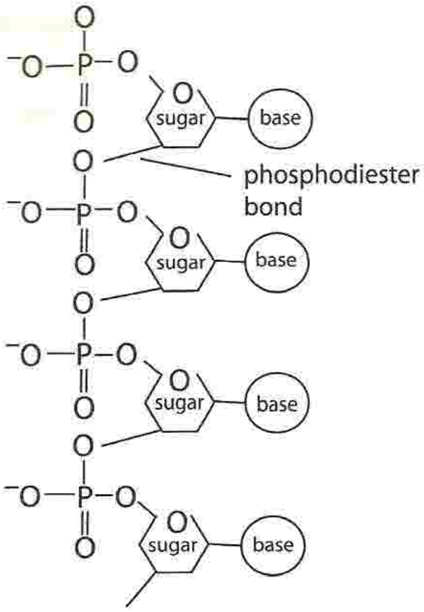
Therefore the tertiary structure of protein is broken and the enzyme is denatured.

24.6 Nucleotides and Nucleic acids

- A nucleotide contains a phosphate group, a pentose sugar group and an organic base. There are generally five nucleotide bases which are adenine (A), cytosine (C), guanine (G), thymine (T) and uracil (U).

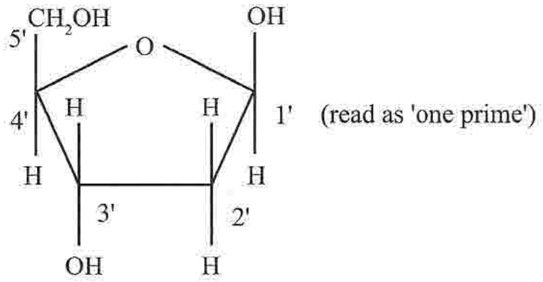
A nucleic acid is a polyester chain of nucleotides formed by enzyme catalysed condensation reactions. The phosphate of one nucleotide combine with the –OH group on the third carbon of the sugar of another nucleotide. Water molecule is released. Thus as the condensation polymerisation continues, a backbone of alternate sugar and phosphate group is formed with the nitrogenous bases emerging from the backbone. This is shown below.

The sequence of the base stores the genetic information of the organism.



STRUCTURE OF THE DNA

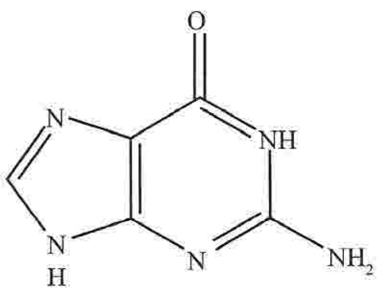
- The DNA is a double-stranded polynucleotide.
- Each nucleotide consists of a pentose sugar, deoxyribose, a phosphate group and one of the four organic bases, namely adenine (A), cytosine (C), guanine (G) and thymine (T).
- The carbon atoms in the pentose sugar are numbered from 1′(one prime) to 5′ as shown below:-



Deoxyribose

- The organic bases can be classified as purines and pyrimidines.
- The purines are double-ringed planar structures, with a 5-member ring of C and N atoms and a 6-member ring of C and N atoms. The 2 purines present in DNA are adenine(A) and guanine(G)

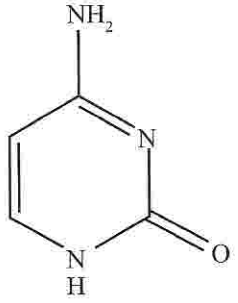
Adenine (A)



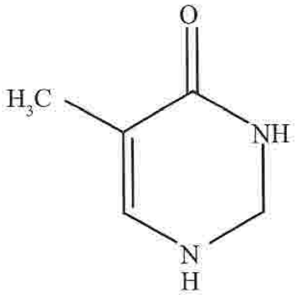
Guanine (G)

- In block diagrams, the purines are represented by a rectangle, as follows:-

- The pyrimidines are single-ringed planar structures with a 6-member ring of C and N atoms.
- The two pyrimidines found in DNA are cytosine(C) and thymine(T)



cytosine (C)

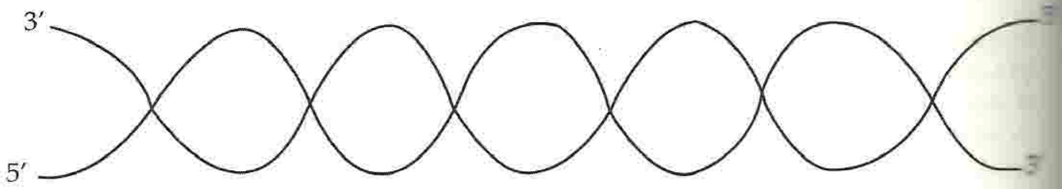


Thyamine (T)

- In block diagrams, the pyrimidines are represented by a smaller rectangle, as follows:- 
- During the formation of a polynucleotide, the –OH group of the phosphate residue found on the 5′ carbon of one nucleotide react with the –OH group at the 3′ of the next nucleotide. A condensation reaction takes place and it leads to the formation of a linkage between the two nucleotides which is known as the phosphodiester linkage.
- Therefore in the polynucleotide, the nucleotides are held together by the phosphodiester linkage.

COMPLEMENTARY BASE PAIRS

- The DNA is a double stranded polynucleotide.
- The two polynucleotides are antiparallel.



- The two ploynucleotides are held together by hydrogen bonds formed between the organic bases,
- Hydrogen bonds can only be formed between a purine and a pyrimidine.
- It has been found that:-

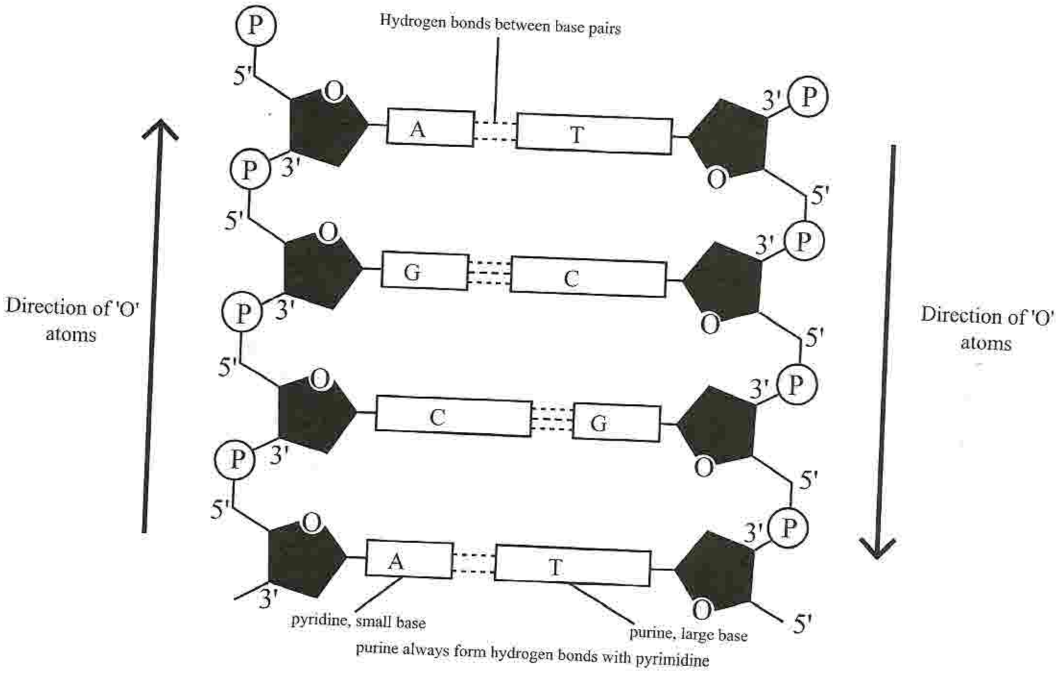
a) Adenine always forms hydrogen bonds only with thymine. The two organic bases are held together by a double hydrogen bonds.

$$A = T$$

b) guanine always forms a triple hydrogen bonds with cytosine

$$C \equiv G$$

- Adenine/ thymine and guanine/cytosine are said to be complementary base pairs.
- Hence the DNA consists of a double stranded antiparallel polynucleotide woven around each other to form two antiparallel helical structure.
- The DNA may be represented as follows:-



- All DNA contains the same sugar-phosphate backbone. They differ only in the sequence of bases. Therefore a DNA strand can be represented only by the sequence of bases in the strand.

For example, part of a DNA strand may be represented as follows:-

A-C-C-A-G-T-A-T-A-G-C-C-A-G-A-

It can be deduced that the base in the fourth nucleotide is adenine(A)

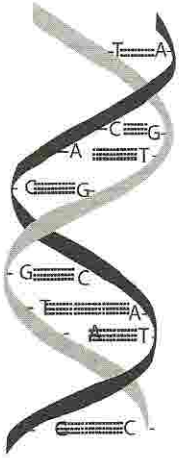
REPLICATION OF THE DNA

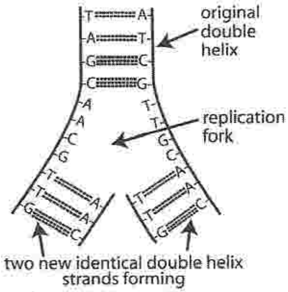
- Every time a cell divides, an exact copy of the DNA is made.
- DNA replication is a process during which the DNA in a cell copies or replicates itself.
- The following steps are involved in DNA replication:-

(i) the enzyme DNA helicase slides along the DNA and breaks the hydrogen bonds and the instantaneous-induced dipole attraction which are present between complementary base pairs. The strands separate or are unzipped at one end. Each strand acts as a mould or template for the synthesis of a new strand containing complementary bases.

(ii) When the two strands are unzipped, the DNA bases are exposed. Free nucleotides found in the cytoplasm enters the nucleus and assemble on the template DNA according to the law of base pairing.

(iii) When the new nucleotides have aligned on each template, they are joined together with the help of the enzyme DNA polymerase.. A new sugar phosphate backbone is formed on each template.Two new DNA molecules are formed.





Replication of DNA

A = T, C ≡ G

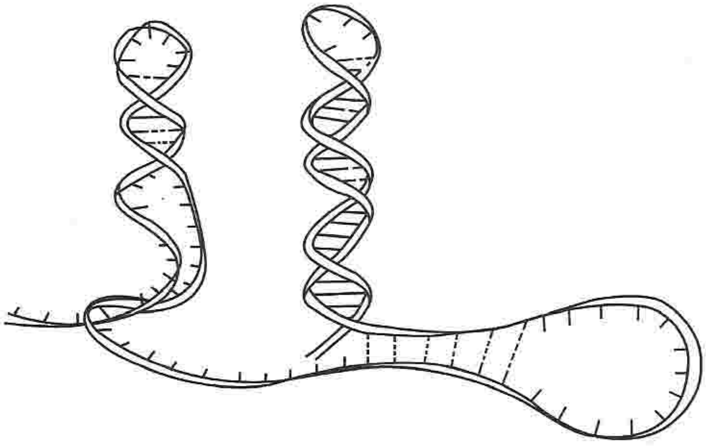
The DNA double helix

RIBONUCLEIC ACID, RNA

RNA(ribonucleic acid) occurs in the human cells. RNA are abundant in rapidly growing cells where large quantities of protein are synthesised.
The RNA molecules are polymers also made up of repeating base – sugar – phosphate nucleotides units. But the sugar in RNA is ribose though three of the bases are the same as in DNA, the fourth one is uracil instead of thymine.

- The RNA are generally single strands with some regions of the base pairing when part of the molecule folded onto itself via hydrogen bonding.

- There are three types of ribonucleic acids which are involved in protein synthesis. They are:
  (i) The mRNA (messenger RNA) which is formed during transcription and which codes for protein synthesis
  (ii) The tRNA(transfer RNA) which carries aminoacids to the ribosome during protein synthesis and
  (iii) The rRNA(ribosomal RNA) which is the site for protein synthesis.



DIFFERENCES BETWEEN DNA AND RNA

	DNA	RNA
1	It is double-stranded	It is single-stranded
2	It contains the deoxyribose sugar	It contains the ribose sugar
3	It contains the base thymine	It contains the base uracil
4	It is found only in the nucleus	mRNA is formed in the nucleus. Afterwards it moves into the cytoplasm where tRNA and rRNA are also found.

RNA AND PROTEIN SYNTHESIS

Protein synthesis involves two major steps. They are:-

(i) transcription
(ii) translation

TRANSCRIPTION

- During transcription, part of the DNA strand, corresponding to a gene is copied to form a complementary copy of the strand which is known as the mRNA (messenger RNA). The formation of mRNA, that is transcription, takes place through the following steps :

(i) Part of the DNA corresponding to the gene unravels with the help of the enzyme RNA polymerase

(ii) One of the DNA strand acts as a template for mRNA synthesis

(iii) Nucleotides containing ribose sugar and with corresponding complementary bases bind with the template

(iv) The complementary bases for the RNA are as follows

Base in DNA	Complementary base in RNA
A	U
C	G
G	C
T	A

(v) The enzyme RNA polymerase then helps formation of bonds between adjacent nucleotides. A m-RNA is formed.

For example the mRNA that will be formed when part of a DNA is transcribed is shown below:

DNA base sequence: —A —A –C –T –G –G –T –A –C –C—G—
mRNA base sequence: —U —U—G –A –C –C –A –U –G –G –C –

(vi) The DNA releases the mRNA and forms back its double helical structure, while the newly formed mRNA leaves the nucleus and move into the cytoplasm. Transcription is completed.

- The mRNA carries the genetic message to the ribosome, where it will be decoded by a process known as translation.

THE TRIPLET CODE

- The triplet code is a set of three nucleotides arranged in a specific order which codes for a specific amino acid. For example the triplet code CUA codes for the amino acid leucine.
- The triplet codes are also referred to as codons.
- Some amino acids are coded by more than one triplet code. This offers a certain protection against genetic mutation. For example leucine is coded by six triplet codes.
- The triplet code AUG codes for the amino acid methionine. It gives the start signal for protein synthesis. It is known as the start codon. Protein synthesis starts only when the start codon encounters the ribosome, which is the site for protein synthesis.
- Three triplet codes, namely UAA, UAG and UGA do not code for any amino acid. They are referred to as stop codons. They indicate when protein synthesis stops.
- The mRNA consists of a set of non-overlapping triplet codes which codes for a specific sequence of aminoacid residues for a polypeptide.
- The triplet codes for all the twenty amino acids which are involved in protein synthesis are shown in the table below:- (in book – pg 485)

TRANSLATION

- After transcription the mRNA moves into the cytoplasm and it carries the genetic message to the ribosome, the site for protein synthesis.
- The ribosome can hold only two triplet codes at a time.
- Translation takes place in three steps. They are:-

(i) The initiation step

When the ribosome encounters the start codon, AUG, protein synthesis starts. This step is called the initiation step. The mRNA appeals to a tRNA having the appropriate anticodon, namely UAC and which carries the amino acid ,methionine. Protein synthesis starts.

(ii) The elongation step

- The mRNA moves one step forward and another codon enters the ribosome. The tRNA with the correct anticodon will bind with a specific amino acid and will bring it to the ribosome.
- The mRNA moves one step ahead and the first codon which codes for methionine moves outside the ribosome. At this moment a peptide linkage is formed between the methionine and the adjacent amino acid with the help of enzymes and the tRNA releases the methionine residue and is free to move in the cytoplasm.
- As the mRNA moves forward through the ribosome more amino acids are brought successively to the ribosome and the length of the polypeptide chain increases.This step is called the elongation step.

(iii) The termination step

When the ribosome encounters a stop codon, protein synthesis is completed. This step is known as the termination step. The polypeptide chain is released in the cytoplasm where it acquires its secondary and tertiary structures.

24.7 RNA and protein synthesis

The complete sequence of bases in human DNA has been determined. This is shown below.

UUU	Phe	UCU	Ser	UAU	Tyr	UGU	Cys
UUC	Phe	UCC	Ser	UAC	Tyr	UGC	Cys
UUA	Leu	UCA	Ser	UAA	Terminator	UGA	Terminator
UUG	Leu	UCG	Ser	UAG	Terminator	UGG	Trp
CUU	Leu	CCU	Pro	CAU	His	CGU	Arg
CUC	Leu	CCC	Pro	CAC	His	CGC	Arg
CUA	Leu	CCA	Pro	CAA	Gln	CGA	Arg
CUG	Leu	CCG	Pro	CAG	Gln	CGG	Arg
AUU	Ile	ACU	Thr	AAU	Asn	AGU	Ser
AUC	Ile	ACC	Thr	AAC	Asn	AGC	Ser
AUA	Ile	ACA	Thr	AAA	Lys	AGA	Arg
AUG	Met	ACG	Thr	AAG	Lys	AGG	Arg
GUU	Val	GCU	Ala	GAU	Asp	GGU	Gly
GUC	Val	GCC	Ala	GAC	Asp	GGC	Gly
GUA	Val	GCA	Ala	GAA	Glu	GGA	Gly
CUG	Val	GCG	Ala	GAG	Glu	GGG	Gly

The genetic code carried by RNA

The order in which the RNA molecules are called up for proteins synthesis, depends upon the sequence of bases along the mRNA chain. Thus:

GAU is the code for aspartic acid
UUU, phenylalanine
GUG, valine

Note that more than one codon can call up the same amino acids, since the 64 combinations of three-lettered words (codons) are for twenty amino acids. Thus:
CUU and CUC for Leucine
GAA and GAG for glutamic acid.
This is shown in the genetic code in the given table.

24.8 DNA mutation and genetically related diseases

- Since the amino acid sequence on the protein is dependent on the base sequence in the DNA molecule, any misreading of the code causes a change in the amino acid sequence on the new DNA strand. For example a segment of the DNA chain where the codon GUG appears instead of GAG leads to a genetic modification. This is the cause of sickle-cell, anemia known as pernicious anemia. The shapes of haemoglobin molecules are altered.
- At times antibiotics alter the ribosomes. Then misreading of the code occurs and defective proteins are produced. This causes the death of the organism.

- The nature of the base on the DNA may also change by chemical reactions. These may be due to oxidation or alkylation. Then the size of the base and its hydrogen-bonding capacity are altered such that base-paring between DNA strands are impaired. Then DNA mutation occurs.

For example:

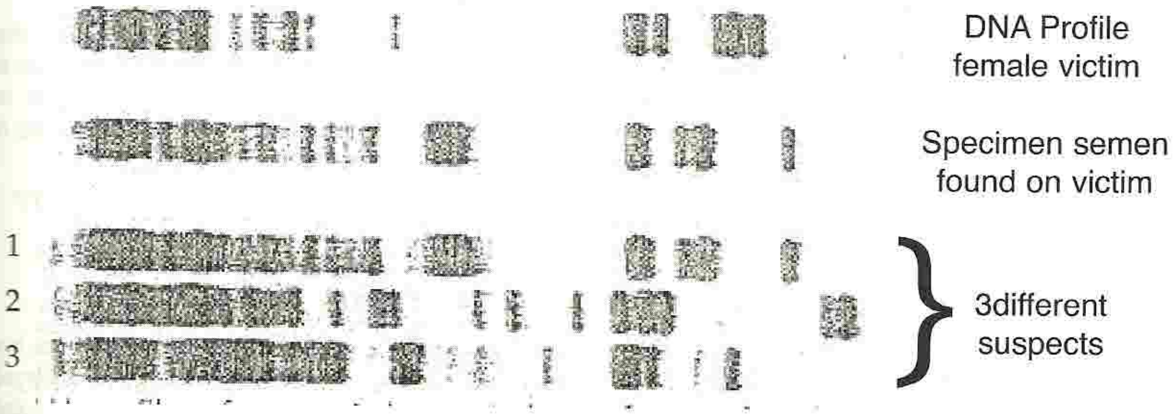
(i) carcinogenic compounds can undergo chemical reactions such as nucleophelic substitution with the basic nitrogen of the amino acid or electrophilic reaction or even form epoxide. Such mutations of the DNA causes development of cancerous cells.
(ii) a changed base sequence may give rise to non-harmful genetic change. These may change hair and eye colour. Therefore the structure of the nucleic acid molecules affect the structure of the newly formed protein molecules which in turn control the living organism.

- ***DNA profiling***

DNA profiling is a process that produces a genetic fingerprint. The key to DNA profiling is that all cells from the same organism create the same DNA profile. A small sample of the cellular material of the organism is required. This may be saliva, hair, blood or semen from which the DNA is extracted and broken down into small fragments known as **minisatellites**. Enzymes known as restriction enzymes are used which can cut the large DNA molecules at specific base pairs sequence.

Different persons have different lengths of the minisatellites. Now the fragments are separated into bands by gel electrophoresis. Since DNA has negatively charged phosphate groups, it is attracted towards the positively charged end. The smaller fragments move faster. Thus a band patten is obtained. Hence the fragments are separated into bands or zones. An electropherogramm is formed. The electropherogram is then treated with radioactive phosphorous, ^{32}P to determine the position of the different bands or zones.

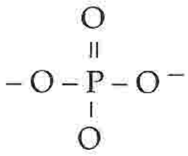
A photograph is taken to show the number and position of the bands. The DNA pattern is unique for each individual but some bands in the pattern are shared between related people. This is how DNA profiling is used in court cases to positively identify murderers and rapists from body fluids and also to prove paternity. It is also used to identify particular genes which are likely to carry certain diseases. Palaeontologists use DNA patterns to identify and map extinct species.



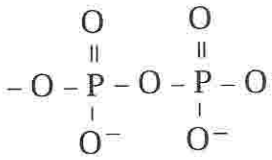
DNA Profiles of a rape victim, a specimen of semen found on her, and three different suspects. Which one was the rapist?

24.8 A.T.P.

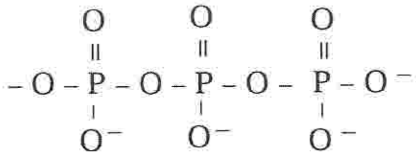
- The base adenine can form three types of phosphate ester with the sugar ribose. All of them occur in the living cells.



(i) Adenine ribose $-\mathrm{O}-\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{O}}{|}}{\mathrm{P}}}-\mathrm{O}^{-}$: Adenosine monophosphate AMP

(ii) Adenine-ribose  : Adenosine diphosphate ADP

$$-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}-O^-$$

(iii) Adenine-ribose  : Adenosine triphosphate ATP

$$-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}-O^-$$

The – P – O – P bond of ATP is liable to hydrolyse to form ADP, an inorganic phosphate, P_i and a large amount of energy is released in the cells. Such energy is used in muscle contraction, synthesis of large molecules and the transport of substances across the cells membranes.

$$ATP + H_2O \rightleftharpoons ADP + P_i \qquad \Delta H = \text{-ve}$$

ATP can be regenerated by the metabolism of glucose which happens in rapidly contracting muscles.

$$C_6H_{12}O_6 + 2ADP + 2P_i \longrightarrow 2CH_3CH(OH)COOH + 2ATP + 2H_2O$$

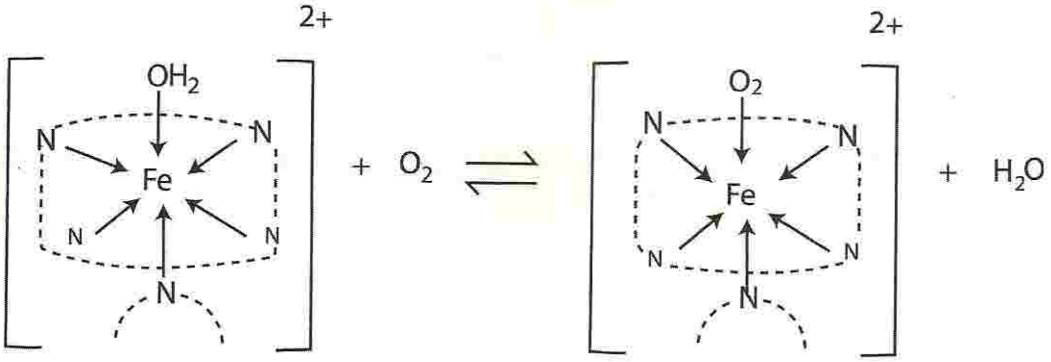
This process is exothermic. In another process which generate a much larger amount of energy, glucose undergoes aerobic oxidation to carbon dioxide and water. Through a series of reactions, called the citric acid cycle, a total of thirty-eight ATP molecules can be formed from the oxidation of one glucose molecule.

$$C_6H_{12}O_6 + 6O_2 + 38ADP + 38P_i \longrightarrow 6CO_2 + 44H_2O + 38ATP$$

• Metal ions in the chemistry of life

A large number of metal ions play important biological roles in the body. The function they carry out depends on their chemical and physical properties. For example their charge densities, their ability to exhibit variable oxidation states and their ability to form complexes by bonding with ligands.

Consider haemoglobin, the whole giant haem molecule contains four large polypeptide groups, and four iron(II) ions. Each iron(II) has a coordination number 6, at 5 positions nitrogen from protein chains act as electron donors (ligands) and the 6th position is usually bonded to water molecule.



At high oxygen concentration, oxygen bond at the 6th position as a ligand. Thus the haem transport oxygen to the tissue.
Carbon monoxide and cyanide ions are poisonous because they are strong ligands and form irreversible complexes with the iron ion of haem. Thus the transport of oxygen is hindered.

• Sodium / Potassium balance

Mammalein cells have a much higher concentration of potassium ions inside the cells and a much higher concentration of sodium ions outside the cells. This is because protein synthesis which occurs inside the cells requires potassium ions while nerve impulses need an optimum K^+/Na^+ concentration gradient.

- The cell wall acts as a semi permeable membrane to maintain the required concentrations of the K^+/Na^+ by osmosis. This is referred to as the K^+/Na^+ pump and the energy required is obtained by the conversion of ATP to ADP.
  The cell wall has a protein structure. Due to its lower charge density, , K^+ ions can diffuse more easily across the cell membrane whereas the Na^+ ions bind more tightly to parts of the cytoplasm.

- The transmission of nerve impulses involves electro-chemical signals. A nerve impulse is the depolarization of a section of the cell membrane which moves down the nerve fiber of a nerve cell and is transmitted to other cells. Na^+ ions participate in the propagation of the impulse down the nerve fiber (axon). As the cell membrane is depolarised, Na^+ ions rush in momentarily. Then the ions are pumped out as the cell membrane is repolarised. Thus the nerve impulses are sent effectively when the Na^+ and K^+ ions are balanced.
- Metal ions such as zinc increases the efficiency of enzyme catalysis by acting as a cofactor, behaving as a nucleophile. The Zn^{2+} ions bind with groupings on the substrate and act as a strain producing agent by forming a chelate intermediate. Thus the activation energy of the catalysed reaction is lowered.

- Three heavy metals mercury, cadmium and lead are examples of metabolic poisons. They interfere with biological metabolism either by reducing or even stopping the function of an important process. They interfere with enzymes which bond with metal ions. These ions reach us by entering the food chain. The table below shows the major sources and effects of these heavy metal ions.

Heavy metal	Sources	Health effects	Food chain
Mercury	From : batteries, cell in the extraction of chlorine, from fungicides	Causes paralysis and mental disorders	Via fish and sea food to man
Cadmium	From: rechargeable Ni/Cd cells, metal plating pigments	Causes brittleness of bones, kidney and lung cancer	From sea food to man
Lead	From lead paints exhaust fumes containing lead compounds where tetraethyl lead is used as an antiknock	Causes respiratory problems in infants and old people, disorder of the nerveous system	From plants and animals in the food chain to man

Exercises 24

1. Describe and explain the primary, secondary, tertiary and quaternary structures of proteins.

2. List four ways in which parts of the amino acid chains interact to stabilise the structure of the tertiary protein.

3. What are the major functions of the different types of protein in the body.

4. With respect to enzymes, explain the following terms:
   (a) substrate,
   (b) active site,
   (c) lock and key model.

5. (a) Explain how enzymes work
   (b) Some fabrics are damaged when washed with biological washing powders, suggest in chemical terms why.

6. (a) Draw a block diagram of the double helix of DNA showing three repeated units.
   (b) Explain how DNA:
   (i) replicates itself,
   (ii) leads to the formation of RNA
   (iii) A sequence of bases on one strand of DNA is

   – T – G – G – A – C – T- A – A – G

Complete the corresponding base sequence in
   (i) the complementary strand of DNA,
   (ii) the RNA derived from this complementary strand of DNA.

7. When DNA partially uncoils in the process of transcription, only one of the separated strands serves as a template for RNA synthesis. What would happen if both separated strands were to act as templates?

8. (a) Describe simply the role of m-RNA.
   (b) Explain the following terms:
   (i) transcription
   (ii) translation
   (iii) triple code.

9. Describe the principles and uses of DNA profiling.

10. Describe the importance of the difference in Na^+ and k^+ ions concentration across cell membrane.

CHAPTER

25

Applications of Analytical Chemistry

Syllabus Objectives

In this chapter you should be able to:

- describe the process of electrophoresis
- understand the technique of DNA fingerprinting
- describe and explain the use of NMR spectra
- understand the partition coefficient
- describe different chromatographic method
- describe and explain the use of mass spectroscopy
- interprete and analyse data from environmental monitoring

Electrophoresis

Separating and characterising in cell

Principle of NMR

Distribution between phases

Chemical Analysis

Mass Spectroscopy

Isotopic ratios in ice cores

PCBs in the atmosphere

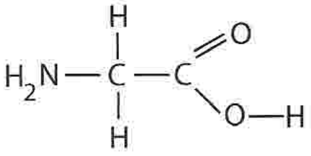
APPLICATIONS OF ANALYTICAL CHEMISTRY

25.1 Electrophoresis

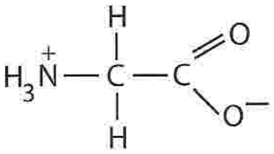
- Electrophoresis is a technique used to separate (and sometimes purify) macromolecules (that is very large molecules which do not contain a regular sequence of units), mainly proteins and nucleic acid that differ in size, charge or conformation .It is also used to separate mixture of aminoacids.
- It involves the movement or migration of ions in an electric field.
- When charged molecules or particles are placed in an electric field, they migrate towards either the positive electrode (the anode) or the negative electrode (the cathode) according to their charge.
- Separation by electrophoresis is based on differences on solute velocity in an electric field.
- The different ions in a mixture will move or migrate at different rates. Therefore they can be separated.
- The rate at which they move depends on the charges and masses of the ions. Thus:-
  1. a highly charged ion will move faster in an electric field
  2.. a large ion will move more slowly in an electric field
- Electrophoresis is carried out within a 'matrix' or a gel.
- A gel consists of polymer molecules arranged randomly such that spaces or pores are left between them.
- Molecules of the solutions under analysis will move through the empty spaces.
- The commonly used gel is either agarose gel or polyacrylamide gel (also known as PAGE- **p**oly**a**crylamide **g**el **e**lectrophoresis).
- Polyacrylamide gels are used extensively for separating and characterizing mixtures of proteins.
- In all electrophoresis processes, a pair of electrodes is positioned at opposite ends of the plate.
- Fragments of linear DNA migrate through agarose gels with a mobility that is **inversely proportional** to the their molecular weight.
- Circular forms of DNA migrate in agarose distinctly different from linear DNAs of the same mass. Typically uncut plasmids will appear to migrate more rapidly than the same plasmid when linearized.

Effect of pH on migration of ions

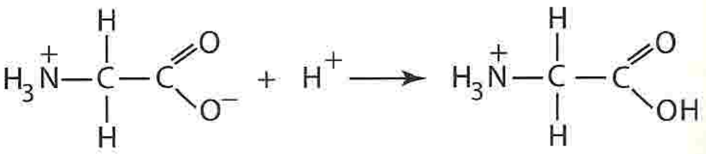
- Aminoacids can have a net positive or negative charge, depending upon the pH of the solution in which they are found. Hence molecules can migrate towards the anode or the cathode.
  For example consider the aminoethanoic acid molecule



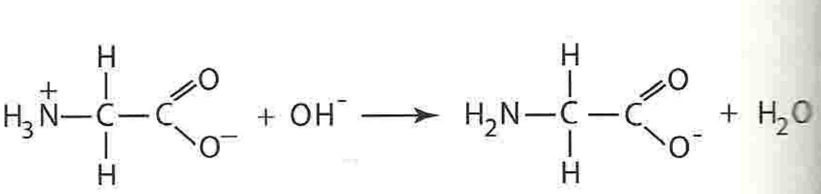
[a] In aqueous medium , the aminoacid exists mainly as a zwitterions



[b] If an acid is added to a solution of aminoethanoic acid, the H^+ ion from the added acid will protonate the CO_2^- ion. As a result it will become a positively charged ion. In presence of an electric field it will migrate towards the negative electrode- the cathode



[c] If a base is added to the solution of the aminoacid, the OH^- ion will react with the NH_3^+ group and will remove proton from this group



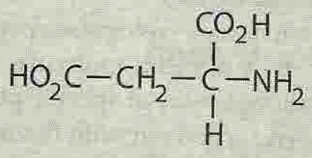
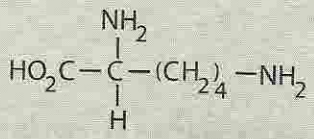
As a result the aminoacid will acquire a negative charge and in an electric field it will move towards the positive electrode, namely the anode.

- From above, it can be deduced that if the pH changes during electrophoresis, there is a risk that the net charge of the aminoacid may change (as a result of which the direction in which migration takes place may be reversed). Hence electrophoresis must always be carried out in a carefully buffered solution or gel.

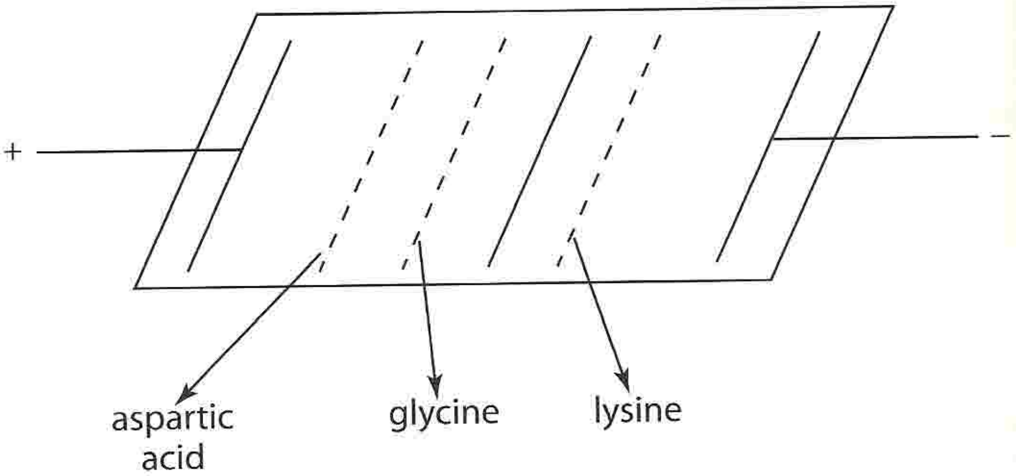
- At a given pH ,an aminoacid will have no net charge. This pH is called the isoelectric point of the aminoacid.
- The isoelectric point of an aminoacid can be determined by electrophoresis.
- By determining the isoelectric point of an aminoacid and comparing it with a Data Bank, the identity of the aminoacid can be known.
- If an aminoacid is placed in a buffer solution found at a pH less than the isoelectric point, that is the buffer pH is more acidic than the isoelectric point of the aminoacid, the latter will acquire a positive charge and will migrate towards the cathode.
- If an aminoacid is placed in a buffer solution found at a pH greater than the isoelectric point of the protein, that is the buffer pH is less acidic than the isoelectric point of the aminoacid the latter will acquire a negative charge and will migrate towards the anode.
- As different aminoacids have different isoelectric point, at a given buffered pH they may have different net charge. When they are found in an electric field they will move at different speeds and some aminoacid molecules will move towards the cathode and others will move towards the anode. Hence electrophoresis can be used to separate aminoacids, based on their net charge in a given buffered solution and on their mass.

Electrophoresis of aminoacids

Consider a mixture of three aminoacids, namely aspartic acid, glycine and lysine, separated by electrophoresis using a buffered gel at pH 7.00.

Amino acid	**Aspartic acid**	**glycine**	**lysine**
Structural formula	 $HO_2C-CH_2-\overset{CO_2H}{\underset{H}{C}}-NH_2$	$HO_2C-CH_2-CH_2-NH_2$	 $HO_2C-\overset{NH_2}{\underset{H}{C}}-(CH_2)_4-NH_2$
Isoelectric point	2.77	5.97	9.94
Charge of aminoacid at buffered pH=7.00	Negative [isoelectric point < than pH of buffer solution]	Negative [isoelectric point < than pH of buffer solution]	Positive [isoelectric point > than pH of buffer solution]

- When a potential difference is applied, glycine and aspartic acid will migrate towards the anode(positive electrode) as they have acquired a negative charge.
- Since aspartic acid has a larger negative charge than glycine, it will move faster than the latter.
- Lysine migrates towards the negative electrode since it has a net positive charge at pH 7.00.
- Hence the aminoacids separate out.



Electrophoresis of DNA- Genetic fingerprinting

- DNA have always a net negative charge, mainly due to their phosphate backbone. Hence they always migrate towards the positive electrode, namely the anode.
- The DNA of a person is extracted from a sample tissue, bone, saliva or blood.
- The DNA extracted is then treated with a group of enzymes known as the ***restriction endonucleases***.
- The restriction endonucleases recognise specific sequences in the DNA and therefore they act as a molecular scissors and cut the DNA chain in a predictable way at specific places.
- Electrophoresis is then carried out with the resulting fragments. A given pattern, known as the DNA fingerprinting, will be obtained that will be unique for each person.

Practical steps to carry out electrophoresis of DNA

1. Some agarose powder are dissolved in a hot buffer solution.
2. Pour the hot agarose solution in a mould (the mould has tape on each end where the electrodes will be found)
3. Place a comb in the hot gel solution on one end.
4. The gel is allowed to cool and solidify. As the gel cools tiny holes will form in it.

4. The bands from the analysed DNA sample are compared with the bands of known length from the DNA size standard. As a result the DNA length of the DNA strands can be known.

OR

The gel is treated with radioactive phosphorous, ^{32}P to determine the position of the different bands.

Note that electrophoresis cannot be used to determine the exact DNA length of DNA strands. It just gives a good estimate of the length.

Factors affecting reproducibility of electrophoresis are:-

1. changes in temperature [therefore process must be carried out in a thermostat]
2. changes in buffer composition mainly due to electrolysis or buffer evaporation [therefore there must be a constant supply of buffer solution]
3. variation in applied voltage [therefore a voltage stabilizer may be used]

Factors determining the mobility of DNA fragments in agarose gels are:-

1. **The agarose concentration**- high concentration of agarose facilitates separation of small DNAs, while low agarose concentration facilitates separation of larger DNAs
2. **The voltage used**-as the voltage applied to the gel is increased, larger fragments migrate proportionally faster than small fragments.
3. **The elctrophoresis buffer**- the buffer serves not only to establish a stable pH but also to provide ions to support conductivity.
4. **The use of tracking dyes**, mainly ethidium bromide, that binds with the DNA will alter the mass ,rigidity and mobility of the molecule.

Applications of DNA fingerprinting

1. In forensic science

- The pattern obtained on the electropherogram can be used to :-

1. identify an individual from a tissue,flake of skin or trace of blood left at the scene of a crime by comparing the pattern obtained with that obtained by electrophoresis of hair, tissue,flake of skin or blood of the individual. Usually a sample of cell is taken from the inside of the suspects cheek. The genetic fingerprint of the sample is then made .The electropherogram obtained is compared with that obtained from a sample the tissue,flake of skin ,trace of blood or any other biological sample of left at the scene of a crime. If the two electropherograms are perfectly identical , the presence of the suspect at the scene of crime is confirmed.

2. common features between the DNA fingerprints of two persons can be used to establish hereditary relationships, such as paternity of the child.

Note: the DNA decays rapidly. In this case some of the DNA sites that would be cut by the restriction endonuclease may no more be available

In medicine

- Electrophoresis is also used in medicine to identify genes that are responsible for diseases. Genes consist of DNA molecules and can be identified from the pattern their segments produce in electrophoresis. If a harmful gene is detected in an individual it is sometimes possible to provide medical treatment for it.
- Genetic fingerprinting is also used in the treatment of leukaemia. Leukaemia is a cancer of the bone marrow. If the bone marrow is diseased, it can be removed and replaced by bone marrow from a donor. The success of the operation can then be judged by determining the genetic fingerprint of the patient's blood.

In archaeology

- The ability to perform DNA analysis on ancient organic material has provided archaeologists with a powerful tool to help understand the past. It provides a means of identifying proteins in ancient samples. For if proteins can be detected then DNA, in sufficient quantities for analysis, should also be present.
- Genetic fingerprinting can be used in the reconstruction of precious documents.
- Electrophoresis can be used to provide independent identification of residues and work as a complementary means of analysis to a number of existing techniques.

Other uses of genetic fingerprinting

- To detect genetically modified foods
- The precise order of the aminoacids in a particular protein can also be known by making use of enzymes which break peptide links one at a time, starting from either the amino or the carboxyl end of the molecule. But the process is very time consuming.

25.2 Separating and characterising in cell

- Proteins have a major role in all the main aspects of cell structure and functions. They show physiological as well as pathophysiological processes in a cell or an organism.
- Proteins are complex, dynamic systems constantly changing in number and structure in response to physiological and environmental stimuli, for example stress or drug effects
- A large scale study of protein involving the screening and identification of new proteins is carried out through the science of proteomics.
- Proteomics enables the proteome(the complete **prote**in complement expressed by the gen**ome**) of a cell to be displayed and studied.
- The main purpose of proteomics is to uncover the function of new proteins thereby providing new targets for drug intervention.
- The ultimate goal in proteomics is to isolate, characterise, identify and assign function to every protein produced by the human body.
- Protein levels in different cells vary extensively. Certain low level proteins are particularly difficult to detect and isolate.
- Disease mechanism and drug effects both affect a protein profile and vice versa, characterising protein profiles reveals information for the understanding of disease and therapy.
- Thus:-
  1. by determining the presence or altered levels of particular proteins, certain diseases can be detected
  2. pharmaceutically active drugs alter the presence or abundance of certain proteins
  3. drug resistant bacteria contain different proteins to those in their drug susceptible counterparts.
- Differences in protein structure , such as those obtained from cells at various developmental stages can provide information which is invaluable in obtaining a better understanding of the cellular mechanisms involved.
- By separating and characterising the proteins in a cell, it is possible to identify the protein differences between samples such as :
  1. canceronous and non-canceronous tissue
  2. pathogenic and non-pathogenic bacteria
- The technical challenge is the complete coverage of the physicochemical properties for thousands of molecules.
- Techniques are available to separate thousands of proteins in one run, and their identification can be achieved within minutes.

Separation of proteins

- The most widely used tool for separating and visualizing proteins in a sample is **two dimensional polyacrylamide gel electrophoresis** (2D PAGE).
- Proteins labelled or unlabelled are firstly separated by isoelectric focusing in one direction and then at right angles to the first run by molecular weight.
- The gel is then developed giving an array of protein spots suspended in the gel.
- Selected protein spots can be physically cut from the gel .
- The protein in the gel is then dissolved in a suitable solvent.
- Further investigations or identification using mass spectrometer (in conjunction with peptide databases) may be carried out.
- However gel electrophoresis can affect functional analysis because of the denaturing conditions of the gel. Protein-to-protein interactions may be damaged.
- 2D-PAGE is also unsuitable for the analysis of membrane-bound proteins as these are insoluble without detergents.
- Some proteins may also be separated by partitioning in aqueous systems. This system is used industrially for the separation of recombinant and enzyme proteins.

NUCLEAR MAGNETIC RESONANCE

25.3 Principle of NMR

- In nuclear magnetic resonance (nmr) experiments are performed on the nuclei of atoms and not on the electrons.
- Subatomic particles [protons, neutrons and electrons] are spinning on their axes.
- A spinning charge, for example a proton ($^{1}_{1}H^{+}$), generates a local magnetic field.
- In many atoms these spins are paired against each other as a result of which the nucleus of the atom has no net magnetic field or no overall spin.
- The overall spin (denoted by I) depends on the number of protons and neutrons in the nucleus of the atom as shown in the table below:-

Number of neutron	Number of proton	Nucleon number	Overall spin
even	even	even	No net spin
even	odd	odd	Nucleus will have half integer spin1/2, 3/2 , 5/2...
odd	even	odd	Nucleus will have half integer spin :1/2, 3/2 , 5/2...
odd	odd	even	Nucleus will have an integer spin: 1,2 ,3...

- According to quantum mechanics , a nucleus of overall spin I will have 2I +1 possible orientations. For example a nucleus with spin =1/2 will have 2(1/2) + 1 = 2 possible orientations .
- Isotopes which are of particular interest and use to organic chemists are ^{1}H , ^{13}C , ^{19}F and ^{31}P all of which have spin I =1/2. From above, all these isotopes will have two possible orientations.
- A spinning charge generates a local magnetic field.
- The resulting spin-magnet has a magnetic moment (μ) proportional to the spin.
- In the absence of an external magnetic field, the two possible orientations of the ^{1}H , ^{13}C , ^{19}F and ^{31}P nuclei will have the same energy. The two spin states of the given nucleus are of equivalent energy: they are said to be degenerate.
- However in the presence of an external magnetic field, the spin states are no longer of the same energy.
- The magnetic moments generated by the charge and the spin of the nucleus may either align or oppose the applied field.
- Therefore the nuclei may align themselves in the magnetic field in two ways:-
  (i) the nuclei are aligned in the same direction as the magnetic field
  (ii) the nuclei are aligned in the opposite direction to the magnetic field, that is against the external magnetic field
- Hence the degenerate spin states split into two energy levels in the presence of an external magnetic field.
- If the magnetic moment generated by the charge and spin of the nucleus is in the same direction as the applied external field, the spin state is assigned a +1/2 state.
- If the magnetic moment generated by the charge and spin of the nucleus is in the opposite direction to the applied external field, the spin state is assigned a -1/2 state
- The spin state of +1/2 has a slightly lower energy than that of spin state –1/2 (Fig 1).

Energy levels for a nucleus with quantum 1/2

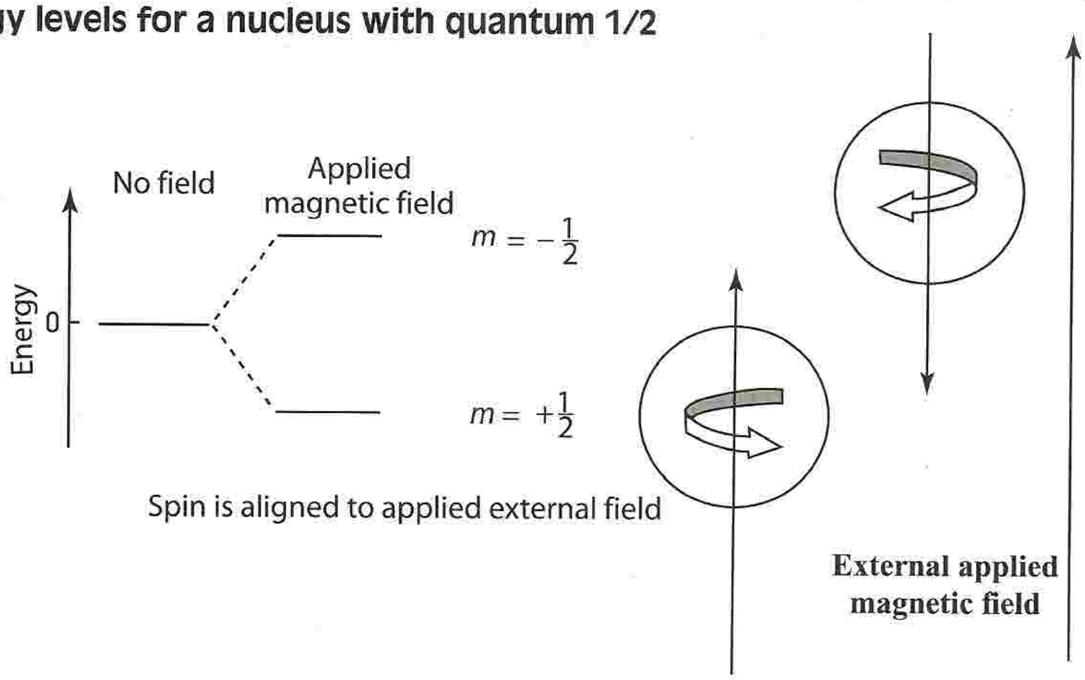


Fig 1

- The magnetic moment of the lower energy +1/2 state is aligned with the external field, but that of the higher energy -1/2 spin state is opposed to the external field.
- The difference in energy between the two spin states depends on the external magnetic field. It is always very small.
- As the strength of the applied magnetic field increases, the difference in energy between the two spin states increases.

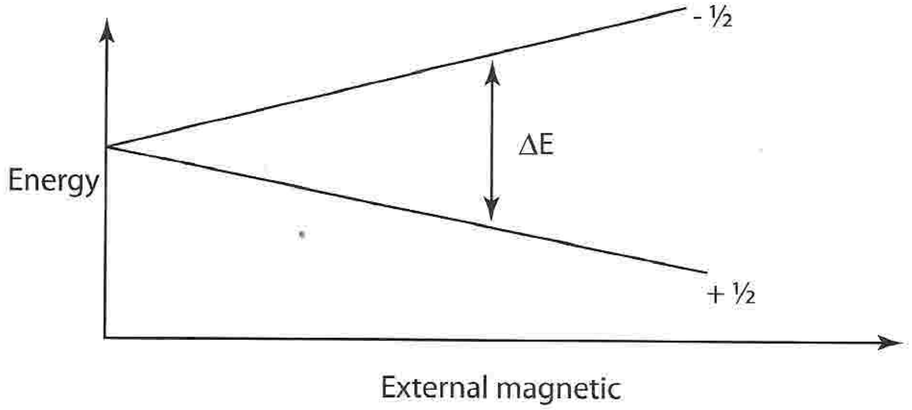


Fig 2

$$\Delta E = E_{-1/2} - E_{+1/2} = hf$$

where:- h = plancks constant
f = frequency of radiowave

- The difference in energy between the two spin states corresponds to a particular frequency in the radiowave frequecy.
- The proton undergoes resonance. The frequency at which the proton undergoes resonance is called the resonance frequency.
- The resonance frequency of a proton depends on its chemical environment. It is determined using the NMR spectrometer.

The magnitude of the difference in energy depends on the nucleus concerned, the chemical environment of the nucleus and on the external magnetic field strength applied.

- **The energy difference corresponds to the radio-frequency of the electromagnetic spectrum.**
- NMR spectroscopy is based on the net absorption or emission of energy in the radiofrequency region by the nuclei of those elements that have an overall spin.
- Irradiation of a sample with radiowave frequency energy corresponding exactly to the spin state separation of a specific set of nuclei will cause excitation of those nuclei in the +1/2 state to the higher -1/2 spin state. The proton undergoes resonance. This electromagnetic radiation falls in the radio and television broadcast spectrum and will be absorbed by the nuclei.
- The frequency at which absorption of energy occurs is determined using the NMR spectrometer.
- The high energy nuclei or protons will then return to the low energy state. When doing so , they emit radiowaves of a specific frequency.The radiowave emitted by the sample when resonance occurs may also be detected by the NMR spectrometer. This is displayed as an NMR spectrum.

The nmr- spectrometer

- The basic parts of the nmr spectrometer are:-
  (i) a powerful magnet that will provide a powerful magnetic field (of about 20T)
  (ii) sweep coils that will vary the magnetic field
  (iii) a sweep generator
  (iv) a radio-frequency transmitter that will emit radiowave of a certain frequency
  (v) a radio-frequency receiver and transmitter
  (vi) a recorder

1. Powerf
2. Sweep
3. Sweep
4. Radio f
transm
5. Radio f
receive
transm
6. Contro
and re
7. Spinni

Fig 4

- The nmr spectrometer can be represented as shown below:-

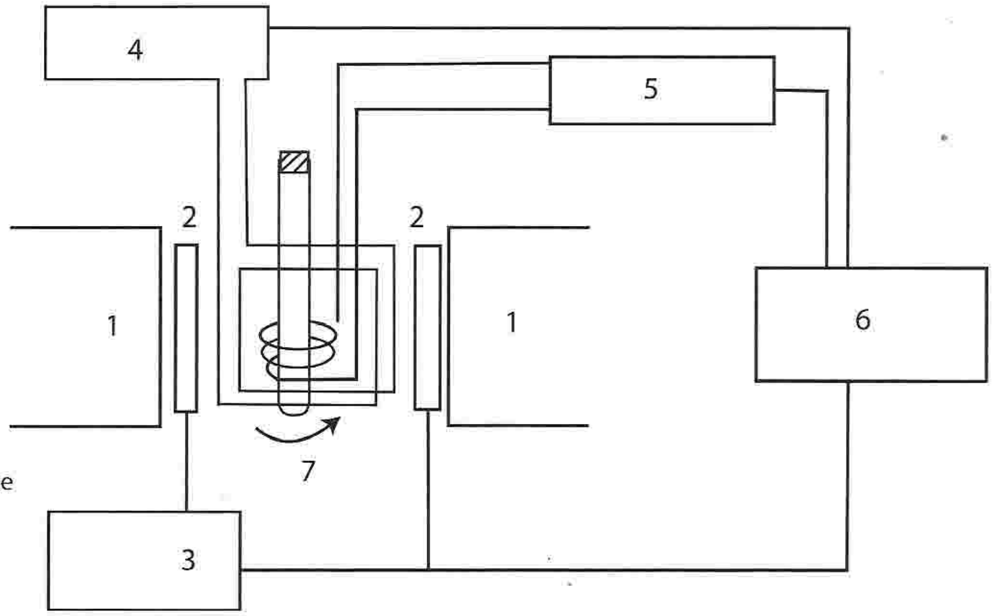


Fig 4

Action of the nmr spectrometer

A solution of the sample is prepared by dissolving the sample in a solvent having no proton, for example CCl_4. Other solvents that contain deuterium ^2H instead of the usual hydrogen atom , ^1H can also be used since ^2H has no overall spin. A small amount of tetramethylsilane, $(CH_3)_4$ Si, is added to act as a reference .

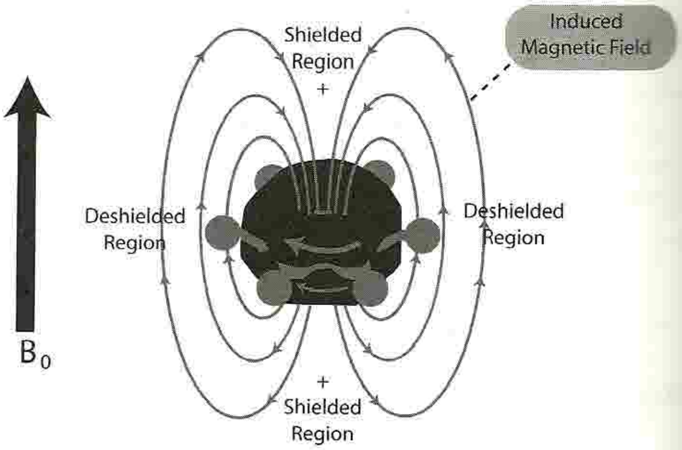
- The solution is then placed in a uniform 5mm diameter glass tube.
- The tube is placed between the poles of the powerful magnet (Fig 4).
- It is spun at a high frequency so as to average any magnetic field variations and tube imperfections.
- An intense variable frequency radiowave is broadcast into the sample from an antenna coil, also referred to as oscillator coil. The radio frequency radiation provides energy for the nuclear spins to flip from spin state + 1/2 to spin state –1/2.
- A receiver coil , placed at right angle to the radio frequency coil, surrounds the sample tube. It acts as a detector. It is connected to a detector and a recorder (computer).
- When energy is not being absorbed by the sample, the detector coil will not pick up any energy from the oscillator coil.
- However when the sample absorbs energy, the reorientation of the nuclear spins induces a signal in the detector coil which is recorded as a resonance signal.
- Alternatively the radiation emitted by the sample when resonance occurs is detected and measured.
- By varying or sweeping the magnetic field over a small range, protons in different chemical environment can be brought into resonance. Hence an NMR spectrum can be obtained.

- This radiation emitted or absorbed at resonance has two features:
  (i) the frequency of the radiowaves emitted or absorbed at resonance depends on the chemical environment of the hydrogen atom(eg H atoms in O—H group and H atoms in CH_3—group produce or absorb radiowaves of slightly different frequencies)
  (ii) the amount of radiation(its intensity) depends on the number of hydrogen atoms found in a given chemical environment (eg the H atoms in a CH_3—group produce or absorb 3 times as much radiation as a H atom in an O—H group).

Shielded and deshielded protons

- Since electrons are charged particles, they move in response to the external magnetic field (B_0) so as to generate a secondary field that opposes the much stronger applied field. Therefore the nucleus will experience a reduced overall field .This secondary field will be said to **shield** the nucleus from the applied field, so B_0 must be increased in order to achieve resonance (absorption of radio frequency energy).
- If a molecule contains π -electrons, specially if it is delocalized like in aromatic molecules, the electron circulation generates another magnetic field (like the magnetic field generated by an electric current in a conductor). The magnetic field generated by the π – electron generates an opposing field at the center of the ring and a supporting field at the edge of the ring. Consider the **benzene molecule** (fig 5)

Fig 5



- Regions in which the induced fields supports or adds to the external fields are said to be **deshielded [designed by a '–' sign]** because a slightly weaker external field will bring about resonance for nuclei in such areas .
- Regions in which the induced field opposes the external fields are said to be **shielded[designed by a '+' sign]** , because a slightly stronger external field will bring about resonance for nuclei in such areas.
- Therefore each type of proton in a molecule experiences a slightly

different magnetic field and the energy required for resonance will vary slightly depending upon the chemical environment of the proton. **This slight variation is the key to the determination of organic structure.**

- By varying or sweeping the magnetic field over a small range, protons in different chemical environment can be brought into resonance. Hence an nmr spectrum can be obtained
- An nmr spectrum can also be obtained by maintaining a constant external magnetic field but by varying the applied radio frequency.

The nmr spectrum

- NMR resonance signals is dependent on both the external magnetic field applied and the radiowave frequency used. As two magnets will never have exactly the same magnetic field strength ,a reference standard is used.
- The commonly used reference standard is tetramethylsilane, $(CH_3)_4Si$, usually referred to as TMS.
- The characteristics that make TMS suitable as a reference standard are:-
  1. it gives only one single sharp and intense nmr signal even at low concentrations(having 12 protons in magnetically equivalent position) that does not interfere with the resonance normally observed for organic compounds even at low concentration.
  2. it has a low boiling point and hence it can be easily removed from the sample after measurements, mainly if a valuable organic compound is being analysed.
  3. it is chemically unreactive
  4. it is soluble in most organic solvents and hence can be added to a sample solution (about 1%)as an internal standard
  5. it is non-toxic
  6. the frequency at which TMS absorbs radiowaves is far from the frequencies of hydrogen atoms in organic compounds, so the TMS peak is not confused with the NMR spectrum

  Note: TMS is not soluble in water or in D_2O: for solutions in this solvent the sodium salt of 3-[trimethylsilyl)-propanesulphonic acid $(CH_3)_3SiCH_2CH_2CH_2SO_3^-Na^+]$ is used.
- All other signals are compared by quoting the shift away from the standard TMS line. This is called the chemical shift (δ).

Chemical shift

- Magnetic environment of a proton is measured as its chemical shift.
- The chemical shift of a nucleus is the difference between the resonance frequency of the nucleus and the standard ,namely tetramethyl silane (TMS).
- The chemical shift is a measure of how far the absorbed radiowave frequency is shifted from the standard, that is from the signal of TMS

- The chemical shift (denoted by the symbol δ)is measured in ppm (parts per million)
- For TMS , the chemical shift $\delta = 0$
- The protons in most organic molecules exhibit chemical shifts in the range 0 to 10 δ.
- The chemical shift gives a very precise indication of the chemical **environment** around the nucleus.
- In the nmr spectrograph, the chemical shift increases **from right to left**.
- Chemical shift values depend on the chemical environment of the protons concerned: different environments generate local magnetic fields of different strengths. For example in phenol, the electronegativity of oxygen reduces the electron density in the proton in –OH. Hence the chemical shift will be relatively high. Therefore the chemical shift from an nmr spectroscopy can be used to determine the chemical environment of a proton.
- The chemical shift can be calculated using the expression

$$\textbf{Chemical shift } \delta = (\Delta B \times 10^6) / B_0$$

$$B_0 = \textbf{applied magnetic field}$$

Where , ΔB = difference in field [in ppm]
B_0 = applied magnetic field

- Highly shielded protons have low δ values .
- Deshielded protons have high δ values.[for example the H nuclei in –OH alcohols is deshielded as the oxygen atom is very electronegative . Therefore it will have a high chemical shift].
- The dependence of chemical shift on the chemical environment of protons is indicated on the two molecules below:-

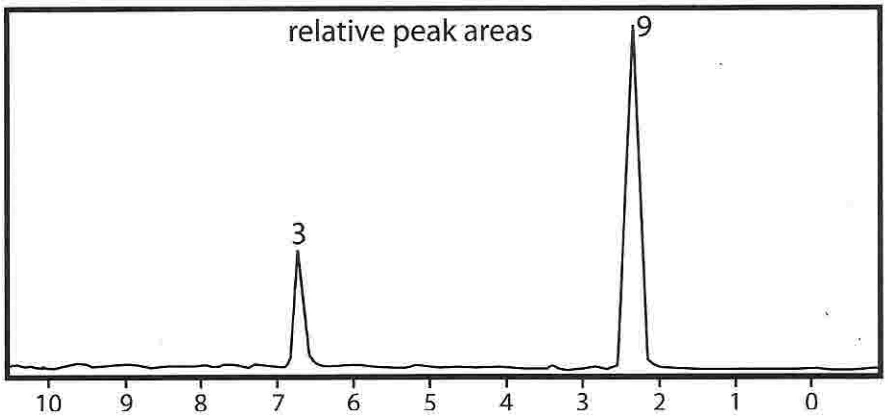
Fig 5

Analysis of the nmr spectrum

- The magnitude or intensity of nmr resonance signals is displayed along the vertical axis of a spectrum.
- The area under each peak is proportional to the number of equivalent hydrogen nuclei.

- The area is usually displaced as integrated intensities.
- The relative integrated intensities are usually displayed on a given signal.
- The integrated intensities in the nmr spectrum can be displayed as shown below:-

Fig 6



The nmr spectrum above shows that:-

[a] there are two sets of protons found in different chemical environment

[b] there are nine hydrogen atoms (at δ =2.2) found in the same chemical environment. These nine hydrogen atoms will be said to be chemically equivalent

[c] there are three hydrogen atoms (at δ =6.9).The three hydrogen nuclei will be chemically equivalent.

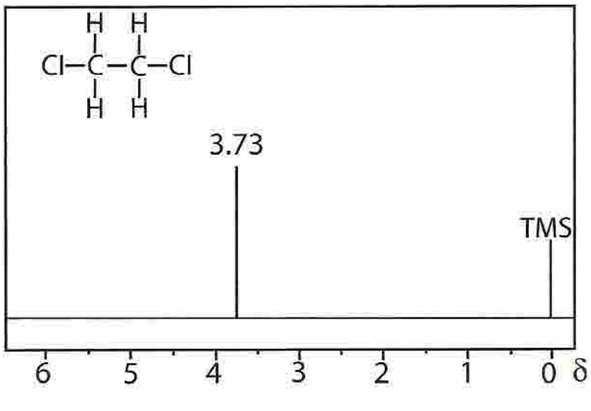
Interpretation of NMR spectra

The following general rules summarise important requirements and characteristics for the interpretation of nmr specta.

1. Nuclei having the same chemical shift, that is equivalent nuclei do not interact with each other.

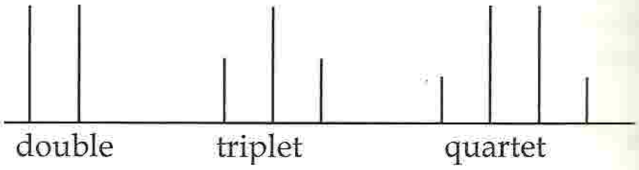
Ex1: In 1,2-dichloroethane, the 4 H-atoms are found in the same chemical environment. Therefore they do not exhibit spin-split. Hence only one signal will be observed in the NMR spectrograph.

Fig 7



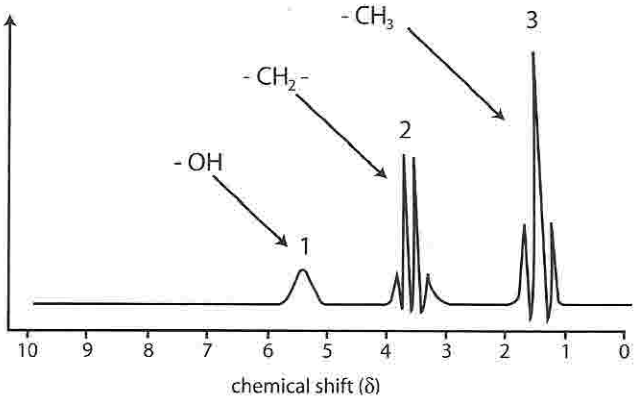
2. Nuclei separated by **three or fewer bonds** will usually exhibit **spin-spin interaction or coupling** (provided they have different chemical shifts), whereby the spin of one nuclei will interact with the spin of the other nuclei. As a result the signal in the NMR will be splitted and a splitting pattern will be observed. The splitting patterns are symmetrically distributed on both sides of the proton chemical shift, and the central lines are always stronger than the outer lines. The most commonly observed patterns have been given descriptive names, such as **doublet** (two equal intensity signals), **triplet** (three signals with an intensity ratio of 1:2:1) and **quartet** (a set of four signals with intensities of 1:3:3:1). Three such patterns are shown below:-

Fig 8



The line separation is always constant within a given multiplet, and is called the coupling constant (J). The magnitude of J, usually given in units of Hz, is magnetic field independent. It helps to distinguish between a splitted signal (where J is constant) and another signal, mainly when the signals are quite close to each other, that is when the difference between the chemical shifts for neighbouring peaks are small or less than 2 ppm and signal from another proton (where the J will not be constant).Consider the nmr spectrum of ethanol below:-

Fig 9



To see why the methyl peak is splitted into a triplet, consider the **methylene [CH$_2$]** protons. There are two of them, and each can have one of two possible orientations (aligned with or opposed against the applied field). This gives a total of four possible states.

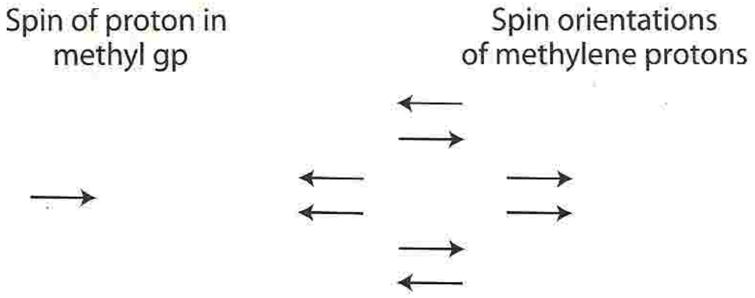


Fig 10

In the first possible combination, spins are paired and opposed to the field. This has the effect of reducing the field experienced by the **methyl** protons; therefore a slightly higher field is needed to bring them to resonance, resulting in an upfield shift. Neither combination of spins opposed to each other has an effect on the methyl peak. The spins paired in the direction of the field produce a downfield shift. Hence, the methyl peak is split into three, with the ratio of areas 1:2:1.

Similarly, the effect of the methyl protons on the methylene protons is such that there are eight possible spin combinations for the three methyl protons;

Out of these eight groups, there are two groups of three magnetically equivalent combinations. The methylene peak is split into a quartet. The areas of the peaks in the quartet have the ration 1:3:3:1.

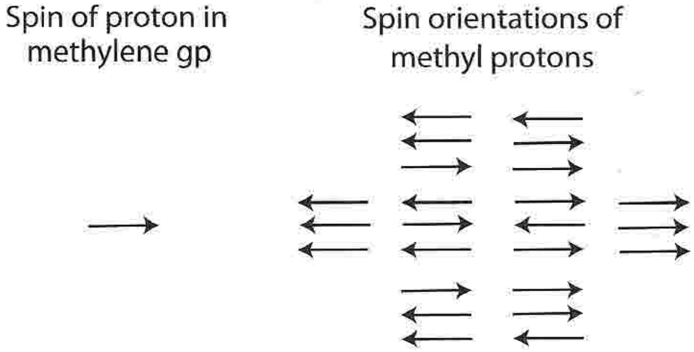
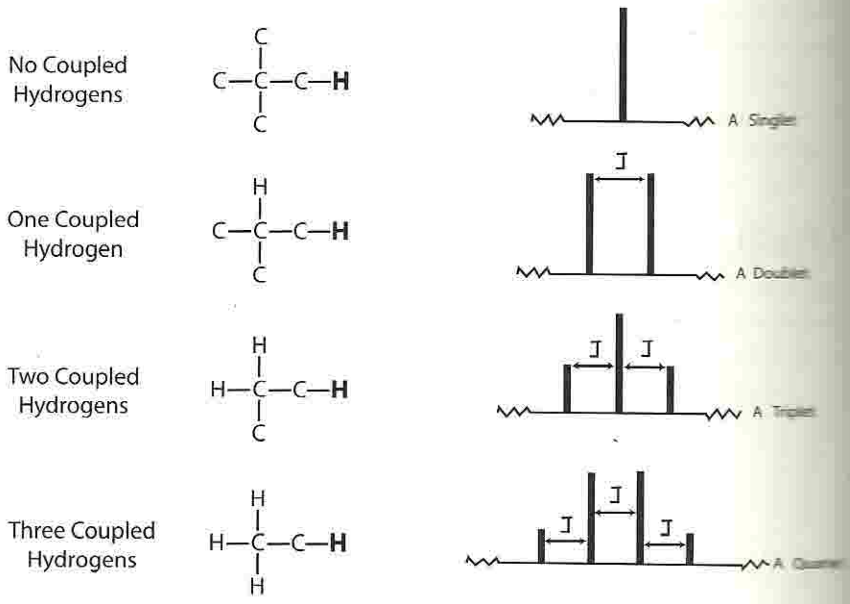


Fig 11

3. The splitting pattern of a given nucleus (or set of equivalent nuclei) can be predicted by the **n+1 rule**, where n is the number of neighbouring spin-coupled nuclei.Thus:-
   - (i) a peak is split into 2 (producing a doublet) if there is one neighbouring H atom
   - (ii) a peak is split into 3 (producing a triplet) if there are two neighbouring H atom
   - (iii) a peak is split into 4 (producing a quartet) if there are three neighbouring H atom
   - **(iv)** In all cases the central line(s) of the splitting pattern are stronger than those on the periphery.

Fig 12



[J is a constant known as the coupling constant]

Usually

[i] a doublet indicates the presence of a single H-atom on an adjacent carbon atom bonded to hydrogen atoms

[ii] a triplet shows the presence of a –CH_2 group on an adjacent carbon atom bonded to hydrogen atoms

[iii] a quartet shows the presence of a --CH_3 group on adjacent carbon atom bonded to hydrogen atoms

[iv] if there is a triplet and a quartet it shows the presence of the --CH_2CH_3 group

[v] presence of benzene group may be shown by the presence of a distorted splitting

- Thus the interpretation of nmr depends on three features: the chemical shifts(which shows the chemical environment of the proton), the multiplicities of the signals (which indicates the number of equivalent protons on adjacent carbon atom) and the integrated peak areas(which shows the number of equivalent protons).

Consider the nmr spectra of ethanol and 2-methylphenol

1. NMR spectrum of ethanol

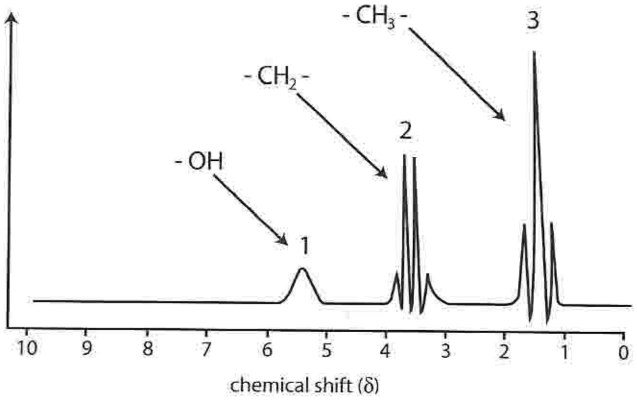


Fig 13

Analysis of spectrum

[i] at δ = 5.8, there is a singlet. It corresponds to an isolated hydrogen. It is probably the hydrogen atom in –OH group

[ii] the quartet at δ = 3.8 corresponds to the CH_2 group which is splitted into 4 signals by the 3 neighbouring atoms in the $-CH_3$ group

[iii] the triplet at δ =1.2 corresponds to the $-CH_3$ group which is splitted into 3 by the $-CH_2$ group.

Note : the splitting signal gives an indication of the number of hydrogen atoms present on the adjacent carbon atom. For example :-

[a] quartet shows that the adjacent carbon atom contains three hydrogen atoms

[b] a triplet shows that the adjacent carbon atom contains 2 hydrogen atoms

[c] a doublet shows that the adjacent carbon atom contains only one hydrogen atom

2. NMR spectrum of 2-methylphenol

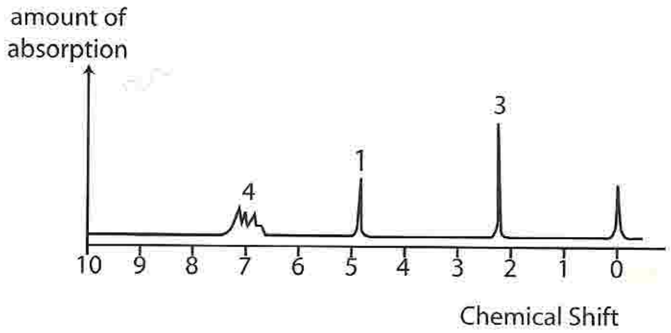


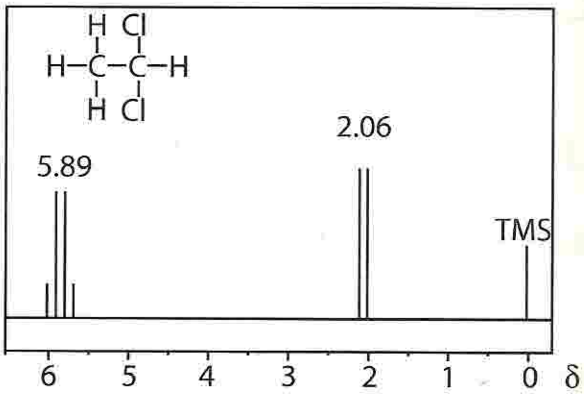
Fig 14

The nmr spectrum of 2-methylphenol is as shown above (fig 14):-
From the nmr spectrum above it can be deduced that:-

1. there are three types of protons: one isolated proton, three equivalent and four equivalent protons
2. absorption due to three equivalent proton indicates the presence of the $-CH_3$ group
3. complex absorption of four equivalent protons suggests the presence of a disubstituted benzene ring.
4. absorption due to one proton is due to the –OH group in phenol

3. NMR spectrum of 1,1-dichloroethane

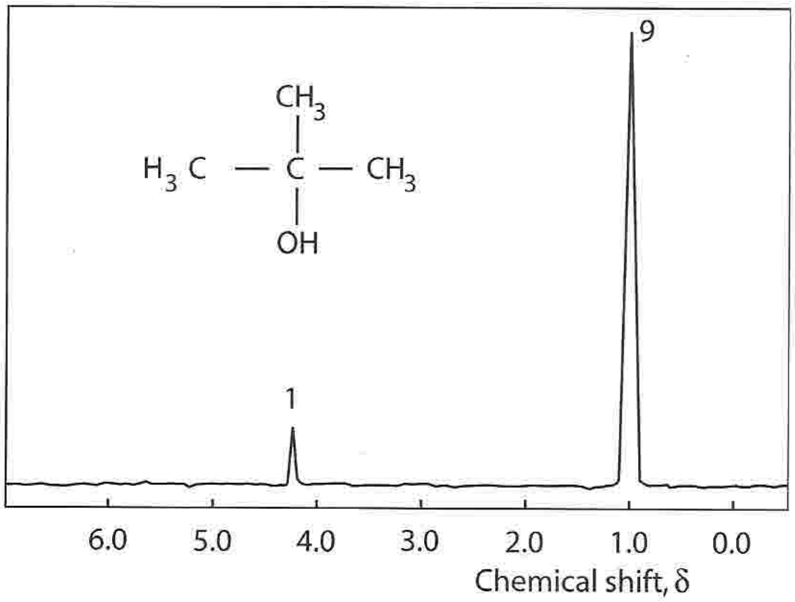
Fig 15



The following information can be deduced:-

1. There are two sets of signals. Hence the molecule contains H-atom in two different chemical environment.
2. Both signals are splitted. Therefore it can be deduced that the two H-nuclei exhibit spin-spin interaction. Hence the two nuclei are more likely to be on adjacent carbon atoms.
3. Atδ=2.06 [chemical shift =2.06] the signal is splitted into two. Using the n +1 rule, it implies that the adjacent carbon atom contains only 1 H-atom[number of splitted signals – 1]. It will be a CH-group. The splitted signal represents the CH_3 group.
4. Atδ=5.89, the signal is splitted into 4 lines. Using the n + 1 rule, it implies that the adjacent carbon atom will contain 4-1 = 3 equivalent hydrogen atoms. It will be a CH_3 group. Hence the signal represents the –CH group. Due to spin-spin splitting, the signal is splitted into 3+1 = 4 signals.

4. NMR spectrum of 2-methyl propan-2-ol



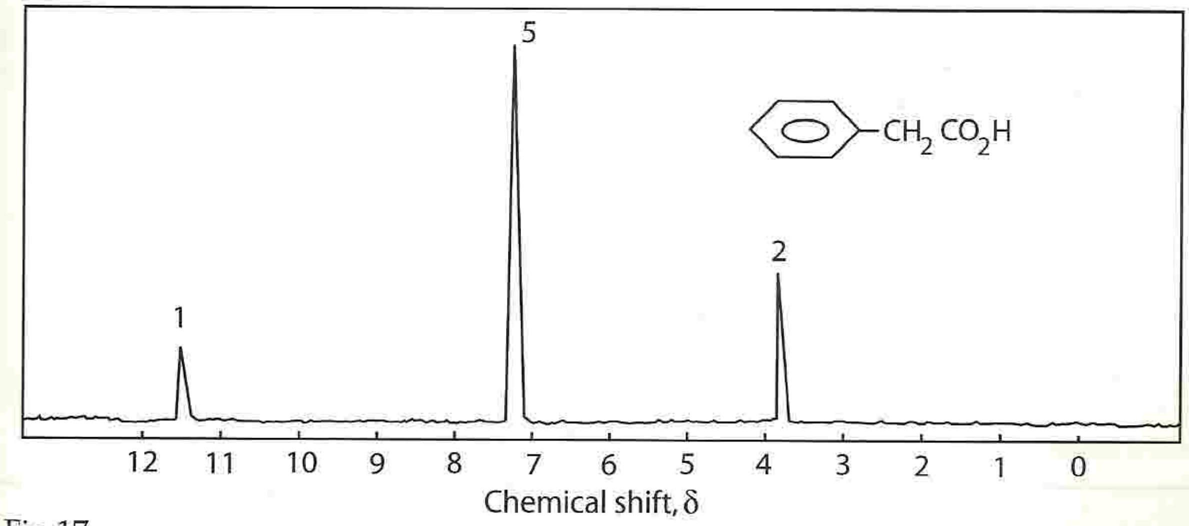
▸ Fig 16

In the above spectrum there are two signals which are not splitted. It implies that there are two sets of hydrogen atoms in the molecule and they are far enough to prevent spin-spin splitting form taking place. By considering the integration values [1 and 9] above the signals , it can be deduced that the ratio of equivalent hydrogen atoms in different chemical environment is 1:9.

The signal at d = 4.2 correspond to an isolated hydrogen atom. This isolated H atom is from the –OH group

The signal at d = 1.2 corresponds to 9 equivalent hydrogens, that is to 3 methyl groups.

5. NMR spectrum of phenyl ethanoic acid



▸ Fig 17

- A single peak of integral height five at δ =7.3 indicates a phenyl group
- A single peak at δ=3.7 suggests the presence of the $-CH_2$ group
- No spin-spin interaction occurs between the protons from the phenyl group and those from the methylene group. Therefore the two groups are not on adjacent carbon atoms.
- A signal at δ = 11.5 shows the presence of a proton in the carboxylic group ($-CO_2H$) .

Uses of D_2O in NMR spectroscopy

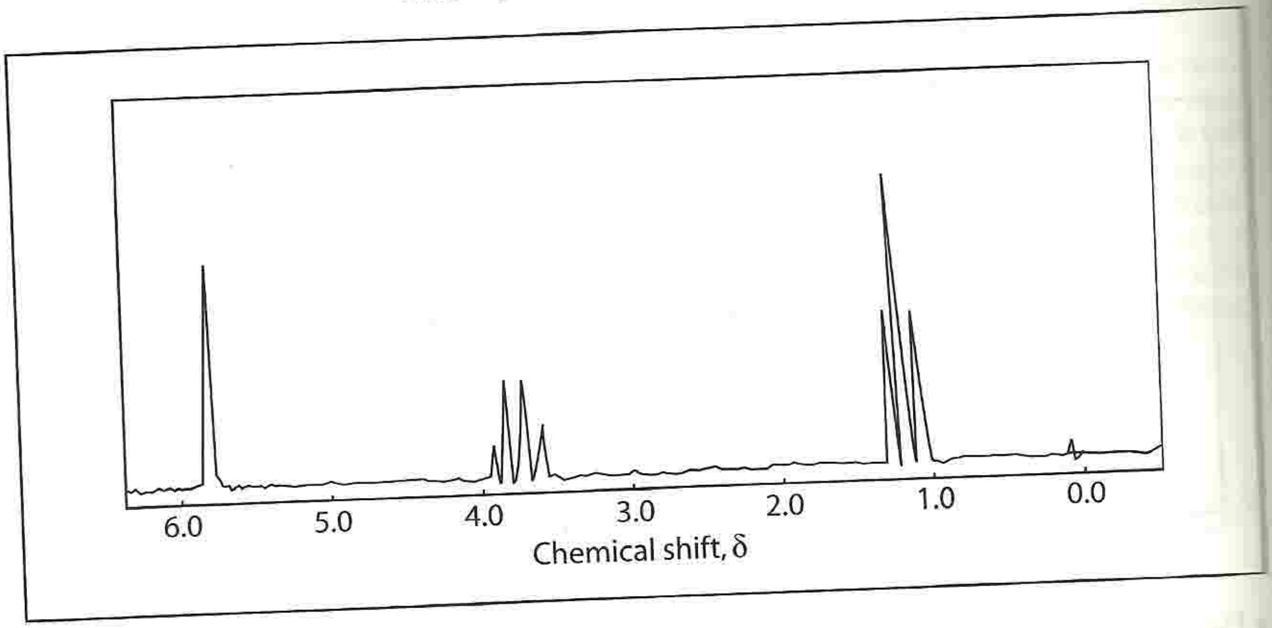
- The—OH signal in the nmr spectrum [fig 18] appears as a single peak. It is not splitted by the protons on the neighbouring—CH_2— group. This is because the proton in the –OH group changes rapidly with protons in traces of water. This exchange is so rapid that the signal for the—OH proton becomes a single peak.

- The signal for the—OH group can be easily removed from the spectrum by adding a small amount [a few drops]of deuterium oxide D_2O[heavy water] to the nmr sample. The deuterium atoms in D_2O exchange reversibly with the protons in the –OH groups.

$$\text{R-O-H} + D_2O \rightleftharpoons \text{R-O-D} + \text{D-O-H}$$

- As deuterium atoms do not absorb in the same region of the spectrum as protons, the–OH signal disappears from the nmr spectrum, as shown in the two nmr spectra below: (fig. 18 and 19)

NMR spectrum of ethanol in absence of D_2O below



▸ Fig 18

NMR spectrum of ethanol in the presence of D_2O

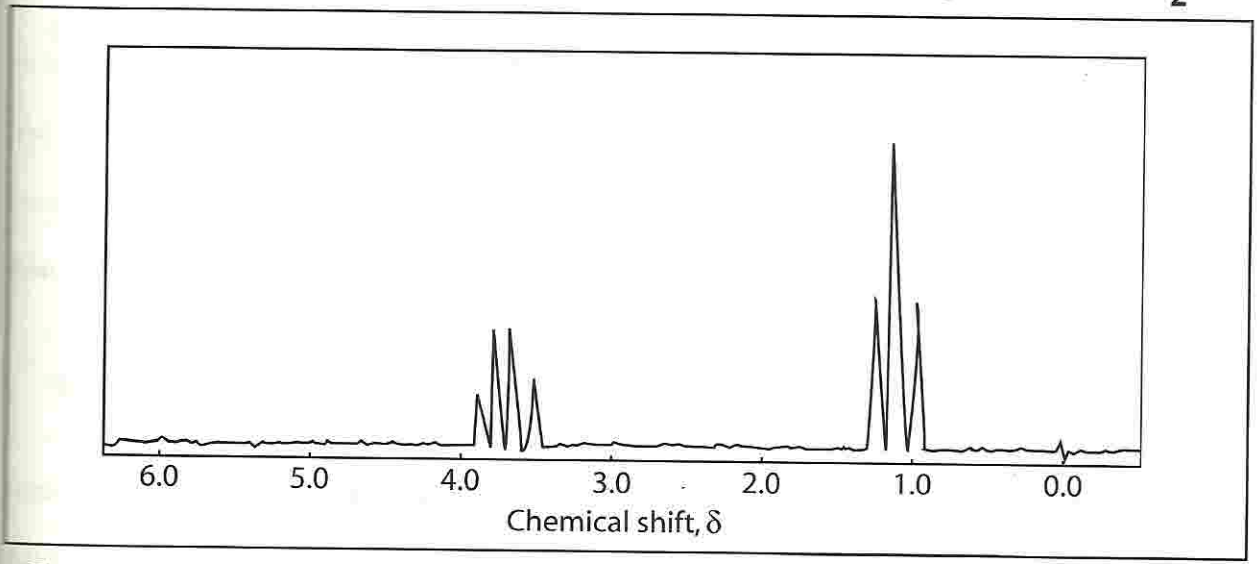


Fig 19

- Hence Rapid exchange of these hydrogens with heavy water would cause the low field signal to disappear.
- By comparing the nmr spectrum of a sample in absence of D_2O and in presence of D_2O, the signal corresponding to the—OH group can be identified.
- These hydrogen atoms that can be very rapidly be replaced by deuterium atoms are known as labile hydrogen atoms or labile protons.
- Labile protons are hydrogen- bonded hydrogen atoms. The hydrogen atoms involved in hydrogen bonding can move from one electronegative atom to another. Due to their continuous mobility they do not interact with hydrogen atoms in neighbouring $-CH_2$ or $-CH_3$ groups.
- Labile protons are found in such groups as –OH , –NH , –SH and so on.
- The addition of D_2O to a sample is widely used to detect the presence of –OH , – NH , –SH in organic molecules.
- Although hydroxyl protons have been the focus of this discussion, it should be noted that corresponding N-H groups in amines and amides also exhibit hydrogen bonding nmr shifts, although to a lesser degree. Furthermore, OH and NH groups can undergo rapid proton exchange with each other; so if two or more such groups are present in a molecule, the nmr spectrum will show a single signal at an average chemical shift. For example, 2-hydroxy-2-methylpropanoic acid, $(CH_3)_2C(OH)CO_2H$, displays a strong methyl signal at $\delta = 1.5$ and a 1/3 weaker and broader OH signal at $\delta = 7.3$ ppm.
- Hydrogen bonding shifts the resonance signal of a proton to lower field (higher frequency).

Uses of nmr in medicine

- Nmr is a non-invasive technique-tissue sample is not required.
- The nmr radiation is not absorbed by tissues, unlike ir (infra-red or ultra-violet radiation).
- As radio waves are used and they are low radiation energy, they will not cause any damage to tissue.
- nmr spectroscopy can be 'tuned' to look at particular organ , tissue proton or process.
- As nmr radiation is not absorbed by bones, it will not be obscured by bones.

Use of nmr and X-ray crystallography in determining the structure of macromolecules

- Hydrogen is the most highly abundant element in organic molecules
- Biological nmr helps to identify the chemical environment of the hydrogen atoms in proteins
- The chemical bond connectivity and the spatial orientation as well as geometry of large biological molecules can be determined.
- Secondary and tertiary protein structure can be determined by two methods: X-ray crystallography and nuclear magnetic resonance.
- To obtain optimum results the protein must be more than 95% pure
- To carry out nmr spectroscopy, crystallization of the protein is not necessary
- But to carry out X-ray crystallography , only crystalline protein must be used, which in certain case is very difficult to be produced.
- NMR spectroscopy has the following advantages in the study of structure of proteins:-
    a) it reveals easily details about specific sites of molecules without having to solve their entire structure
    b) it is sensitive to motions on the time scale of most chemical events. Therefore it allows the direct examination of motions on the millisecond to second range and indirect studies of motions on the nanosecond to microsecond range
    c) it may reveal how active sites of enzymes work
- In X ray – crystallography, X-rays are directed at a crystal of a protein or a derivative of the protein containing a heavy metal.
- The rays are scattered in a pattern, depending upon the electron densities in different portions of a protein
- Electron density maps are obtained
- By superimposing the electron density maps on one another, a model of the protein can be constructed.
- Hence by using X-ray crystallography and nmr spectra, the structure of protein may be determined.
- X-ray crystallography is very time consuming, expensive and

requires specialized equipments and training to be carried out successfully.

- Nevertheless , it reveals very precise structural data about amino acid orientation.
- Knowing the amino acids orientation, protein interactions can be understood and ultimately drugs can be designed in structure based design drug.

X-ray crystallography cannot determine the position of hydrogen atom since the electron density around the proton is too low and it cannot scatter the X-ray sufficiently to be detected. Hence to obtain the full crystalline structure of protein:-

(i) NMR spectroscopy is used to determine chemical environment of the protons, and hence their position in the crystal
(ii) X-ray crystallography is used to determine the position of the remaining atoms.

25.4 Distribution between phases

Partition Coefficient

- If a solute, S, is shaken with two immiscible solvents X and Y (which form two phases), the solute dissolves in both solvents (ie in both phases). An equilibrium is established in which the ratio of the concentrations of the solute S in the two solvents is equal to a constant.
- This constant, K, is called the partition coefficient for the particular

  $$\frac{[S]\ \text{in X}}{[S]\ \text{in Y}} = \text{constant, k}$$

  solute and the two solvents. This relationship is known as the partition law. K has no units.
- The partition coefficient of a solute between two immiscible solvents is defined as the ratio of the concentration of the solute in one solvent to the concentration of the solute in the other solvent at a given temperature.
- The partition coefficient varies with temperature.
- The value of the partition coefficient is independent of the total solute concentration.
- The magnitude of the partition coefficient shows the relative solubility of a solute in the two immiscible solvents.

For example if the partition coefficient of bromine between tribromoethane , $CHBr_3$ and water at 25 ^{0}C is 67, that is

$$\frac{[Br_2]\ \text{in}\ CHCl_3}{[Br_2]\ \text{in}\ H_2O} = 67$$

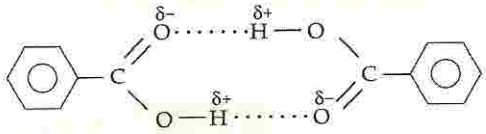
This implies that bromine is 67 times more soluble in $CHBr_3$ than in water.

- The partition law only holds if the solute particles are the same in both solvents.

There are two general cases when the partition law does not hold:

(a) when the solute molecules dissociate or ionise in one solvent but not in the other;

(b) when the solute molecules join together (associate) in one solvent but not in the other. For example, in the distribution of benzoic acid between water and benzene, the solute particles in water are almost entirely C_6H_5COOH molecules. But in benzene, the solute particles pair up to form $(C_6H_5COOH)_2$ molecules because of hydrogen bonding (Fig 20).



▸ Fig 20 Hydrogen bonding of benzoic acid in benzene

When the solute particles are different in the two solvents, the ratio of the two concentrations varies with concentration.

Question

A quantity of iodine was shaken with water and tetrachloromethane in a separating funnel until the iodine had dissolved and equilibrium had been reached. The two solutions were allowed to settle and then separated. 25.0 cm^3 of the aqueous layer required 39.4 cm^3 of 0.02 mol dm^{-3} $S_2O_3^{2-}$ for titration using starch indicator. 5.0 cm^3 of the CCl_4 layer required 15.0 cm^3 of 0.1 mol dm^{-3} $S_2O_3^{2-}$ for titration.
Calculate the partition coefficient for iodine distributed in the water and tetrachloromethane.

Answers

In the CCl_4 layer: $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

Number of moles of $S_2O_3^{2-}$ required $= \dfrac{15.0 \times 0.1}{1000}$ mole

From the equation, the number of moles of I_2
$= \dfrac{1}{2}$ number of moles of $S_2O_3^{2-} = \dfrac{1}{2} \times \dfrac{15.0}{1000} \times 0.1$ mole

Hence the concentration of I_2 in CCl_4

$$= \frac{\frac{1}{2} \times \frac{15.0}{1000} \times 0.1}{\frac{5}{1000}} = 0.15 \text{ moldm}^{-3}$$

In the H_2O layer
number of moles of $S_2O_3^{2-}$ required $= \dfrac{39.4}{1000} \times 0.02$ mole

From the equation, the number of moles of I_2

$$= \frac{1}{2} \times \frac{39.4}{1000} \times 0.02 \text{ mole}$$

Hence the concentration of I_2 in H_2O

$$= \frac{\frac{1}{2} \times \frac{39.4}{1000} \times 0.02}{\frac{25}{1000}} = 0.016 \text{ mol dm}^{-3}$$

$$\text{The partition coefficient} = \frac{[I_2] \text{ in } CCl_4}{[I_2] \text{ in } H_2O} = \frac{0.15}{0.016} = 9.4$$

It implies that iodine is 9.4 times more soluble in CCl4 than in water at the temperature that the experiment was carried out.

Note: The partition coefficient can be written the other way round.

$$\frac{[I_2] \text{ in } H_2O}{[I_2] \text{ in } CCl_4}$$

(this gives $K = 0.11$).

Usually, the larger concentration is written as the numerator (top).

Solvent Extraction

- In the preparation of organic compounds, the organic compound is often produced in a dilute aqueous solution. To obtain the organic compound, the solution is shaken with a suitable extraction solvent. The organic compound goes from the water into the extraction solvent. The latter is then separated (with a separating funnel) from the water. The organic compound is then obtained by evaporating the solvent, leaving behind the pure organic compound (Fig 21).

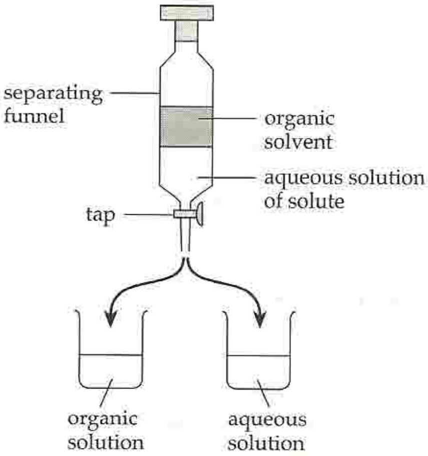


Fig 21 Solvent extraction

The efficiency of solvent extraction depends on:-

(i) the solvent used, that is the partition coefficient of the solute between the solvent and water. A large value of the partition coefficient will lead to a better extraction.

(ii) on the relative volumes of the two immiscible liquids used. Usually by using small portions of liquids several time rather by using the same total volume of liquid only once, a more efficient extraction occurs.

- A good general solvent for the extraction of organic compounds from aqueous solutions should have the following properties:

(a) it must be insoluble in water (or almost insoluble);

(b) it must have a high solubility for organic compounds (it will then have a large partition coefficient);

(c) it must have a low boiling point so that it can easily be evaporated at low temperature and

(d) it must be chemically unreactive with most organic compounds.

- A good solvent for solvent extraction of organic compounds is ethoxyethane (ether). Ether has all of the desirable properties of an extraction solvent.

  However ether has two disadvantages:

  (a) it is a serious fire risk as it is very flammable. It can only be used in laboratories without naked flames or sparking electrical equipment;

  (b) the vapour of ether is harmful to people.

- Solvent extraction is used industrially:-

  (i) to obtain aromatic compounds, or essential oils, from flowers, grasses and plants.

  (ii) To separate and purify low grade and complex ores.

Question

500 cm^3 of water contains 6.0 g of the organic compound caffeine. The solution is shaken with 100 cm^3 of trichloromethane to extract the caffeine.

Calculate:

(a) the mass of caffeine extracted into the organic solvent, and

(b) the percentage of caffeine removed from the water.

[Partition coefficient for caffeine distributed between trichloromethane and water = 10]

Answer

Let *x* g be the mass of caffeine extracted into the trichloromethane.
Then the mass of caffeine remaining in the water = (6 – *x*) g

$$\text{Partition coefficient} = 10 = \frac{[\text{caffeine}]\text{ in trichloromethane}}{[\text{caffeine}]\text{ in water}}$$

$$= \frac{\frac{x}{100}}{\frac{(6-x)}{500}}$$

$$5x = 60 - 10x$$

$$x = 4\text{ g}$$

Thus (a) the mass of caffeine extracted by the trichloromethane = 4 g,

(b) the percentage of caffeine removed from the water

$$= \frac{4}{6} \times 100\% = 67\%$$

Note: The units of solubility in the expression for the partition coefficient can be in g dm^{-3} or mol dm^{-3}.

- Solvent extraction is more efficient with several small portions of solvent, rather than one large portion.

Question

20 g of an organic compound is dissolved in 100 cm^3 of water. If the organic compound is extracted with ethoxyethane (ether), show that the quantity extracted by two 25 cm^3 portions of ethoxyethane is larger that that extracted by one 50 cm^3 portion.
(Partition coefficient = 4)

Answers

(a) Let x be the mass of organic compound extracted by one 50 cm^3 portion of ethoxyethane.
Then the mass of organic compound remaining in the water is (20 – x) g.

$$\frac{\text{[organic compound] in ethoxyethane}}{\text{[organic compound] in water}} = \frac{\frac{x}{50}}{\frac{(20-x)}{100}} = 4$$

Hence x = 13.3 g.

(b) Let y be the mass of organic compound extracted by one 25 cm^3 portion of ethoxyethane.
Then the mass of organic compound remaining in the water = (20 – y) g.

$$\frac{\text{[organic compound] in ethoxyethane}}{\text{[organic compound] in water}} = \frac{\frac{y}{25}}{\frac{(20-y)}{100}} = 4$$

Hence y = 10 g.

Let z be the mass of organic compound extracted by the second 25 cm^3 portion of ethoxyethane.
Then the mass of organic compound remaining in the water = (10 – z) g.

$$\frac{\text{[organic compound] in ethoxyethane}}{\text{[organic compound] in water}} = \frac{\frac{z}{25}}{\frac{(10-z)}{100}} = 4$$

Hence z = 5.0 g.
The total mass of organic compound extracted by two 25 cm^3 portions of ethoxyethane.
= (10 + 5) g = 15g.
This is larger than the 13.3 g extracted by one 50 cm^3 portion of ethoxyethane.

25.5 Chemical Analysis

Chromatography

- Chromatography is a method used to separate different components of a mixture based on a difference in the physical property of the mixture such as solubility of components in a given solvent, volatility of the components or their adsorptivity on a given surface.
- During chromatography the components of a mixture distribute themselves between two phases, namely a stationary phase and a mobile phase. As the different components have different distribution coefficient between the two phases, they go in the mobile phase at different rates. Hence the components will separate out.
- Chromatography is a method of separating mixtures by distributing the mixture between two immiscible phases, one stationary and one moving. The method consists of putting the mixture onto the stationary phase (which is usually a solvent absorbed on a solid) and then passing the other phase over it (this other phase is either liquid or gaseous). The moving phase dissolves the components of the mixture and carry them with it. The components move at different speeds depending on their solubility in the moving phase, and are thus separated.
- Chromatography is particularly useful for detecting, identifying and separating complicated organic compounds present in very small amounts, such as drugs in urine samples, dyes in food and herbicides in vegetables. It can also be used to identify inorganic substances such as metal ions from alloys and minerals.
- There are several types of chromatography, such as paper chromatography, thin layer chromatography, column chromatography, high performance liquid chromatography and gas-liquid chromatography.

Paper Chromatography

- In paper chromatography, a liquid solvent moves up (or down) a strip of paper. The paper has a layer of water attached to its fibres which acts as the stationary phase.
- Paper chromatography is used to separate a mixture of solutes in a liquid solvent.
- An example of paper chromatography is the separation and identification of individual dyes from a mixture of dyes (Fig 22).
    (a) Spots of known dyes are placed on a pencil line (the start line) at positions 1 and 2.
    (b) A spot of the dye mixture is placed on the start line at position 3.
    (c) The paper is placed in a suitable basin so that the solvent can move up the paper. A lid prevents loss of solvent by evaporation.

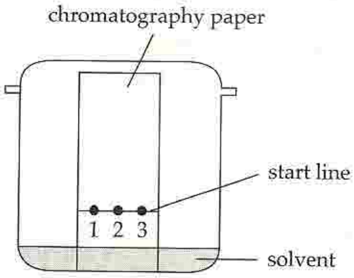


Fig 22 Paper chromatography

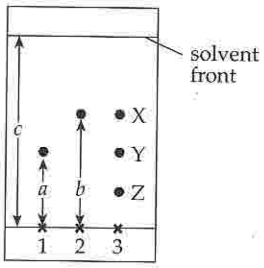


Fig 23 Chromatogram showing separation of dyes

(d) The result after some time is shown in Fig 23. This is called the chromatogram. The solvent front marks the final position of the solvent on the chromatogram.

(e) For each dye, the ratio

$$\frac{\text{distance moved up the paper by the dye}}{\text{distance moved up the paper by the solvent}} = \textbf{a constant, } \mathbf{R_f}$$

The constant R_f is called the R_f value for the dye. It is a constant for that particular dye under particular conditions of solvent and temperature. In Fig 23, the R value for dye 1 is a/c, and for dye 2 it is b/c.

- Dyes (and other substances) can be identified from their R values. This can be done by looking up the R_f values in a reference data book, or by direct comparison with known dyes on the chromatogram. Dyes which are the same have the same R_f value and hence will have moved the same distance up the paper.
  For example, in Fig 23, spot X has moved the same distance as the spot of dye 2, so it must have the same R_f value and must be the same dye. Similarly, spot Y must be dye 1. Spot Z is a dye with an R_f value different from dye 1 or 2, so it must be a different dye.
  The experiment shows that the mixture placed at position 3 is made up of three dyes: dyes 1 and 2 and a third (unknown) dye.

- Paper chromatography (and thin layer chromatography) can be used in industry to test the purity of manufactured chemicals, such as drugs. A pure compound will produce a single spot on the chromatogram. An impure compound produces two or more spots. Even tiny amounts of impurities can be observed as faint spots.
- In School laboratories paper chromatography is used to separate mixture of dyes such as ink or mixtures of aminoacids.

Thin Layer Chromatography (TLC)

1. TLC is a chromatographic method, similar to paper chromatography, but the stationary phase is a finely divided solid, usually silica , powdered cellulose or alumina spread as a thin layer on a supporting flat surface such as a plastic, aluminium or glass plate

- The mobile phase must be a very pure solvent as TLC is a very sensitive analytical technique.
- In practice, TLC is carried out as follows:-
  i. a small volume of the mobile phase is placed in a tall tank or chamber, which is covered and allowed to stand for some minutes so that the atmosphere becomes saturated with the solvent vapour
  ii. a very tiny drop of the mixture sample is spotted on the TLC plate along a line near the base of the plate (at about 1cm from the base).
  iii. the plate is then carefully lowered in the tank in such a way that the spot is above the surface of the mobile phase
  iv. the mobile phase will then move up the plate by capillary force
  v. as the mobile phase moves over the sample, the different components of the mixture will distribute themselves between the stationary phase and the mobile phase.
  vi. due to the difference in solubility of the different components in the mobile phase and the difference in their adsorptivity on the stationary phase, the different components will move up the plate at different rate. Hence they start to separate out.
  vii. before the solvent front reaches the top of the plate, the latter is removed from the tank and is dried in a current of warm air
  viii. the solute spots are than located either by its colour or if it is colourless, by using a suitable locating agent or by viewing the plate under ultraviolet light.
  ix. Each component of the mixture is characterised by its R_f value. By determining the R_f value and comparing it with available Data, the identity of the component may be known.

- Thin layer chromatography is usually superior to paper chromatography because the 'spots' are more compact on the chromatogram. Therefore:
  (a) there is better separation and
  (b) smaller amounts of mixture can be separated and identified.

Uses of TLC

1. It is used in the biochemical, pharmaceutical, clinical and forensic areas for qualitative analysis.
2. It is used to check for purity of substances
3. It is used to monitor the course of certain industrial reactions
4. It is used to separate organic compounds

Advantages of TLC over gas-liquid chromatography[GLC] and HPLC[high performance liquid chromatography

1. A large number of samples can be run simultaneously.
2. All components, including those that have very low R_f value can be detected
3. The process is relatively cheap, versatile,reliable and quick.

Column Chromatography

- Column chromatography is similar to thin layer chromatography. The inert material (eg aluminium oxide) is packed into a glass tube. A little of the substance to be separated (eg a solution of plant pigments) is poured into the top of the tube. A solvent is then allowed to run slowly down the tube. The mixture to be separated dissolves in the solvent and moves down the tube: the components of the mixture move at different speeds and so are separated into bands, one band for each component in the mixture. The components are identified from their positions in the column.

- Column chromatography is a good way of collecting samples of the components in the mixture for further analysis. Each component can be collected as it comes out the bottom end of the tube. The identity of each component (eg if it is an organic compound) can then be found out by other techniques such as mass spectrometry.

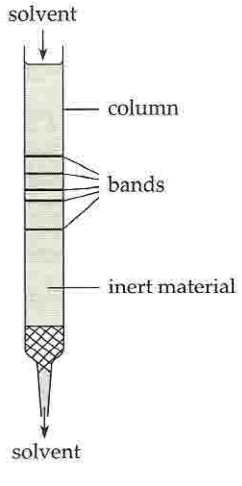


Fig 24 Column chromatography

Gas-Liquid Chromatography (GLC)

- Gas-liquid chromatography is used to separate and identify substances that are gaseous or which can be vapourised easily (this includes most organic compounds),and which thermally stable.

- An example of a simple gas-liquid chromatography apparatus is shown in Fig 25.

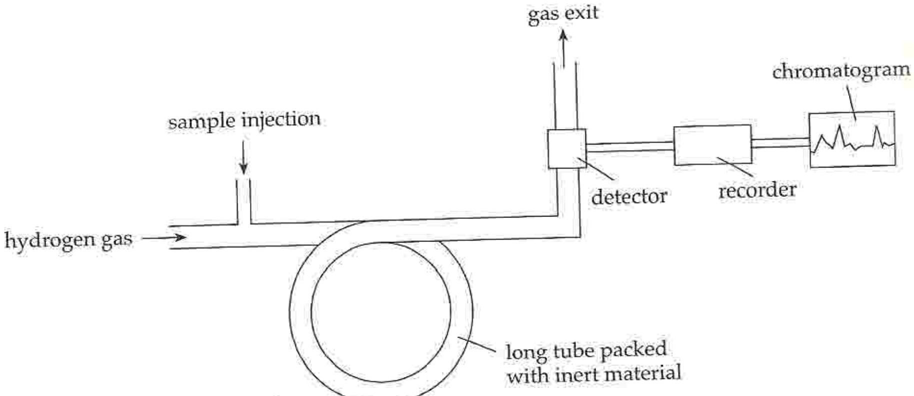


Fig 25 Gas-liquid chromatography apparatus

In the apparatus:

(a) Hydrogen gas, argon or nitrogen gas (the moving phase) is passed through a long tube packed with inert material which is coated with a suitable liquid. This is the stationary phase.

(b) The sample to be analysed is vapourised and injected into the hydrogen gas stream. The sample is carried through the long tube found in a thermostat over the inert material by the hydrogen gas. The components of the sample move at different speeds and are separated. The components come out of the end of the tube at different times.

(c) As each component leaves the tube, it is detected by its effect on the conductivity of the hydrogen gas, which is measured by a sensitive ammeter.

(d) The recorder prints a graph of ammeter reading against time from injection of the sample. This graph is called a gas chromatogram.

- In a gas chromatogram:
  (a) Each component appears as a peak.
  (b) The time at which a component emerges from the tube is characteristic of a component. Hence a component can be identified from the position of its peak in the chromatogram.
  (c) The area under each peak is a measure of the amount of that component that is present. Hence a small peak means a very small amount of that component is present, and a large peak means the presence of a large quantity of the component.

- A gas chromatogram is shown in Fig 26 for a mixture of straight-chain alkanes in an oil sample. The numbers indicate the number of carbon atoms per molecule.
  (a) The smaller alkane molecules have shorter times than the bigger molecules because they move through the inert material more quickly.
  (b) The C29 peak is bigger than the C19 peak, which shows that there is much more of the C29 alkane present in the sample.

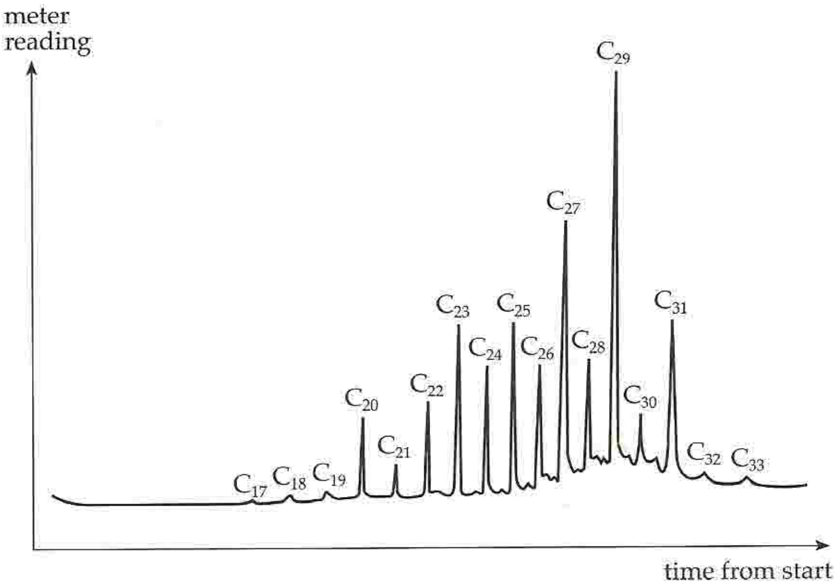


Fig 26 Gas chromatogram of an oil sample

- Gas-liquid chromatography is routinely used in the detection and identification of drugs. For example, it is used in drug-testing of athletes in international competitions such as the Olympic Games. It can also be used to identify the sources of an oil sample (eg from an oil slick at sea dumped from a passing ship) as it usually has a unique composition which produces a distinctive chromatogram.

High Performance Liquid Chromatography (HPLC)

- HPLC is a separation technique whereby different components of a mixture, dissolved in the mobile phase, are forced to move through a column packed with microparticles by applying high pressure, usually between 20 to 200 atmosphere.
- In HPLC, the stationary phase is held in a column (about 25 cm long) and the mobile phase is forced is forced through the column under pressure.
- A common stationary phase consists of silica particles with long-chain alkane adsorbed onto their surfaces. Other commonly used stationary phases are magnesium oxide , activated charcoal and alumina.
- A common mobile phase is methanol.

- An example of a simple high performance liquid chromatography apparatus is shown below:-

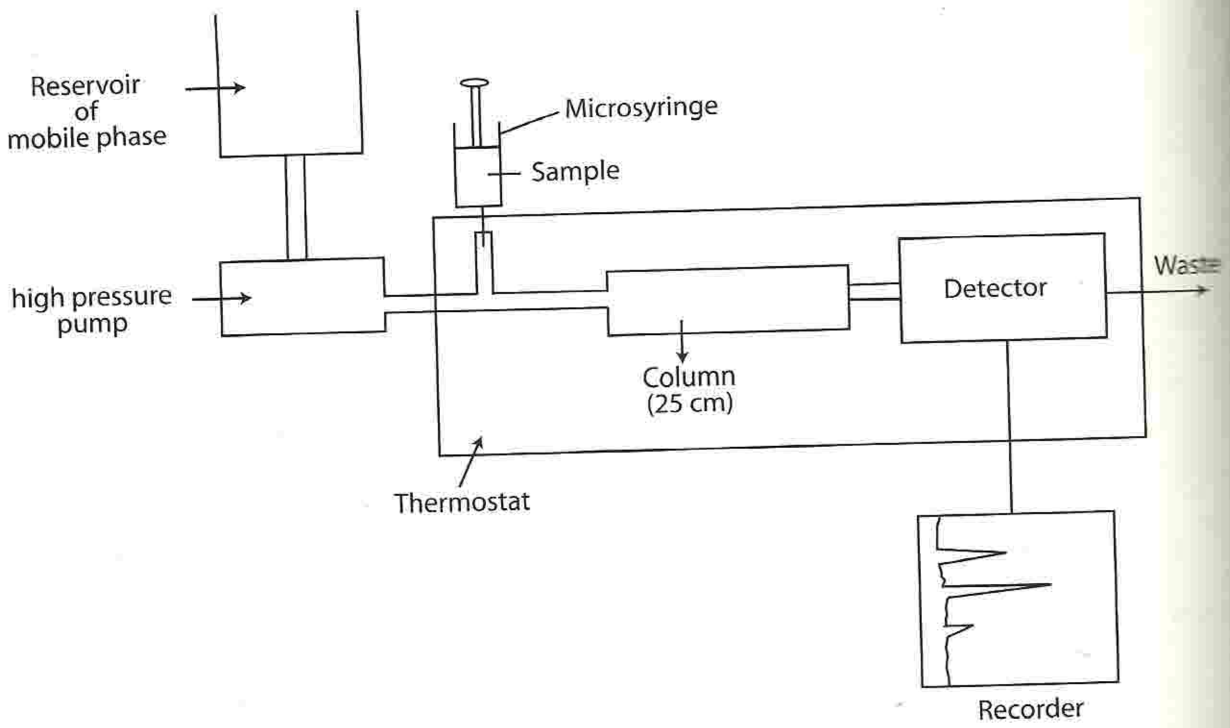


Fig 27

- Due to the difference in solubility of components in the mobile phase and their adsorptivity on the stationary phase the different components will move through the column at different rate and hence they will elute out at different rate.
- As the different components elute out, they pass through a detector, usually an ultraviolet spectrophotometer and an output appears as a series of peaks.
- The **elution time**, which is the time between injection and the appearance of a peak on the chromatogram is used to identify the component. Under similar conditions, a given substance will have the same elution time.
- HPLC is a rapid method of separation and identification of substances.
- It is usually interfaced with mass spectrometer. The end of the column is connected to the ionisation chamber of the mass spectrometer, which identifies the elutant rapidly.
- HPLC is a highly reproducible analytical tool .The reproducibility is ensured by having a constant flow of the mobile phase through the column.
- The area under the peak is proportional to the amount of a component in the mixture.

Uses of HPLC

1. In the rapid identification of drugs or doping substances such as the presence of steroids and stimulants blood or urine of competing athletes or racehorses.
2. In the analysis of pharmaceutical products before packaging to ensure the absences of undesirable substances
3. In determining the nature and amount of insecticides and pesticides in plants.

25.6 Mass spectroscopy

To deduce the number of carbon atoms in a molecule using the M+1 peak

- All organic compounds contain carbon atoms.
- There are three isotopes of carbon. They are ^{12}C , ^{13}C and ^{14}C.
- The relative abundance of ^{13}C in Nature is 1.1% that of ^{12}C
- Therefore in the mass spectra of carbon containing substances, apart from the peak representing the molecular peak M, there will be a neighbouring peak of m/e value of M+1.
- The relative abundance of the M+1 peak increases linearly with the number of carbon atoms. For example for a molecule with 2 carbon atoms, a molecule of mass M+1 will occur 2x1.1%, that is 2.2% of the time. Therefore a t M+1 there will be a peak with an abundance of 2.2% that of the molecular ion peak.
- Hence the M+1 peak shows the number of carbon atoms present in the molecule. This can be practically determined using the following steps

Step 1 : Measure the height of the molecular ion peak, M^+. Let it be 98mm

Step 2: Measure the height of the molecular ion peak M+1. Let it be 5.4mm

Step 3: Calculate the percentage of the height of peak at M+1 relative to the height of peak at M^+

$$\frac{\text{height of peak (M+1)}}{\text{height of peak (M)}} \times 100 = \frac{5.4}{98} \times 100 = 5.5\%$$

Step 4: As there are 1.1% of carbon-13 in Nature, the number of carbon atom in the molecule is determined as follows

The number of carbon atoms in the molecule is 5.5 /1.1 = 5

- In general the number of carbon atoms in a molecule may be deduced using the expression below:-

$$n = \frac{\text{height of peak (M+1)}}{\text{height of peak (M)}} \times \frac{100}{1.1}$$

To determine the presence of bromine and chlorine atoms using the M+2 peak

- Chlorine occurs in two isotopic forms: chlorine-35 (^{35}Cl) and chlorine-37(^{37}Cl).
- The natural abundance of chlorine –37 is 33% that of chlorine –35
- Bromine occurs in two isotopic forms : bromine-79(^{79}Br) and bromine-81(^{81}Br)
- The natural abundance of bromine –81 is 98% that of bromine-79 [that is both ^{79}Br and ^{81}Br have almost the same natural abundances]
- If chlorine or bromine atom is present in a molecule, there will be extra peaks due to the presence of the different isotopes of the chlorine or bromine atoms.
- The extra peak will appear at M+2, as the difference in relative isotopic mass between the two isotopes of chlorine and bromine is only 2 units in each case.
- In the presence of chlorine atom, the ratio of the height of the peak at M to that at M+2 must be approximately 3:1
- Hence if in a mass spectrum there are two peaks which differ in mass by exactly two units and the ratio of the height of their peaks is 3:1, it shows that the compound contains a chlorine atom.
- In the presence of bromine atom, the ratio of the height of the peak at M to that at M+2 must be approximately1:1
- Hence if in a mass spectrum there are two peaks[of almost similar height] which differ in mass by exactly two units and the ratio of the height of their peaks is1:1, it shows that the compound contains a bromine atom.

Fragmentations in mass spectrograph

- When a molecule is bombarded with very energetic electrons, it may lose an electron and undergo ionization only.
- But the molecule may also absorb enough energy to break the internal covalent bond in the molecule. As a result the molecule breaks into fragments. This process is referred to as fragmentation
- Fragments of similar m/e values will appear as a peak in the mass spectrograph.
- The different peaks may be assigned a particular atom or group of atoms as shown below:-

Fragment	Specific mass (m/e)
CH_3^+	m-15
OH^+	m-17
CN^+	m-26
$H_2C=CH_2^+$	m-28
$CH_2CH_3^+$	m-29
OCH_3^+	m-31
$C1^+$	m-35
$OCH_2CH_3^+$	m-45
$C_6H_5^+$	m-77
$C_6H_5CH_2^+$	m-91

If the specific mass (m) of the molecule is known, by considering the decrease in mass indicated by different peaks in the spectrograph, the fragments responsible for these decrease in mass can be known as indicated by the table above.

Hence the identity of different groups present in the molecule can be known.

ANALYSIS OF SOME MASS SPECTRA

An organic compound A was analysed using mass and nmr spectroscopy. The spectra obtained are shown .

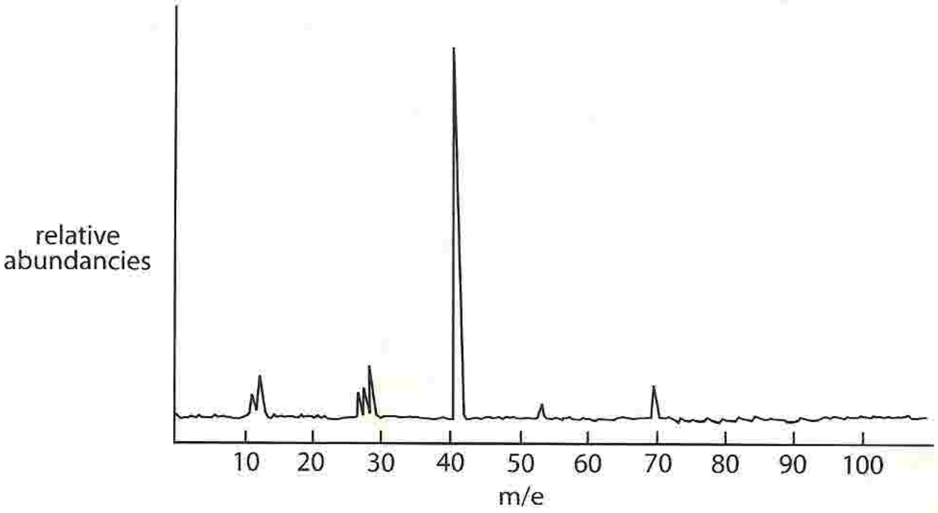
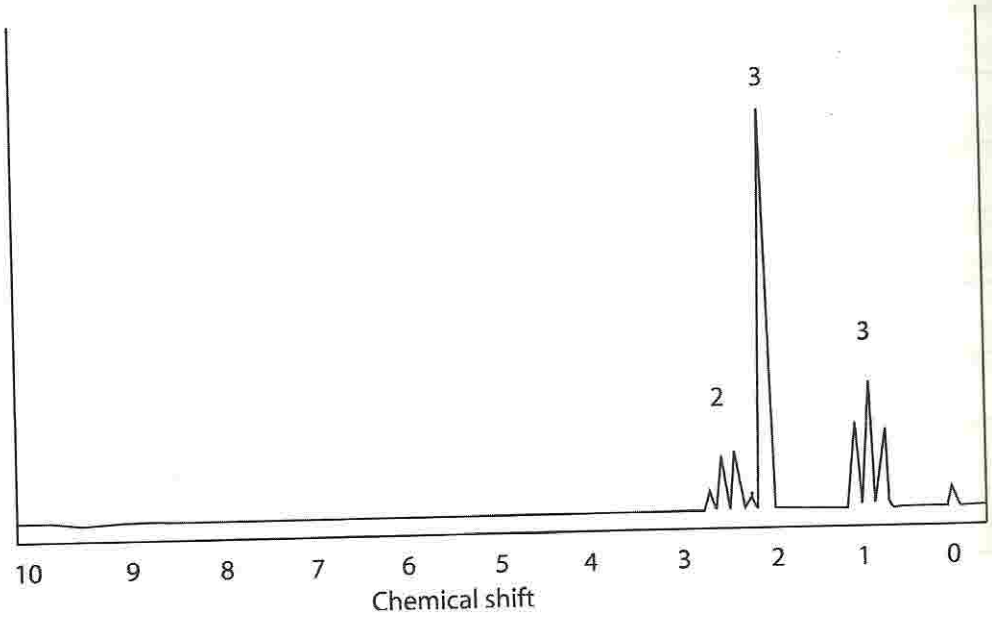


Fig 29

Fig 30



Using this information, deduce what you can about the nature of A, indicating clearly what evidence you are using in each case.

From the mass spectrum the following information can be obtained:-

[a] the last signal is at m/e value of 72. Therefore the relative molecular mass of compound A is 72.

[b] number of carbon atoms in the molecule can be calculated using the relative abundances of the 'M' and 'M+1' peaks as follows:-

Relative abundancy at peak M =14.5
Relative abundancy at peak 'M+1' = 0.66

$\therefore$n = [0.66 x 100] / [14.5 x 1.1] =4.1
$\therefore$number of carbon atoms = 4

From the nmr spectrum , the following information may be obtained:-

1. there are protons in three different chemical environment
2. there are three protons at chemical shift δ = 2.1 which did not undergo splitting
3. the presence of the quartet at δ =2.4 shows the presence of a $-CH_2$ group which has been splitted by three hydrogen atoms found on an adjacent carbon atom
4. the presence of a triplet at δ = 1.0 shows the presence of a $-CH_3$ group that has been splitted by two hydrogen atoms found on the adjacent carbon atom
5. therefore the presence of a triplet and a quartet in an nmr indicates presence of the $-CH_2CH_3$ group in the molecule

From the mass spectrum, the molecule contains 4 carbon atoms and has a relative molecular mass of 72.

From the nmr spectrum , the molecule A has 8 hydrogen atoms only.

To identify any other element present in A, the unaccounted mass is determined. It will be equal to [72 –4(12) –8(1)] = 16. This mass corresponds to the atomic mass of the oxygen atom. Hence it may be deduced that oxygen atom is present in A.

Hence the molecular formula of A is C_4H_8O. Furthermore from the nmr spectrum, it was found that the molecule A contains the groups $-CH_2CH_3$ and $-CH_3$.Hence a possible structural formula for A is $CH_3CH_2COCH_3$.

The main fragments in the mass spectrum are at m/e 72,43, 29 and 15.They correspond to the following fragments

m/e	Corresponding fragments
15	CH_3^+
29	$CH_3CH_2^+$
43	CH_3CO^+
57	$CH_3CH_2CO^+$
72	$CH_3CH_2COCH_3^+$

Hence compound A is probably butanone, $CH_3CH_2COCH_3$

25.7 Isotopic ratios in ice cores

- The two main isotopes of oxygen are ^{16}O and ^{18}O. All other isotopes of oxygen have very short half lives or are found in very small amount in nature.
- The ^{16}O : ^{18}O ratio in modern environments is about 500 : 1. Therefore about 0.2% of oxygen in natural circulation is ^{18}O
- The vapour pressure of $H_2{}^{16}O$ is higher than that of $H_2{}^{18}O$.Therefore during evaporation, the lighter $H_2{}^{16}O$ evaporates preferentially.
- During condensation ,as the vapour pressure of $H_2{}^{18}O$ is lower than that of $H_2{}^{16}O$, the heavy water $H_2{}^{18}O$ condenses out more-readily.
- Therefore atmospheric oxygen becomes preferentially richer in ^{16}O whereas oceanic oxygen becomes enriched in ^{18}O.
- As water vapour moves towards the pole, it condenses gradually as

temperature falls. However the $H_2{}^{18}O$ condenses more rapidly than $H_2{}^{16}O$. As a result , while moving towards the polar regions, there is a fractionation of the $H_2{}^{18}O$ and $H_2{}^{16}O$ vapours, as a result of which the vapour will have an increasingly lower amount of $H_2{}^{18}O$.

- As the rate of condensation depends on the rate of cooling of the vapour, the greater the fall in temperature, the greater will be the condensation rate and the greater will be the proportion of $H_2{}^{18}O$ in the liquid.
- Hence the isotope concentration in the condensate is a function of the temperature at which condensation has taken place.
- When the water vapour reaches the polar region, most of the heavy water has already condensed out. As a result the proportion of heavy water in the condensate at polar region is very small.
- Therefore the relative proportion of ^{18}O and ^{16}O in the ice core may be used to determine the temperature at which the ice was formed.

Information that can be obtained from ice cores

1. The changes in isotopic composition of water are mostly influenced by temperature. By measuring water isotopes in ice cores, the temperatures when the snow originally fell can be determined.
2. The solid and dissolved impurities in the snow [such as traces of dust, pollutants, volcanoes , forest fires and so on] can be used to detect major environmental changes as well as variations in the chemistry and circulation of the atmosphere.
3. As the snow is compressed, air is trapped between the flakes. As a result bubbles are formed in the ice cores. Once the bubbles have formed they will act as an indicator of the atmosphere when they were trapped. Hence by extracting the air from the bubbles in the ice cores, changes in the past atmosphere can be studied.
4. As snow and ice accumulates on polar ice caps, it lays down a record of the environmental conditions at the time of its formation.

25.8 PCBs in the atmosphere

- PCBs –polychlorinated biphenyls-are chlorinated hydrocarbons.
- Among their main characteristics are high melting point, high degree of stability, low flammability and low electrical conductivity.
- PCBs are mainly used as dielectric fluids in electric transformers and capacitors, plasticizers and additives in lubricating and cutting fluids
- PCBs are non-biodegradable. They are very persistant both in the environment and in living tissue..
- The manufacture of PCBs has been banned during the 1970's.

However, Because of their persistence and toxicity to organisms ranging from algae to human beings, they still pose a serious threat to the environment.

- When released into the environment, they persist for many years, bioaccumulate, and bioconcentrate in organisms.
- Exposure to PCBs in humans may cause liver damage, nausea, dizziness eye irritation and bronchitis.
- PCBs may enter the body through the lungs, the gastrointestinal tract and the skin.
- After absorption, PCBs are circulated in the blood throughout the body and are stored in fatty tissues and a variety of organs including liver, kidneys, lungs, adrenal glands, brain, heart and skin.
- PCBs pervade the environment. They may be detected in soils , water, fish, milk and human tissue.
- Hence the use of PCBs is hazardous to the environment.
- The pace of PCBs phase out has nowadays been speed up as awareness of its danger is more understood by policy makers.

EXERCISE 25

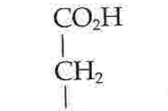
Q1. (a) (i) With the aid of a diagram describe the use of electrophoresis in the separation of peptides and amino acids.

(ii) Explain how peptides and amino acids are identified by this method.

(b) Suggest and explain the relative movement during electrophoresis at a pH of 7.0 of the following amino acids.

(i) $H_2NCH_2CO_2H$
aminoethanoic acid

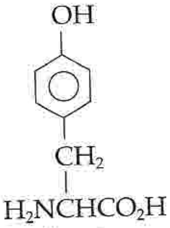
(ii)



$$\begin{array}{c} CO_2H \\ | \\ CH_2 \\ | \\ H_2NCHCO_2H \end{array}$$

aspartic acid

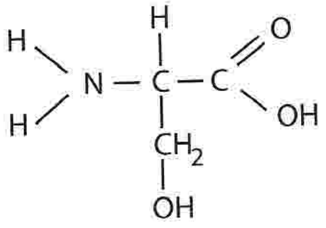
(iii)



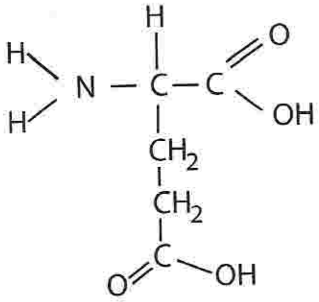
tyrosine

(c) Briefly describe two examples of the use of electrophoresis other than in protein analysis.

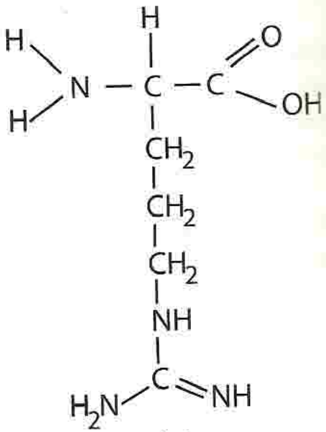
Q2. The amino acids serine, glutamic acid and arginine have the structures shown below:-



Serine



glutamic acid



arginine

(a) Explain why the serine molecule is amphoteric in nature.

(b) Show how the serine, iosleucine and phenylalanine molecules may join together to form a tripeptide.

(c) (i) Suggest the possible isoelectric points for serine, glutamic acid and arginine.

(ii) Describe how the above three aminoacids may be separated by electrophoresis, suggesting the approximate pH of the buffered gel required.

Q3 Explain the following:-

(a) The agarose gel must always be buffered to carry out electrophoresis.

(b) During electrophoresis the pH at which the agarose gel is buffered will determine the direction in which aminoacids will migrate.

(c) When electrophoresis is carried out, a coloured dye is usually added to the mixture of aminoacids.

4. Two coins have the following compositions:

coin 1 : 75% element X, 25% element Y

coin 2 : 70% element X, 30% element Z

Drops of nitric acid were placed on each coin to form solutions of the metals in the coins. The metals present were identified by paper chromatography. The results together with five other metal ions as standards are shown in the diagram.

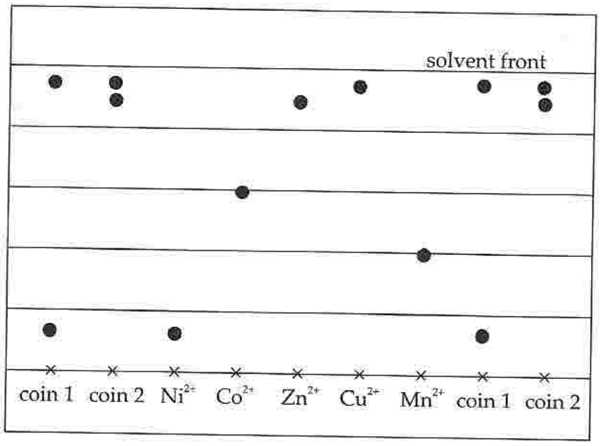


Fig 31

(a) Identify elements X, Y and Z in the two coins.

(b) Name the alloy from which coin 2 is made of.

(c) What is the physical appearance of coin 1?

(d) Why are two drops of liquid from each coin separated on the chromatogram?

(e) (i) What is the Rf value for cobalt ions, Co2+, in this experiment?

(ii) Which one of the following changes in the experiment would you expect to have the biggest effect on this Rf value?

— changing the temperature;

— running the solvent up the paper for a longer time;

— using a different solvent;

— using a different quantity of cobalt ions.

5 (a) A mixture of alcohols, consisting of methanol, ethanol and propan-1-ol, was separated by gas-liquid chromatography. The chromatogram is shown in Fig 32.

(i) Identify the other two peaks, explaining your reasoning.

(ii) Which alcohol in the mixture is present in the greatest amount?

(iii) Copy the chromatogram and indicate how it might be changed if the alcohol mixture also contained a small amount of butan-1-ol.

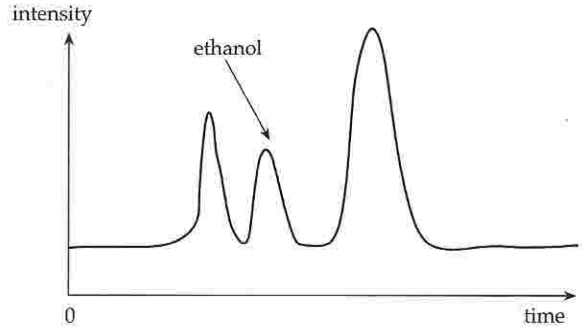


Fig 32

6 (a) What do you understand by the term partition coefficient for the distribution of a solute between two immiscible liquids?

(b) State and explain the conditions under which the partition coefficient of a solute between two immiscible liquids will be a constant.

(c) The partition coefficient of a solute X between ether and water is 20.0 at 25 °C.

A solution contains 10.00g of X dissolved in 100 cm^3 of aqueous solution .

(i) What can you deduce about the relative solubilities of the solute X between ether and water?

(ii) Calculate the mass of X extracted in 100 cm^3 of solution by 100 cm^3 of ether.

(iii) Calculate the mass of X extracted in 100 cm^3 of solution by two successive portions of 50 cm^3 of ether.

7. (a) Explain how solvent extraction can be used to extract an organic substance from an aqueous solution.

(b) The organic solvent which is usually used to carry out solvent extraction is ether (usually ethoxy ethane , also known as diethyl ether, $C_2H_5OC_2H_5$).

(i) State three reasons why ether is particularly useful for the extraction of organic compounds from aqueous solution .over other organic solvents.

(ii) State one main drawback of ether as an organic solvent and state how this drawback may be overcome.

(c) The partition coefficient of butanoic acid between ether and water is 3.0

(i) Calculate the mass of butanoic acid that can be extracted from 100 cm^3 of solution containing 6.00g of butanoic acid using 100 cm^3 of ether.

(ii) Calculate the mass of butanoic acid extracted in 100 cm^3 of solution by two successive portions of 50 cm^3 of ether.

(d) Do you expect the partition coefficient of hexanoic acid between ether and water to be greater or less than that of butanoic acid between ether and water.

(e) State two uses of solvent extraction.

8. (a) Outline the main principle of chromatography.

(b) (i) Explain briefly how high performance liquid chromatography is carried out.

(iii) Suggest two advantages of high performance liquid chromatography over thin layer chromatography.

(c) State two uses of high performance liquid chromatography.

9. One commonly used chromatographic method in school is paper chromatography.

(a) State the stationary and a possible mobile phase used in paper chromatography.

(b) Name a mixture that can be suitably separated by paper chromatography .

(c) In order to obtain a good paper chromatogram, a set of precautions must be taken. Some of these precautions are:-

- (i) a very tiny droplet of mixture must be placed on the starting line
- (ii) the starting line must be drawn using a pencil instead of a pen.
- (iii) a long sheet of chromatograpy paper must be used preferentially.
- (iv) while carrying out the process, the vessel containing the chromatography paper must be closed.

Explain how each of the above precautions will help in obtaining a sharp chromatogram.

(d) Explain how paper chromatography can be used to:-
- (i) determine the number of components in a mixture,
- (ii) identify the components in the mixture.

(e) State an industrial use of paper chromatography.

10. Electrophoresis is a process that can be used to separate mixtures of aminoacids.

(a) (i) Describe , with the help of a diagram, the main features of electrophoresis for separating a mixture of aminoacids.

(ii) Suggest why a dye is usually added together with the mixture of aminoacids before carrying out electrophoresis.

(b) All aminoacids have a characteristic point known as the isoelectric point.
- (i) What do you understand by the term 'isoelectric point'?
- (ii) Suggest how electrophoresis can be used to identify different aminoacids.
- (iii) Suggest how electrophoresis can be used to estimate the relative molecular mass of different aminoacids.

11. (a) Describe and explain the method of gas liquid chromatography.

(b) Discuss the relative advantages of using gas-liquid chromatography and high performance liquid chromatography.

(c) Give two examples of modern applications of gas-liquid chromatography .

Q12 (a) Sketch the expected form of the nmr spectrum for:
- (i) methanol
- (ii) ethanoic acid
- (iii) propanal
- (iv) propanone

(b) There are three isomers of pentane.
- (i) Draw the displayed formula of the three isomers of pentane.
- (ii) How can nmr spectrum be used to distinguish the three isomers of pentane?

Q13. The empirical formula of a compound X is C_2H_4O.

The nmr spectrum of X shows a triplet at 1.3ppm, a singlet at 2.0 ppm and a quartet at 4.1 ppm in the ratio 3:3:2.

(a) Deduce the molecular formula of X.

(b) Give a possible structure for X , explaining your reasoning.

Q14 (a) Explain why partition is the basis of paper chromatography.

(b) Outline and explain the technique of high performance liquid chromatography.

(c) Explain why in carrying out HPLC, the column is placed in a thermostat.

(d) State three uses of HPLC.

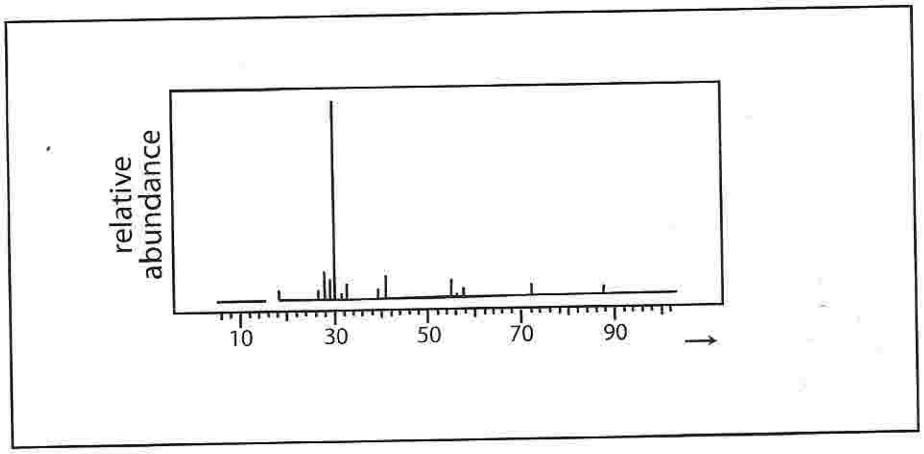
Q15. Explain how the spectrograph of a substance may be used to:-

(i) determine the number of isotopes that can exist for an element
(ii) determine the number of atoms which is found in one molecule of an element
(iii) calculate the relative atomic mass of an element
(iv) determine the relative molecular mass of a compound
(v) determine the number of carbon atoms present in an organic molecule
(vi) determine the number of chlorine atoms present in a molecule
(vii) determine the number of bromine atoms present in a molecule

Q16. A sample of chlorine(I)oxide containing ^{35}Cl , ^{37}Cl and ^{16}O was analysed in a mass spectrometer.

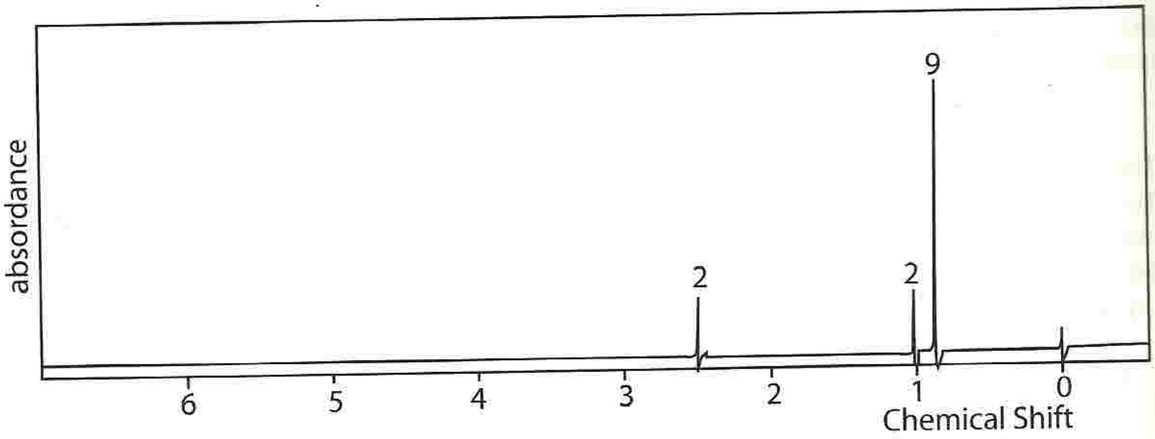
(a) Write down all the peaks that will be observed in the mass spectrograph.
(b) Calculate the ratio of the height of peaks that correspond to the molecular Cl_2O.

Q17. (a) Mass spectrum shown below was obtained from a sample of compound L, CxHyNz.



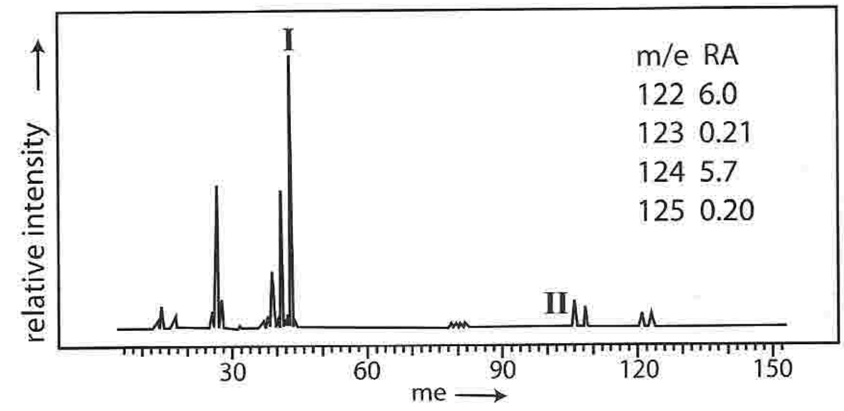
(i) Use this spectrum to deduce a molecular formula for L.
(ii) Suggest what species is responsible for the peak at m/e 30.

(b) The n.m.r. spectrum shown below was obtained from the same sample of L.



Interpret this spectrum and hence deduce a structural formula for L.

Q18. A sample of 2-bromopropane , C_3H_7Br, was analysed in a mass spectrometer. The mass spectrum obtained is shown below:-



m/e	RA
122	6.0
123	0.21
124	5.7
125	0.20

(a) (i) Identify the species responsible for the peaks labeled I and II on the spectrum, indicating any charge present.

(ii) Explain the relative heights of the M and (M+2) peaks.

(b) Show how you could use the M and (M+1) peaks to confirm that 2-bromopropane contains three carbon atoms.

(c) Suggest two differences you might expect in the mass spectrum of 1-bromobutane.

(d) Comment on the relative heights of the M and (M+2) peaks of 2-chloropropane.

Q19 Polychlorinated biphenyls(PCB) are very hazardous to the environment.

(a) (i) Draw the structural formula of a PCB of your choice

(ii) State the main characteristics of PCBs which makes them useful.

(iii) State the main uses of PCB.

(iv) Why are PCBs considered to be very hazardous to the environment?

(b) The manufacture of PCBs has been banned during the 1970's.

(i) Explain why PCBs is still a serious threat to the environment today.

(ii) State the health problems which may arise on exposure to PCBs.

Q20 Oxygen exists in two main isotopic forms namely 16_O and 18_O in the ratio 500:1

(a) A sample of water is analysed using a mass spactrometer.

(i) Determine the number of peaks that will appear in the mass spectrograph.

(ii) Calculate the relative abundancies of the unfragmented water molecules.

(b) (i) Explain why the vapour pressure of $H_2{}^{16}O$, $H_2{}^{18}O$ are different.

(ii) Explain why as water vapour moves towards the pole, the amount of $H_2{}^{18}O$ decreases.

(iii) How can the change in proportion of $H_2{}^{16}O$ and $H_2{}^{18}O$ while moving towards the pole be used to determine the temperature at which a sample of ice was formed?

(c) A sample of ice was collected at a depth of about 5m from the surface.

(i) What information can be obtained from the ice sample?

(ii) To what extent is the information obtained from a study of the ice cores be reliable?

CHAPTER

26

Design and Materials

Syllabus Objectives

In this chapter you should be able to:

- explain the uses of drugs and medicines to combat diseases and their side effects
- understand the stereo chemistry in drugs design
- described methods of drugs delivery
- deduce the properties and structure of polymers
- show awareness of nanotechnology and its applications
- indentify environmental problems and propose solutions
- discuss the importance of effective use of resources

The Effect of drugs and medicines

Stereochemistry in drug action and design

Drugs administration

Polymerisation

Nanotechnology

The Ozone Layer

Oil spillage

Sewrage treatment

Effective use of resources

26.1 The Effects of drugs and medicines

- The terms drug and medicine varies across cultures. In some countries drug and medicine are interchangeable. But in others drugs are considered as harmful and medicine as beneficial. Generally a drug or a medicine is any chemical, natural or synthetic, which has one or more of the following effects:
  (i) alters incoming sensory sensation
  (ii) alters the physiological state of consciousness, co-ordination and
  (iii) the general activity of the individual
  (iv) alters moods or evolutions.

Here drugs and medicines will be considered interchangeable.

- Drugs and medicines are taken to improve health. They do this by assisting the body's natural process of healing. However they have unwanted side effects. To minimize side effect, other substances are often included. For example antacids are used to combat excess acid in the stomach. To do this they contain simple bases such as metal hydroxides, $Al(OH)_3$, metal oxides, MgO, a carbonate or hydrogen carbonate, $NaHCO_3$. They neutralise the excess acid in the stomach and prevent inflammation of the stomach lining and relieve pain and discomfort. Thus antacid prevents and heals stomach ulcers.

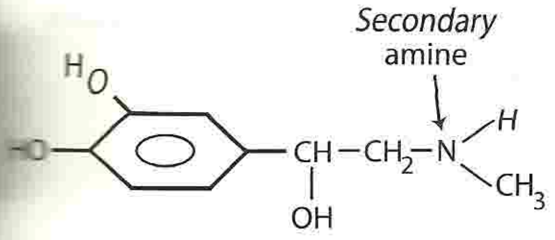
$$Al(OH)_3(s) + \underset{\nearrow\ \text{From gastric juice}}{3HCl(aq)} \rightarrow AlCl_3(aq) + 3H_2O(l)$$

$$MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l)$$

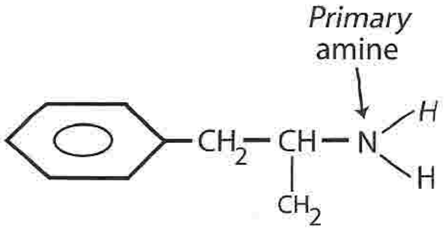
$$NaHCO_3(s) + HCl(aq) \rightarrow NaCl(aq) + CO_2(g) + H_2O(l)$$

Yet antacids have side effects such as flatulence due to the carbon dioxide, magnesium compounds cause diarrhea whilst aluminum compounds cause constipation. This is why antacids contain anti foaming agents and the concentrations of magnesium and aluminum compounds are adjusted to minimise their side effects.
Stimulants are drugs that increase a person's mental alertness. A natural stimulant in the body is the adrenaline hormone secreted by the adrenaline glands. This hormone is known as the 'fight and flight' hormone

since it stimulates the sympathetic nervous system which deals with the subconscious nerve responses such as speeding the heart rate and sweating. The amphetamines are stimulant drugs administered to people suffering from mild depression. They have been given to pilots during World War II to combat sleep and fatigue. They have similar chemical structures to adrenaline. Both are derived from phenylethylamine structure as is shown below.

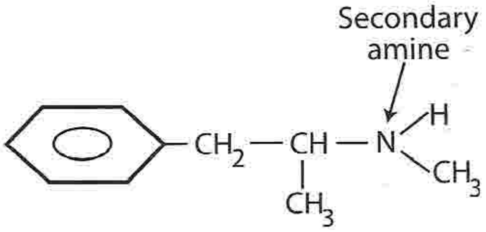


Adrenaline



Amphetamine

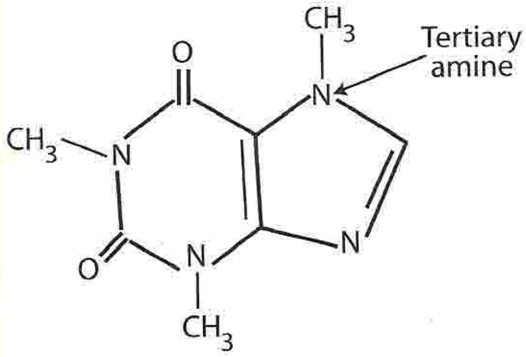
Modification of the structure of amphetamine have produced several designer drugs. For examples metamphetamine which has a much more pronounced psychological effect. This drug is commonly called speed.



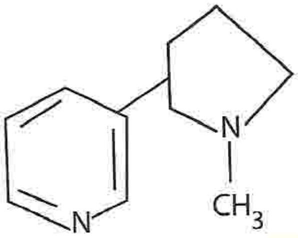
Metamphetamine

Another variety of these is ecstasy also known as 'E'. In controlled dose, it relieves the symptoms of Parkinson's disease. But when abused, it produces hallucinations and may even be fatal.

- Caffeine is a stimulant present in coffee, tea, chocolate and cola drinks. In moderate doses it enhances alertness, motivation and concentration. Thus it sustains intellectual efforts and is relatively harmless. Many common painkillers contain caffeine since it



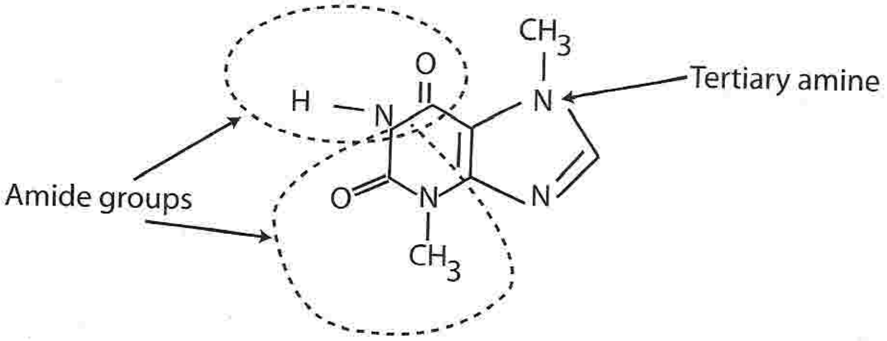
Caffeine



Nicotine

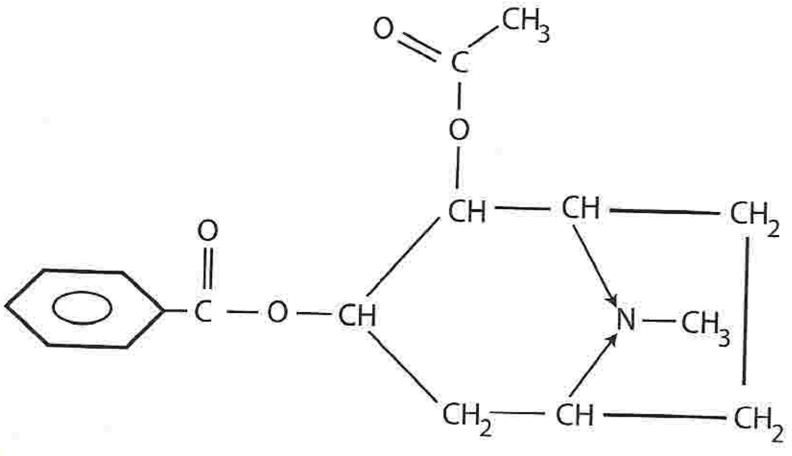
speeds up their effects. Caffeine is an alkaloid that is a nitrogen – containing compounds of plant origin with heterocyclic rings and a tertiary amino group. Other alkalioids are nicotine, morphine, codeine and cocaine.

- Like amphetamines, nicotine is sympathomimetic.
  It increses concentration and relieves tension. The side effects include increased heart rate, blood pressure and reduction in urine output.
- Chocolate contains theobromine a structure similar to caffeine

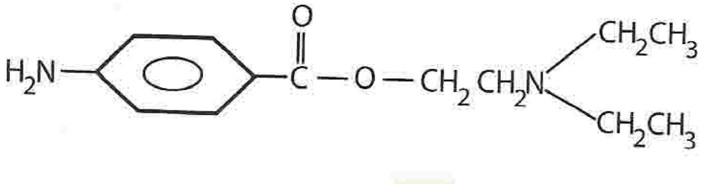


Notice that theobromine contains no bromine!

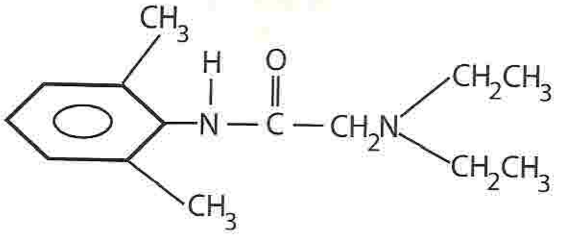
- Cocaine is another stimulant, it occurs in the leaves of certain plants which are chewed by the locals to deaden pain and increase endurance. Due to undesirable side effects, derivatives of cocaine are synthesised which retain their anesthetic properties but do not affect the brain as a stimulant. The two most important compounds are procaine and lidocaine. They have similar structure to cocaine and are used in minor surgery.



Cocaine



Procaine

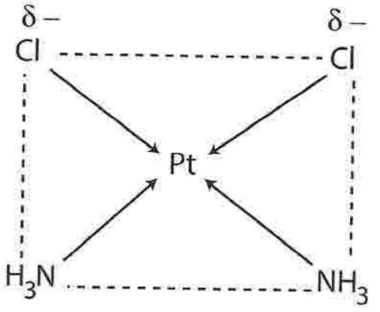


Lidocaine

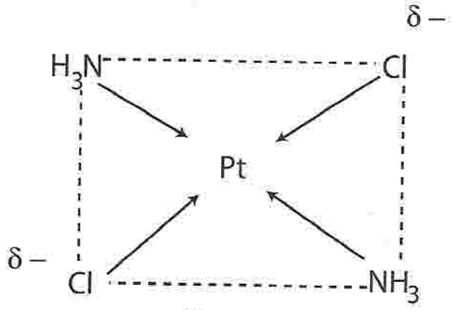
26.2 Stereochemistry in drug action and design

Stereoisomers have the same molecular formula, same structural formula but different arrangement of atoms in space. These are geometric and optical isomers.

- **Geometrical isomers** occur when there is hindrance of rotation about a point in the molecules. Quite often this is due to a C = C. Then cis and trans isomers occur. Geometrical isomers may have the same chemical properties since they contain the same functional groups but they have different physical properties such as polarity, solubility, melting and boiling points. This is why they can have different pharmacological effects. Geometrical isomers can exist in both organic and inorganic complexes. For example the complex $Pt(NH_3)_2Cl_2$ is square planer and exists as cis and trans forms.



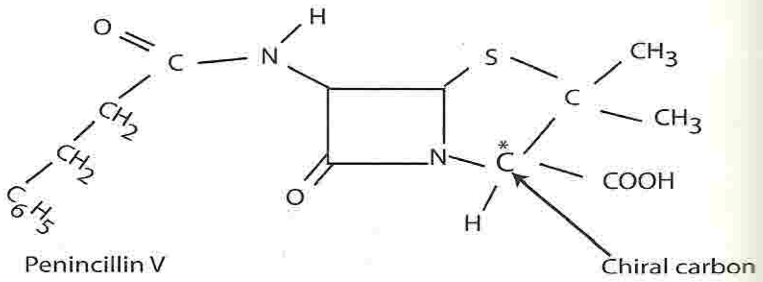
Cis



Trans

However only the cis form, known as cisplatin is effective in the treatment of cancer. This is because it has an overall dipole and can diffuse through the cancerous cell membrane. It enters the cell nucleus, binds with the DNA. Thus the cancer cell's DNA is altered and it cannot be copied correctly during DNA replication, the cell dies.

- **Optical isomers** differ from geometrical ones by being chiral and are non-superimposable on their mirror images. The two are called enantiomers. Each rotate the plane of a polarised light to the same extent but in different directions. The enantiomers behave in totally different ways in the body. Many drugs come from natural sources where they are fond as only one enantiomer which is chiral. An example is Penicillin V which is isolated from penicillin mould.

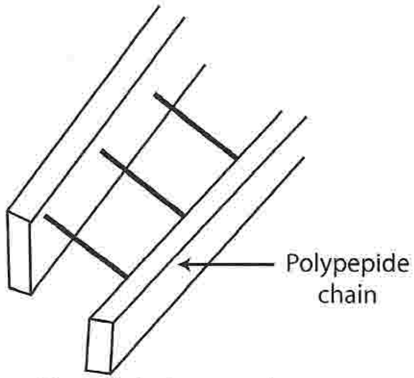


Penincillin V

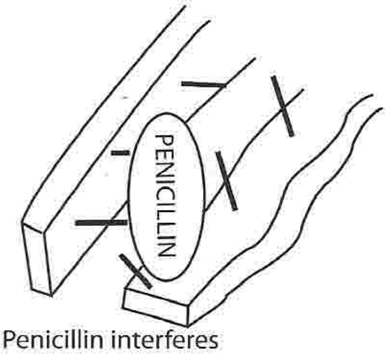
Once the structure of penicillin was determined, chemists were able to synthesise different types of penecillin and antibiotics in the laboratory.

- **How penicillin works?**

The cell walls of some bacteria are reinforced by a series of three dimensional chemical cross-links. Penicillin interferes with their cross-links. The bacterial shape is unable to hold its shape and size. Water diffuses into it by osmosis, such that the cell expands and bursts the bacteria dies.



Cross-links in normal bacterial cell



Penicillin interferes with the cross-links

- **Vaccines** which are to combat diseases, are periodically modified to challenge the changes in the configuration of the viruses.
  Vaccines for flue are yearly modified because the flue virus changes to nullify the effect of the vaccines.
  A vaccine for HIV has not yet been successfully developed because the HIV virus continues to change its configuration.

26.3 Drugs Administration

In order to reach the site where their effects are needed, the majority of drugs must be absorbed in the blood stream.

There are four main methods for administrating drugs and each has its advantages and disadvantages. The four main route of drug delivery in the system are: oral, rectal, inhalation and parenteral, i.e. by injection.

• Oral, that is by mouth

Though a convenient method yet the effect is influenced by the rate of absorption of the drug which in turn depends on the drug concentration and stomach content. Usually absorption occurs from the mouth to the intestine. Except for alcohol, percentage absorption in the stomach is small. Most drug which are taken orally, are primarily absorbed in the small intestines.

A drug that is partially soluble is absorbed slowly. The rate of absorption also depends on whether the drug is a solid or a liquid and whether it is taken on an empty stomach or with food.

In order not to flood the system with a high concentration of the drug, very often it comes in the form of time release capsules. The latter have various coating to ensure gradual release over time. Thus the drug is more effective and safer to use.

• Rectal that is via the rectum

This method is effective when the patient has side effects and is unable to take the drug orally. The drug is absorbed into the bloodstream and bypass the stomach.

Anti inflammatory pills are given rectally for patients suffering from stomach ulcers. Also drugs that are likely to be destroyed by the pH of the stomach are preferentially delivered rectally. Drugs which have systemic effects, that is those that can affect any part of the body, can be given as suppositories via the rectum.

• Inhalation that is breathing in

Drugs administered by this route have systemic effect for example general anesthesia. Delivery is rapid due to the extensive network of blood vessels in the lungs in which the drug is absorbed into the blood stream to produce an effect in the brain and the whole body.

Those suffering from asthma achieve quick relief from such delivery since the respiratory tract is rapidly dilated.

• Parenteral that is by injection

This consists of three routes of delivery.

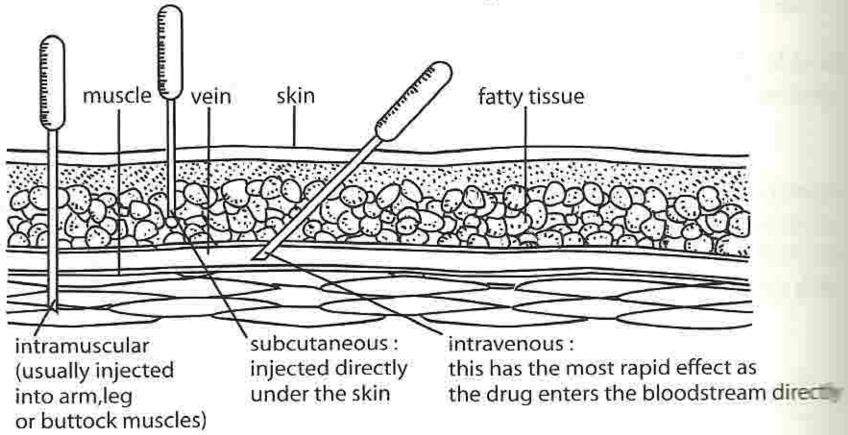
(i) Subcutaneous that is beneath the skin where absorption of drug is slow. Dental injections are often subcutaneous.

(ii) Intra muscular, i.e. into the muscles, this route is used when a large volume of a liquid needs to be injected. This method is relatively safe but response to the drug is not immediate.
Many vaccines are delivered by this method.

(iii) Intravenous that is directly into the blood stream. The drug is introduced directly into the blood stream and the effect is almost instantaneous. The advantage of this method is that precise amounts can be delivered.

Note that drugs may also be applied topically so that the effect is limited to the site of the problem, such as the surface of the skin. Such drugs may be in the form of creams, ointments and sprays.

The three different methods of injection



Advantages of injections

1. It ensures the speed delivery of drug to target organ
2. The drug does not pass through the stomach. Therefore it avoids the hydrolysis of the drug (which may take place if the drug reaches the stomach)
3. It allows a smaller dose of drug to be used
4. The patient does not have to be conscious
5. Small dose of drugs can be administered regularly for a long time period through the use of drips.

Better-targeted delivery of drugs allows smaller amounts to be used, which brings significant advantages.
The main advantages of using smaller doses of drugs are:-

1. It is more economic since drugs are relatively expensive
2. There will be less side effect and less risk of harming healthy tissue
3. There will be less chance of overdose
4. The probability for allergic reactions will be reduced

26.4 Polymerisation

- Polymers (Gr. polys,many and meros, parts) are long chain molecules formed by reaction between smaller molecules known as monomers (Gr. monos, single and meros, parts).
- Polymers are very large molecules made up of many repeat units.

- The two main classes of polymers are natural polymers and synthetic polymers.
- Some natural polymers are starch, fat, proteins (a polymer of amino acids), natural rubber, DNA (a polymer of nucleotides) and enzymes.
- Synthetic polymers are classified as addition polymers and condensation polymers
- There are two main processes that are used to convert monomer to polymer. They are addition polymerisation (also known as chain-growth polymerisation) and condensation polymerisation (also known as step-growth polymerisation).

Addition polymerisation

- Addition polymerisation is a process during which a large number of unsaturated hydrocarbons (which are alkenes or their derivatives) combine together to give only one product, namely the addition polymer.
- The reactive group in the alkene or its derivatives is the carbon-carbon double bond (C=C).
- Addition polymerisation occurs through a free radical mechanism. It is a free-radical polymerisation process.
- In the initiation step, a free radical species is generated. Usually benzoyl peroxide is used for this purpose.
- Benzoyl peroxide undergoes homolytic fission on heating or in the presence of light to generate free radicals (Fig 1)

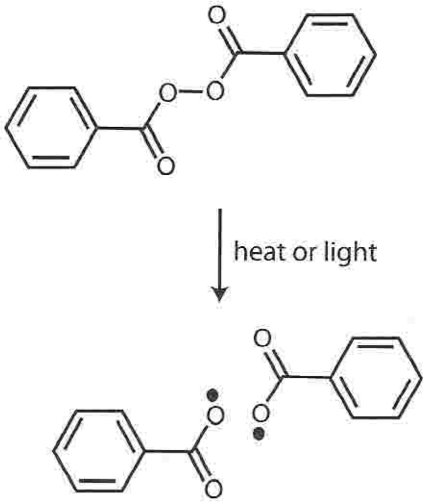


Fig 1

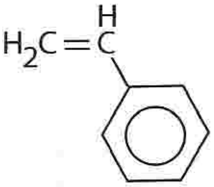
- The radical, represented by $R^\cdot$grabs an electron from a-C=C- bond, as a result of which the double breaks, leaving behind a single bond and a new radical.For example consider the reaction of the radical with ethene,

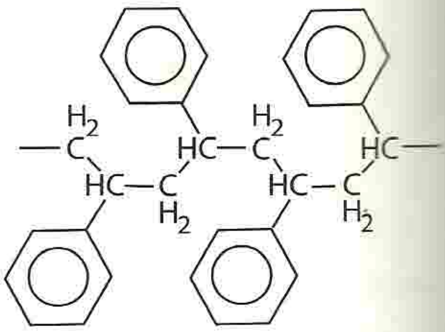
$$R^\cdot + CH_2{=}CH_2 \rightarrow R{-}CH_2CH_2^\cdot$$

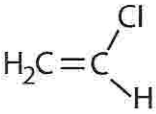
- The new radical will attack another ethene as a result of which a chain reaction occurs and the length of the chain increases continuously.

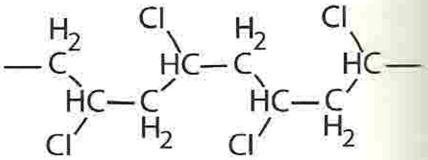
$$R{-}CH_2CH_2^\cdot + CH_2{=}CH_2 \rightarrow R{-}CH_2CH_2\,CH_2CH_2^\cdot$$

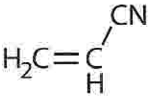
- In theory the chain reaction will keep going until all the monomer has been used up.
- However in practice, as there is a lot of free radicals in the mixture, they will run into each other as a result of which they will be used up, thereby terminating the chain. For example
  $R—[CH_2CH_2]_nCH_2CH_2^{\cdot} + {}^{\cdot}CH_2CH_2[CH_2CH_2]_m—R \rightarrow$
  $R—[CH_2CH_2]_nCH_2CH_2CH_2CH_2[CH_2CH_2]_m—R$
  The chain contains between 10^4 to 10^6 carbon atoms
- Addition polymerisation is a relatively fast process and it generates lots of energy.
- Examples of common addition polymers are poly(ethene), poly(vinyl chloride), polystyrene and polyacrylonitrile, PTFE. Some of their monomers and polymers are given below:-

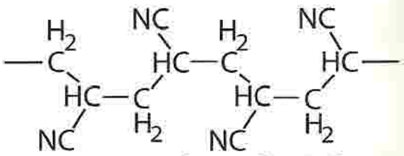

Styrene


Polystyrene

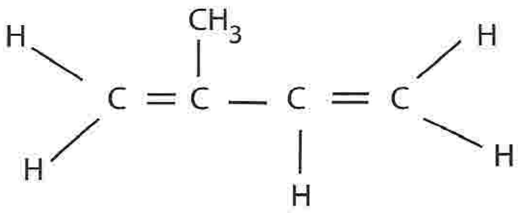

Vinyl chloride

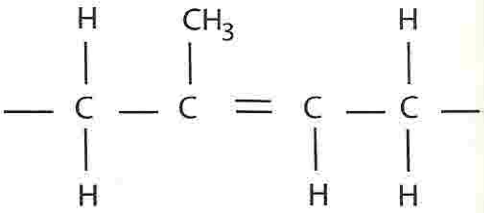

Poly (vinyl chloride)


acrylonitrile


poly acrylonitrile

- An example of a natural addition polymer is rubber. The monomer is 2-methyl buta-1,3-diene.





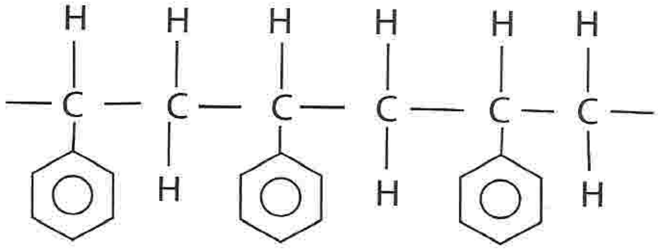
- Monomers of rubber are non-polar hydrocarbon molecules. Therefore their polymers are also non-polar and the polymeric molecules will be held together by only weak intermolecular forces of attraction.
- Although the intermolecular forces of attraction between the molecules are weak, the individual polymer molecules are large enough that even with the weak forces between them, they are solid at room temperature
- However if the monomer contains a polar atom(eg –Cl atom, like in PVC) or group of atoms, the intermolecular forces of attraction between the polymeric chain will be stronger, making the polymer mechanically stronger.
- Poly(vinyl chloride) is a rigid polymer . It is used to make PVC piping.
- Although many chlorinated hydrocarbons are toxic, PVC is not toxic since the polymer molecules are very large and it is impossible for them to interact with living cells and harm them.
- When substances , known as plasticisers are added, the polymer PVC becomes more elastic or rubbery. This is because the plasticisers help the chains to move past one another more easily.
- As indicated above, ethene can be polymerised to polyethene. However the property of the polymer formed will vary according to the conditions used for its preparation as indicated in the table below:-

POLYMER	METHOD OF PREPARATION	TYPE OF STRUCTURE	USES
Low density polyethene[LPDE]	High pressure [about 1400 atm], high temperature [170 ^{0}C], use of an initiator, such as benzoyl peroxide	The polymer molecules will have numerous branches, which prevent the polyethene from packing closely together, making it relatively soft	Whenever a soft plastic is required, for example in the making of plastic bag, collapsible 'squeezy' bottles
High density polyethene [HDPE]	Relatively low temperature[70 ^{0}C] and low pressure [2 atm]. A catalyst, known as the Ziegler-Natta catalyst is used. It is a mixture of trialkyl aluminium[for exampleAl$(C_2H_5)_3$] and titanium (IV) chloride, $TiCl_4$ [dissolved in an alkane solvent]	The polymer is not branched. It is a linear polymer. Therefore the polymer molecules will be more closely packed together. The polymer will have a more crystalline structure than LDPE. It will be harder.	Use to make rigid bottles and bottle crates
Linear low density polyethene[LLDPE]	LLDPE is a polymer made by copolymerisation with other alkenes that has only short branches, using the Zieggler-Natta catalysts.	Although it will have a low density, it will have a better mechanical strength than LDPE	It is used in making of polyethene films.

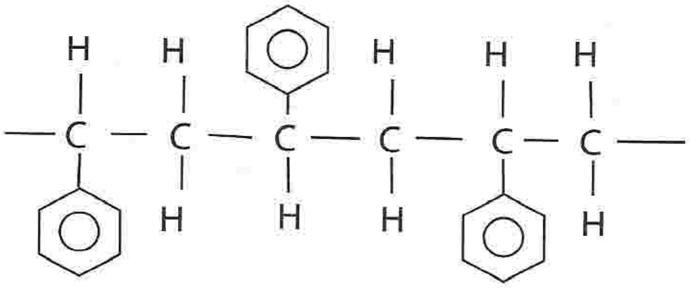
- Chain length and chain branching in polyethene affect the physical properties of the polymer material.
- Stiffness is mainly influenced by the way in which the polymer chain interact with each other.
- The presence of a side group is in the alkene (such as –Cl in PVC or C_6H_5 in polystyrene) will influence the interaction between the chains and hence will influence the properties of the addition polymer.
- **The side group may:-**
    1. cause the polymer chains to align themselves as a result of which the material becomes more crystalline. For example polyethene lacks regularity in its structure. It is relatively amorphous. However the presence of the phenyl group, as in polystyrene, causes the polymers molecules to be more regularly arranged as a result of which the polymer will have a more crystalline structure.

    2. form polymers in which the side groups are arranged differently. By varying conditions under which polymerisation is carried out, the side group may be found on the same side of the chain (isotactic polymer), the side group may altenate regularly from one side of the chain to the other (syndiotactic polymer).Atactic and syndiotactic polymers are called stereoregular polymers.
    In the presence of radicals, polymerisation occurs randomly as a result of which the side group are arranged randomly along opposite sides of the chain(atactic polymer).
    The three types of polymers will have different physical properties such as tensile strength and the softening temperature as the type and extent of interaction between the chains will be different.

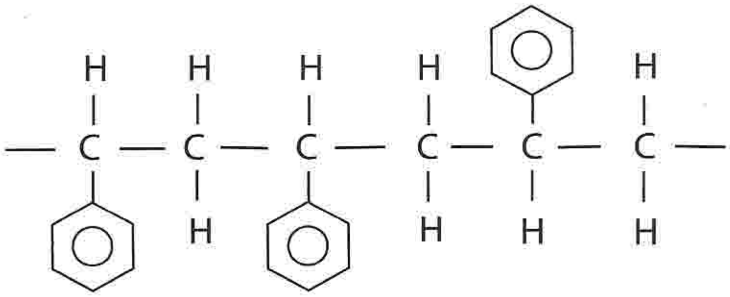
Isotactic



Syndiotactic



Atactic



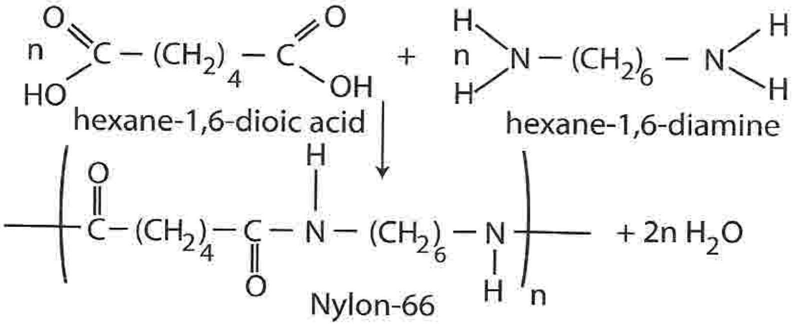
Disposal of plastics

- The simple plastics are non-biodegradable (they are resistant to most chemicals and to bacteria) and stays in the environment for a long period of time
- They may be recycled but recycling is a relatively expensive process.
- They are potentially good fuels and so may be used as a source of energy. Technology is now available to burn the plastic materials cleanly with much less pollutants than with traditional methods of combustion.
- Note that there are plastics that are biodegradable. Among such biodegradable plastics are starch-filled plastics, photodegradable plastics, soluble plastics and bacterial thermoplastic.
- When the starch filled plastic is buried, bacteria and fungi will feed on the starch as a result of which the plastic breaks down in tiny pieces.
- In photodegradable plastic, the polymer chain is designed so as to include a carbonyl group, which is a good absorber of part of light energy (near the ultra-violet region of the electromagnetic spectrum). As the polymer absorb energy, bonds near the carbonyl group will break down. Hence the polymer will break into tiny pieces.
- Water soluble plastics are polymers that will dissolve in water at different temperatures depending upon their composition.

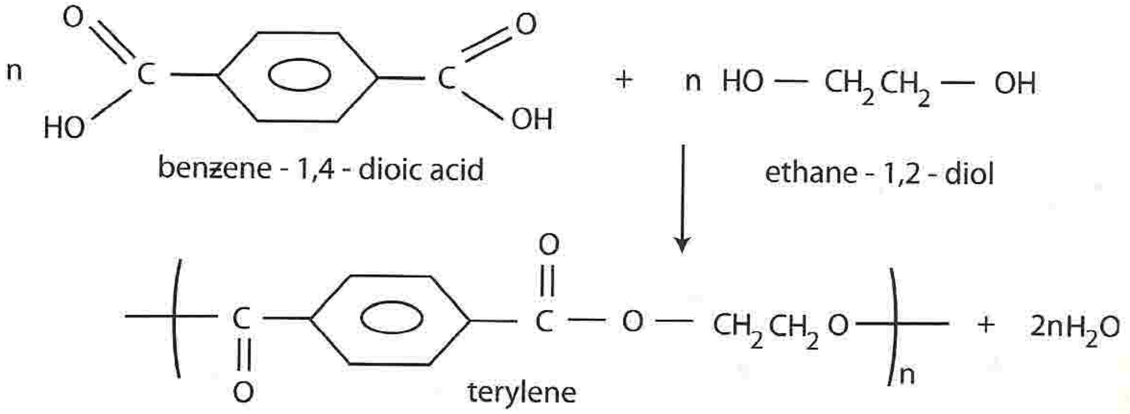
Condensation polymerisation

- In condensation polymerisation , reactive groups on both ends of each monomer react with one another.
- A growing chain still has a reactive group on each end. Therefore if two such chains join together, the length of the chain gets much larger.
- Two monomer molecules react together to form a dimer that reacts with another molecule to form a trimer and so on. The reaction proceeds further as a result of which long polymer is formed. That's why condensation polymerisation is also known as step-growth polymerisation.
- Two different functional groups are involved in any condensation polymerisation.

- The two functional groups may be on two different monomer species(for example one monomer may be hexane-1,6-diamine and the other monomer may be hexane-1,6-dioic acid) or on the same monomer(for example aminoacids).
- During condensation polymerisation, a small molecule such as water or hydrogen chloride may be eliminated. For example consider the condensation polymerisation involved in the preparation of nylon-66, in which a peptide bond is formed.



- The amino group undergoes a condensation reaction with a carboxylic group. A –C—N bond is formed and a small molecule such as water is eliminated. The amide group will link the carbon chain in the polymer.
- Hydrogen bonds are present between the different polymeric chain. This provides for strength and elasticity of nylon.
- Condensation polymerisation are used to make polyesters, nylon and polyurethane.
- Polyesters are made by the condensation polymerisation reaction between ethane -1,2-diol and benzene-1,4-dioic acid at a temperature of about 280 °C and in the presence of antimony(III)oxide, acting as catalyst.



- The presence of groups at the 1,4 position in the benzene ensures that the polymer will be relatively linear. Therefore the polymeric chain will pack more closely, producing stronger intermolecular forces of attraction, thereby making the polymer more rigid.

- A natural condensation polymer is spider silk.

- Silk is for more than 50% a polymerized protein called fibroine with a molecular weight of 200.000 - 300.000. When looking at silk at a molecular scale one can see that the proteins strands are regularly orientated.hence the force of attraction between the polymeric material will be very strong.
- Spider silk is an extremely strong material and is on weight basis stronger than steel.
- The silk is used by the spider for a lot of different uses. Constructing their webs, the production of egg sacs, wrapping in their prey, as a life line when jumping, or dropping to escape, in drag lines marked with pheromones, as a shelter in which it can retreat.
- A comparative table for condensation and addition polymerisation is given below:

	CONDENSATION	ADDITION
1.	Any two molecular species can react if they contain two active functional group	Molecular species can react only with active centers, that is if they are unsaturated
2.	Chains start short and steadily grow	Chains are long at all times
3.	Most monomer gone early in reaction	Some monomer remains until end of reaction
4.	Reactions relatively slow, generate little heat	Reactions relatively fast, generate lots of heat

Properties of polymers

- The properties of polymers depends on several factors such as :-

i. Length of carbon chain: the tensile strength and melting point increase with increase in length of carbon chain until there are about 500 monomer units in the chain. Further increase in length of carbon chain has little effect on the properties of the polymer.

ii. The presence of side group on the carbon chain: side chain effectively act as branches. Therefore the polymeric material cannot pack together as regularly as straight chain polymers. Hence presence of a branch on the carbon chain will lead to a lowering of the melting point and tensile strength of the polymer.

iii. The degree of compactness or crystallinity of the polymer

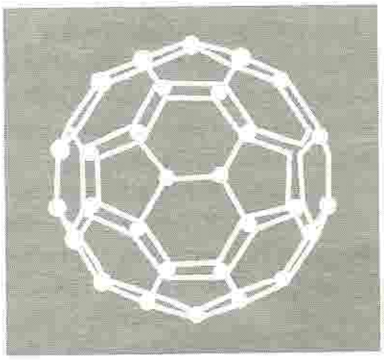
iv. The type and strength of intermolecular forces of attraction between the polymeric chain. This factor will largely determine the properties of the polymer.

v. Cross-linking between polymeric chains will make the polymeric material hard, rigid and relatively brittle.

- The two main properties of polymers are tensile strength and softening temperature.
- The tensile strength determines the main uses of the polymer.
- The softening temperature determines the way the polymer can be moulded.
- The tensile strength and softening temperature are controlled mainly by the forces of attraction between the polymer chains, which in its turn depends on the atoms or group of atoms bonded to the carbon skeletal structure

26.5 Nanotechnology

- Nanotechnology refers to work at the atomic and molecular(nanometer) level.
- A nanometre has the size of 10 hydrogen, or 5 silicon atoms and almost as wide as a DNA molecule .
- Nanotechnology was triggered by the discovery of another allotrope of carbon , namely buckminsterfullerene sometimes simply referred to as fullerene.
- The common fullerene molecule resembles a soccer ball and consists of 60 carbon atoms and can be represented by the structure below:-



- Graphite can be rolled into tubes only a few nanometers(1 nanometer =1 x 10^{-9} m) in diameter. These tubes are called nanotubes
- The uses of carbon nanotubes as superconductors, material strengtheners and ion storage for batteries are being studied.
- Nanotubes can be used to make threads and cables of extreme strength, called nanofibres.
- Nanotechnology is dealing with the smallest parts of matter that we can manipulate. The essence of nanotechnology is the ability to work on an atomic, molecular and supramolecular level, i.e. on a scale of length from 1-100 nanometre.
- Molecular nanotechnology, applies to building organic and inorganic materials into defined structures, atom-by-atom or molecule-by-molecule, often by self-assembly or self-organisation.
- Chemists are involved in numerous areas of nanotechnology such as :-
  1. the synthesis of inorganic, organic and hybrid nano-materials for use in nano-devices
  2. the development of new nano-analytical techniques
  3. the manipulation of biological molecules such as DNA and
  4. the evolution of molecular machines.
- Nanotechnology is the engineering of tiny machines, for example motors , robot arms and so on, on the scale of molecules, a few nanometers wide-far smaller than the cell .
- Nanotechnology is often referred to as a general-purpose technology since in the future it will have significant impact on almost all industries and all areas of society.
- Nanotechnology is expected to offer better built, longer lasting , cleaner, safer and smarter products for the home, communications , medicine , transportation, agriculture and for industry in general.
- Nanotechnology provides the potential for significant advances over the next 50 years. Applications will be broad, including health care, medicine, security, electronics, communications and computing as indicated in the table below.

	CURRENT	1-5 YEARS	6-10 YEARS	10-50 YEARS
Medicine	Sun screens	Biological nano-sensors for diagnostics	artificial muscle	Engineering of artificial organs
Energy	nano-catalyst enhanced fuels for better efficiency	nanomaterials for fuel cells	more efficient solar cells using nanotechnology	nanomaterials for hydrogen storage fuel cells
Communications and computing			high density data storage using nanomagnetic effects	computing DNA
Other	nanoparticles for pigments	responsive nano-coatings for food packaging	use of nanotechnology for synthesis and catalysis	ultra-light materials for cheaper construction and transportation

- Nanotechnology means something far more ambitious, miniature submarines in the bloodstream, little cogs and gears made out of atoms, space elevators made of nanotubes, and the colonisation of space .
- Many of the initial applications of nanotechnology are materials related, such as additives for plastics, nanocarbon particles for improved steels, coatings and improved catalysts for the petrochemical industry.
- Many of the companies working with nanotechnology are simply applying our knowledge of the nanoscale to existing industries, whether it is improved drug delivery mechanisms for the pharmaceutical industry, or producing nanoclay particles for the plastics industry.
- Shrinking machines down to the size where they can be inserted into the human body in order to detect and repair diseased cells is a popular idea of the benefits of nanotechnology, and one that even comes close to reality. Many companies are already in clinical trials for drug delivery mechanisms based on nanotechnology
- Current medical applications of nanotechnology are far more likely to involve improved delivery methods, such as pulmonary or epidermal methods to avoid having to pass through the stomach, encapsulation for both delivery and delayed release, and eventually the integration of detection with delivery, in order for drugs to be delivered exactly where they are needed, thus minimizing side effects on healthy tissue and cells.

- By controlling the atomic and molecular structure, we are able to invent new materials, components and systems with new attractive features and functions.
- With molecules as building blocks, nanotechnology will create new structures and constructions. Electronic nanocircuits that assemble themselves, intelligent nanocontainers, which are able to apply medicine without side effects and in accordance with the needs of the patient, super-strong materials, or new ecologically desirable catalysts, are just some of the promising opportunities. There is moreover research with new biocompatible materials for implants and with optical nanostructures for fast communications. Nanotechnology is the technology of the future.
- Molecular nanotechnology has been defined as the three-dimensional positional control of molecular structure to create materials and devices to molecular precision.
- More than just an extension of "molecular medicine," nanomedicine will employ molecular machine systems to address medical problems, and will use molecular knowledge to maintain and improve human health at the molecular scale. Nanomedicine will have extraordinary and far-reaching implications for the medical profession, for the definition of disease, for the diagnosis and treatment of medical conditions including aging, and ultimately for the improvement and extension of natural human biological structure and function.
- "Nanomedicine is the preservation and improvement of human health using molecular tools and molecular knowledge of the human body."

26.6 The ozone layer

- Ozone, O_3 is an allotrope of oxygen
- The word 'ozone' comes from a greek word meaning'to smell'.
- While O_2 is an odourless gas, O_3 has a typical pleasant odour.
- It is usually produced during lightning storm
- Ozone is chemically more reactive than oxygen.
- It is commonly used in the purification of water and in the bleaching of wood pulp
- However in the troposphere, the region where we live, ozone causes photochemical smog.
- But in the stratosphere ,at an altitude of about 20-30km, the ozone acts as a filter for energetic, short wavelength ultra-violet (UV)light which can cause damage to plants and animals especially crops leading to food shortage and skin cancer in humans.
- Ozone is formed by the following reactions involving free-radicals
- Solar UV radiation decomposes oxygen molecules into oxygen atoms $O_2 \rightarrow O\cdot + O\cdot$

  The oxygen atom(or oxygen radical) react with further oxygen molecules to produce ozone $O\cdot + O_2 \rightarrow O_3$
- In fact both the stratospheric oxygen(O_2) and ozone (O_3) molecules absorb UV light of different wavelength.
- Stratospheric oxygen molecules absorb UV light of wavelength less than 242 nm.

- On the other hand the stratospheric ozone molecules, being more reactive than diatomic oxygen will absorb effectively UV –light of longer wavelength (less than 320nm) .
- Hence the ozone molecules and oxygen molecules in the stratosphere act as an effective screen against UV radiation on the earth's surface.
- However the screening effect is not perfect. A small fraction of the UV light does reach the troposphere.

Biological effects of UV radiation

- The effects of UV-radiation on living things depends on the intensity of the UV-radiation and the sensitivity of different organisms to that radiation.
- UV radiation of wavelength less than 300nm are very energetic and will damage living tissues considerably as well as the DNA molecules. Such solar radiation are almost completely absorbed by O_2 and O_3 molecules found in the stratosphere.
- However recent studies have shown that the concentration of ozone in the stratosphere has dropped considerably.
- Hence the capacity of the stratosphere to screen UV radiation of wavelength less than 320nm has been greatly reduced. Living things are now exposed to a larger amount of energetic UV light.
- If the trend continues, the number patients suffering from skin cancer and skin-related cancers will increase considerably.
- The natural concentration of ozone in the stratosphere is not uniform.
- The depletion of the ozone layer has a natural as well as man-made origin.
- The major natural cause of ozone depletion involves water vapour and its breakdown products.
- When a few molecules of water reaches the stratosphere they absorb a UV photon and they breakdown homolytically to produce radicals as shown below:-

$$H_2O \rightarrow H^{\cdot} + OH^{\cdot}$$

- Some of these radicals ultimately convert ozone molecules into oxygen molecules.
- Similarly nitrogen monoxide is a radical which also reacts with ozone molecules.
- However NO molecules are formed naturally (during lightening) as well as through human activities, for example during combustion of fuels.
- Nevertheless , the major cause of the depletion of the ozone layer is the use of chlorofluorocarbons(CFCs)- compounds containing atoms of carbon, fluorine and chlorine .
- CFCs are not produced in nature. They are man-made.
- The mainly used CFCs are CF_2Cl_2 and $CFCl_3$.
- CFCs are volatile, chemically inert, nontoxic , non-flammable and cheap substances.
- CFCs are use as refrigerants (in refrigerators and air-conditioner), aerosol propellants, in fire extinguishers (mainly those CFCs which

contain bromine atoms), as solvents for grease and oil and as sterilizers for surgical instruments.

- Studies have shown that as the consumption of CFCs has increased, the stratospheric ozone concentration has decreased.
- The inertness of CFCs allows their molecules to reach the stratosphere.

Action of CFCs in the stratosphere

- It takes more than 100 years for a molecule of CFC to be destroyed but it takes less than 7 years for a molecule of CFC to reach the stratosphere.
- In the stratosphere the energetic UV light provides enough energy to break the C—Cl bond homolytically, thereby forming radicals.

$$\text{CF}_2\text{Cl}_2 \rightarrow {}^{\cdot}\text{CF}_2\text{Cl} + \text{Cl}^{\cdot}$$

- The chlorine radical, being very reactive, will react with an ozone molecule

$$\text{Cl}^{\cdot} + \text{O}_3 \rightarrow {}^{\cdot}\text{ClO} + \text{O2} \qquad [1]$$

- A pair of chlorine monoxide radicals combine together as shown below

$$^{\cdot}\text{ClO} + {}^{\cdot}\text{ClO} \rightarrow \text{ClOOCl} \qquad [2]$$

- The ClOOCl molecule than further absorb UV radiation and decomposes to liberate back the chlorine radicals

$$\text{ClOOCl} \rightarrow 2\text{Cl}^{\cdot} + \text{O}_2 \qquad [3]$$

- From equations [1], [2] and [3], it can be seen that all the radicals are intermediate in the reaction. The overall equation for the reaction is obtained by eliminating all these radicals and it will be:

$$2\text{O}_3 \rightarrow 3\text{O}_2$$

Alternatively, the ·ClO formed in [1] will react with an oxygen radical, which comes from the natural decomposition of ozone by UV light.

$$^{\cdot}\text{ClO} + \text{O}^{\cdot} \rightarrow \text{Cl}^{\cdot} + \text{O}_2$$

- Hence the chlorine radical is not used up in the reaction. It acts as a catalyst for the reaction.
- On average a chlorine radical may catalyse the decomposition of 1×10^5 ozone molecules.
- The chlorine radical is ultimately destroyed when it encounters another radical.

Proposed solution

- More than 75% of the chlorine atoms in the stratosphere originates from CFCs.
- Some countries have banned the use of CFCs in aerosol propellants and their use as foaming agents for plastics.
- The production of ozone-depleting compounds was earmarked to be eliminated between 2002 and 2010 and many countries agreed to discontinue completely the manufacture of CFCs in 1995.
- Ideally a suitable substitute must be a substance which is non-flammable, non-toxic and which may be destroyed before it reaches the stratosphere.
- Substitutes to CFCs are now being used. Among these substitutes are fluorocarbons(HFCs). These substances are neither toxic nor flammable. The C—F or C—H bond in FCs are strong enough and hence are not affected by UV radiation. Therefore they will not produce radicals and will not catalyse the depletion of the ozone layer. But on the long run the FCs will accumulate in the stratosphere and will cause global warming.
- An increase in number of hydrogen atoms will lead to an increase in ability of the molecule to be destroyed before it reaches the ozone –rich region of the atmosphere. However, the substance becomes more flammable. Furthermore its boiling point decreases to such a low value that it may not be used effectively as refrigerants.
- Compromised substitutes that is now currently being used are hydrochlorofluorocarbons (HCFCs) namely chlorodifluoromethane ($CHClF_2$) and dichlorofluoroethane(CH_3CFCl_2).
- The HCFCs have similar desirable properties as CFCs but the hydrogen atoms enable the molecules to react with free radicals such as OH in the lower atmosphere, which destroys the compound before it can release its chlorine in the stratosphere, that is , it will decompose more rapidly in the troposphere than the CFCs and hence will not affect the ozone layer.
- Ultimately hydrofluorocarbons (HFCs) will be used as they do not contain any chlorine atom and therefore present no risk for the ozone layer. Furthermore the presence of hydrogen atoms will help it to decompose more easily.

26.7 Oil spillage

- Oil spilling may occur in marine environment or on terrestial environment.
- Oil spillage in marine environment may be intentional-for example some ships release their residual oil illegally to the sea instead of legal disposal in special sites in harbours- or accidental such as accidents in shipping.
- Oil spillage on the terrestial environment may come from petroleum refineries, leaks in pipelines, from tankers, leaks in underground gasoline storage tanks and gas stations, from spills during fuel oil delivery.
- Leaks and spills of fuel oil, gasoline and other petroleum products contaminate the environment in many ways.

- Oil spills pollute groundwater, on which many animals and human beings depend for drinking water.
- Spills seep into streams, lakes, and reservoirs, which are drinking water sources as well as habitat where fish, birds, and other wildlife can be harmed or killed.
- Vapours from spills enter indoor environments where people live and work. Gasoline often contains toxic additives which, along with the gasoline itself, are difficult to clean up and cause environmental problems.
- Some oil spills come from large petroleum refineries, tank farms, tankers, or pipelines. But many more oil spills are the result of leaks from underground gasoline storage tanks at gas stations, from residential fuel oil storage tanks, or from spills during fuel oil delivery.
- Yet it is very important for health and protection of wildlife and the environment, that all these spills are cleaned up promptly and properly.
- Health effects from exposure to petroleum products vary depending on the concentration of the substance and the length of time that one is exposed. Breathing petroleum vapours can cause nervous system effects (such as headache, nausea, and dizziness) and respiratory irritation.
- Very high exposure can cause coma and death. Liquid petroleum products which come in contact with the skin can cause irritation and some can be absorbed through the skin.
- Chronic exposure to petroleum products may affect the nervous system, blood and kidneys. Gasoline contains small amounts of benzene, a known human carcinogen. Animals exposed to high levels of some petroleum products have developed liver and kidney tumors.
- People may be exposed to higher levels for longer periods of time if their drinking water supply becomes contaminated by a petroleum spill.
- Through the food chain of marine creatures like plankton and fishes, eventually even people are affected by the marine oil spilling pollution.
- Fish and crustaceans are poisoned as even very tiny amounts of oil is toxic, killing the fish by damaging their immune system and reproductive system.
- Sea birds are covered with oil and cannot fly.
- Recreational beaches are ruined by oil washed ashore.

Clean-up technology for oil spills

- Among the commonly used steps in trying to control oil spilling are:-

i. The use of booms to contain mechanically the oil spill within an area and then siphoning it up;
ii. The recovery of oil using suitable pumps;
iii. The use of chemicals(dispersing agents) and biological methods, such as biostimulation;
iv. Shoreline cleanup of oil spills using natural (evaporation, oxidation, biodegradation) and physical processes(wiping with sorbent material, pressure washing, raking or bulldozing);

v. Soaking up the oil with absorbent materials such as straw.

- The effectiveness of treating oil spilling depends on several factors such as :-
  i. The characteristics of the oil
  ii. Natural conditions such as weather, water temperature, salinity, water depths and bottom material.

Ground water contamination

- Drinking water normally comes from either surface water or groundwater.
- Surface water includes lakes, rivers and reservoirs.
- Surface water are usually treated- sedimentation, flocculation[aluminium sulphate and calcium hydroxide are added. They react to form a sticky gel, aluminium hydroxide which collects suspended particles such as clay and dirt particles. The aluminium hydroxide settles slowly, thereby carrying suspended particles with it at the bottom of the tank], filtration [through sand and gravel to remove any remaining particles], chlorination[using either chlorine gas, sodium chlorate(I) or calcium chlorate(I).In water all the three substances produce chloric (I) acid which is an antibacterial agent] and activated carbon[to remove any taste or odour from the water]- before they are used as drinking water. Sometimes , instead of chloric acid and activated charcoal, ozone or UV light is used to purify the water. It leaves no taste or odour. However , they do not protect the water from contamination after that the water leaves the treatment plant.
- Ground water is the water which is pumped from deep wells that have been drilled into underground aquifers[water bed].
- Usually ground water does not contain harmful contaminants.
- The degree of safetiness of the clean water used for drinking purposes largely determines the public health.
- However due to excessive use of fertilizers, the ground water is contaminated with nitrates and other polluting ions.
- Presence of nitrate or nitrite ion in water limit the ability of blood to carry oxygen.
- Ground water contamination are predominantly industrial in nature. They may involve crude or refined petroleum released from storage tanks, pipelines, transportation accidents, centralised sewage-treatment works, landfills, and a variety of other industrial, military or laboratory facilities.
- Other sources of ground water contamination are from household septic tanks, over-application of fertilizers and pesticides and urban runoff
- Prevention of ground-water pollution is always more cost effective and technically achievable than remediation.
- Ground-water Discharge Permits are required to prevent pollution from discharges onto or below the ground surface.
- A variety of manufacturing, processing, and distribution industries have polluted ground water with halogenated and aromatic solvents, petroleum hydrocarbons, nitrate and metals. Examples include electroplating plants, chemical manufacturers, chemical distributors and power generation stations.

- Many landfills contains large amounts of liquid and/or industrial waste. Ground-water contamination is likely to occur. Contaminants include chloride, nitrate, and chlorinated solvents.

Treatment of ground water contamination

- The treatment of ground water depends mainly upon the contaminants present in the water.
- Some degree of natural biodegradation probably occurs at every site of crude and refined petroleum-product contamination. Several cases of petroleum-product contamination are undergoing bioremediation enhanced by the addition of oxygen, and sometimes nutrients.
- Some physical treatment methods, such as pumping, are used to remove floating non-aqueous phase liquids, such as hydrocarbons.
- Some indigenous ground-water bacteria, stimulated with sodium acetate as a carbon energy source, reduce nitrate to harmless nitrogen gas.
- Contaminated ground water may be used for non-domestic purposes such as irrigation

Waste Management

26.8 Sewrage treatment

- Sewage is over 90% water, together with a complex mixture of organic and inorganic matter and water. Sewage also contains harmful microorganisms.
- Sewage is treated in a series of steps:
    - (a) solid matter is allowed to settle and the sludge aerated to decompose organic matter which lowers its biological oxygen demand (BOD);
    - (b) chemicals are added to precipitate specific ions such as phosphates;
    - (c) activated charcoal is used to absorb offensive odours;
    - (d) the treated sewage is released into rivers or the sea, provided its BOD is adequate.
- Disposal of untreated sewage into the sea is potentially harmful. Pollutants in the sewage can poison fish and the sewage can be washed back ashore, contaminating water supplies.

Ion-exchange treatment

- Waste water from many industries contain harmful metal ions such as silver, mercury and nickel. Traces of these ions are removed by ion-exchange before the water is released into the sewage system. In ion-exchange, the water flows over resin beads. The metal ions are absorbed on the surface of the beads and hydrogen ions are released back into the water to take their place.

  A similar exchange occurs with anions: these are replaced with hydroxide ions which combine with the released hydrogen ions to produce water. The result is the removal of metal salts from water and their replacement with pure water.

Land-filling

- Land-filling is an important method of disposing household and other wastes. The waste is buried in pits and covered with a 2-metre depth of soil.
- Two problems associated with land-filling are summarised below:
  - (a) heavy metals (and other toxic chemicals) can leach out of the dumps and contaminate nearby water supplies;
  - (b) toxic hydrogen sulphide and explosive methane gases can be produced in the anaerobic conditions in land-fill sites. Methane is a greenhouse gas.

Disposal of Waste by Incineration

- One advantage is the production of heat which can be used to generate electricity.

Radioactive Wastes

- Radioactive wastes cannot be destroyed by chemical reactions as the radioactivity is a nuclear property.
- Most radioactive wastes has a very long half-life. For example, radium-226 sources, sometimes used in hospitals for cancer treatment, have a half-life of 1600 years, meaning that it takes 1600 years for half of a radium sample to disappear. As a result, these wastes must be stored in a safe place where it will not be disturbed for thousands of years. It cannot be disposed of in land-fills as there is always a long term risk of radioactive atoms being released into the environment in the event of floods or earthquakes.

26.9 Effective use of resources

Our natural resources are limited and very often they are non-renewable. Therefore ways and means must be found so as to extend their life. Some ways through which natural resources may be spared are:-

(a) through recycling
(b) through a more rational use of the resources
(c) by using alternative resources

Recycling

During recycling already used materials are reconverted into useful materials. Among materials which are being recycled are steel, aluminium, plastics and paper. The recycling of these materials helps to preserve the resources from which they are made. Thus:-

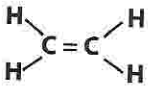
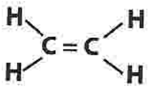
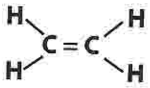
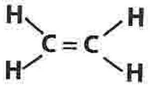
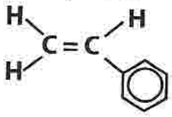
(i) the recycling of metals such as steel and aluminium will help to preserve the raw materials, namely haematite and bauxite. Environmental damages caused by the presence of heavy metals and their ions are reduced. Furthermore large amount of energy is saved (for example electrical energy is saved by reducing production of new aluminium from ores);

(ii) the use of recycled paper helps to decrease the number of trees pulled down to manufacture papers

(iii) the recycling / or reusing of plastic materials means that there will be less pollutants and far less petroleum will be required for their manufacture. Furthermore recycling helps to decrease the amount of plastic entering the landfill or waste stream. Less new land-fill sites are needed.

However the recycling of plastics is not as straightforward as that of steel or paper. The plastics may be different polymers, such as poly(ethene) , poly(vinyl chloride), poly ethylene terephthalate(PET-mainly used in making of soft-drink bottles and is easy to melt and reuse) and so on. The plastics must first be sorted out.

This is facilitated by labels found on the container as shown in the table below:-

POLYMER		PROPERTIES AND USES
polyethylene terephthalate 1 **PETE**	Ethyleneglycol $HOCH_2CH_3OH$ Terephthalic acid 	Transparent and high impact strength. Unaffected by atmospheric gases and acids Used in clothing and making of soft drink bottle
polyethene(HDPE) 2 **HDPE**	Ethene 	Opaque, soft, chemically unreactive, impermeable to water vapour. Mechanically strong. It is used in making of water jugs, cups and gasoline tanks.
polyvinyl chloride 3 **V**	Vinyl chloride 	Thermoplastic and rigid. It is impervious to oil and most organic substances. It is used in making of plumbing pipes, bubble packages wrap ans as insulators.
polyethene (LDPE) 4 **LDPE**	Ethene 	Soft opaque plastic which does not react with acids or bases but absorbs oils. It is used in the making of plastic bags, toys, and electrical insulators.
polypropene 5 **PP**	Propene 	Opaque plastics with high tensile strength and very low density. It is used in making of bottle caps, and battery cases.
polystyrene 6 **PS**	Styrene 	It is rigid, brittle polymer which is easily manufactured. It is used in making of drinking glasses and styrofoam insulation.

After sorting out, different chemical methods are employed to recycle the plastics.

- Recycling also helps in saving money used for importing new materials, for example plastics.

- Some recycling is not worthwhile, particularly if:
  (a) it is extremely labour intensive;
  (b) the costs of collection and separation are too great;
  (c) the recycled product has unsatisfactory properties (eg it is contaminated with impurities which cannot be removed).

Rational use of resources

1. By making a more intelligent use of certain resources, their lifespan may be extended. For example large hydrocarbon molecules are usually broken down into smaller, industrially more important molecules by cracking or are converted into important aromatic or isomeric molecules by catalytic reforming.
   Thus octane is converted into isooctane which improves the performance of fuel by ensuring a smoother combustion. This process is carried out by passing the octane vapour over platinum, rhodium or palladium catalyst.
   By increasing the amount of isooctane in the fuel, the use of additives such as tetraethyl lead to petrol has become obsolete. As lead oxide emissions from car exhaust was a major source of pollution, an increase in isooctane has lead to the use of unleaded petrol, thereby drastically reducing lead pollution.

2. Due to the limited supply of petroleum , other renewable sources of energy are being considered. Among these sources are materials produced by biological processes, also known as biomass. Ethanol and garbages are considered to be important biomasses for the future energetical requirements.
3. The excessive use of petroleum for cars and different vehicles implies that less petroleum will be available to manufacture important petroleum – based starting materials, such as pharmaceutical products and different polymers .Hence alternative sources of fuels must be identified.

Ethanol as fuel

A mixture of about 10% of ethanol and 90% of gasoline, known as gasohol is currently being used in some countries, such as Brazil. For such a mixture, it is not necessary to modify the standard automobile engines. However if a higher percentage of alcohol is used, the engine must be modified.
Some cars use pure ethanol as fuel.
The advantages of ethanol as fuel are that they can be obtained from fermentation of several raw materials such as corn, wheat , beetroot, rice, potato and so on. Furthermore it is a cleaner fuel than gasoline.
However 1g of ethanol produces less energy than 1 g of gasoline. Furthermore, ethanol may undergo only partial oxidation to produce ethanal, a pollutant partly responsible for photochemical smog.

The use of ethanol as fuel for cars will become increasingly important in the future.

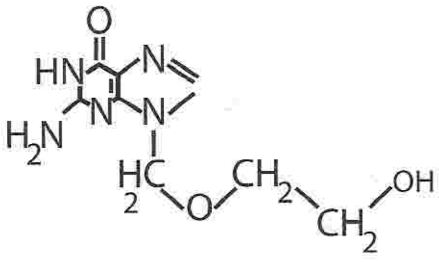
Use of garbage as a source of fuel

Garbage is a potential source of energy which is very cheap, easily available as it is always produced in large amount on a national scale. Furthermore it is always being renewed. The energy released during the combustion of garbages can be converted into different forms of energy such as electrical energy.The emissions that occur during combustion are carefully monitored, such that it does not present any risk to the environment.

Other countries such as China and India have build generators that convert human and animal waste into natural gas, containing about 60% of methane. The gas produced may be used for different purposes such as cooking, heating or generating electricity.

Exercises 26

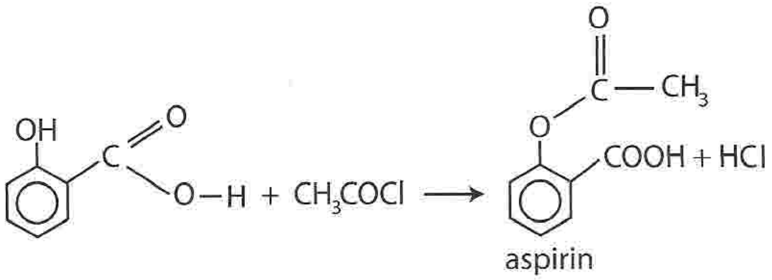
1. Though viral infections are common, yet they are difficult to treat by the use of drugs. Acyclovir is an antiviral drug for cold sores and shingles. Its structure is:



(a) Give two reasons why viruses are so difficult to treat.
(v) Identify the amide group in the structure of Acyclovir by drawing a circle around it.
(c) Explain why Acyclovir is more soluble in dilute acids than in water.
(d) Acyclovir can be taken orally. However some drugs have to be administrated by injection. Suggest two reasons why such drugs cannot be taken orally.

2. Aspirin is an analgesic and can be made from 2-hydroxybenzoic acid by reaction with ethanol chloride.

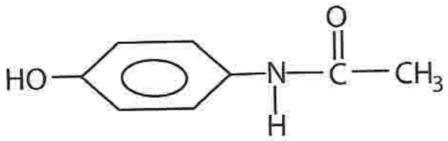
The balance equation is:



(a) Write the molecular formula of 2-hydroxybenzoic acid.

(b) Draw a circle around one of the functional group in the structure of aspirin. Give the name of the group. What is its effect on pH indicator paper?

(c) The structure of paracetamol is shown below:



(i) Draw a circle around the amide group in the structure of paracetamol.

(ii) Name the organic compound that reacts with ethanoyl chloride to produce paracetamol.

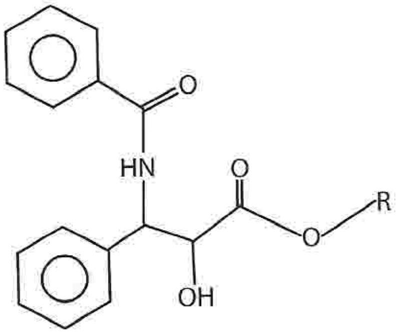
3. (a) Cis platin $Pt(NH_3)_2Cl_2$ is an effective anticancer drug it bonds with guanine in the DNA present in cancer cells and prevents it from replicating.

(i) Draw the structures of cis – and trans-platin.
(ii) What feature of guanine enables it to bond with cisplatin? What type of reaction occurs when the bonds are formed?

(b) Most reactions to form chiral compounds give a racemic mixture which then has to be separated into two different enantiomers.

(i) Explain the term racemic mixture.
(ii) Briefly explain how the desired enantiomer can be separated.

(c) The structure of taxol, an anticancer drug, is show below. Identify with an asterisk two chiral centers.



Q 4 (a) (i) Draw a diagram of two repeat units of nylon-66.
(ii) Kevlar is a synthetic polymer made up by the condensation polymerization reaction be ween benzene –1,4-dioic acid and benzene-1,4-diamine. Draw two repeat units of Kevlar.
(b) (i) Describe the source of intermolecular cohesion in Kevlar.
(ii) Explain why Kevlar is expected to be a very hard solid.
(c) Which of the two polymer, nylon-66 or poly(ethene) would you expect to have a higher me ting point? Explain your answer.
(d) What will be the effect of keeping a nylon rope in aqueous sodium hydroxide for a long time? Give an equation to support your answer.

Q5. (a) Natural rubber (cis-poly(methylbuta-1,3-diene)) and artificial rubber(poly(butadiene)) are similar in that they both contain double bonds.

(i) Draw a section of the structure of natural rubber containing three monomer units.

(ii) Describe how the presence of double bonds in the above polymers determines the phys cal property of the polymer.

(iii) When a rubber bung is used to stopper a vessel containing an organic solvent, such as propanone, it swells. Suggest a reason for this behaviour.

(b) (i) Draw two repeat units for artificial rubber.

(ii) State how the physical properties of natural rubber and artificial rubber may differ and explain why.

Q6 Poly(ethene) is available as HDPE and LDPE.

(a) Describe the main conditions required to produce HDPE and LDPE from ethene.

(b) (i) What is the difference in structure between these two forms?

(ii) How does the differences in structure determine the properties and uses of these two polymers?

(c) What are the main environmental problems linked with poly(ethene) and state how these problems can be minimised?

Q7 (a) Describe the main differences between addition polymerisation and condensation polymerisation, using poly(propene) and terylene as examples.

(b) To what homologous series does poly(propene) belong ?

(c) Explain how the presence of a side chain in a polymer affects the physical properties of the polymer ?

(d) How do you expect the physical properties of poly(ethene) to differ from that of poly (propene) ?

Q8 (a) Buckminsterfullerene is an allotrope of carbon. The buckminsterfullerene contains C_{60} molecules.The structure of C_{60} molecule ressembles a soccer ball with the carbon atoms arranged at the 60 vertices of 32 interconnecting pentagons(12) and hexagons(20).When fullerenes are subjected to intense laser pulses they open their cages to form huge spherical fullerenes. Under suitable conditions fullerene may also be converted into bucky tubes.

(i) What type of bond is present in the fullerene molecule.

(ii) Do you expect the bucky tube to conduct electricity?
Explain your reasoning.

(b) The discovery of the new allotrope of carbon has led to the development of a new field for research, namely the nanotechnology.

(i) What is the nanotechnology?

(ii) How does nanotechnology makes use of the buckminsterfullerene?

(iii) Where is nanotechnology currently being used?

(iv) What are the future prospects of nanotechnology?

Q9 The use of CFCs increased greatly in the second half of the 20th century. Their use is being reduced in the 21st century because of concern about the environmental damage they are causing in the stratosphere.

(a) Outline the importance of the stratosphere to life on the Earth's surface.

(b) By referring to their physical and chemical properties, explain the increased use of CFCs in the 20th century.

(c) CFCs damage the environment by first undergoing photochemical dissociation and then causing a free-radical chain reaction.

(i) A typical CFC has the formula CF_2Cl_2. Write a balanced equation for the photochemical dissociation of this CFC in the stratosphere.

(ii) Write a balanced equation for the first stage in the free-radical chain reaction.

(iii) The strength of the C–F bond is 467 kJ mol–1. By reference to the Data Tables at the back of this book, explain why CFCs such as CF_2Cl_2 are being replaced with fluorohydrocarbons such as $C_2H_2F_2$.

(iv) Give the chemical name or formula of another compound, which can cause similar damage to the stratosphere and state one source of this compound.

Q10 (a) Nitrogen dioxide is a pollutant present in the exhaust fumes from the engines of motor vehicles. Name two other polluting gases found in the exhaust fumes.

(b) Outline, using balanced equations, how nitrogen dioxide causes

(i) the formation of sulphuric acid in the atmosphere, leading to acid rain;

(ii) the formation of ozone, leading to photochemical smog.

(c) What is meant by a lean burn engine and what is the advantage of such an engine?

Q11 (a) Table 25.5 provides some data on CFCs and possible replacement compounds. Each compound has its own code number for easy reference. ODP is the ozone depletion potential which measures the compound's ability to destroy ozone in the stratosphere.

(i) The three CFCs listed in the table have high retention times. What is the significance?

(ii) How would you expect the retention times of the replacement compounds to compare with those of the CFCs?

Table 25.5

CFCs			**Replacement compounds**		
code number	**chemical formula**	**ODP**	**code number**	**chemical formula**	**ODP**
CFC-11	CCl_3F	1.0	HCFC—22	$CHClF_2$	0.05
CFC-12	CCl_2F_2	1.0	HFC—134a	CF_3CH_2F	0
CFC-113	CCl_2FCClF_2	0.8	HCFC—123	CF_3CCl_2H	0.02

(iii) CFC-11 is being replaced with HCFC-123. Explain the difference in the ODP of these two compounds.

(iv) Why does HFC-134a have an ODP of zero?

(b) Table 25.6 provides some data on greenhouse gases.

(i) Suggest the main cause of the CO_2 increase from 1765 to 1990.

(ii) Suggest one non-natural cause for the increase in atmospheric CH4 from 1765 to 1990.

(iii) Why is the amount of 'all CFCs' zero in 1765?

Table 25.6

Greenhouse gas:	CO_2	CH_4	N_2O	all CFCs
amount in air in 1765/ppm	279	790	285×10^{-3}	0
amount in air in 1990/ppm	354	1720	310×10^{-3}	680×10^{-6}
contribution to atmospheric greenhouse effect/%	66	18	4	12

(iv) The amount of atmospheric CFCs in 1990 was a tiny fraction of the amount of N_2O present, yet the contribution to atmospheric greenhouse effect is larger.
Explain this apparent discrepancy.

Q12 Domestic waste can be disposed of by land-filling or by recycling.

(a) One problem with land-filling is the formation of 'landfill gases', which consist mainly of a mixture of carbon dioxide and methane. Explain how these gases are formed and state why there is environmental concern about the large-scale release of these gases.
(b) Plastic is recyclable. State one advantage and a disadvantage of recycling plastics.
(c) Smoke detectors contain radioactive americium, with a half-life of 458 years. Explain why old smoke detectors must not simply be buried in landfill sites and how they should disposed of.
(d) Explain one way in which oil spillages at sea can harm marine creatures.

Q13. Water is an essential commodity to life.

(a) State three uses of water in the industries.
(b) The final stage in the purification of water is chlorination.
    (i) State the steps involved in the purification of water starting with the water supply from the dam.
    (ii) What do you understand by the term 'chlorination'?
    (iii) State one main advantage and one main disadvantage of use of chlorine in water treatment.
(c) Bottled water is often purified using ozone.
    (i) State the advantage of using ozone in bottled water.
    (ii) Why do you think ozone is not used to purify water used for domestic purposes.

Q14. (a) Emissions from car exhausts contain some polluting gases such as carbon monoxide, oxides of nitrogen and unburnt hydrocarbons.
    (i) State the origin of each of the above pollutants.
    (ii) Give three reasons why oxides of nitrogen are considered to be harmful to the environment.
(b) One way of reducing the amount of oxides of nitrogen, carbon monoxide and unburnt hydrocarbon in the environment is to use a catalytic converter. The catalytic converter usually consists of a steel casing packed with a ceramic support which is covered by platinum and rhodium powder which act as catalyst.
    (i) Explain why the catalytic converter does not contain only one catalyst.
    (ii) Write down equations for the reactions which take place in the catalytic converter that help to reduce emission of polluting gases in the environment.
    (iii) State two main problems that are associated with catalytic converters.
(c) The ozone layer is also being damaged by the presence of nitrogen monoxide in the atmosphere and stratosphere. Explain how nitrogen monoxide leads to the gradual depletion of the ozone layer.

Q15. Comment on the environmental impact of :-

(a) excessive use of ammonium salts in agriculture.
(b) the use of chloroflorocarbons(CFCs) in air conditioners and others.
(c) the disposal of chlorinated materials by incineration.
(d) the spilling of oil in the sea .
(e) the disposal of organic material by land-filling.

Q16. The resources available in nature is limited.

(a) Explain the main problems that are associated with an excessive use of crude oil.
(b) One way of limiting use of crude oil is to use alternative sources of energy. State some alternative sources of fuel that may be used .
(c) Recycling of plastic materials may also help in decreasing the dependence on crude oil.
    (i) Explain what is meant by the term 'recycling'.
    (ii) Explain briefly the difficulties that are associated with recycling.

Q17 There is actually a very intensive use of natural resources in the manufacturing industries.
(a) State two reasons why the use of natural resources is increasing continuously.
(b) What problems are associated with the excessive use of natural resources?
(c) State and explain three ways by which the lifetime of natural resources may be increased.

Answers

Exercise 1

Multiple Choice Questions

Section I

1	C	2	C	3	B	4	B	5	D
6	C	7	D	8	A	9	B	10	B
11	B	12	C	13	B	14	D	15	C

Section II

16	D	17	B	18	D

Structured Questions

1 (a) see text

(b) (i) ^{107}Ag: 47 protons and 60 neutrons;

^{109}Ag: 47 protons and 62 neutrons

(ii) $A_r = \frac{(51.4 \times 107) + (48.6 \times 109)}{100}$

2 (a) (i) $^{69}_{31}Ga$ and $^{71}{}_{31}Ga$ (ii) 69.8

(b) (i) Ga_2O

(ii) $Ga_2O_3 + 4Ga \rightarrow 3Ga_2O$

3 (a) $^1H_2{}^{16}O$ *or* $^1H^1H^{16}O$; $^1H^2H^{16}O$; $^2H^2H^{16}O$ *or* $^2H_2{}^{16}O$

(b) $^2H^2H^{16}O$

(c)

relative mass	*formula of ion*
1	$^1H^+$
2	$^2H^+$ or $^1H^1H^+$
3	$^1H^2H^+$
4	$^2H_2{}^+$
17	$^1H^{16}O^+$
18	$^1H_2{}^{16}O^+$ or $^2H^{16}O^+$
19	$^1H^2H^{16}O^+$
20	$^2H_2{}^{16}O^+$

4 (a) I = $^2_1H^+$; II = $^2_1H_2{}^+$; III = $^{81}_{35}Br^+$;

IV = $^2_1H\,^{81}_{35}Br^+$; V = $^{81}_{35}Br_2{}^+$

(b) The hydrogen and bromine reacted together before ionisation.

5 (a) (i) $\frac{2.3}{46} = 0.05$ mole

(ii) $0.05 \times 6.0 \times 10^{23} = 0.3 \times 10^{23}$

(iii) $0.3 \times 10^{23} \times 6 = 1.8 \times 10^{23}$

(b) (i) $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

(ii) $0.05 \times 3 = 0.15$ mole

(iii) $44 \times 2 \times 0.05 = 4.4$ g

(iv) $0.05 \times 3 \times 6.0 \times 10^{23} = 0.9 \times 10^{23}$

6 (a) 10 cm^3 (b) 90 cm^3 (c) 60 cm^3

(d) C_3H_6 (e) 42

7 (a) – (c): see text

(d)

relative mass	28	29	30
relative intensity	8910	1080	10

Descriptive Questions

1 (a) see text

(b) A_r of boron = $\frac{(10 \times 1) + (11 \times 4)}{(1 + 4)} = 10.8$

(c) BH_2; B_8H_{16}

2 (a) relative mass 50: $^{12}C^1H_3{}^{35}Cl^+$ ion

relative mass 52: $^{12}C^1H_3{}^{37}Cl^+$ ion

Chlorine consists of two isotopes, ^{35}Cl and ^{37}Cl.

(b) The molecular formula of sulphur is S_8, with relative molecular mass = 8 × 32 = 256. This produces the line at mass = 256 (due to $S_8{}^+$).

The S_8 ring easily breaks open and the molecule breaks up into fragments. There are seven different fragments, each producing a line in the mass spectrum:

fragment	*relative mass*
$S_7{}^+$	224
$S_6{}^+$	192
$S_5{}^+$	160
$S_4{}^+$	128
$S_3{}^+$	96
$S_2{}^+$	64
S^+	32

3 (a) Please refer to text

(b) Z can be butanone, $CH_3—CH_2—CO—CH_3$.

4 (c)

m/e	Ions
1	H^+
15	$CH_3{}^+$
29	$CH_3CH_2{}^+$
43	CH_3CO^+
46	$CH_3CH_2O^+$
59	$CH_3CO_2{}^+$
88	$C_4H_8O_2{}^+$

5 (a) (i) 78.7% (ii) 24.0

(b) (i) ^{63}Cu = 80%

Exercise 2

Multiple Choice Questions

Section I

1	A	2	D	3	D	4	D	5	D
6	C	7	C	8	B	9	B	10	D
11	C	12	B	13	A	14	A	15	C
16	A	17	D	18	D	19	C		

Section II

20	C	21	C	22	D

Structured Questions

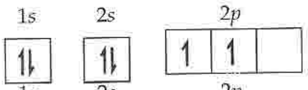
1 (a) 1 = screen; 2 = battery or high voltage source; 3 = vacuum pump; 4 = protons; 5 = neutrons; 6A = negative terminal; 6B = positive terminal

(b) [moves towards positive terminal]

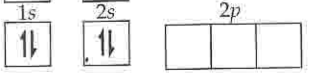
2

particle	number of protons	number of electrons	number of neutrons
^{79}Br	35	35	44
$^{81}Br^{+}$	35	34	46
$^{16}O^{2-}$	8	10	8
$^{16}O_2$	16	16	16
$^{16}O_2^{+}$	16	15	16

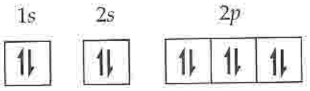
3 (a) (i)



(ii)



(iii)



(b) (i) H^-, because the electron arrangement is $1s^2$, like in the noble gas helium.

(ii) P^{3-}, because the electron arrangement is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$, like in the noble gas argon.

4 (a) orbitals B, D and E

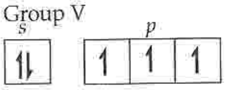
(b) (i) 6

(ii) approximately twice the atomic number ie 12

(c) 2+

5 (a) (i) Group V

(ii)



(iii) Q has at least eight electrons and so the atomic number of Q must be ≥ 8.

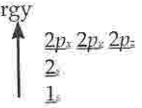
Nitrogen has atomic number 7.

(b) As electrons are removed, the net positive charge on the atom increases. Thus the attractive force on the remaining electrons is greater. Hence more energy is required to remove the electrons.

(c) The first five electrons are in the outer shell. The sixth electron is in an inner shell, much closer to the nucleus and hence more strongly held.

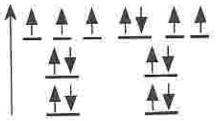
(d) phosphorus $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$

6 (a) (i) Energy



(ii)

(b) (i) Energy



(ii) Nitrogen has exactly a half-filled and stable 2p subshell, so more energy is needed to remove an electron.

(iii) N^{3-} and O^{2-}

(iv) The ionisation energy is too high to remove five electrons from N and six electrons from O to form N^{5+} and O^{6+}.

Descriptive Questions

1 (a) Please refer to text

(b) First four electrons in the outer shell — ionisation energy increases because, as electrons are removed, the net positive charge on the atom increases and the attractive force on the remaining electrons becomes stronger.

Last two electrons in the inner shell — closer to nucleus.

Big increase in ionisation energy between 4th and 5th electrons because these electrons are from different shells. 5th electron from the inner shell — more energy is required to remove it.

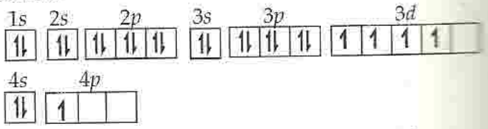
Electronic configuration $1s^2\ 2s^2\ 2p^2$.

(c) see text

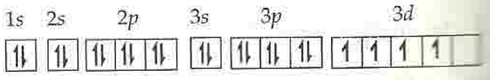
2 (a) ^{56}Mn (same number of protons but one more neutron than in an atom of ^{55}Mn)

(b) No difference — because isotopes have the same chemical properties.

(c) (i)



(ii)



3 Please refer to text

4 (d) (i) 0.9^0 (ii) 10^0

Exercise 3A

1 (a) 0.0625 mol dm^{-3} (b) 6.125 g dm^{-3}

2 20.8 cm^3

3 (a) 0.2 mol dm^{-3} (b) 3.4 g

4 250 cm^3

5 (a) 0.08 mol dm^{-3} (b) 5.04 g dm^{-3}

6 0.25 mol dm^{-3}

7 (a) $SO_2Cl_2 + 2H_2O \rightarrow H_2SO_4 + 2HCl$ (b) 0.54 g

8 (a) $CH_3COCl + H_2O \rightarrow CH_3COOH + HCl$ (b) 333 cm^3

9 %of zine = 73.1

Exercise 3B

1 (a) 0.1 mol dm^{-3} (b) 127

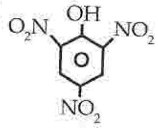
2 (a) 146 (b) $n = 4$

3 $x = 2$

4 (a) 0.04 mol dm^{-3} (b) $x = 8$

5 62.8; 11.8

6 (a) 0.12 mole (b) 4.68 g
(c)



(d) Weak acid, because phenolphthalein changes colour in an alkaline solution.

Exercise 3C

1 (a) 0.0035 mole of NaH_2PO_4; 0.007 mole of OH^-
(b) $NaH_2PO_4 + 2NaOH \rightarrow Na_3PO_4 + 2H_2O$

2 (a) 5×10^{-3} mole
(b) and (c):

equation	M_r	A_r
$1\ H_3MO_3 + 1\ OH^-$	31	−20
$1\ H_3MO_3 + 2\ OH^-$	62	11
$1\ H_3MO_3 + 3\ OH^-$	93	42

(d) $A_r = 11$ is most reasonable (boron).

3 31 or 151

Exercise 3D

1 (a) 0.00107 mol
(b) 0.0107 mol
(c) 1.13 g
(d) 57%

2 (a) $NaOH + HCl \rightarrow NaCl + H_2O$
(b) (i) 14.0 cm^3 (ii) 36.0 cm^3
(c) $2HCl + CaCO_3 \rightarrow CaCl_2 + H_2O + CO_2$
(d) (i) 0.009 mole (ii) 0.9 g (iii) 90%

Exercise 3E

1 (a) 0.05 mol dm^{-3} (b) 1.7 g dm^{-3}

2 11.1 cm^3

3 (a) 134 g dm^{-3} (b) 0.02 mole

4 120 cm^3

5 (a) $ClO_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O$
(b) $ClO_3^- + 6Fe^{2+} + 6H^+ \rightarrow Cl^- + 6Fe^{3+} + 3H_2O$
(c) (i) dilute H_2SO_4
(ii) 0.016 mol dm^{-3}
(iii) 0.627 g

6 (a) (i) 0.112 g (ii) 5.60 g
(b) 44%

7 44.3 g

Exercise 3F

1 (a) (i) The solution remained pink at the end-point (the MnO_4^- was no longer decolourised).
(ii) The solution in the titration flask must be heated.
(b) 124; 18
(c) NH_4^+

2 (a) $2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$
(b) 0.2 mole
(c) 55

3 (a) 0.0267 mol dm^{-3}
(b) 23

Exercise 3G

1 4.82 g dm^{-3}

2 40

3 85.6; rubidium

4 (a) $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$
(b) 2.67 g dm^{-3}

5 (a) 0.00135 mole (b) 0.27 mole (c) 9.86 g

6 (a) 0.015 mol dm^{-3} (b) 0.015 g dm^{-3}

Exercise 3H

1 (a) 0.00125 mole (b) 0.000625 mole
(c) 2 moles (d) equation (ii)

2 (a) N_2O (oxidation number of N is +1)
(b) 0.01 mole
(c) 0.03 mole
(d) 3 moles
(e) equation (iii)
(f) Solution would appear brown due to formation of $Fe(NO)^{2+}$ ('brown ring').

3 (a) [In writing these half-equations, assume that any extra oxygen becomes H_2O in the products: add H^+ to react with this oxygen to make the water.]
$NO_2^- + 2H^+ + e^- \rightarrow NO + H_2O$
$NO_2^- + 4H^+ + 3e^- \rightarrow \frac{1}{2} N_2 + 2H_2O$

(b) (i) 2×10^{-3} mole (ii) 6×10^{-3} mole (iii) 3 moles
(c) NO_2^- was reduced to N_2;
$NO_2^- + 4H^+ + 3Ti^{2+} \rightarrow 3Ti^{3+} + 2H_2O + \frac{1}{2}N_2$

Exercise 3I

1 (a) 0.0005 mole (b) 0.0003 mole (c) $\frac{5}{3}$ moles
(d) 3 electrons so that $5V^{2+}$ will react with $3MnO_4^-$.
(e) +5

2 (a) 0.0008 mole Cr^{2+}; 0.0004 mole $[CuCl_4]^{2-}$
(b) 0.5 mole
(c) 2
(d) (i) +2 (ii) 0 (iii) $[CuCl_4]^{2-} + 2e^- \rightarrow Cu + 4Cl^-$

3 Equal number of moles of Ce^{4+} and $[Fe(CN)_6]^{4-}$ react together; $[Fe(CN)_6]^{4-}$ gives up one electron, Ce^{4+} must accept one electron, hence n+ = 3+.

4 (a) +6
(b) (i) 0.002 mole (ii) 0.0008 mole (iii) $\frac{5}{2}$ moles
(iv) 2 electrons, so that $5U^{z+}$ react with $2MnO_4^-$
(v) z = 4
(c) $UO_2^{2+} + 4H^+ + 2e^- \rightarrow U^{4+} + 2H_2O$

5 (a) (i) 2 moles
(ii) increase of 2
(iii) N_2O

Exercise 4

Multiple Choice Questions

Section I

1	D	2	B	3	D	4	B	5	A
6	B	7	C	8	C	9	C	10	D
11	D	12	B	13	B	14	B	15	D
16	B	17	B	18	D				

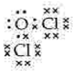
Section II

19	B	20	D	21	C

Structured Questions

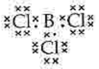
1 (a)

(b)

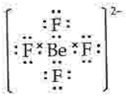


(c)

(d)



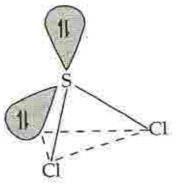
(e)



(f)

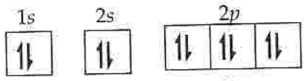
2 (a) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$ (b)

(c) (i) two bond pairs (ii) two lone pairs
(d) Sulphur atom is surrounded by four electron pairs (two bond pairs and two lone pairs) arranged in tetrahedral arrangement. Therefore, the molecule SCl_2 has a bent shape.

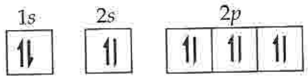


(e) H_2O, H_2S

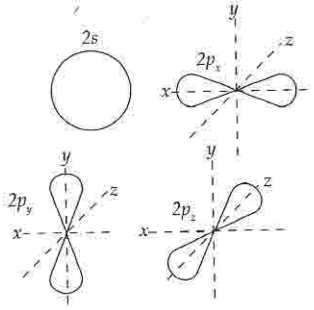
3 (a) (i)



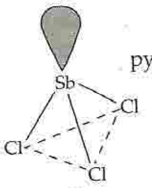
(ii)



(b)

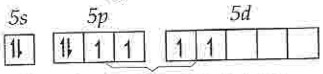


(c) (i) $SbCl_3$ and $SbCl_5$
(ii) one lone pair and three bond pairs



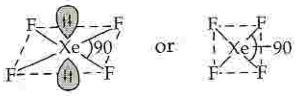
pyramidal shape

4 (a) (i)



four single electrons to form four covalent bonds

(ii) two lone pairs (iii) six electron pairs
(iv)

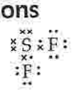


(b) XeF_2 (three lone pairs); XeF_6 (one lone pair); XeF_8 (no lone pair)

5 (a) (v)
$BeCl_2 + 2NH_3 \rightarrow BeCl_2(NH_3)_2$

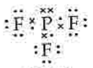
Descriptive Questions

1 (a) *briefly:* (i)



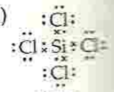
shape: bent as the four electron pairs have tetrahedral arrangement

(ii)



shape: pyramidal

(iii)



shape: tetrahedral

(b) Please refer to text

2 (a) Please refer to text (b) Please refer to text
(c) The white solid is $BCl_3.NH_3$, like $BF_3.NH_3$.
(d) The C—I bond energy is less than the C—Cl bond energy, so the C—I bonds are weaker and CI_4 decomposes more easily.

3 (a) (i) H_3O^+ ion; oxygen is surrounded by 4 electron pairs in both particles, but the bond angle is larger in H_3O^+ as there is only one lone pair compared with two lone pairs in H_2O.
(ii) NH_4^+ ion; the bond angle is larger in NH_4^+ because NH_4^+ has no lone pair but NH_3 has one lone pair.
(iii) BF_4^- ion; the bond angle in BF_4^- is smaller ($109\frac{1}{2}$°) than in BF_3 (120°) because there are four electron pairs around the boron atom in BF_4^- and three electron pairs around the boron atom in BF_3.
(b) Please refer to text

Exercise 5

Multiple Choice Questions

Section I

1 C	2 A	3 A	4 C	5 D
6 D	7 C	8 B	9 C	10 B

Section II

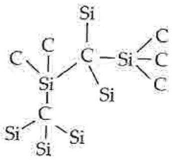
11 C	12 C	13 C	14 D	15 A
16 A	17 B			

Structured Questions

1

solid	lattice particles	main force
SiO_2	Si, O atoms	covalent bonds
CH_4	CH_4 molecules	Van der Waals
H_2O	H_2O molecules	hydrogen bonds
NH_4Cl	NH_4^+, Cl^- ions	electrovalent bonds
H_2	H_2 molecules	Van der Waals
Al_2O_3	Al^{3+}, O^{2-} ions	electrovalent bonds
Cr	Cr atoms	metallic bonds

2 (a) (i) giant molecular
(ii) It has a high melting point so the lattice forces are strong; it is a compound of two non-metals.
(b) (i)



(ii) Silicon carbide should be very hard — like diamond; it could be used for saws and drills and as an abrasive.

3 (a) 166.2 kPa (b) (i) 33.2 kPa (ii) 133 kPa
(c) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$
(d) Total number of moles of gas at the end of the reaction remains unchanged, hence the pressure is the same ie 166.2 kPa.

4 (a) Van der Waals forces
(b) covalent bonds
(c) It will not conduct electricity and it will be insoluble in water.

(d) CCl_3F should have higher melting point and boiling point because the molecules are larger (a chlorine atom is larger than a fluorine atom as atomic radius increases down the group).
(e) As a propellant for aerosol cans, in air-conditioners or refrigerators.

Descriptive Questions

1 (a) Please refer to text (b) Please refer to text
(c) see text for General Gas Equation;
(i) 0.00802 mole of gas (ii) 0.241×10^{23} atoms

2 (a) *briefly:*
propane: molecular structure; C_3H_8 molecules; weak Van der Waals forces, hence low boiling point; no delocalised electrons, therefore does not conduct electricity when in solid or molten state
ethanol: molecular structure; CH_3CH_2OH molecules; hydrogen bonds, hence higher boiling point than propane; no delocalised electrons, therefore does not conduct electricity when in solid or molten state
chromium: metallic structure; large metal atoms (or positive ions) surrounded by delocalised electrons; strong metallic bonds, hence high boiling point; delocalised electrons, therefore conducts electricity in both solid and molten states
potassium chloride: ionic structure; K^+ and Cl^- ions; strong electrovalent bonds, hence high boiling point; conducts electricity in molten state because ions can move; does not conduct electricity in solid state
(b) Sodium chloride is soluble in water because water molecules are polar and so can form electrostatic bonds with the ions [see Fig 5.7 in text]. Tetrachloromethane is not polar and so cannot form these bonds.

3 *briefly:*
(a) high melting point because of strong electrovalent bonds; the ions cannot move to conduct electricity in the solid state
(b) hydrogen bonds in liquid ammonia (only weak Van der Waals forces in liquid methane)
(c) Please refer to text
(d) Ceramics are mainly giant molecular with very strong covalent bonds (hence they have very high melting points).

4 Please refer to text

5 Please refer to text

9 mass of argon = 20.19g

10 (b) % of Na_2CO_3 =86.2

Exercise 6

Multiple Choice Questions

Section I

1 D	2 C	3 D	4 A	5 D
6 B	7 D	8 B	9 C	10 A
11 A	12 B	13 B	14 D	15 C
16 B	17 A	18 A	19 C	

Section II

20 D *21* A *22* D

Structured Questions

1 (a) (i) enthalpy change of atomisation of Na
 (ii) ionisation energy of Na
 (iii) enthalpy change of formation of NaI
(b) (i) Smaller, because ionisation energy decreases down the Group.
 (ii) no change
 (iii) Smaller, because the bigger potassium ions would produce weaker electrovalent bonds.
(c) –800 kJ mol^{-1}

2 (a) In ΔH_f ←, an electron is added to a negative ion (energy must be supplied to overcome the force of repulsion).
(b) More energy is required to take away an electron from a positive ion than from a neutral atom (greater force of attraction in the first case).
(c) –3441 kJ mol^{-1} (d) magnesium oxide

3 (a) ΔH_1 ← = minus lattice energy;
ΔH_2 ← = enthalpy change of solution of KCl;
ΔH_3 ← = enthalpy change of solvation of K^+ ion
(b) +15 kJ
(c) ΔH_1 ← would become smaller; the bromide ion is larger than the chloride ion, so the forces between the ions would be weaker.
ΔH_4 ← would become smaller; the enthalpy change of solvation would become smaller as the size of the ion increases.

4 (a) oxidation numbers: +1, +2, +3;
formula: P_2O_5 or P_4O_{10}
(b) (i) $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightarrow NO(g)$;
$\Delta H_f = +90.4$ kJ mol^{-1}
 (ii) Heat from the car engine causes this endothermic reaction to take place.
(c) The formation of nitrogen oxides is endothermic because a large amount of energy needs to be absorbed to break the very strong N N bond.
(d) –98.8 kJ

5 (a) –592 kJ mol^{-1}
(b) –588 kJ mol^{-1}
(c) bond enthalpies are only averages and not for the particular compounds

6 (b) (ii) 1.61KJ (iii) 1.53×10^{-2}
 (iv) 2.50×10^{-2} (v) ΔH = -105KJmol^{-1}
(c) –1110.5 kJ mol^{-1}

7 (c) (ii) ΔH = -495KJmol^{-1}

8 (b) (ii) lattice energy = -1992KJmol^{-1}

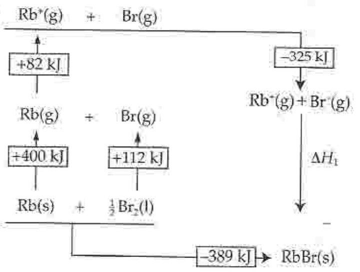
9 (b) (ii) ΔH = -60KJmol^{-1}

Descriptive Questions

1 (a) +329 kJ mol^{-1} (b) –1775 kJ mol^{-1} (c) –196 kJ mol^{-1}
(d) +440 kJ mol^{-1} (e) +42 kJ mol^{-1} (f) –301 kJ mol^{-1}

2 (a) –422 kJ mol^{-1} (b) –129 kJ mol^{-1}

3 (a) see text (b) see text
(c)



Lattice energy, ΔH_1
$= -389 - 82 - 400 - 112 + 325$
$= -658$ kJ mol^{-1}

(d) The lattice energy of RbI would be smaller than that of RbBr because the larger I^- ion would make the electrovalent bonds weaker.

4 (a) (i) see text
(b) (ii) see text (eg finding ΔH for the reaction
C + O2 → CO
(b) –237 kJ mol^{-1}
$\frac{1}{2}$

5 (a) bent or non-linear (like water)
(b) $Cl_2O_6 + 2OH^- \rightarrow ClO_3^- + ClO_4^- + H_2O$
(c) +76 kJ mol^{-1}; this is unusual because it is endothermic whereas the decomposition of Cl_2O is exothermic. Cl_2O would decompose easily and might explode if heated.

6 (a) Please refer to text
(b) –430 kJ
(c) RbF is soluble in water (unlike SF_4) and conducts electricity when molten (unlike SF_4).

7 (b) (i) 23.1°C (ii) 2.25KJ
 (iii) 2.50×10^{-2} (iv) 4.00×10^{-2}
 (v) ΔH = –112KJmol^{-1}

9 (a) (i) briefly: MgF_2 has strong ionic bonds; SF_2 has a simple molecular structure with only weak intermolecular forces
 (ii)
 ‥ ‥ ‥ ‥
$[Mg]^{2+}$ 2[: F :]– : F : S : F :
 ‥ ‥ ‥ ‥

(b) –112 kJ mol–1
[note: need to use F—F bond enthalpy and 1st and 2nd ionisation energies of Mg]
(c) the ionisation energies for the removal of the 3rd and 4th electrons are too high

10 (a) entropy increases because an ordered solid is producing a disorderly gas

(b) (i) +131 kJ mol^{-1}
(ii) +178 kJ mol^{-1}
(iii) +0.161 kJ mol^{-1} K^{-1}

(c) (i) ΔG is positive (it must be negative for a spontaneous reaction)
(ii) a temperature above $\frac{\Delta H}{\Delta S} = \frac{178}{0.161} = 1105\ K$

11 (a) (i) +142.7 kJ mol^{-1} (ii) +0.216 kJ mol^{-1} K^{-1}
(b) it is positive because more gas is being produced
(c) (i) no effect
(ii) becomes more negative
(d) (i) the reaction will not take place at these conditions as ΔG is a large positive number
(ii) a big increase in temperature would make less negative so that it will eventually become a positive value and the reaction will take place to produce a large amount of hydrogen

Exercise 7

Multiple Choice Questions

Section I

1	D	*2*	A	*3*	D	*4*	B	*5*	A
6	C	*7*	A	*8*	B	*9*	D	*10*	D
11	D	*12*	D	*13*	D	*14*	C	*15*	C
16	A	*17*	B	*18*	C				

Section II

19	B	*20*	B

Structured Questions

1 (a) +4 (b) –2 (c) +5 (d) +7
(e) –4 (f) +4 (g) +3 (h) +1
(i) +6 (j) +2 (k) +1

2 (a) (i) –2 (ii) +5
(b) (i) increase (ii) decrease
(c) (i) 0.12 mole (ii) 1.2 dm^3

3 (a) **A**: silver metal; **B**: 1.0 mol dm^{-3} $Ag^+(aq)$;
C: salt bridge; **D**: sensitive voltmeter;
E: platinum wire or electrode;
F: hydrogen gas at 101 kPa pressure;
G: 1.0 mol dm^{-3} $H^+(aq)$.
(b) (i) $2Ag^+(aq) + H_2(g) \rightarrow 2Ag(s) + 2H^+(aq)$
(ii) +0.80 V
(c) (i) at the platinum electrode
(ii) at the silver electrode
(iii) at the silver electrode

4 (a) The solution would turn brown.
(b) (i) $2I^- \rightarrow \underset{\text{brown}}{I_2} + 2e^-$
(ii) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
(c) From electrode **X** through the wire and voltmeter to electrode **Y**.
(d) (i) $2MnO_4^- + 16H^+ + 10I^- \rightarrow 5I_2 + 2Mn^{2+} + 8H_2O$
(ii) $E^{\leftarrow} = +0.98$ V
(e) The voltage reading would increase as more I^- would react to place more electrons on the electrode **X**, making **X** more negative.

5 (a) Hydrogen from liquid hydrogen rocket fuel and oxygen from liquid oxygen are used as oxidisers for the fuel.
(b) (i) $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
(ii) $2H_2 + O_2 \rightarrow 2H_2O$
(c) It acts as a catalyst for the reactions.
(d) The fuel cell will work indefinitely on fuel from the rocket fuel tanks (a battery has a fixed lifetime — it stops when its electrode materials are used up); the fuel cell produces water which is needed by astronauts.

6 (a) reactions II, IV and V (b) reaction V

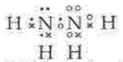
7 (a) (i) $E^{\leftarrow} = +0.43$ V
(ii) in the Cu^{2+} | Cu half-cell: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
in the Fe^{3+} | Fe^{2+} half-cell: $Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$
overall equation is:
$Cu(s) + 2Fe^{3+}(aq) \rightarrow Cu^{2+}(aq) + 2Fe^{2+}(aq)$
(b) The $E^{\leftarrow}$ value for the reaction is positive and more positive than +0.3 V.
(c) The new half-cell can consist of a platinum electrode dipping into a solution containing a mixture of aqueous chlorine and aqueous sodium chloride. This half-cell has a standard redox potential of +1.36 V and is thus more positive than the Fe^{3+} | Fe^{2+} half-cell. The cell is
$Pt(s) \mid Fe^{3+}(aq), Fe^{2+}(aq) \because Cl^-(aq), Cl_2(aq) \mid Pt(s)$

8 (a) (i) at anode: $2Br^- \rightarrow Br_2 + 2e^-$
at cathode: $Sr^{2+} + 2e^- \rightarrow Sr$
(ii) to protect the hot strontium from reaction with oxygen in the air
(iii) 18 000 coulombs; 8.17 g
(iv) hydrogen from water is produced at the cathode instead of strontium because H^+/H_2 electrode potential is more positive than that of Sr^{2+}/Sr

Descriptive Questions

1 (a) and (b): see text
(c) $Co(s) + 2Ag^+(aq) \rightarrow Co^{2+}(aq) + 2Ag(s)$;
$E^{\leftarrow} = +1.08$ V
The e.m.f. would increase.

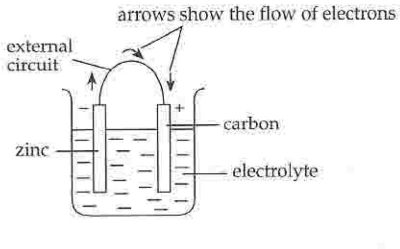
2 (a)



$$\begin{array}{c} H : \ddot{N} : \ddot{N} : H \\ \ \ H \quad H \end{array}$$

(b) $N_2H_5^+(aq) + 2Cl_2(aq) \rightarrow N_2(g) + 5H^+(aq) + 4Cl^-(aq)$; $E^{\leftarrow} = +1.53$ V
(c) The C—C bond energy is 350 kJ which is much larger than the N—N bond energy of 160 kJ; hence the C—C bond in ethane is much stronger and less easily broken.

3 (a) (i)



(ii) at the zinc electrode:
$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$; $E^{\leftarrow} = +0.76$ V
at the carbon electrode:
$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$; $E^{\leftarrow} = +0.40$ V

overall equation:
$2Zn(s) + O_2(g) + 2H_2O(l) \rightarrow 2Zn(OH)_2(s)$
[Note: The $Zn(OH)_2$ is formed by reaction of $Zn^{2+}(aq)$ with $OH^-(aq)$.]
The e.m.f. of the cell is +1.16 V.
(iii) aqueous sodium chloride
(b) 5683 cm^3

5 (b) (i) 0.7cm^3 (ii) 5.03g
(iii) 2.80 x 10^{4}C (iv) 5604s(or 1.56h)

Exercise 8

Multiple Choice Questions

Section I

1 D 2 C 3 A 4 B 5 C
6 C 7 D 8 C 9 C 10 D
11 B 12 B

Section II

13 D 14 A 15 D 16 D 17 D

Structured Questions

1 (a) reactions forward and backward are containing, and the rate forward = the rate backward
(b) (i) it would become paler
(ii) the composition would shift to the left, producing more N_2O_4
(c) the forward reaction is endothermic as the equilibrium shifts to the right when the temperature is increased

(d) (i) $K_p = \dfrac{(P_{NO_2})^2}{P_{NO_2O^4}}$

(ii) $K_p = 5.04$ Pa

2 (a)

reaction	amount of product(s) at equilibrium
$A \rightleftharpoons 2B$	decrease
$A + B \rightleftharpoons 2C$	no change
$4A + 5B \rightleftharpoons 4C + 6D$	decrease
$3A + B \rightleftharpoons 2C$	increase

(b) there will be less C and D
(c) Haber Process; A = H_2, B = N_2, C = NH_3

3 (a) (i) $K_c = \dfrac{[NO]^2}{[N_2].[O_2]}$ (ii) $x = 6.0 \times 10^{-3}$ mole

(c) (i) There will be more N_2 and O_2 and less NO.
(ii) No effect on the composition of the equilibrium mixture because pressure changes do not affect this reaction.

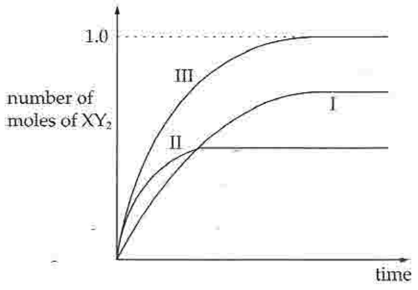
4 (a) (i) 0.200 mole (ii) 0.200 mole
(iii) 0.200 mole (iv) 0.300 mole
(v) 0.300 mole

(b) (i) $K_c = \dfrac{[CH_3CH_2COOCH_2CH_3].[H_2O]}{[CH_3CH_2OH].[CH_3CH_2COOH]}$ (ii) 2.25

(c) (i) The reaction did not reach equilibrium.
(ii) Add a little concentrated sulphuric acid as catalyst.

5 (a) (i) higher pressure — smaller percentage of **B** and **C**
(ii) higher temperature — larger percentage of **B** and **C**
(b) Endothermic, because higher temperature favours the decomposition of **A**.
(c) The graphs show that the reaction is affected by pressure changes. The reaction $2HI \rightleftharpoons H_2 + I_2$ is not affected by pressure changes.
(d) (i) 300°C would produce a larger amount of **A**, but the process would require a longer time to reach equilibrium. Hence 500°C would be better as the process would reach equilibrium faster. However, a smaller percentage of **A** would be obtained.
(ii) At a very low temperature, the rate of reaction would be very slow. A very long time would be needed for the process to reach equilibrium and to produce a large amount of **A**.

6 (a) Because the temperature was higher, so the rate of reaction was faster.
(b) Equilibrium had been reached.
(c) ΔH must be exothermic, because less XY_2 was produced at a higher temperature.
(d)



(e) (i) $\frac{0.6}{1.7}$ P (ii) $\frac{0.7}{1.7}$ P (iii) $\frac{0.4}{1.7}$ P

(f) $K_p = \dfrac{P^2 x\, y_2}{Px_2 \,.\, Py^2{}_2}$
$= 2.73 \times 10^{-2}$ kPa

Descriptive Questions

1 (a) (i) iron
(ii) nitrogen from air, hydrogen from petroleum
(iii) air
(iv) No more ammonia can be made from the equilibrium mixture until it is removed.
(b) (i) 200°C produces a larger percentage of ammonia. The reaction is too slow below 500°C.
(ii) 150 atmospheres. A very high pressure requires expensive pumps and extra thick pipes and containers.

2 (a) $K_c = \dfrac{[CH_3OH]}{[CO][H_2]^2}$ dm^6 mol^{-2}

(b) (i) low temperature
(ii) high pressure
(c) (i) the reaction would be too slow

(ii) 300°C is a moderate temperature; it is a compromise, although the yield is reduced, it is fast enough

(d) the equilibrium is pushed to the left, producing more methanol at equilibrium

3 (a) Please refer to text

(b) *briefly:* (i) less NH_3 at equilibrium

(ii) more H_2 and CO and less H_2O at equilibrium

(iii) more $Cr_2O_7^{2-}$ and less CrO_4^{2-} at equilibrium

(c) (i) $Kc = \frac{[NO_2]^2}{[NO_2][O_2]^2}$

(d) (i) 1.25×10^{-2} $mol^{-1}dm^3$

(i) 8.94 $mol^{-\frac{1}{2}}dm^{-\frac{3}{2}}$

4 (c) (ii) 0.03 (iii) 0.03 (iv) 0.065

(v) number of moles of water = 0.07, number of moles of ester = 0.035

(vi) 2.93

5 (a) (i) 50% (ii) 0.17atm (iii) 0.33atm

Exercise 9

Multiple Choice Questions

Section I

1 C 2 C 3 B 4 B 5 D
6 D 7 D 8 C 9 B 10 C
11 B 12 A 13 D 14 D 15 C
16 D 17 B

Section II

18 D 19 D 20 C

Structured Questions

1 (a) (i) 0.001 mol dm^{-3}

(ii) 3.16×10^{-5} mol dm^{-3}

(iii) 1.58×10^{-11} mol dm^{-3}

(b)

solution	[H^+]	pH	[OH^-]
HCl	0.0001	4.0	1.0×10^{-10}
H_2SO_4	0.1	1.0	1.0×10^{-13}
NaOH	1.0×10^{-12}	12.0	0.01
HNO_3	3×10^{-3}	2.52	3.3×10^{-12}
KOH	4×10^{-13}	12.4	0.025

[Note: These are all strong acids and alkalis.]

(c) (i) 9.95×10^{-3} mol dm^{-3} (ii) 2.0

(d) (i) 2.0×10^{-6} mol dm^{-3} (ii) 5.70

(e) 1.8×10^{-4} g dm^{-3}

2 (a) 1.8×10^{-16} mol dm^{-3}

(b) (i) 4.0 (ii) [H^+] = 10^{-3} mol dm^{-3}; pH = 3.0

(c) 4.60

3 (a) Strong acid, because the pH of the pure acid starts at about 1.0.

(b) Weak alkali, because of pH of pure alkali is about 10 – 11, and the end-point is in acid conditions.

(c) 0.30 mol dm^{-3}

(d) Congo red; it changes colour completely when the pH in the titration flask changes from 2 to 6 at the end-point.

(e) After addition of about 6 cm^3 of alkali (ie in the middle section of graph where the gradient is small, so that there is little change in pH when more alkali or acid is added).

4 (a) $K_{sp} = 4x^3$ mol^3 dm^{-9} (b) $400x^3$ mol^3 dm^{-9}

(c) (i) no effect on K_{sp}

(ii) K_{sp} is increased as solubility usually increases with temperature.

5 Solutions (c) and (e)

6 (b) (i) 1.00 (ii) 0.070 (iii) 2.88

(c) (i) 4.76

(ii) Buffer solution

7 (a) (iii) 1.0×10^{-7} $moldm^{-3}$

(iv) 7.00

(b) (ii) endothermic

(iii) degree of dissociation increases

(iv) pH decreases

Descriptive Questions

1 (a) Please refer to text

(b) (i) 1.9 (ii) 3.16

2 *briefly:* (a) K_w increases with temperature [also see text].

(b) The pH range at which methyl orange changes colour is less than 7, but the end-point of the titration for a weak acid with a strong base is alkaline [also see text].

(c) A solution of SO_2 is the same as a solution of H_2SO_3, which is a dibasic acid, giving two end-points — for the reaction producing $NaHSO_3$ and the reaction producing Na_2SO_3 [also see text].

3 (b) (i) 1.32×10^{-3} $moldm^{-3}$ (ii) 1.74×10^{-5} $moldm^{-3}$

(c) (ii) 120cm^3

(d) (i) 1.00 (ii) 120cm^3

5 (e) (i) 1.93×10^{-3}g (ii) 2.58×10^{-7}g

6 (b) 0.136 $moldm^{-3}$

8 (a) (i) 13.00 (ii) 13.30 (iii) 9.31
(c) (ii) 11.11 (iii) 8.92

Exercise 10
Multiple Choice Questions
Section I

1 D *2* B *3* C *4* B *5* A
6 B *7* B *8* A *9* D *10* A
11 D *12* C *13* B *14* A *15* C
16 A *17* A

Section II
18 D *19* A

Structured Questions

1 (a) (i) rate ∝ $[H_2]$ (ii) rate α $[NO]^2$
(b) (i) rate = $k.[H_2].[NO]^2$ (ii) 3
(iii) $mol^{-2} dm^6 s^{-1}$ (iv) 1.67×10^5

2 (a) (i) rate ∝ [propanone]
(ii) The rate is independent of iodine.
(iii) rate ∝ $[H^+]$
(b) 4.5×10^{-6} mol $dm^{-3} s^{-1}$
(c) (i) rate = $k.[CH_3COCH_3].[H^+]$
(ii) 2
(iii) 3×10^{-5}
(iv) $mol^{-1} dm^3 s^{-1}$
(d) Because the concentrations changed with time and would not be known except at the start of the experiment.

3 (a) $mol^{-2} dm^6 s^{-1}$
(b) (i) 2*y*
(ii) 8*y*
(iii) *y* (no change)
(iv) *y* (no change)

4 (i) (graph is a straight line)
(ii) Order = 1(first order), because the rate is directly proportional to $[H_2O_2]$.
(iv) k = gradient = $5.56 \times 10^{-3}\ s^{-1}$
(v) manganese(IV)oxide; heterogeneous catalyst

5 (a) 3
(b) *briefly:*
(i) 2*r* (ii) 8*r* (iii) $\frac{1}{8}r$ (iv) *r*

6 (d) $0.14 min^{-1}$(or $2.3 \times 10^{-3} s^{-1}$)

8 (b) (i) order w.r.t. A = 1, order w.r.t. B = 2
(ii) rate = $K[A][B]^2$ (iii) 2.0 (iv) $mol^{-2}dm^6s^{-1}$
(v) $0.072 mol dm^{-3} s^{-1}$

Descriptive Questions
1 (a) Please refer to text
(b) (i) Graph of rate against $[HI]^2$ is a straight line, so the order = 2.
(ii) $k = 1.3 \times 10^{-5}\ mol^{-1}\ dm^3\ s^{-1}$

3 (iv) $t_{1/2}$ = 14min, rate constant = $4.95 \times 10^{-2} min^{-1}$

4 (b) order w.r.t. CH_3COCH_3=1, I_2=0, H^+=1

5 (a) (ii) order w.r.t. $S_2O_3^{2-}$ = 1, H^+ = 1

6 (b) 42 min
(c) (i) order w.r.t. X =2
(ii) order w.r.t. Y =1
(iii) overrall order =3

7 (b) (i) order w.r.t. A =2
(ii) order w.r.t.B =1

Exercise 11
Multiple Choice Questions
Section I
1 A *2* B *3* A *4* A *5* C
6 D *7* C *8* D *9* D *10* D
11 C *12* D *13* C

Section II
14 A *15* B *16* D

Structured Questions
1 (a) Group IV (b) ZCl_4; +4
(c) $ZCl_4 + 4H_2O \rightarrow Z(OH)_4 + 4HCl$

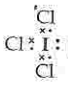
2 *briefly:*
(a) (i) +2 (ii) magnesium oxide
(iii) The high melting point indicates an ionic solid and the +2 oxidation state agrees with Group II.
(b) (i) +6 (ii) sulphur trioxide
(iii) The formula of ions agrees with sulphuric acid.
(c) (i) +1 (ii) sodium oxide
(iii) It must be an alkaline oxide of Group I to produce ammonia from ammonium salts.
(d) (i) +5 (ii) phosphorus(V) oxide
(iii) The mole ratio agrees with P_4O_{10} and H_3PO_4 has relative molecular mass of 98.

3 *briefly:*
(a) Gallium has a longer atomic radius as atomic radius increases down the Group.
(b) (i) Gallium's is smaller.
(ii) Gallium's is smaller.
(c) (i) Gallium's is smaller.
(ii) Gallium's is larger.
(d) (i) covalent bonds
(ii) +3
(iii) $GaCl_3 + 3H_2O \rightarrow Ga(OH)_3 + 3HCl$ (similar to aluminium chloride)
(e) (i) Ga_2O_3
(ii) amphoteric like Al_2O_3
(iii) Gallium oxide should have a lower lattice energy because Ga^{3+} ions are larger than Al^{3+} ions, so the

electrovalent bonds are weaker.

4 (a) (i) $Si(s) + 2Cl_2(g) \rightarrow SiCl_4(l)$
(ii) $SiCl_4$ would be hydrolysed by water:
$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$
(iii) phosphorus trichloride or sulphur chloride
(b) (i) SCl (ii) 135 (iii) S_2Cl_2
(iv) The chloride must have a molecular structure — the lattice particles must be covalently bonded S_2Cl_2 molecules.

5 (a) **A** and **I**
(b) (i) C_2 (ii) D (iii) G_2O_3
(iv) HCl_4
(c) element **E** (Group I element)
(d) (i) In **B**, two of the *p* electrons are paired so there is increased repulsion and one electron is more easily lost.
(ii) **A** is above **I** in the same group and has a smaller atomic radius, so its outer electrons are more strongly held.

(e) 

$\mathrm{Cl}\,{}^{\times}_{\cdot}\,\overset{\substack{\mathrm{Cl}\\ \times\cdot}}{\underset{\substack{\times\cdot\\ \mathrm{Cl}}}{\mathrm{I}}}\,:$ pyramidal shape because of 4 electron pairs

(f) element **E** (Group I oxide)

6 (a) *briefly:*
(i) Aluminium is a metal with delocalised electrons which can move throughout the metal and carry an electric current.
(ii) Sulphur is a non-metal and has a molecular structure. Its electrons are in fixed positions in the atoms and molecules and cannot move throughout the solid.
(b) (i) $SO_3 + 2OH^- \rightarrow SO_4^{2-} + H_2O$
(ii) $Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O$
The oxides of sulphur do not react with acids, though they will react with the water in hydrochloric acid. [Note: Equations could be written with 'NaOH' instead of ionic equations with OH^-.]

Descriptive Questions

1 Please refer to text

2 (a) $Q_2O + H_2O \rightarrow 2QOH$
$QOH + HCl \rightarrow QCl + H_2O$
(b) 39; so **Q** = potassium

3 (a) period 3
(b) Na Mg Al Si P Ar

5. (a) n = 5
(b) (i) y is a non-metal.
(c) (i) y is phophorus.

$YCl_n = PCl_5$

7 (b) (i) a = 2 b = 7
(ii) x is chlorine
(iii) Cl_2O_7
8. (d) (i) Mg_2 Cl_2 O
(ii) $MgCl_2$ MgO
(iii) Because it is hydrolysed
$MgCl_2.H_2O \rightarrow Mg(OH)Cl + HCl$

Exercise 12

Multiple Choice Questions

Section I

1 B 2 D 3 A 4 C 5 B
6 B

Section II

7 A

Structured Questions

1 (a) $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$
(b) (i) Barium carbonate is more stable.
(ii) The barium ion is larger and less able to polarise the carbonate ion.
(c) (i) $BaO + H_2O \rightarrow Ba(OH)_2$
(ii) No, because magnesium oxide is insoluble in water.
(d) (i) magnesium oxide
(ii) used to line the interior of furnaces
(iii) It has a very high melting point.

2 (a) (i) radium's is less
(ii) radium's is greater
(b) (i) it would react very vigorously, producing bubbles of hydrogen gas
(ii) $Ra + 2H_2O \rightarrow Ra(OH)_2 + H_2$
(c) (i) $Ra(NO_3)_2$
(ii) $2Ra(NO_3)_2 \rightarrow 2RaO + 4NO_2 + O_2$
(iii) radium stability increases down group as cation becomes larger

Descriptive Questions

1 *briefly:*
(a) Barium carbonate is more thermally stable as thermal stability increases down the Group [also see text].
(b) Reactivity of metals increases down the Group as standard electrode potentials become more negative, so barium rapidly corrodes in air.
(c) The thermal stability of beryllium nitrate is very low as it is at the top of Group II and thermal stability of nitrates decreases up the Group.

Exercise 13

Multiple Choice Questions

Section I

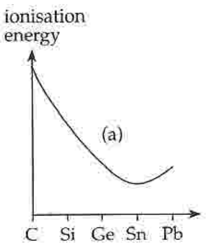
1 C 2 A 3 D 4 C 5 B
6 A 7 C 8 C

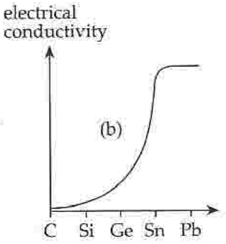
Section II

9 D 10 D

Structured Questions

1



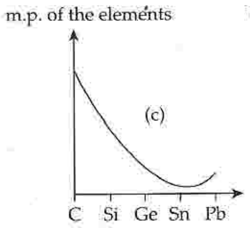


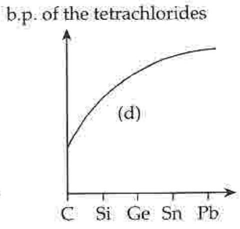
Atoms become larger so the outer electrons are less strongly held,

(a) hence electrons can be removed easily.

(b) hence electrons can be delocalised easily, and elements become better conductors.

(c) hence bonds with other atoms become weaker, and melting points decrease.





(d) Molecules become larger from CCl_4 to $PbCl_4$. Van der Waals forces increase, hence boiling points increase.

2 (a) Germanium should have a lower ionisation energy because ionisation energy decreases down the Group as atoms become larger and outer electrons become less strongly held by the nucleus.

(b) (i) GeO_2

(ii) Germanium should be like silicon and tin — the +4 oxidation state of Ge in GeO should be more stable than the other oxidation states.

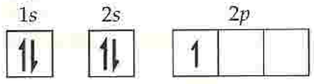
(iii) giant molecular with covalent bonds — like SiO_2

(c) (i) tetrahedral shape because of 4 electron pairs around the germanium atom

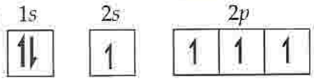
(ii) $GeCl_4 + 2H_2O \rightarrow GeO_2 + 4HCl$

Descriptive Questions

1 (a) (i)



(ii)



(b) To form electrovalent bonds, four electrons must be lost or gained to obtain a stable ion. This requires a large amount of energy.

Carbon forms the C^{4-} ion in a few compounds. However this is not very stable because of repulsion between the eight outer electrons in a small anion.

(c) (i) CO_2 is molecular; only weak Van der Waals forces exist between the molecules. SiO_2 has a giant covalent structure; strong covalent bonds must be broken to melt it.

(ii) Si—Si covalent bonds are weaker than C—C covalent bonds.

2 (a) It should conduct electricity well as it should be a metal like lead.

(b) Tetrahedral shape. Very unstable to heat. The thermal stability of tetrachlorides decreases down the group, because

— the +4 oxidation state becomes less stable than the +2 state;

— the covalent bonds become weaker as atoms become larger.

(c) UnqO (like PbO); UnqO should dissolve in nitric acid to produce a solution of $Unq(NO_3)_2$:

$$UnqO(s) + 2H^+(aq) \rightarrow Unq^{2+}(aq) + H_2O(l)$$

(d) A white precipitate of $Unq(OH)_2$ should be formed:

$$Unq^{2+}(aq) + 2OH^-(aq) \rightarrow Unq(OH)_2(s)$$

The precipitate should dissolve in excess NaOH to give a colourless solution:

$$Unq(OH)_2 + 2OH^- \rightarrow UnqO_2^{2-} + 2H_2O$$

This should happen as the oxide and hydroxide of unquadium should be amphoteric like lead oxides.

(e) More negative. Unq atoms should be larger than lead atoms — thus the outer electrons would be less strongly held.

3 Please refer to text

4 (a) *briefly:* Lead — metallic; lead(IV) chloride — covalent; lead(II) chloride — ionic. The low melting point of $PbCl_4$ is due to weak Van der Waals forces between the molecules. Metallic and electrovalent bonds are stronger and so the melting points of lead and lead(II) chloride are much higher.

(b) The +4 oxidation state of lead is less stable than the +2, so lead(IV) oxide decomposes into oxygen and the more stable lead(II) oxide. The +4 state of tin is more stable than the +2 state so tin(IV) oxide does not decompose.

(c) The two redox potentials are:

$$Pb^{2+} + 2e^- \qquad Pb;\ E^{\leftarrow} = -0.13\ V$$

$$O_2 + 2H_2O + 4e^- \qquad 4OH^-;\ E^{\leftarrow} = +0.40$$

So $2Pb + O_2 + 2H_2O \rightarrow 2Pb^{2+} + 4OH^-;\ E^{\leftarrow} = +0.53\ V$

The Pb^{2+} and OH^- ions then combine together to give a precipitate of $Pb(OH)_2$. From the equation, the water must contain dissolved oxygen (from air) for the reaction to take place.

5 Please refer to text

Exercise 14

Multiple Choice Questions

Section I

1 B *2* C *3* D *4* D *5* B
6 C *7* B *8* D *9* C

Section II

10 B *11* A *12* B

Structured Questions

1 (a) At_2; $6s^2 6p^5$; about 230°C; about 0.237 nm; about 880 kJ mol^{-1}; about 2.2

(b) (i) black solid
    (ii) Lowest lattice energy as At^- ion is very large.
    (iii) HAt; it would easily decompose on heating.
    (iv) $HAt + H_2O \rightarrow H_3O^+ + At^-$

Descriptive Questions

1 *briefly:*
  (a) hydrogen bonding in liquid HF
  (b) Concentrated H_2SO_4 oxidises Br^- to Br_2.
  (c) HI decomposes when heated strongly due to a relatively weak H—I covalent bond.

2 (a) $NaClO = +1$
  $CCl_4 = -1$
  $NaClO_3 = +5$
  $NaClO_4 = +7$

  (c) (ii) $KMnO_4 : KI$ as 2 : 1
    (iii) Final oxidation number of iodine is +5.

Exercise 15

Multiple Choice Questions

Section I

1 B 2 A 3 B 4 A 5 B
6 D

Section II

7 B 8 D 9 A

Structured Questions

1 (a) (i) A lot of heat energy is needed to break the strong covalent triple bond in N_2.
    (ii) Mg_3N_2
    (iii) ionic
  (b) (i) magnesium hydroxide
    (ii) $Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$

2 (a) NH_3: −3; NO_2: +4; N_2H_4: −2
  (b) (i) NO
    (ii) A large amount of energy is required to break the strong N N bond before the products can be formed.
    (iii) NO_2
    (iv) The reaction of NO with O_2 to produce NO_2 is reversible and exothermic. A low temperature is needed to favour the forward reaction to produce NO_2.

  (c) $2NO_2 + \frac{1}{2}O_2 + H_2O \rightarrow 2HNO_3$

  (d) $N_2H_4 + H_2 \rightarrow 2NH_3$; $\Delta H = -142$ kJ
  (e) $N_2H_4 + H_2O \rightarrow N_2H_5^+ + OH^-$

3 (a) (i) iron
    (ii) nitrogen from air, hydrogen from petroleum
    (iii) air
    (iv) No more ammonia can be made from the equilibrium mixture until it is removed.
  (b) (i) 200°C produces a larger percentage of ammonia. The reaction is too slow below 500°C.
    (ii) 150 atmospheres. A very high pressure requires expensive pumps and extra thick pipes and containers.

4 (a) (i) $Fe^{2+} + NO_3^- + 2H^+ \rightarrow Fe^{3+} + NO_2 + H_2O$
    (ii) $E^{\leftarrow} = +0.04$ V
  (b) (i) It oxidises iron(II) in haemoglobin [see text].
    (ii) from the excessive use of nitrogen fertilizers
  (c) NO_2^+

6 (e) (iii) $2.4dm^3$

7 Please refer to text

8 Please refer to text

Descriptive Questions

2 (a) Please refer to text
  (b) Please refer to text
  (c) (ii) 0.16g

Exercise 16

Multiple Choice Questions

Section I

1 B 2 B 3 C 4 C 5 A
6 B 7 B 8 D 9 B 10 D
11 B 12 A

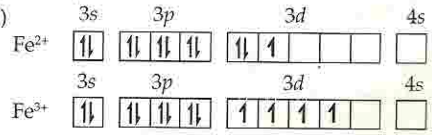
Section II

13 B 14 B 15 D 16 C 17 A
18 C

Structured Questions

1 (a) Please refer to text
  (b) Compared with calcium, copper has
    (i) higher first ionisation energy;
    (ii) higher density;
    (iii) higher melting point;
    (iv) smaller ionic radius.
  (c) variable oxidation states
2 (a) Please refer to text
  (b) +4
  (c) (i) it has a lone pair of electrons
    (ii) $[TiCl_6]^{3-}$
  (d) (i) the water ligands splitting the energy of the 3*d* orbitals into two groups; electrons absorb light in moving from the low energy to high energy 3*d*
    (ii) they have no *d* electrons

3 (a) (i) cobalt; 27
    (ii)



(b) (i) *briefly:* The transition elements have higher nuclear charges so the outer 4*s* electrons are pulled inwards by the greater attractive force.

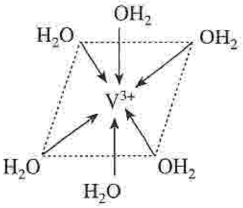
(ii) see textttractive force.

(ii) Please refer to text

4 (a)

3*s*	3*p*			3*d*					4*s*
↑↓	↑↓	↑↓	↑↓	↑	↑				

(b) octahedral shape



(c)

VO_2^+	V^{2+}	VO^{2+}
+5	+2	+4

(d) (i) oxidation state +3

(ii) The solution would change colour from yellow to blue and then to green. A pale yellow precipitate of sulphur would be formed.

(iii) Dilute acid must be added for the reaction to occur as the VO_2^+ ions require H^+ for reduction.

5 (a) (i) reaction **E** (ii) reaction **C**

(b) (i) aqueous sodium hydroxide

(ii) high concentration of OH^- pushes equilibrium to left

(c) (i) yellow to orange

(ii) $2CrO_4^{2+} + 2H+ \rightarrow Cr_2O_7^{2-} + H_2O$

(d) zinc and sulphuric acid

6 (a)

	3*s*	3*p*			3*d*					4*s*	4*p*		
Co^{2+}	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	↑				

	3*s*	3*p*			3*d*					4*s*	4*p*		
Co^{3+}	↑↓	↑↓	↑↓	↑↓	↑↓	↑	↑	↑	↑				

(b) (i) pink (ii) blue

(iii) The enthalpy change of reaction, ΔH, for the forward reaction is endothermic.

(c) (i) $[Co(NH_3)_6]^{2+}$ because the $E^{\leftarrow} = +0.44$ V for the reaction; $[Co(CN)_6]^{4-}$ because the $E^{\leftarrow} = +1.34$ V for the reaction.

(ii) It turns pink as it oxidises water to oxygen gas.

7 (a) (i) $E^{\leftarrow} = +1.11$ V

(ii) The green colour would change to purple and a brown precipitate would be formed.

(iii) Mn is oxidised to MnO_4^- from MnO_4^{2-} (oxidation number increases from +6 to +7). Mn is reduced to MnO_2 from MnO_4^{2-} (oxidation number decreases from +6 to +4).

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

(b) Please refer to text

Descriptive Questions

1 Please refer to text

2 (a) Please refer to text

(b) *briefly:*
$[CuCl_4]^{2-}$ contains copper(II) ions, so electrons can move between the split 3*d* orbitals.
$[CuCl_4]^{3-}$ contains copper(I) ions, so the 3*d* is full. Hence no electrons can move between the split 3*d* orbitals.

(c) K_2FeO_4; contains tetrahedral FeO_4^{2-} ion; oxidation state of iron = +6

Exercise 17

Multiple Choice Questions

Section I

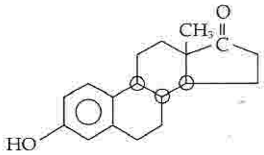
1	A	2	D	3	D	4	C	5	C
6	C	7	B	8	A				

Section II

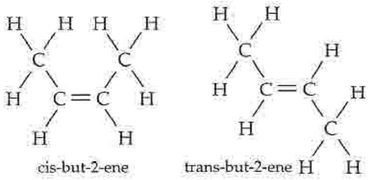
9	A	10	D	11	D	12	B	13	B

Structured Questions

1 (a)



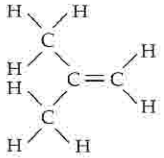
2 (a)



cis-but-2-ene trans-but-2-ene

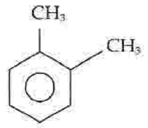
(b) The C C bond cannot be rotated.

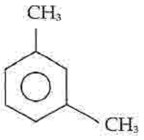
(c) 2-methylpropene



(d) They all have different boiling points.

3 (a)

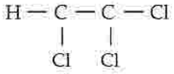




(b) (i) one

(ii) 1,1,2-trichloroethane

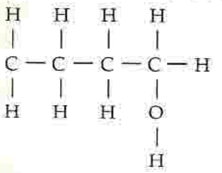
(iii) by fractional distillation

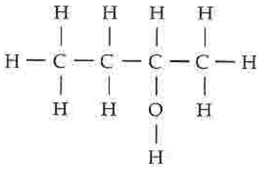


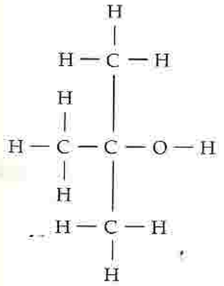
4 (a) (i) **C** (ii) **G** (iii) **B**
(iv) **E** (v) **G** (vi) **A**
(b) **A and C**
(c) **B**

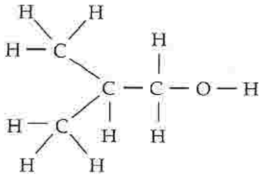
Descriptive Questions

1 (a) Please refer to text for *structural isomerism*





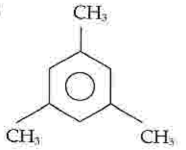




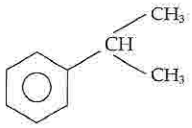
(b) The other functional groups are: amine (—NH_2); acid (—CO_2H); ester (—CO_2CH_3); benzene ring (—C_6H_5)
Optical isomerism (it has a chiral centre).

2 (a) Please refer to text
(b) (i) optical isomerism
(ii) cis-trans isomerism *and* optical isomerism
(iii) *neither* optical *nor* cis-trans isomerism

3 (a) empirical formula = C_3H_4;
molecular formula = C_9H_{12} (M_r = 120)
(b) (i)



(ii)



Exercise 18

Multiple Choice Questions

Section I

1 C 2 B 3 B 4 B 5 B
6 A 7 C 8 A

Section II

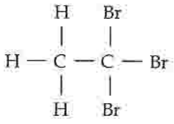
9 A 10 A 11 A 12 D 13 A
14 D

Structured Questions

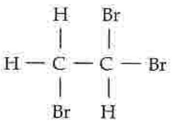
1 Please refer to text

2 (a) $C_2H_6 + Br_2 \rightarrow C_2H_5Br + HBr$
(b) (i) a particle with an unpaired electron
(ii)

(c) With light: a photon breaks the Br—Br bond.
(d) $C_2H_5\cdot + C_2H_5\cdot \rightarrow C_2H_5—C_2H_5$
(e) (theoretically) C_2Br_6
(f)

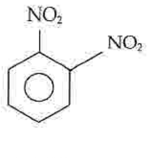


1, 1, 1-tribromoethane



1, 1, 2-tribromoethane

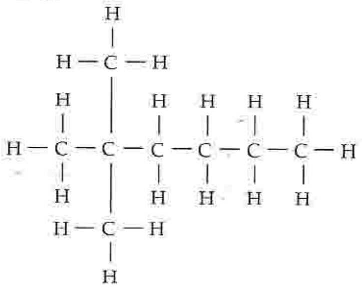
3 (a) (i) $C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O$
(ii) mixture of concentrated H_2SO_4 and concentrated HNO_3 below 60°C
(iii) electrophilic substitution
(b) (i) $HNO_3 + 2H_2SO_4 \rightarrow 2HSO_4^- + NO_2^+ + H_3O^+$
(ii) NO_2^+, an electrophile
(c)



1, 2-dinitrobenzene

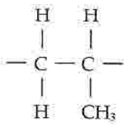
1, 4-dinitrobenzene

4 (a) (i) C_8H_{18}
(ii)

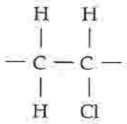


(iii) $C_8H_{18} + 12\frac{1}{2}O_2 \rightarrow 8CO_2 + 9H_2O$
(iv) $CH_3—CH_2$
(b) (i) nitrogen (from air)
(ii) carbon monoxide, hydrocarbons and hydrogen
(iii) The radicals from lead tetraethyl have stopped the combustion.
(iv) lead(II) bromide and nitrogen oxides [see text for harmful effects]

5 (a) (i)



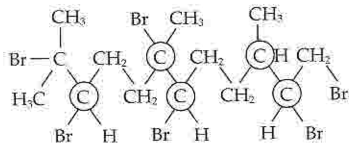
(ii)



(b) (i) They are not biodegradable and hence cause pollution.
(ii) poly(propene) + oxygen → carbon dioxide + oxygen
(iii) Acidic hydrogen chloride would be produced.

6 (a) benzene: electrophilic substitution;
cyclohexene: electrophilic addition;
cyclohexane: free radical chain reaction
(b) (i) cyclohexene
(ii) cyclohexane requires light (eg sunlight);
[see text for benzene]

7 (a)

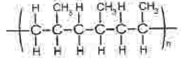


(b) (i) 1.2 g (ii) 13.44 dm^3

8 (a) C_3H_6 (b) Dehydration of either propan 1-o1 or 2-o1

(d) (i) Addition polymerization

(ii)



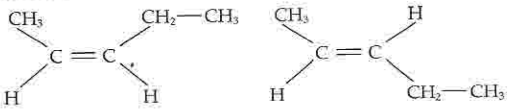
(iii) To manufacture ropes.

9 (b) electrophilic addition reaction

10 (a) Only III

Descriptive Questions

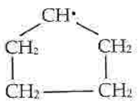
1 (a)



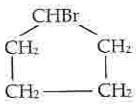
The isomers exist because the C=C bond cannot be rotated.

(b) *for* **W**: (i) The mechanism is free radical substitution.

(ii)

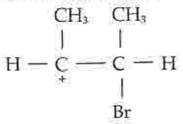


(iii)

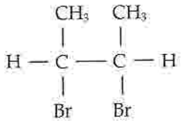


for **X**: (i) The mechanism is electrophilic addition.

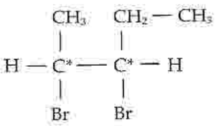
(ii)



(iii)



(c)



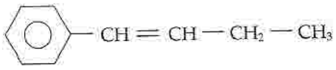
2

reaction	*reagents*	*conditions*
(a)	alkaline $KMnO_4$	cold
(b)	concentrated HNO_3, concentrated H_2SO_4	below 60°C
(c)	chlorine	UV light
(d)	chlorine	UV light
(e)	H_2SO_4, $KMnO_4$	boil for a few hours

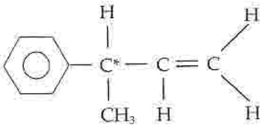
3 (a) 132; $C_{10}H_{12}$

(b) The other acid is CH_3CH_2—COOH;

P is



(c)



4 (b) They are mixtures of hydrocarbons the liquid ones dissolves the solid hydrocarbon with the higher relative molecular mass and the gaseous ones with lower R.M.M.

(c) (i) It is not volatile, it consists of a thick, viscous liquid

(ii) fractional distillation.

(d) (i) cracking, by passing the vapours of the hydrocarbons over a hot catalyst.

(ii) one of the many equation is :

$$C_{13}H_{38} \rightarrow 3C_2H_4 + C_3H_6 + C_4H_{10}$$

(iii) C_2H_4 and C_3H_6

5 (a) (i) -360 kJ

(ii) Benzene is not a cyclic triene but it is more stable because the ring has a delocalized π systems.

(ii) Electrophilic Substition reaction.

6 (a) (i) Electrophilic addition reaction.

(ii)Elimination reaction.

(c) $CH_3CHClCH_2CH_3$ $CH_2ClCH_2CH_3$

2 – Chlorobutane 1 – Chlorobutane

Exercise 19

Multiple Choice Questions

Section I

1 A 2 B 3 D 4 C 5 B

6 D

Section II

7 A 8 D 9 A 10 D

Structured Questions

1 (a) The slow rate determining step involves the fissioning of only one molecule of reactant.

(b) (i) the chlorocompound would react more slowly

(ii) the C—Cl bond is stronger than the C—Br and harder to break

(c) I-Bromo, 2 methyl propane.

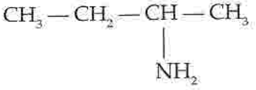
(d) (i) $CH_3CH_2CH_2CH_2Br + CN^- \rightarrow$

$CH_3CH_2CH_2CH_2CN + Br^-$

(ii) nucleophilic substitution

(iii) $CH_3CH_2CH_2CH_2COOH$

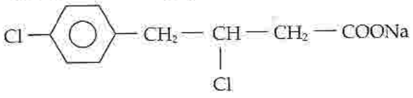
(f)



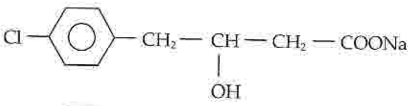
$$CH_3-CH_2-\underset{\underset{NH_2}{|}}{CH}-CH_3$$

2 (a) (i) atom I (ii) atom III

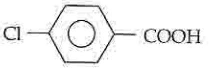
(b) (i)



(ii)

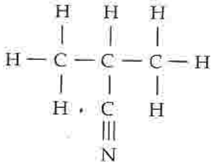


(iii)



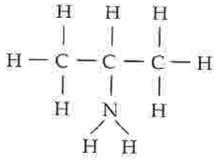
3 (a) aerosol propellants or refrigerants.
  (b) Because it is chemically inert.
  (c) (i) by the action of ultraviolet light from the sun
    (ii) (ii) propanamide, $CH_3CH_2CONH_2$
      phenylpropanoate, $CH_3CH_2COOC_6H_5$
  (d) $Cl\cdot + Cl\cdot \rightarrow Cl_2$
    or $\cdot CFCl_2 + \cdot CFCl_2 \rightarrow CFCl_2{-}CFCl_2$
  (e) from the decomposition of O_2 by light
  (f) Chlorine atoms (Cl·) can destroy the ozone layer so dangerous ultraviolet light could reach the Earth's surface. This light can damage crops and cause skin cancer in people.

4 (a) (i)



$$\begin{array}{ccccccc} & & H & & H & & H & \\ & & | & & | & & | & \\ H & - & C & - & C & - & C & - H \\ & & | & & | & & | & \\ & & H & \cdot & C & & H & \\ & & & & ||| & & & \\ & & & & N & & & \end{array}$$

(ii)



$$\begin{array}{ccccccc} & & H & & H & & H & \\ & & | & & | & & | & \\ H & - & C & - & C & - & C & - H \\ & & | & & | & & | & \\ & & H & & N & & H & \\ & & & & / \ \backslash & & & \\ & & & & H \quad H & & & \end{array}$$

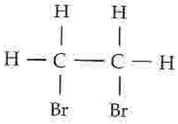
  (b) (i) nucleophilic substitution
    (ii) elimination
    (iii) electrophilic addition
  (c) (i) The number of carbon atoms in the molecule has increased.
    (ii) cyanide ion, CN^-
  (d) lithium aluminium hydride
  (e) (i) boiling dilute sulphuric acid
    (ii) $CH_3CH(CN)CH_3 + 2H_2O \rightarrow$
      $CH_3CH(COOH)CH_3 + NH_3$

5 (a) The slow rate determining step involves the fissioning of only one molecule of reactant.
  (c) I-Bromo, 2 methyl propane.

Descriptive Questions

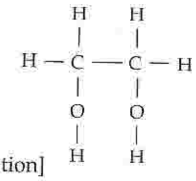
1 (a) boil with aqueous NaOH
  (b) boil with KCN in alcohol, then with dilute H_2SO_4
  (c) boil with KCN in alcohol, then reduce with $LiAlH_4$
  (d) boil with aqueous NaOH, then heat with hot concentrated H_3PO_4 and add bromine

2 (a) **X** is $C_2H_4Br_2$.
  (b) **X** is



$$\begin{array}{ccccc} & & H & & H & \\ & & | & & | & \\ H & - & C & - & C & - H \\ & & | & & | & \\ & & Br & & Br & \end{array}$$

Y is



$$\begin{array}{ccccc} & & H & & H & \\ & & | & & | & \\ H & - & C & - & C & - H \\ & & | & & | & \\ & & O & & O & \\ & & | & & | & \\ & & H & & H & \end{array}$$

[Please refer to text for explanation]

3 (a) PCl_5 or $SOCl_2$ at room temperature.
  (c) (ii) propanamide, $CH_3CH_2CONH_2$
    phenylpropanoate, $CH_3CH_2COOC_6H_5$

Exercise 20

Multiple Choice Questions

Section I

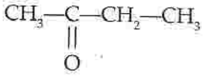
1	A	*2*	D	*3*	B	*4*	A	*5*	B
6	D	*7*	C	*8*	D	*9*	A	*10*	D
11	A	*12*	C						

Section II

13	D	*14*	C	*15*	B	*16*	B

Structured Questions

1 (b) (i) X has four different groups attached to a carbon atom
    (ii) X conatins $CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH^-}}$ or $CH_3{-}\underset{\displaystyle O}{\underset{||}{C^-}}$
    (iii) X must be a secondary alcohol which is oxidised to a ketone
  (c) (i) is butan-2-ol, $CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_2{-}CH_3$
    (ii)

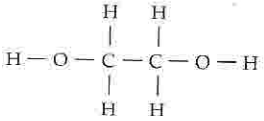


$$CH_3{-}\underset{\displaystyle O}{\underset{||}{C}}{-}CH_2{-}CH_3$$

    (iii) $(CH_3)_3C{-}OH$ (tertiary alcohol)

2 (a) (i) propene
    (ii) propan-1-ol
    (iii) propanoic acid
    (iv) 1-bromopropane
    (v) propylethanoate
  (b) excess hot concentrated sulphuric or phosphoric acid
  (c) oxidation
  (d) (i) $CH_3COCl + CH_3CH_2CH_2OH \rightarrow$
      $CH_3CO_2CH_2CH_2CH_3 + HCl$
    (ii) ethanoic acid and a little concentrated sulphuric acid, reflux

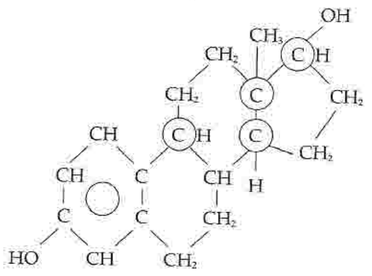
3 (a) empirical formula is CH_3O
  (b) 62
  (c) (i) $C_2H_6O_2$ (ii)



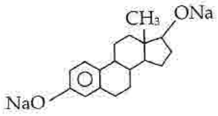
$$\begin{array}{ccccccccc} & & & & H & & H & & \\ & & & & | & & | & & \\ H & - & O & - & C & - & C & - & O - H \\ & & & & | & & | & & \\ & & & & H & & H & & \end{array}$$

  (d) 4.48 dm^3;
    $HO{-}CH_2{-}CH_2{-}OH + 2Na \rightarrow$
      $NaO{-}CH_2{-}CH_2{-}ONa + H_2$
  (e) (i) When heated with a mixture of potassium dichromate(VI) solution and sulphuric acid, compound **P** will be oxidised to HOOC—COOH.
    (ii) When heated with a mixture of sodium bromide and concentrated sulphuric acid, compound **P** will become $Br{-}CH_2{-}CH_2{-}Br$.

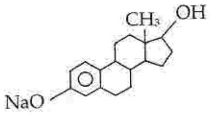
4 (a)



(b) (i)

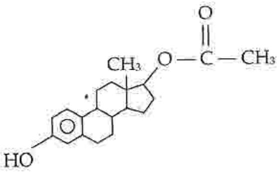


(ii)



(iii)

(iv)



5 (a) By dripping an ethanol/sodium dichromate mixture onto the hot dilute sulphuric acid.

(b) B : refluxed with a mixture of sodium dichromate and dilute sulphuric acid.
C : reduce ethanal with $NaBH_4$.

(c) (i) Fermentation of sugar solution.
Hydration of ethene.

(ii) Hydration of ethene because a purer form of ethanol is obtained.

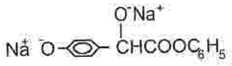
Descriptive Questions

1 (a) Heat ethanol with conc H_2SO_4.
(b) First dehydrate propan-1-ol into propene by heating with phosphoric acid. Then pass the propene into bromine.
(c) Mix butan-1-ol with ethanoic acid and a little concentrated H_2SO_4, and then boil for a few minutes.
(d) Boil ethanol with excess potassium dichromate(VI) and H_2SO_4.
(e) First boil 2-bromopropane with aqueous NaOH to make propan-2-ol. Then heat the propan-2-ol with potassium dichromate(VI) and H_2SO_4 to oxidise it to propanone.

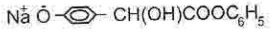
2 *briefly:*
(a) Add a little dilute H_2SO_4 and potassium dichromate(VI) solution to each compound and heat — butan-1-ol is oxidised so the dichromate changes colour from orange to green. The other compound is a tertiary alcohol and will have no effect.
(b) Add dilute NaOH and iodine solution to each compound, and warm — pentan-2-ol will give a yellow precipitate of CHI_3. Pentan-3-ol will give no reaction.

3 (b) (i) $CH_3CH_2CH_2CH_2OH$
$CH_3CH(OH)CH_2CH_3$
$CH_3CH(CH_3)CH_2OH$
$CH_3C(CH_3)(OH)CH_3$

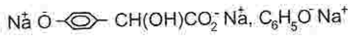
4 (a) (i)



(ii)

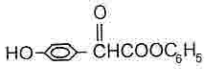


(iii)

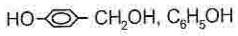


(iv)

(v)



(vi)



5 (a) The cumene process using benzene, propene and $AlCl_3$ as catalyst
$CH_3COOH > C_6H_5OH > CH_3OH$

Exercise 21

Multiple Choice Questions

Section I

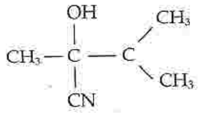
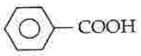
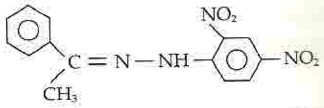
1 C	2 D	3 B	4 B	5 D
6 D	7 A	8 D	9 A	

Section II

10 A	11 D	12 B	13 A

Structured Questions

1

important conditions	organic product
slightly alkaline	
reflux	
boil	$CH_3—CH_2—COOH$
dilute HCl as catalyst	

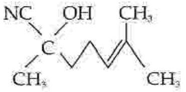
2 (a) (i) aldehydes and acids
(ii) ketones
(iii) none

(b)

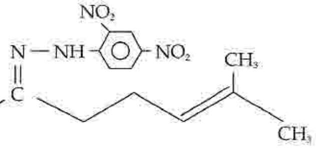
alcohol	tube X	tube Y
primary	solution changed from orange to green	yellow or orange precipitate
secondary	solution changed from orange to green	yellow or orange precipitate
	no change	no change

(c) (i) Fehling's solution *or* a mixture of silver nitrate solution and ammonia
   (ii) If Fehling's solution is used, a red-brown precipitate; if mixture of silver nitrate and ammonia is used, a precipitate of silver.
   (iii) no change

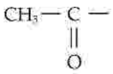
3 (a) (i) **A** would rapidly decolourise the bromine when shaken with it. **B** would not react.
   (ii) **A** would give a yellow precipitate of CHI_3. **B** would not react.
(b) no (the C = C has *two* CH_3 groups on one end)
(c) (i)



(ii)

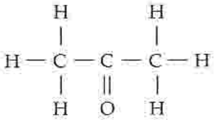


4 (a) C_3H_6O (b) C_3H_6O
(c) (i) CHI_3 (ii)



$$CH_3-\underset{\underset{O}{\|}}{C}-$$

(d)



$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\underset{\underset{O}{\|}}{C}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H$$

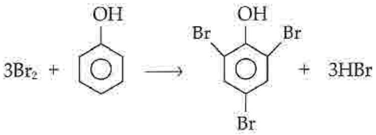
(e) Add 2,4-dinitrophenylhydrazine solution to **P**: a yellow/orange precipitate will be produced.
(f) React **P** with hydrogen cyanide and then reflux with dilute sulphuric acid.

6 (a) (iii) Zn/Hg conc. HCl (Clemensen reaction)

Descriptive Questions

1 *briefly:*

for phenol: Add aqueous bromine to each bottle. The bottle with phenol will give a white precipitate of tribromophenol and decolourise the bromine.



for propanal: Boil a little of each solution with silver nitrate and ammonia, $[Ag(NH_3)_2]^+$. Only propanal produces a shiny precipitate of silver metal.

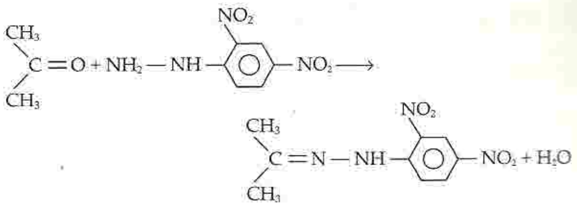
$$CH_3—CH_2—CHO + 2[Ag(NH_3)_2]^+ + H_2O \rightarrow CH_3—CH_2—COOH + 2Ag + 2NH_4^+$$

Fehling's solution can also be used.

for propan-2-ol: Heat a little of each solution with iodine and aqueous sodium hydroxide. Only propan-2-ol will give a yellow precipitate of triiodomethane, CHI_3.

[Note that solid PCl_5 cannot be used as a test for alcohols in this question. All the organic compounds are in aqueous solution, so the PCl_5 would react with the water.]

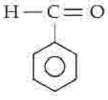
for pentan-3-one: Add 2,4-dinitrophenylhydrazine solution and a little hydrochloric acid to each solution. Warm. Only pentan-3-one will give an orange precipitate (propanal has already been eliminated above).



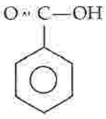
for phenylmethanol: Boil a little of each compound with alkaline $KMnO_4$. Then filter the products and acidify the filtrate with hydrochloric acid. Only phenylmethanol will give a white precipitate of benzoic acid.

2. *briefly:*
(a) **A** is butanone
(b) **B** is

C is



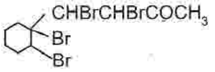
D is



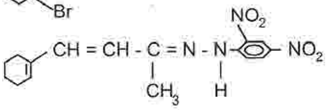
(c) **E** is

(d) **F** is $CH_3—CH_2—CHO$

3 (a) (i) Geometrical isomerism.
(b) (i)

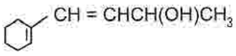


(ii)



(iii)

(iv)



4 (a) aqueous sodium hydroxide and aqueous iodine; yellow precipitate.

Exercise 22

Multiple Choice Questions

Section I

1 A	*2* D	*3* A	*4* B	*5* B
6 C	*7* C	*8* B	*9* C	*10* D
11 B				

Section II

12 A	*13* A	*14* B	*15* A

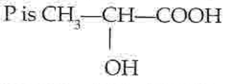
Structured Questions

1 (a) (i) propanone, $CH_3—CO—CH_3$
   (ii) propanoic acid, $CH_3CH_2CO_2H$
   (iii) propaneitrile, CH_3CH_2CN
   (iv) propanoyl chloride, CH_3CH_2COCl
(b) (i) reflux with mixture of sulphuric acid and potassium dichromate(VI) solution
   (ii) reflux with dilute sulphuric acid

(c) hydrolyse it by reflux with dilute hydrochloric acid

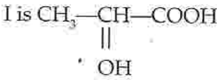
2 (a) (i) **W** is sodium benzoate, C_6H_5—COONa
(ii) **X** is benzoic acid, C_6H_5—COOH
(iii) **Y** is benzoyl chloride, C_6H_5—COCl
(iv) **Z** is ethylbenzoate, C_6H_5—$COOCH_2CH_3$
(b) it is a catalyst and increases yield of ester by absorbing water

3 (b) (i) **P** has 4 different groups attached to one carbon atom
(ii) **P** contains CH_3—CO— or CH_3—CH(OH)—
(iii) **P** is an acid, containing —COOH
(c) (i) an alcohol group and carboxylic acid group [note it cannot contain a carbonyl group as the empirical formula would not fit]
(ii) P is



$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-COOH$

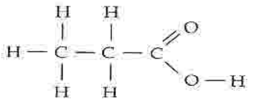
(d) (i) I is



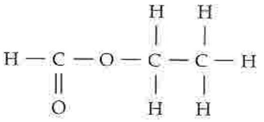
$CH_3-\underset{\displaystyle OH}{\underset{\|}{CH}}-COOH$

(ii) add 2,4-dinitrophenylhydrazine reagent; **Q** gives an orange precipitate.

4 (a) propanoic acid

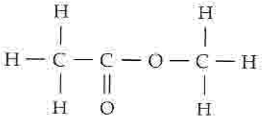


ethyl methanoate



$H-\underset{\displaystyle O}{\underset{\|}{C}}-O-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H$

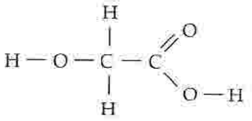
methyl ethanoate



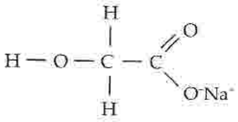
$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\underset{\displaystyle O}{\underset{\|}{C}}-O-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H$

(b) Warm separately the products of reactions A and B with iodine and aqueous NaOH. A yellow precipitate of CHI_3 will be produced by the ethanol in the products of reaction B.
The products of reaction A will *not* give a yellow precipitate.

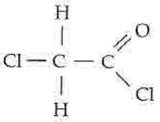
5 (a) $C_2H_4O_3$
(b) (i) 76 (ii)



(c) (i)

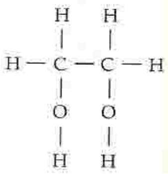


(ii)



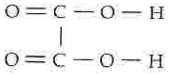
6 (a) (i) potassium dichromate(VI) and sulphuric acid
(ii) ethanoyl chloride
(b) (i) acylation (ii) neutralisation
(c) (i) *either* add aqueous bromine (the —OH group should decolourise the aqueous bromine as bromine atoms substitute onto the benzene ring) *or* add universal indicator (the —OH should give an acid pH)
(ii) *either* add 2,4-dinitrophenylhydrazine reagent (the —CHO group gives an orange precipitate) *or* heat with silver nitrate and ammonia (the —CHO group produces a precipitate of silver)
(d) Dispirin is ionic, aspirin is molecular.
(e) The direct route may be cheaper (**A** into **C**) because:
(i) CO_2 is cheaper compared to NaOH;
(ii) it is a one stage process, so less compound is lost (the more the stages, the less the final yield as some solid is lost at every stage).

7 (a) CH_3O
(b) (i) 62 (ii) $C_2H_6O_2$ (iii)



$H-\overset{\displaystyle H}{\underset{\substack{|\\ O\\ |\\ H}}{C}}-\overset{\displaystyle H}{\underset{\substack{|\\ O\\ |\\ H}}{C}}-H$

(c) (i)



$\begin{array}{l} O=C-O-H \\ \quad\;\, | \\ O=C-O-H \end{array}$

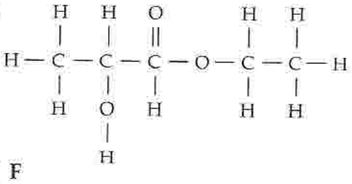
(ii) $5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$

8 (b) Decreasing acidic sequence is:

$CCl_3COOH > CHCl_2COOH > CH_2ClCOOH > CH_3COOH$

Due to the electron withdrawing ability of the electronegative chlorine atom(s). But CH_3 is electron repelling.

9 (a) **W** - hot phosphoric acid or concentrated H_2SO_4;
X - potassium dichromate(VI) and H_2SO_4;
Y - sodium metal;
Z - phosphorus pentachloride.
(b) ethanoic acid
(c)



$H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\substack{O\\ |\\ H}}{C}}-\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle H}{C}}}-O-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-H$

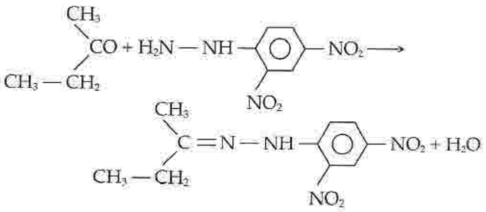
(d) **F**
(e) **B, C, D, E** and **F**
(f) (i) **A** (ii) **G** (iii) **E** (an acyl achloride)
(g) Addition of HCN then hydrolyse the product with boiling dilute H_2SO_4.

10 (a) $C_8H_{10}O$
(b) (i) 122 (ii) $C_8H_{10}O$
(c) alcohol, —OH
(d) (i) **Q** = C_6H_5—CH_2—CH_2OH
(ii) **R** = C_6H_5—CH_2—COOH
(iii) **S** = C_6H_5—CH = CH_2
(e) None do (none have a carbon atom attached to four different groups).

Descriptive Questions

1 *briefly:*

(a) Add 2,4-dinitrophenylhydrazine solution; butanone gives an orange precipitate (propanoic acid does not react):

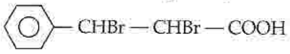


(b) Add silver nitrate solution; ethanoyl chloride gives a white precipitate of AgCl (chlorobutane does not react):
$CH_3COCl + H_2O + AgNO_3 \rightarrow CH_3COOH + AgCl + HNO_3$

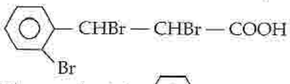
(c) Add water, and then dilute HCl; C_6H_5COCl produces a white precipitate of benzoic acid — the HCl helps to ensure precipitation by reducing the solubility of the benzoic acid (CH_3COCl reacts with water, but does not give a precipitate):
$C_6H_5COCl(l) + H_2O(l) \rightarrow C_6H_5COOH(s) + HCl(aq)$

(d) Add iodine and aqueous NaOH; a yellow precipitate of CHI_3 is produced by $CH_3COCH_2CH_3$ (the other compound does not give a precipitate).

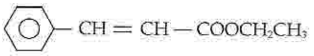
2 (a) (i) With bromine only, the product is



With bromine and iron catalyst, the product is

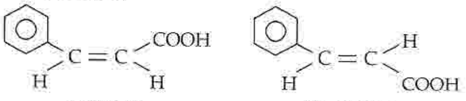


(ii) The product is



(Heat cinnamic acid with ethanol and a little H_2SO_4 catalyst.)

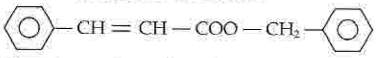
(b)



cis-isomer trans-isomer

The C=C bond cannot be rotated, so one isomer cannot be converted into the other.

(c)



The cinnamic acid can be made by boiling the ester with dilute H_2SO_4 or dilute NaOH. The ester is hydrolysed.

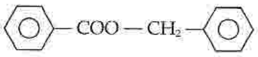
3 (a) *briefly:* Cl_3C—COOH (strongest); ClH_2C—COOH; CH_3—COOH (weakest)

(b) (i) Boil with aqueous NaOH, then heat with acidified dichromate(VI).

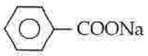
(ii) Boil with KCN in alcohol, then boil with dilute H_2SO_4.

(iii) Add HCN and then boil the product with dilute H_2SO_4.

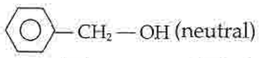
4 **P** is



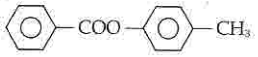
X is



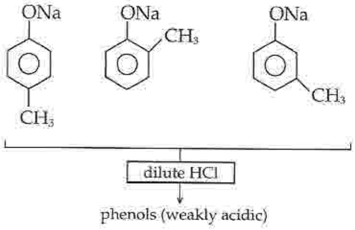
Y is



Q can be



Z can be



5 (a) (i) $CH_3COCl + H_2O \rightarrow CH_3COOH + HCl$

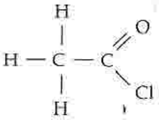
(ii) $CH_3COCl + CH_3CH_2OH \rightarrow CH_3COOCH_2CH_3 + HCl$

(iii) $CH_3COCl + C_6H_5$—$OH \rightarrow CH_3COO$—$C_6H_5 + HCl$

(iv) $CH_3COCl + C_6H_5$—$NH_2 \rightarrow$
CH_3CO–NH—$C_6H_5 + HCl$

(b) 0.628 g

6 (a) **P** is ethanoyl chloride:



CH_3—$COCl + H_2O \rightarrow CH_3$—$COOH + HCl$
HCl makes the solution strongly acidic.

(b) **Q** is an ester. It must be methyl benzoate. Methyl benzoate is hydrolysed by boiling aqueous NaOH:
C_6H_5—COO—$CH_3 + NaOH \rightarrow$
C_6H_5—$COO^-Na^+ + CH_3OH$
The sodium benzoate reacts with hydrochloric acid to produce **R** , which is benzoic acid (the white precipitate).

(c) M_r of **U** = 46 (using General Gas Equation). **S** must be an ester (because it produces two organic compounds in the reaction with hydrochloric acid). So **T** and **U** are an acid and an alcohol respectively.

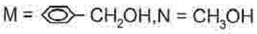
U must be ethanol (the only possible compound with M_r = 46). **T** would then be an acid with one carbon ie methanoic acid.

S is $HCOOCH_2CH_3$. Boiled with HCl:
$HCOOCH_2CH_3 + H_2O \rightarrow HCOOH + CH_3CH_2OH$

7 (a) C_3H_6O; $CH_3(CH_2)_4COOH$; **Z** is $CH_3(CH_2)_4CN$.

8 (a) CH_3OH, few drops of concentrated H_2SO_4 and refluxed.

(b) M =



(c) PCl_5 or $SOCl_2$

(d) L =

(f) (i) Hydrolysis.

(ii) sodium benzoate,
sodium phenoxide,

(iii) the phenol is displaced by the strong acid and distils over.

Exercise 23

Multiple Choice Questions

Section I

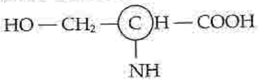
1 A 2 C 3 D 4 D 5 A
6 D 7 D 8 D 9 D 10 A
11 C 12 C 13 D 14 C

Section II

15 B 16 A

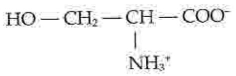
Structured Questions

1 (a)



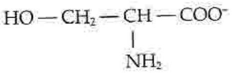
$HO-CH_2-\underset{NH}{\text{\textcircled{C}}}H-COOH$

(b) (i)



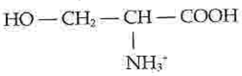
$HO-CH_2-\underset{NH_3^+}{CH}-COO^-$

(ii)



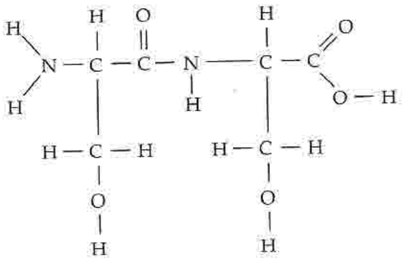
$HO-CH_2-\underset{NH_2}{CH}-COO^-$

(iii)



$HO-CH_2-\underset{NH_3^+}{CH}-COOH$

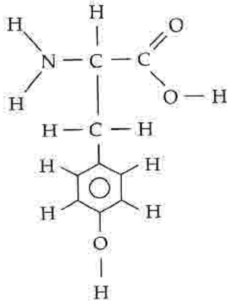
(c) (i)

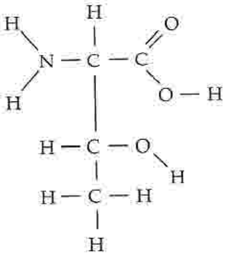


(ii) condensation

(iii) polypeptide or protein

2 (a)

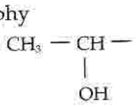




(b) (i) boil the dipeptide with dilute HCl

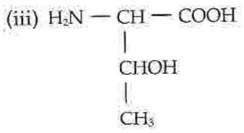
(ii) by chromatography

(c) (i) CHI_3 (ii)



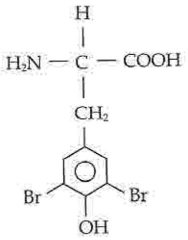
$CH_3-\underset{OH}{CH}-$

(iii)

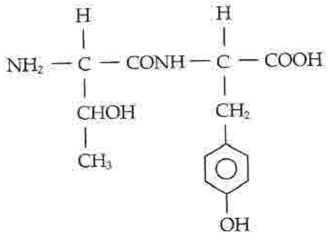


$H_2N-\underset{\underset{CH_3}{CHOH}}{CH}-COOH$

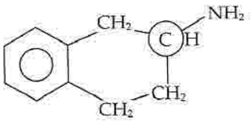
(d)



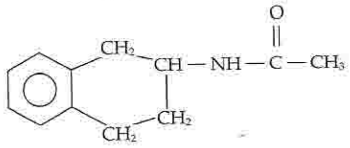
(e)



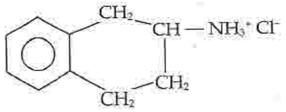
3 (a)



(b)

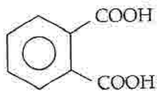


(c) (i)

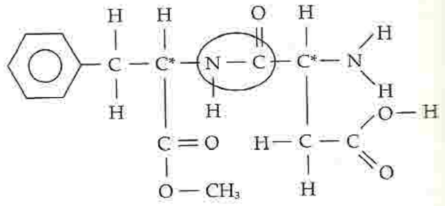


(ii) The —NH_2 group accepts a proton from the acid to form —NH_3^+.

(d)



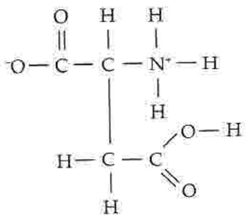
4 (a) and (b)



(c) (i) reaction with water
(ii) boiling with aqueous hydrochloric acid
(iii) methanol

(d) Use a drop of the drink in a paper chromatography experiment. The chromatogram should show two spots due to amino acids if they are present.

(e)



5 (a) (i) C_3H_9N

(ii) A=$CH_3CH_2CH_2NH_2$, propylamine

(b) (ii) B is propan 1-ol, $CH_3CH_2CH_2OH$

(c) (ii) propyl ammonium chloride: $CH_3CH_2CH_2NH_3Cl^-$

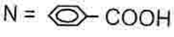
6 (a) (i) Step I: $LiAlH_4$ in dry ether

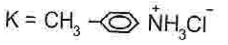
(ii) Step II: CH_3COCl

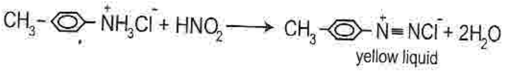
(b) the lone pair on the nitrogen of the -NH_2 group accepts protons

7 (a) The phenyl ring, 

The amide group, —CONH—

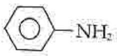
(b) (ii) 



(c) (i) 

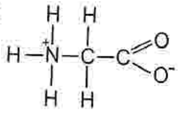
Descriptive Questions

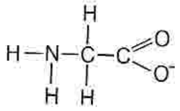
1 (a) Compound **A** is CH_3—CO—NH_2.
(b) Compound **B** is N_2N—CH_2—COOH
(c) Compound **C** is nitrobenzene C_6H_5—NO_2.
Compound **E** is phenylamine

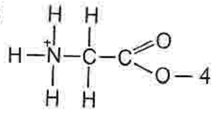
2 (a) add aqueous bromine;  gives a white precipitate

(b) **P** is . 

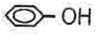
First, reflux the dinitrobenzene with tin and hydrochloric acid. Then add ethanoyl chloride to the pure **P**.

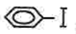
3 (a) (ii) 

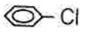
(b) (i) 

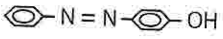
(ii) 

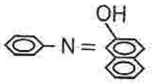
4 (a) 

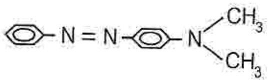
(b) (i)  , phenol

(ii)  , iodobenzene

(iii)  , chlorobenzene

(d) (i) 

(ii) 

(iii) 

Exercise 24

1. Please refer to text

2. Please refer to text

3. (a) Fibrous proteins serves as the chief structural materials of animals tissues. Their main functions are related to their insolability in water and fiber-forming tendency.
Examples:
(i) Keratin in skin, nail hair, feathers, wool etc.
(ii) Collagen in tendons.
(iii) Myosin in muscles.

(b) Globular proteins are involved in the maintenance of the body. They regulate life processes. This is due to their relative more solubility in water. They make up all the enzymes, many hormones such as insulin.

5. This is because the linkages within the fibres undergo hydrolysis with the attacking agents in the washing powder. These attacking agents may be nucleophiles or even electrophiles and enzymes.

6. Please refer to text

7. Two different RNA strands would be formed. Therefore they would call for different set of amino acids to build the protein.

8. Please refer to text

9. Please refer to text

10. Please refer to text

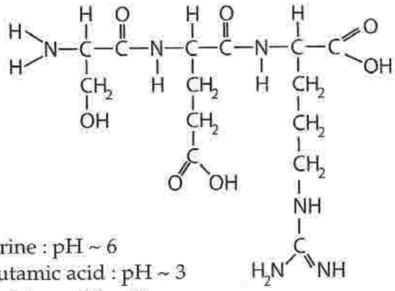
Exercise 25

1. (a) Please refer to text
(b) (i) aminoethanoic acid moves slightly towards the anode.
(ii) aspartic acid moves faster towards the anode.
(iii) tyrosine will move towards the anode faster than (i) but less rapidly than (ii).
(c) separation of a mixture of metal cations by dissolving an

alloy in acid and separation of DNA fragments in 'DNA finger printing'

2. (a) it contains both a basic group, -NH_2 and an acidic group – CO_2H.

(b)



(c) Serine : pH ~ 6
glutamic acid : pH ~ 3
arginine : pH ~ 10

3. Please refer to text

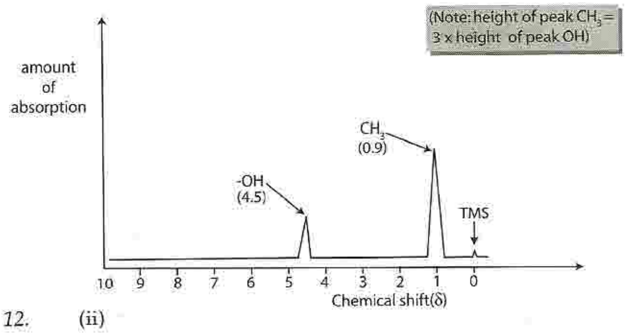
4. (a) Copper, nickel, zinc
(b) brass
(c) silver (it is made of cuprorickel)
(d) in case of error with one drop
(e) (i) 0.6
(ii) using a different solvent.

6. (c) (ii) 9.52g (iii) 9.92g

7. (c) (i) 4.50g (ii) 5.20g

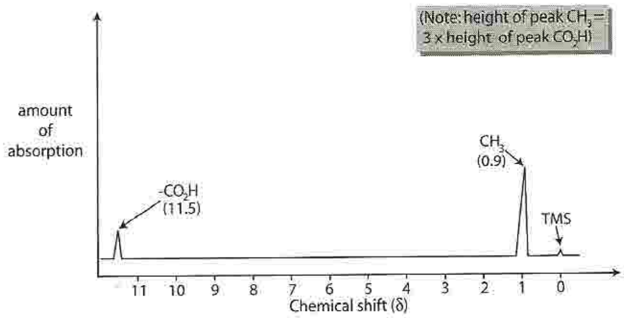
8. Please refer to text

12. (a) (i)



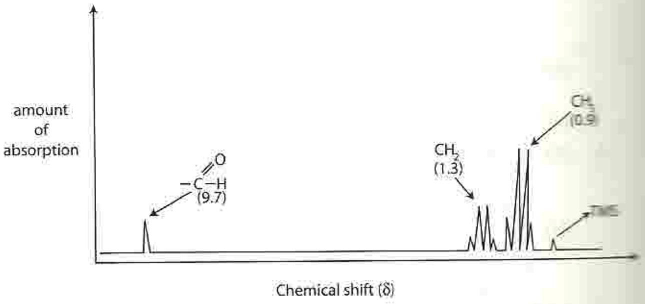
(Note: height of peak CH_3 = 3 x height of peak OH)

12. (ii)

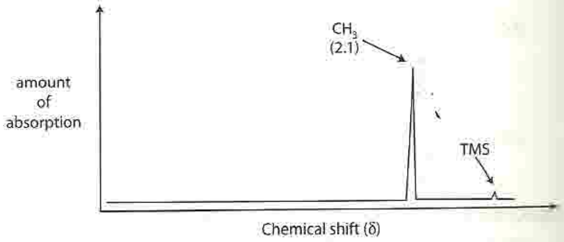


(Note: height of peak CH_3 = 3 x height of peak CO_2H)

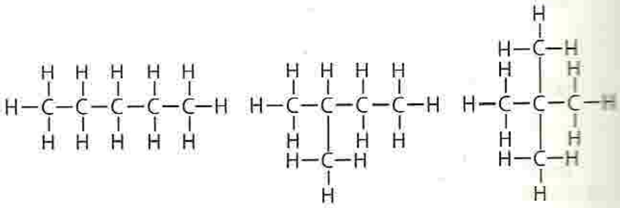
12. (iii)



12. (iv)

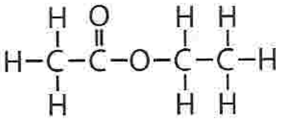


12. (b) (i)



12. (b) (ii) Absorption occurs at different chemical shift values

13. (a) $C_4H_8O_2$



Reason : $\underbrace{CH_3}_{\substack{\downarrow \\ \text{singlet} \\ \text{(2.0 ppm)}}}\ CO_2\ \underbrace{CH_2}_{\substack{\downarrow \\ \text{quartet} \\ \text{(4.1ppm)}}}\ \underbrace{CH_3}_{\substack{\downarrow \\ \text{triplet} \\ \text{(1.3 ppm)}}}$

14. Please refer to text

15. (a) (i) (M + 1) peak is used to determine the number of carbon atoms in the molecule.
(ii) (M + 2) peak indicates presence of Br-atom in the molecule.
(iii) (M + 4) peak indicates presence of 2 Br atoms in the molecule.

(b) 2 (i) Carry out the mass spectrograph of the ester. Use the molecular peak and the different fragments to identify the ester.

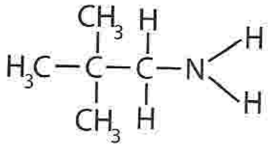
(ii) Carry out hydrolysis of the ester and study mass spectrograph of products of hydrolysis.

16. (b) $^{35}Cl_2O^+ : {}^{35}Cl^{37}ClO^+ : {}^{37}Cl_2O^+ = 9:6:1$

17. (a) (i) $C_5H_{13}N$

(ii) $-CH_2NH_2$

(b)



18.(a) (i) Peak I :

(ii) Bromine exists in two isotopic forms ^{79}Br and ^{81}Br in equal isotopic abundances. Therefore the peak M and M + 2 will have the same height.

(b) number of c-atoms = $\frac{0.21 \times 100}{6.0 \times 1.1}$ = 3.18 = 3

(c) (i) the molecular peak will be at 136 and 138.

(ii) the number of fragments will increase.

(d) Please refer to text

19. Please refer to text

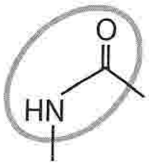
20. Please refer to text

Exercise 26

1. (a) (1) They replicate quickly giving a high viral population.

(2) They are constantly undergoing mutation.

(b)



(c) (i) The :NH_2 groups lone pairs nd they are protonated by the acid to form +vely charged ions which attract the polar water molecules.

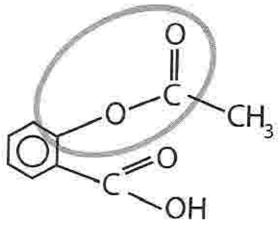
(ii) The O-H group forms H—bonds with water molecules.

(d) (i) Some drugs are decomposed by the acid medium of the stomach.

(ii) Water-solube drugs are not readily absorbed via the fatty tissue of the stomach wall.

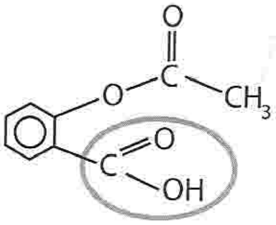
2. (a) $C_7H_6O_3$

(b)



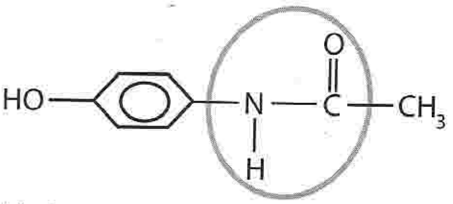
Ester group, pH=7

or



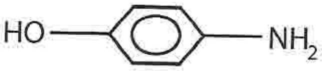
Carboxylic group pH=2-3

(c) (i)

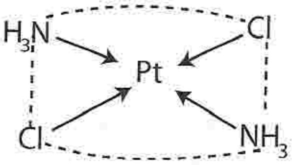


(ii) 4-hydroxyphenylamine

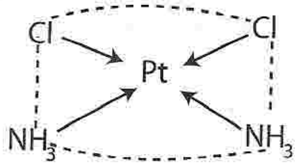
i.e



3. (a) (i)



Cis.



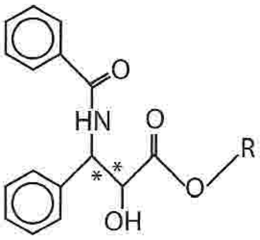
Trans.

(ii) The lone pair on the nitrogen atoms can form dative covalent bonds with the cisplatine.

The type of reaction is an acid/base reaction where lone pairs are shared.

(b) (i) A racemic mixture consists of an equimolar amount of the two enantiomers. The racemic mixture is then of no use as a disease treatement.

(ii) The racemic mixture is made to react with another optically active substance. The latter would bond with the unwanted enantiomers. Then the required chiral molecule can be isolated.



4. (a) Please refer to text

(b) (i) hydrogen bonds
(ii) When drawn into fibres intra-chain hydrogen bonds are broken and inter-chain hydrogen bonds are formed.
(iii) it has relatively high melting point.
(c) Nylon-6 will have a higher melting point.
(d) Please refer to text
(e) In making of fabrics, tents, cable covering, spectacle frames.

5. (a) (i) Please refer to text
(ii) Presence of double bonds helps in the formation of cross-links. When natural rubber, which is a viscous liquid is heated with sulphur, the latter establishes short links between the chains.
(iii) Molecules of rubber in bung absorb molecules of solvent. This causes the bung to swell.
(b) better packing.

6. Please refer to text

7. Please refer to text

8. Please refer to text

9. (a) Please refer to text
(b) Please refer to text

10. (a) unburnt hydrocarbons; carbon monoxide
(b) Please refer to text
(c) Please refer to text

11. (a) (i) they are not quickly destroyed in the environment and so reach the stratosphere where they can slowly destroy the ozone layer
(ii) much shorter as the hydrogen atoms make them more easily destroyed by the atmosphere (especially by OH· radicals)
(iii) HCFC-123 has less chlorine but also it contains H atoms so that it can be destroyed by OH· radicals in the air
(iv) it contains no chlorine so it cannot form Cl· radicals to destroy ozone
(b) (i) increased combustion of fossil fuels die to industrialisation
(ii) leakage of methane from natural gas wells and pipelines
(iii) CFCs are non-natural compounds which were only manufactured in the 20th century
(iv) a CFC molecule has many more bonds than $N_2O$and so is much more able to absorb infrared radiation

12. (a) carbon dioxide is produced from decay of organic material; methane is produced when carbon dioxide is reduced in anaerobic conditions
(b) advantage: saves expense of buying more oil to make new plastic (or reduces visual pollution and potential damage to fish when plastic items are thrown into the sea)
(c) The americium will remain radioactive and dangerous for thousands of years; over this time, due to land movement, water might reach the americium which could contaminate water supplies.
The americium should be removed from the smoke detectors first by a suitable chemical process, before disposal of the rest of the detector.
(c) They can be poisoned so that abnormal growth takes place or their reproductive organs are damaged.

13. (a) (i) removes bits of solid which can harbour poisonous chemicals
(ii) aluminium ions form aluminium hydroxide which binds with very fine particles to precipitate them
(b) metal ions such as Al^{3+} are absorbed by the ion-exhange resin, which releases other (harmless) ions in their place, such as H^+ or Na^+
(c) (i) $Cl_2(aq) + H_2O(l) \rightleftharpoons HClO(aq) + H^+ + Cl^-(aq)$ …..equilibrium 1
The HOCl molecules kill bacteria.
(ii) HClO from the equation in (i) ionises:
$HClO \rightleftharpoons H+ + OCl^-$ ….. equilibrium 2
The HClO molecule is much more effective than the OCl^- ion in killing bacteria. By Le Chatelier's Principle, if the pH is high, [H+] is reduced so the equilibrium 2 shifts to the right, reducing [HClO] and making the water less effective at killing bacteria. If the pH is low, [H+] is increased, but this shifts equilibrium 1 to the left, reducing the amount of HClO.
So the pH must not be too low nor too high.
(iii) Chlorine can substitute hydrogen atoms making poisonous chloro compounds.

14. (a) briefly: decay of organic material uses up oxygen; this can create anaerobic conditions (with a very high BOD), in which the CO_2 produced from the decay of organic material is reduced to CH_4.
(b) (i) $O\cdot + H_2O \rightarrow 2HO\cdot$
(ii) $\mathrm{H}\,\dot{\times}\,\underset{\cdot}{\ddot{\mathrm{O}}}\colon$
(iii) $CH_4 + 2NO + 2O_2 \rightarrow HCHO + 2NO_2 + H_2O$
(c) It is produced by the reaction of CH_4 and NO from car exhausts reacting with HO· radicals, which are a catalyst. The HO· radicals are initially produced by the action of sunlight on NO_2 molecules. So the reactions producing the smog do not occur in overcast conditions. Also, on bright days, the reactions do not start until the sun has risen high enough to provide the sunlight to produce the HO· radicals.
(d) This shows the HO radical is very reactive and is removed from the air so quickly that it is not present in the absence of bright sunlight

15. (a) Please refer to text

(b) Please refer to text

16. (a) (i) *briefly:* decaying organic material produces flammable methane gas
(ii) briefly: carcinogenic dioxins are produced if the temperature is not high enough
(b) Please refer to text

17. Please refer to text

Glossary

Glossary of Chemical Terms

This is a brief summary. For a fuller explanation of each term and for further examples, use the index to find the relevant section in the book.

Abundance, isotopic: The abundance of an isotope is the percentage of the isotope in the naturally occurring mixture of isotopes that an element consists of.
example: The abundance of ^{37}Cl is 24.5%. This means that 24.5% of the atoms in a sample of chlorine are ^{37}Cl (the other 75.5% are of the isotope ^{35}Cl).

Acid: An acid is a substance that donates hydrogen ions (protons).
example: In the reaction:

$$HCl + NH_3 \rightarrow NH_4^+ + Cl^-,$$

HCl is an acid because it gives a hydrogen ion to NH_3 to produce NH_4^+.

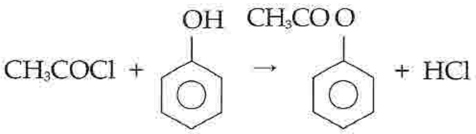
Acid dissociation constant, K_a: A weak acid, HA, ionises in water:

$$HA \rightleftharpoons H^+ + A^-$$

At equilibrium, $\frac{[H^+][A^-]}{[HA]}$ = a constant, K_a

Activation energy: The activation energy for a reaction is the *minimum* energy required for colliding particles to react.

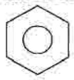
Acylation: Acylation is a reaction in which the R—CO— group of atoms is substituted into an organic compound.
example: Acylation takes place in the reaction of ethanoyl chloride with phenol:

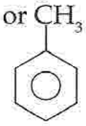


Addition reaction: An addition reaction is an organic reaction in which two or more molecules combine together to form a *single* molecule as the only product.
example: The reaction of ethene with steam to produce ethanol is an addition reaction:

$$CH_2{=}CH_2 + H_2O \rightarrow CH_3CH_2OH$$

Adiabatic system (thermodynamic): a closed sysytem that is thermally insulated from its surroundings.

Aromatic compounds: An aromatic compound is an organic compound containing a benzene ring.
examples: Benzene, C_6H_6 or  ; methylbenzene, CH_3—C_6H_5 or CH_3 are both aromatic compounds.



Aromatic hydrocarbons are also called *arenes*.

Avogadro constant, *L*: The Avogadro constant is the number of atoms in exactly 12 grams of carbon-12 (about 6 10^{23} atoms).

Azeotropic mixture: An azeotropic mixture is a mixture of two liquids which on boiling gives a vapour with the same composition as the boiling liquid.

Base: A base is a substance that accepts hydrogen ions (protons).
example: In the reaction:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-,$$

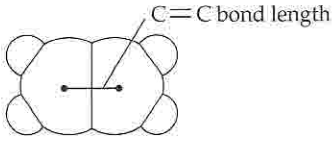
NH_3 is a base because it accepts a hydrogen ion from the H_2O to produce NH_4^+.

Biological oxygen demand (BOD): The amount of oxygen taken up by a sample of water. It is a measure of the organic matter present. Unpolluted water (free of dissolved organic matter) has a very low BOD

Bond energy: The bond energy is the amount of energy required to break the covalent bond between two atoms, per mole of bonds.
example: The bond energy for the H—Cl bond is 431 kJ. This amount of energy is absorbed in the reaction:

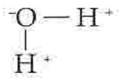
$$H{-}Cl \rightarrow H + Cl$$

Bond length: The covalent bond length is the distance between the nuclei of the two atoms in a covalent bond.
example: The C═C bond length is 0.134 nm. This is shown below in a molecule of ethene.



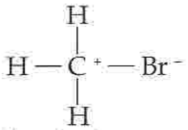
ethene molecule, C_2H_4

Bond polarity: In a covalent bond between atoms of different elements, the bond electrons are displaced towards the more electronegative atom. The more electronegative atom acquires a small negative charge (-) and the other atom acquires a small positive charge (+). The bond is then said to be *polarized*.
examples: The O—H bond in water and the C—Br bond in bromomethane are polarized:



$$\begin{array}{l} {}^{-}O - H^{+} \\ \;| \\ H^{+} \end{array}$$

oxygen is more
electronegative
than hydrogen



$$\begin{array}{c} H \\ | \\ H - C^{+} - Br^{-} \\ | \\ H \end{array}$$

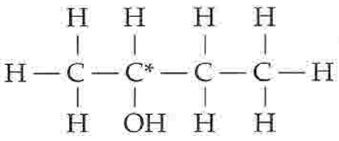
bromine is more
electronegative
than carbon

Buffer: A buffer solution is one which shows little change in pH when a small amount of acid or alkali is added to it.
example: A mixture of ethanoic acid and sodium ethanoate is a buffer. The CH_3COOH molecules act as an acid and neutralise additional alkali, and the CH_3COO^- ions from CH_3COONa act as a base and neutralise additional acid.

Catalyst: A catalyst is a substance that increases the rate of a chemical reaction without itself being chemically changed. A catalyst provides an alternative route for the reaction with a lower activation energy.

Chemical shift ( ): A measure of how much a proton n.m.r. absorption signal is displaced from TMS used as a standard with = 0.

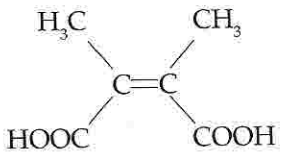
Chiral centre: A chiral centre in an organic compound is an atom which is bonded to four different groups of atoms. This results in the compound existing as two optical isomers.
example: The carbon atom marked with an asterisk (*) in butan-2-ol is a chiral centre:



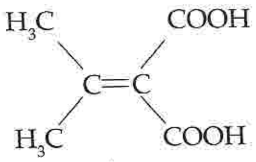
$$\begin{array}{ccccccccc} & & H & & H & & H & & H & \\ & & | & & | & & | & & | & \\ H & - & C & - & C^* & - & C & - & C & - & H \\ & & | & & | & & | & & | & \\ & & H & & OH & & H & & H & \end{array}$$

[Note: see *Optical isomers*]

Cis-trans isomers: Organic cis-trans isomers are different compounds with the same molecular formula. In such compounds, the groups attached to a C=C bond have different orientations.
example:

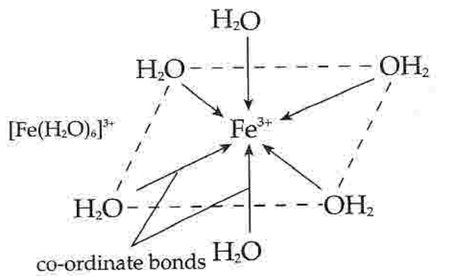


cis-isomer



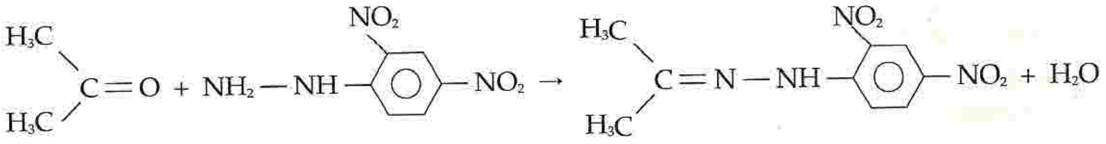
trans-isomer

Complex ion: A complex ion consists of a metal cation joined by co-ordinate (dative) bonds to a number of ligand particles around it.
examples: $[Al(OH)_4]^-$; $[Fe(H_2O)_6]^{3+}$; $[Cu(NH_3)_4]^{2+}$

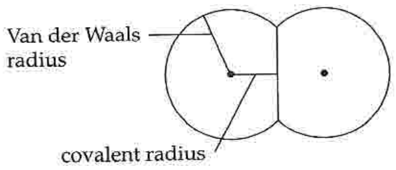


[Note: see *Ligand*]

Condensation reaction: In a condensation reaction, two organic molecules combine together to produce an organic molecule plus a small inorganic molecule such as H_2O or HCl.
example: 2,4-dinitrophenylhydrazine reacts with propanone to form one organic molecule and one H_2O molecule in a condensation reaction:



Covalent radius: The covalent radius of an atom is the radius of an atom in a covalent bond.
example: The covalent radius for iodine is 0.133 nm. This is shown below. When the two atoms in the covalent bond are the same, the covalent radius = half the covalent bond length.



iodine molecule, I_2

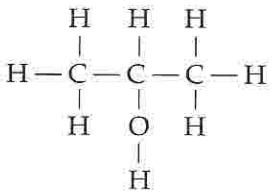
[Note: see also *Van der Waals radius*]

Cracking: Cracking is a reaction in which big hydrocarbon molecules are broken into smaller hydrocarbon molecules by heat. In a typical cracking reaction, a big alkane molecule from petroleum is broken into an alkene molecule and a smaller alkane molecule.
example: $C_{20}H_{42} \rightarrow C_{12}H_{24} + C_8H_{18}$

Dehydration: Dehydration is a reaction in which water is removed (eliminated) from a compound.
example: Ethanol is converted to ethene in dehydration:

$$C_2H_5OH \quad CH_2{=}CH_2 + H_2O$$

Displayed formula: The displayed formula of an organic compound shows how all the atoms and bonds are arranged in a molecule.
example: The displayed formula of propan-2-ol is



[Note: see *Structural formula*]

Disproportionation: Disproportionation is a redox reaction in which a substance is both oxidised and reduced in the same reaction.
example: The reaction of chlorine with aqueous sodium hydroxide:

$$Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$$

Half of the Cl_2 is reduced to Cl^- (its oxidation number decreases from 0 to –1). The other half of the Cl_2 is oxidised to ClO^- (its oxidation number increases from 0 to +1).

Electron affinity: The electron affinity of an element is the heat change when one mole of separate gaseous negative ions is formed from its separate gaseous atoms, at standard state conditions.
example: The electron affinity of bromine is –342 kJ. This amount of energy is given out in the reaction:

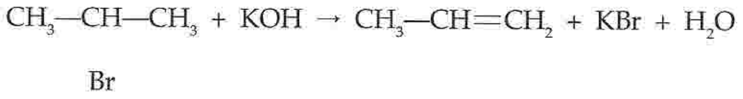
$$Br(g) + e^- \rightarrow Br^-(g)$$

Electronegativity: The electronegativity of an element is its attractive power for electrons in covalent bonds.
example: The electronegativity of oxygen is 3.5.

Electronic structure: The electronic structure of an atom or simple ion shows the arrangement of electrons in the orbitals of the atom.
example: The electronic structure of nitrogen is $1s^2\ 2s^2\ 2p^3$.

Electrophile: An electrophile is a particle that is attracted to a concentration of negative charge (high electron density) in an organic compound.
example: The NO_2^+ ion is an electrophile in the reaction of benzene with a mixture of concentrated nitric and sulphuric acids.

Elimination reaction: In an elimination reaction, a small molecule is removed from an organic compound.
example: In the reaction of 2-bromopropane with a solution of potassium hydroxide in ethanol, hydrogen bromide is removed:



$$CH_3\text{—}\underset{\displaystyle Br}{CH}\text{—}CH_3 + KOH \rightarrow CH_3\text{—}CH\text{=}CH_2 + KBr + H_2O$$

Endothermic change: An endothermic change is one in which heat energy is absorbed.
examples: Breaking a covalent bond and the decomposition of calcium carbonate into calcium oxide and carbon dioxide by heating are both endothermic changes.

Energy (thermodynamic): The capacity to do work.

Enthalpy change of atomisation, ΔH_a: The enthalpy change of atomisation is the heat change required to produce one mole of separate gaseous atoms from the element, at standard state conditions.
example: ΔH_a for sodium is +109 kJ mol^{-1}. This is the enthalpy change of the reaction:

$$Na(s) \rightarrow Na(g)$$

Enthalpy change of combustion, ΔH_c: The enthalpy change of combustion is the heat change when one mole of a compound is completely burnt in oxygen, at standard state conditions.

example: ΔH_c for methane is –882 kJ mol^{-1}. This is the enthalpy change of the reaction:

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

Enthalpy change of formation, ΔH_f: The enthalpy change of formation is the heat change when one mole of a compound is made from its elements, at standard state conditions.
example: ΔH_f for sodium chloride, NaCl, is –411 kJ mol^{-1}. This is the enthalpy change of the reaction:

$$Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s)$$

Enthalpy change of hydration: The enthalpy change of hydration is the heat change when one mole of aqueous ions is formed from the separate gaseous ions, at standard state conditions.
example: The enthalpy change of hydration of Na^+ ion is –406 kJ mol^{-1}. This is the enthalpy change of the reaction:

$$Na^+(g) + \text{water} \rightarrow Na^+(aq)$$

Enthalpy change of neutralisation: The enthalpy change of neutralisation of an acid is the heat change when one mole of an acid reacts completely with an alkali.
example: The enthalpy change of neutralisation of HCl with NaOH is –57.3 kJ mol^{-1}. This is the enthalpy change of the reaction:

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

Enthalpy change of reaction, ΔH: The enthalpy change of reaction is the heat given out or absorbed in a reaction, for the number of moles given in the equation.
example: 184 kJ of heat is given out in the reaction of 1 mole of N_2 and 3 moles of H_2.

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3;\ \Delta H = -184\ \text{kJ}$$

Enthalpy change of solution: The enthalpy change of solution is the heat change when one mole of an ionic solid dissolves completely in excess water.
example: The enthalpy change of solution of potassium nitrate is +34.9 kJ mol^{-1}. This is the enthalpy change of the reaction:

$$KNO_3(s) + \text{water} \rightarrow KNO_3(aq)$$

Entropy (thermodynamic): A measure of the disorder of a system.

Entropy change (ΔS) (thermodynamics): Change in entropy, for example, in a chemical reaction..

Equilibrium constant, K_c: For the reversible reaction:

$$aA + bB \rightleftharpoons cC + dD$$

$$K_c = \frac{[C]^c.[D]^d}{[A]^a.[B]^b} \text{ at equilibrium}$$

Equilibrium constant, K_p: For the reversible gas reaction:

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$$

$$K_p = \frac{(p_C)^c(p_D)^d}{(p_A)^a(p_B)^b} \text{ at equilibrium}$$

Esterification: Esterification is a reaction of an alcohol with a carboxylic acid to produce an ester.
example: $CH_3CH_2OH + CH_3COOH \rightarrow CH_3COOCH_2CH_3 + H_2O$
ethanol + ethanoic acid → ethyl ethanoate + water

Eutectic: The eutectic is a mixture of two substances with the composition that gives the minimum freezing point. This minimum temperature is called the **eutectic temperature**.
example: The freezing point of a molten mixture of tin and lead depends on its composition. The lowest freezing point is –183°C, obtained for a mixture containing 61.9% tin, which is the eutectic.

Exothermic change: An exothermic change is one in which heat energy is produced.
examples: Making a covalent bond and combustion reactions are both endothermic changes.

Faraday constant, *F*: The Faraday constant is the charge on one mole of electrons (96 500 coulombs mol^{-1}).

Free energy change (thermodynamic): see Gibbs free energy

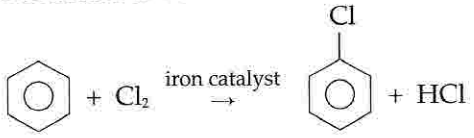
Free radical: A free radical is a particle containing a single unpaired electron.
examples: The chlorine atom, Cl and methyl radical, $CH_3\cdot$ are both free radicals.

Functional group: A functional group is the reactive group of atoms in an organic compound.
examples: The C=C part of but-1-ene, $CH_3CH_2CH{=}CH_2$; the —OH part of propan-1-ol, $CH_3CH_2CH_2OH$; the Cl atom in chloroethane, CH_3CH_2Cl are functional groups. Organic compounds are usually classified according to their functional groups.

Gibbs free energy change (Δ*G*) (thermodynamic): $G = \Delta H - T\Delta G$

Half-life: The half-life of a chemical reaction is the time in which the initial concentration of a reaction decreases by half.

Halogenation: Halogenation is a reaction in which a halogen atom (eg chlorine) is substituted into a benzene ring.
example: Halogenation occurs in the reaction of benzene with chlorine:



Henry's Law: The solubility of a gas in water is proportional to its partial pressure, or:

Hess' Law: Hess' Law states that when a reaction consists of a number of steps, the overall heat energy change is equal to the sum of the heat energy changes for all the individual steps.

Heterolytic fission: In heterolytic fission, a covalent bond is broken such that the two electrons in the bond are *both* taken by the same atom. This produces a positive ion and a negative ion:

$$X:Y \rightarrow X^+ + Y^-$$

Homolytic fission: In homolytic fission, a covalent bond is broken such that each atom receives one of the two bond electrons. This produces two free radicals:

$$X:Y \rightarrow X\cdot + Y\cdot$$

Hydrolysis: Hydrolysis is a reaction of a compound with water.
example: $CH_3{-}COCl + H_2O \rightarrow CH_3COOH + HCl$

Initiation: Initiation is the first step in a free radical chain reaction.
example: The initiation step in the reaction of chlorine with methane is:

$$Cl_2 \rightarrow Cl\cdot + Cl\cdot$$

Internal energy (thermodynamic): The sum of the kinetic and potential energies of all the molecules in a system.

Ionic radius: The ionic radius is the radius of an ion.
example: The ionic radius of the Mg^{2+} ion is 0.065 nm. This is the radius of the Mg^{2+} ion in, for example, the ionic solid magnesium oxide.

Isotopes: Isotopes are atoms of the same element, but with different numbers of neutrons.
example: Carbon has three isotopes:

$^{12}_{6}\mathrm{C}$	$^{13}_{6}\mathrm{C}$	$^{14}_{6}\mathrm{C}$
six neutrons	seven neutrons	eight neutrons

Ionic product of water, K_w: In an aqueous solution:

$$K_w\text{, constant} = [\mathrm{H^+}][\mathrm{OH^-}]$$

Ionisation energy: The ionisation energy of an element is the energy required to remove an electron from a gaseous atom, per mole of atoms.
example: The ionisation energy of carbon is 1090 kJ mol^{-1}. This is the enthalpy change, ΔH, for the reaction:

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

Isoelectronic: Atoms, ions or molecules which are isoelectronic contain the same number of electrons.
example: The Ne atom; $\mathrm{O^{2-}}$ ion; $\mathrm{Na^+}$ ion; HF molecule each contains 10 electrons. So they are all isoelectronic.

Labile protons: Hydrogen-bonded protons in, for example, liquid alcohols which can rapidly exchange between molecules.

Lattice energy: The lattice energy of an ionic solid is the heat change when one mole of the solid is formed from its separate gaseous ions, at standard state conditions.
example: The lattice energy of potassium chloride is –701 kJ mol^{-1}. This is the enthalpy change of the reaction:

$$\mathrm{K^+(g)} + \mathrm{Cl^-(g)} \rightarrow \mathrm{KCl(s)}$$

Law of Conservation of Energy (thermodynamic): The sum of all the energy in an isolated system is constant (or, simply: energy cannot be created or destroy). [Also known as the **First Law of Thermodynamics**.]

Le Chatelier's Principle: Le Chatelier's Principle states that when an equilibrium mixture is disturbed, the composition of the mixture will change so as to remove the disturbance.

Ligand: A ligand is a molecule or anion that uses a lone pair of electrons to form a co-ordinate (dative) bond with a metal cation in a complex ion.
examples: $\mathrm{H_2O}$ molecules are ligands in the $[\mathrm{Cu(H_2O)_6}]^{2+}$ complex ion; CO and $\mathrm{O_2}$ molecules are ligands in their reactions with haemoglobin.
[Note: see *Complex ion*]

Metallic radius: The metallic radius of an element is the radius of one of its atoms in its metallic lattice.
example: The metallic radius of sodium is 0.186 nm. This is the radius of a sodium atom in a crystal of solid sodium.

Mole: One mole of a substance is that amount of the substance that contains the same number of particles as in the Avogadro Constant.

Molecular formula: The molecular formula of an element or compound shows the number of atoms of each element in one molecule.
example: The molecular formula of propan-2-ol is $\mathrm{C_3H_7OH}$.
[Note: see also *Displayed formula* and *Structural formula*]

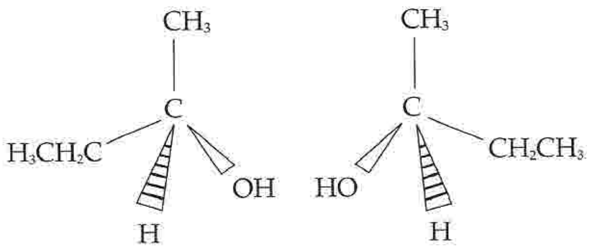
Nuclear spin: A property of protons and some other nuclei, which gives the nucleus a magnetic moment in turn which can have two different energy alignment in an external magnetic field. It causes NMR spectra.

Nucleon number: The nucleon number is the sum of the protons and neutrons in the nucleus of an atom. It is the same as *mass number*.

Nucleophile: A nucleophile is a particle that is attracted to a high concentration of positive charge in an organic compound. It is usually a negative ion (anion) or neutral molecule with a lone pair of electrons which is used to form a co-ordinate (dative) bond with an atom in an organic molecule.

example: The OH^- ion is a nucleophile in the substitution reaction of 1-bromobutane with aqueous sodium hydroxide to produce butan-1-ol.

Optical isomers: Optical isomers are two compounds with the same molecular formula and are mirror images of each other.
example: Butan-2-ol exists as two optical isomers:



Order of reaction: For the chemical reaction:

$$A + B \rightarrow C + D$$

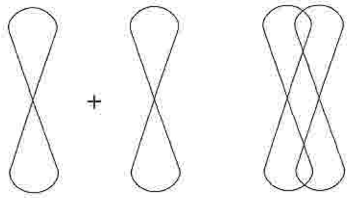
rate = $k[A]^m[B]^n$; the order of the reaction = $(m + n)$.

Oxidation: Any one of the following changes in a chemical reaction is oxidation:
(i) gain of oxygen; (ii) loss of hydrogen; (iii) loss of electrons; (iv) increase in oxidation number.

Oxidation number: The oxidation number of an atom in a compound is equal to its theoretical charge if all the atoms were joined together by electrovalent bonds.
example: If a H_2O molecule were ionic, it would consist of two H^+ ions and one O^{2-} ion. So the oxidation number of oxygen in water is –2.

pH: $pH = -\log[H^+]$, where $[H^+]$ = concentration of hydrogen ions in an aqueous solution.

Pi bond (bond): A bond is formed when orbitals overlap *sideways* in a covalent bond:



p orbital *p* orbital two *p* orbitals in a covalent bond (bond)

examples: The delocalised 'ring' of electrons in benzene; part of the C=C bond in ethene are bonds.
[Note: see *Sigma bond* for comparison]

pK_a: $pK_a = -\log K_a$
[Note: see *Acid dissociation constant,* K_a]

Polymerisation: Polymerisation is a reaction in which large numbers of similar small molecules (known as *monomers*) are joined together to form one large molecule (known as a *polymer*).
example: Making poly(ethene) from ethene:

$$n(CH_2{=}CH_2) \rightarrow \text{+}CH_2{-}CH_2\text{+}_n$$

where n = about 10 000

Propagation: A propagation step in a free radical chain reaction is one which continues the chain reaction after it has started (been initiated).
example: A propagation step in the reaction of chlorine with methane is

$$Cl\cdot + CH_4 \rightarrow CH_3\cdot + HCl$$

Proton number: The proton number is the number of protons in the nucleus of an atom. It is the same as *atomic number*.

Rate constant, *k*: (see *Rate equation*)

Rate-determining step: Most chemical reactions consist of a number of steps. One of the steps is usually a lot slower than all the other steps. This slow step controls the overall speed of reaction and is called the *rate-determining step*.

Rate equation: The rate equation describes mathematically how the rate of a reaction depends on the concentrations of the reactants. For the reaction: A + B → C + D, the rate equation is:

$$\text{rate} = k[\text{A}]^m[\text{B}]^n$$

where m and n are whole numbers and k is the *rate constant* for the reaction.

Reduction: Any one of the following changes in a chemical reaction is reduction:
(i) loss of oxygen; (ii) gain of hydrogen; (iii) gain of electrons; (iv) decrease in oxidation number.

Relative atomic mass, A_r: The relative atomic mass of an element is the average mass of one atom of the element compared with one-twelfth of the mass of one atom of carbon-12:

$$A_r = 12 \; \frac{\text{average mass of one atom of the element}}{\text{mass of one atom of carbon-12}}$$

Relative formula mass: The relative formula mass of a substance is the average mass of all the atoms in the formula compared with one-twelfth of the mass of one atom of carbon-12.

Relative isotopic mass: The relative isotopic mass of an isotope is the mass of one atom of the isotope compared with one-twelfth of the mass of one atom of carbon-12.

Relative molecular mass, M_r: The relative molecular mass of a molecular substance is the average mass of one molecule of the substance compared with one-twelfth of the mass of one atom of carbon-12:

$$M_r = 12 \; \frac{\text{average mass of one molecule of the substance}}{\text{mass of one atom of carbon-12}}$$

R_f value: The R_f value is a term used in paper and thin layer chromatography. The R_f value of a single substance on a chromatogram is:

$$R_f = \frac{\text{distance moved by the substance from the start}}{\text{distance moved by the solvent front from the start}}$$

Residence time: The average time a molecule remains in the atmosphere before being removed or destroyed:

$$\text{residence time} = \frac{\text{steady state atmospheric concentration}}{\text{rate of removal of the gas}}$$

examples:

molecules	residence time
carbon dioxide, CO_2	4 years
hydroxyl radical, HO•	1 second

Second law of Thermodynamics: The entropy of the universe tends to increase.

Sigma bond (bond): A bond is formed when orbitals overlap *head-on* in a covalent bond.

examples: The C—C bond in ethane and the Cl—Cl bond in Cl_2.
[Note: see *Pi bond* for comparison]

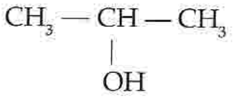
Solubility product, K_{sp}: In a saturated solution of a slightly soluble ionic compound, M_aX_b:

$$K_{sp}\text{, constant} = [M^+]^a[X^-]^b$$

Standard cell potential, $E^{\ominus}_{cell}$: The standard cell potential is the potential difference between two standard half-cells, measured at standard state conditions.

Standard electrode potential, $E^{\ominus}$: The standard electrode potential of a metal is the potential difference between the metal and a 1.00 mol dm^{-3} aqueous solution of its ions, at standard state conditions, relative to a standard hydrogen half-cell.

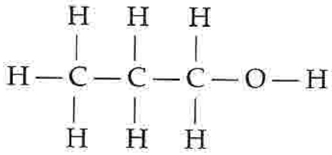
Structural formula: The structural formula of an organic compound is an abbreviated displayed formula. The displayed formula can be deduced from the structural formula.
example: The structural formula of propan-1-ol is



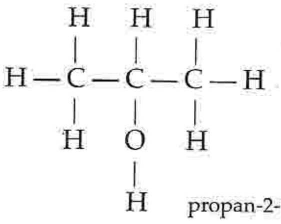
$$CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_3$$

[Note: see *Displayed formula*]

Structural isomers: Structural isomers are different organic compounds with the same molecular formula. Some atoms are bonded to different atoms in the two compounds.
example: C_3H_7OH has two structural isomers:



propan-1-ol



propan-2-ol

Substitution reaction: In a substitution reaction, one or more atoms of an organic molecule are replaced with one or more other atoms.
example: The reaction of iodoethane with aqueous sodium hydroxide:

$$CH_3CH_2I + NaOH \rightarrow CH_3CH_2OH + NaI$$

iodine in iodoethane is replaced with —OH

Termination: A termination step in a free radical chain reaction is one that stops the chain reaction.
example: A termination step in the reaction of chlorine with methane is:

$$H_3C^{\cdot} + {}^{\cdot}CH_3 \rightarrow H_3C{-}CH_3$$

TMS: Abbreviation for tetramethylsilane, $(CH_3)_4Si$. Used as a reference standard in NMR spectroscopy.

Triple point: The triple point shows the conditions of temperature and pressure at which all three states of a substance can exist together at equilibrium.
example: The triple point of water is at 611 Pa and 0.008°C. Ice, liquid water and steam can exist together at this point.

Van der Waals radius: The Van der Waals radius of an element is the radius of an atom of the element when it is joined to neighbouring atoms by Van der Waals forces.
example: The Van der Waals radius of argon is 0.192 nm. This is the radius of an atom in a crystal of solid argon.
[Note: the difference between the covalent radius and the Van der Waals radius in an iodine molecule was shown earlier, see *Covalent radius*]

Work (thermodynamic): A transfer of energy that is used to change the potential energy of something.

Data Tables

CHEMICAL CONSTANTS

molar gas constant	R	=	$8.31\ \text{J K}^{-1}\ \text{mol}^{-1}$
Faraday constant	F	=	$9.65 \times 10^{4}\ \text{C mol}^{-1}$
Avogadro constant	L	=	$6.02 \times 10^{23}\ \text{mol}^{-1}$
Planck constant	h	=	$6.63 \times 10^{-34}\ \text{J s}$
speed of light in a vacuum	c	=	$3.00 \quad 10^{8}\ \text{m s}^{-1}$
mass of proton, ${}^{1}_{1}\text{H}$	m_p	=	$1.67 \times 10^{-27}\ \text{kg}$
mass of neutron, ${}^{1}_{0}\text{n}$	m_n	=	$1.67 \times 10^{-27}\ \text{kg}$
mass of electron, ${}^{0}_{-1}\text{e}$	m_e	=	$9.11 \quad 10^{-31}\ \text{kg}$
electronic charge	e	=	$-1.60 \times 10^{-19}\ \text{C}$
molar volume of gas	V_m	=	$22.4\ \text{dm}^{3}\ \text{mol}^{-1}$ at s.t.p.
		=	$24\ \text{dm}^{3}\ \text{mol}^{-1}$ under room conditions [where s.t.p. is 101 kPa, approximately, and 273 K (0°C)]
ionic product of water	K_w	=	$1.00 \times 10^{-14}\ \text{mol}^{2}\ \text{dm}^{-6}$ (at 298 K (25°C))
specific heat capacity of water		=	$4.18\ \text{kJ kg}^{-1}\ \text{K}^{-1}$
		=	$4.18\ \text{J g}^{-1}\ \text{K}^{-1}$
1 standard atmosphere		=	101 kPa

QUANTITIES, SYMBOLS AND UNITS

Quantity	Symbol	SI units
mass	m	gram, g
		kilogram, kg
length	l	metre, m
		centimetre, cm (1 cm = 10^{-2} m)
		nanometre, nm (1 nm = 10^{-9} m)
volume	V	m^3 (for gases)
		dm^3 (for gases and solutions; 1 dm^3 = $10^3\ \text{m}^3$)
		cm^3 (for gases and solutions; 1 cm^3 = $10^{-3}\ \text{dm}^3$ = $10^{-6}\ \text{m}^3$)
time	t	second, s (1 hour = 60 minutes = 3600 s)
amount of substance	n	mole
current	I	ampere, A
potential difference	V	volt, V
electric charge		coulomb, C
energy		joule, J
		kilojoule, kJ
temperature	t	°C
		K
density	ρ	g cm^{-3}
		kg m^{-3}
concentration	c	g dm^{-3}
		mol dm^{-3} ([B] means concentration of B in mol dm^{-3})

pressure	P	pascal, Pa kilopascal, kPa (1 standard atmosphere = 760 mm Hg = 101.3 kPa)
partial pressure	p	pascal, Pa kilopascal, kPa (p_B means partial pressure of B in a mixture of gases)
Avogadro constant	L	mol^{-1}
Faraday constant	F	$C\ mol^{-1}$
gas constant	R	$J\ K^{-1}\ mol^{-1}$
rate constant	k	*first order:* s^{-1} *second order:* $dm^3\ mol^{-1}\ s^{-1}$ *third order:* $dm^6\ mol^{-2}\ s^{-1}$
rate of reaction		$mol\ dm^{-3}\ s^{-1}$
equilibrium constant	K	(depends on particular case)
(in concentrations)	K_c	
(in partial pressures)	K_p	
acid dissociation constant	K_a	$mol\ dm^{-3}$
base dissociation constant	K_b	$mol\ dm^{-3}$
ionic product of water	K_w	$mol^2\ dm^{-6}$
enthalpy change		
of reaction	$\Delta H^{\ominus}$	kJ
of formation	$\Delta H_f^{\ominus}$	$kJ\ mol^{-1}$
of combustion	$\Delta H_c^{\ominus}$	$kJ\ mol^{-1}$
electrode potential	$E^{\ominus}$	V
proton number	Z	–
number of neutrons	N	–
solubility product	K_{sp}	(depends on particular case)
relative atomic mass	A_r	–
relative molecular mass	M_r	–

PREFIXES FOR NUMBERS

multiple	prefix	symbol
10^9	giga	G
10^6	mega	M
10^3	kilo	k
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p

MISCELLANEOUS SYMBOLS

neutron	n
proton	p
electron	e
approximately equal to	$\approx$
greater than	$>$
less than	$<$
logarithm to base 10	log or $\log_{10}$
natural logarithm	ln or $\log_e$
proportional to	$\propto$

THE PERIODIC TABLE

Key: a
X
b

a = relative atomic mass
X = atomic symbol
b = proton (atomic) number

Group																	
I	II											III	IV	V	VI	VII	O
							1.0 **H** 1										4.0 **He** 2
6.9 **Li** 3	9.0 **Be** 4											10.8 **B** 5	12.0 **C** 6	14.0 **N** 7	16.0 **O** 8	19.0 **F** 9	20.2 **Ne** 10
23.0 **Na** 11	24.3 **Mg** 12											27.0 **Al** 13	28.1 **Si** 14	31.0 **P** 15	32.1 **S** 16	35.5 **Cl** 17	39.9 **Ar** 18
39.1 **K** 19	40.1 **Ca** 20	45.0 **Sc** 21	47.9 **Ti** 22	50.9 **V** 23	52.0 **Cr** 24	54.9 **Mn** 25	55.8 **Fe** 26	58.9 **Co** 27	58.7 **Ni** 28	63.5 **Cu** 29	65.4 **Zn** 30	69.7 **Ga** 31	72.6 **Ge** 32	74.9 **As** 33	79.0 **Se** 34	79.9 **Br** 35	83.8 **Kr** 36
85.5 **Rb** 37	87.6 **Sr** 38	88.9 **Y** 39	91.2 **Zr** 40	92.9 **Nb** 41	95.9 **Mo** 42	- **Tc** 43	101 **Ru** 44	103 **Rh** 45	106 **Pd** 46	108 **Ag** 47	112 **Cd** 48	115 **In** 49	119 **Sn** 50	122 **Sb** 51	128 **Te** 52	127 **I** 53	131 **Xe** 54
133 **Cs** 55	137 **Ba** 56	La to Lu	178 **Hf** 72	181 **Ta** 73	184 **W** 74	186 **Re** 75	190 **Os** 76	192 **Ir** 77	195 **Pt** 78	197 **Au** 79	201 **Hg** 80	204 **Tl** 81	207 **Pb** 82	209 **Bi** 83	- **Po** 84	- **At** 85	- **Rn** 86
- **Fr** 87	- **Ra** 88	Ac to Lr	- **Rf** 104	- **Db** 105	- **Sg** 106	- **Bh** 107	- **Hs** 108	- **Mt** 109	- **Unn** 110	- **Uuu** 111	- **Uub** 112		- **UUq** 114		- **Uuh** 116		- **Uuo** 118

Lanthanides	139 **La** 57	140 **Ce** 58	141 **Pr** 59	144 **Nd** 60	- **Pm** 61	150 **Sm** 62	152 **Eu** 63	157 **Gd** 64	159 **Tb** 65	163 **Dy** 66	165 **Ho** 67	167 **Er** 68	169 **Tm** 69	173 **Yb** 70	175 **Lu** 71
Actinides	- **Ac** 89	- **Th** 90	- **Pa** 91	- **U** 92	- **Np** 93	- **Pu** 94	- **Am** 95	- **Cm** 96	- **Bk** 97	- **Cf** 98	- **Es** 99	- **Fm** 100	- **Md** 101	- **No** 102	- **Lr** 103

IONISATION ENERGIES
(1st, 2nd, 3rd and 4th) of selected elements, in kJ mol^{-1}

	Proton number	First	Second	Third	Fourth
H	1	1310	–	–	–
He	2	2370	5250	–	–
Li	3	519	7300	11800	–
Be	4	900	1760	14800	21000
B	5	799	2420	3660	25000
C	6	1090	2350	4610	6220
N	7	1400	2860	4590	7480
O	8	1310	3390	5320	7450
F	9	1680	3370	6040	8410
Ne	10	2080	3950	6150	9290
Na	11	494	4560	6940	9540
Mg	12	736	1450	7740	10500
Al	13	577	1820	2740	11600
Si	14	786	1580	3230	4360
P	15	1060	1900	2920	4960
S	16	1000	2260	3390	4540
Cl	17	1260	2300	3850	5150
Ar	18	1520	2660	3950	5770
K	19	418	3070	4600	5860
Ca	20	590	1150	4940	6480
Sc	21	632	1240	2390	7110
Ti	22	661	1310	2720	4170
V	23	648	1370	2870	4600
Cr	24	653	1590	2990	4770
Mn	25	716	1510	3250	5190
Fe	26	762	1560	2960	5400
Co	27	757	1640	3230	5100
Ni	28	736	1750	3390	5400
Cu	29	745	1960	3350	5690
Zn	30	908	1730	3828	5980
Ga	31	577	1980	2960	6190
Ge	32	762	1540	3300	4390
Br	35	1140	2080	3460	4850
Sr	38	548	1060	4120	5440
Sn	50	707	1410	2940	3930
I	53	1010	1840	2040	4030
Ba	56	502	966	3390	5000
Pb	82	716	1450	3080	4080

BOND ENERGIES

(a) Diatomic molecules

Bond	Energy/kJ mol^{-1}
H—H	436
D—D	442
N≡N	994
O=O	496
F—F	158
Cl—Cl	244
Br—Br	193
I—I	151
H—F	562
H—Cl	431
H—Br	366
H—I	299

(b) Polyatomic molecules

Bond	Energy/kJ mol^{-1}
C—C	350
C=C	610
C≡C	840
C$\overset{\cdots}{\text{—}}$C (benzene)	520
C—H	410
C—Cl	340
C—Br	280
C—I	240
C—N	305
C=N	610
C≡N	890
C—O	360
C=O	740
N—H	390
N—N	160
N=N	410
O—H	460
O—O	150
Si—Cl	359
Si—H	320
Si—O	444
Si—Si	222
S—Cl	250
S—H	347
S—S	264

ATOMIC AND IONIC RADII

(a) *Period 3*

	Atomic/nm		Ionic/nm	
metallic	Na	0.186	Na^+	0.095
	Mg	0.160	Mg^{2+}	0.065
	Al	0.143	Al^{3+}	0.050
single covalent	Si	0.117	Si^{4+}	0.041
	P	0.110	P^{3-}	0.212
	S	0.104	S^{2-}	0.184
	Cl	0.099	Cl^-	0.181
Van der Waals	Ar	0.192		
(b) ***Group II***				
metallic	Be	0.112	Be^{2+}	0.031
	Mg	0.160	Mg^{2+}	0.065
	Ca	0.197	Ca^{2+}	0.099
	Sr	0.215	Sr^{2+}	0.113
	Ba	0.217	Ba^{2+}	0.135
	Ra^{2+}	0.220	Ra^{2+}	0.140
(c) ***Group IV***				
single covalent	C	0.077		
	Si	0.117	Si^{4+}	0.041
	Ge	0.122	Ge^{2+}	0.093
metallic	Sn	0.162	Sn^{2+}	0.112
	Pb	0.175	Pb^{2+}	0.120
(d) ***Group VII***				
single covalent	F	0.072	F^-	0.136
	Cl	0.099	Cl^-	0.181
	Br	0.114	Br^-	0.195
	I	0.133	I^-	0.216
	At	0.140		
(e) ***First row transition elements***				
single covalent	Sc	0.144	Sc^{3+}	0.081
	Ti	0.132	Ti^{2+}	0.090
	V	0.122	V^{3+}	0.074
	Cr	0.117	Cr^{3+}	0.069
	Mn	0.117	Mn^{2+}	0.080
	Fe	0.116	Fe^{2+}	0.076
			Fe^{3+}	0.064
	Co	0.116	Co^{2+}	0.078
	Ni	0.115	Ni^{2+}	0.078
	Cu	0.117	Cu^{2+}	0.069
	Zn	0.125	Zn^{2+}	0.074

ELECTRONEGATIVITIES

Pauling scale

H 2.1

Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Te 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5
Cs 0.7	Ba 0.9	La 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2
Fr 0.7	Ra 0.9	Ac 1.1														

ELECTRON AFFINITIES

The data applies to the enthalpy change of the reaction:

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

All values in kJ mol^{-1}.

H –73

Li –60	Be –23	B –23	C –123	N 0	O –141	F –322
Na –53	Mg –31	Al –44	Si –120	P –74	S –200	Cl –349
K –48		Ga –36	Ge –116	As –77	Se –195	Br –325
Rb –47		In –34	Sn –121	Sb –101	Te –190	I –295
Cs –46			Pb –101	Bi –101		

Cr –64	Cu –123	Ag –126	Au –223

STANDARD REDOX POTENTIALS, $E^\ominus$ at 298 K (25°C)

(State Symbols Omitted)

Electrode reaction	$E^\ominus$/V
$Ag^+ + e^- \rightleftharpoons Ag$	+0.80
$Al^{3+} + 3e^- \rightleftharpoons Al$	–1.66
$Ba^{2+} + 2e^- \rightleftharpoons Ba$	–2.90
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.07
$Ca^{2+} + 2e^- \rightleftharpoons Ca$	–2.87
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$2HOCl + 2H^+ + 2e^- \rightleftharpoons Cl_2 + 2H_2O$	+1.64
$Co^{2+} + 2e^- \rightleftharpoons Co$	–0.28
$Co^{3+} + e^- \rightleftharpoons Co^{2+}$	+1.82
$[Co(NH_3)_6]^{2+} + 2e^- \rightleftharpoons Co + 6NH_3$	–0.43
$Cr^{2+} + 2e^- \rightleftharpoons Cr$	–0.91
$Cr^{3+} + 3e^- \rightleftharpoons Cr$	–0.74
$Cr^{3+} + e^- \rightleftharpoons Cr^{2+}$	–0.41
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33
$Cu^+ + e^- \rightleftharpoons Cu$	+0.52
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$Cu^{2+} + e^- \rightleftharpoons Cu^+$	+0.15
$[Cu(NH_3)_4]^{2+} + 2e^- \rightleftharpoons Cu + 4NH_3$	–0.05
$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	–0.44
$Fe^{3+} + 3e^- \rightleftharpoons Fe$	–0.04
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
$[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}$	+0.36
$Fe(OH)_3 + e^- \rightleftharpoons Fe(OH)_2 + OH^-$	–0.56
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54
$K^+ + e^- \rightleftharpoons K$	–2.92
$Li^+ + e^- \rightleftharpoons Li$	–3.04

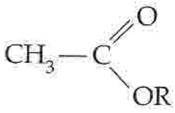
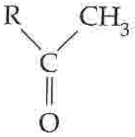
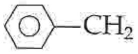
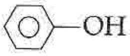
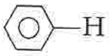
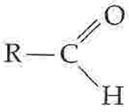
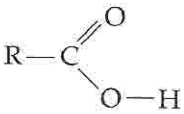
Electrode reaction	$E^\ominus$/V
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	−2.38
$Mn^{2+} + 2e^- \rightleftharpoons Mn$	−1.18
$Mn^{3+} + e^- \rightleftharpoons Mn^{2+}$	+1.49
$MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$	+1.23
$MnO_4^- + e^- \rightleftharpoons MnO_4^{2-}$	+0.56
$MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_2 + 2H_2O$	+1.67
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.52
$NO_3^- + 2H^+ + e^- \rightleftharpoons NO_2 + H_2O$	+0.81
$NO_3^- + 3H^+ + 2e^- \rightleftharpoons HNO_2 + H_2O$	+0.94
$NO_3^- + 10H^+ + 8e^- \rightleftharpoons NH_4^+ + 3H_2O$	+0.87
$Na^+ + e^- \rightleftharpoons Na$	−2.71
$Ni^{2+} + 2e^- \rightleftharpoons Ni$	−0.25
$[Ni(NH_3)_6]^{2+} + 2e^- \rightleftharpoons Ni + 6NH_3$	−0.51
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	+1.77
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	+1.23
$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$	+0.40
$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2$	+0.68
$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$	−0.83
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	−0.13
$Pb^{4+} + 2e^- \rightleftharpoons Pb^{2+}$	+1.69
$PbO_2 + 4H^+ + 2e^- \rightleftharpoons Pb^{2+} + 2H_2O$	+1.47
$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2 + 2H_2O$	+0.17
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	+2.01
$S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-}$	+0.09
$Sn^{2+} + 2e^- \rightleftharpoons Sn$	−0.14
$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	+0.15
$V^{2+} + 2e^- \rightleftharpoons V$	−1.2
$V^{3+} + e^- \rightleftharpoons V^{2+}$	−0.26
$VO^{2+} + 2H^+ + e^- \rightleftharpoons V^{3+} + H_2O$	+0.34
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$	+1.00
$VO_3^- + 4H^+ + e^- \rightleftharpoons VO^{2+} + 2H_2O$	+1.00
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	−0.76

ELECTROCHEMICAL SERIES

(Standard Redox potentials in order of oxidising power)

Electrode reaction	E° / V
$F_2 + 2e^- \rightleftharpoons 2F^-$	+2.87
$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$	+2.01
$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$	+1.77
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	+1.52
$PbO_2 + 4H^+ + 2e^- \rightleftharpoons Pb^{2+} + 2H_2O$	+1.47
$Cl_2 + 2e^- \rightleftharpoons 2Cl^-$	+1.36
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.07
$NO_3^- + 2H^+ + e^- \rightleftharpoons NO_2 + H_2O$	+0.81
$Ag^+ + e^- \rightleftharpoons Ag$	+0.80
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77
$I_2 + 2e^- \rightleftharpoons 2I^-$	+0.54
$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$	+0.40
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	+0.34
$Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$	+0.15
$SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2 + 2H_2O$	+0.17
$S_4O_6^{2-} + 2e^- \rightleftharpoons 2S_2O_3^{2-}$	+0.09
$2H^+ + 2e^- \rightleftharpoons H_2$	0.00
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	–0.13
$Sn^{2+} + 2e^- \rightleftharpoons Sn$	–0.14
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	–0.44
$Zn^{2+} + 2e^- \rightleftharpoons Zn$	–0.76
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	–2.38
$Ca^{2+} + 2e^- \rightleftharpoons Ca$	–2.87
$K^+ + e^- \rightleftharpoons K$	–2.92

Typical Proton Chemical Shift Values (δ) relative to T.M.S. = 0

Type of proton	Chemical shift (ppm)
$R{-}CH_3$	0.9
$R{-}CH_2{-}R$	1.3
R_3CH	2.0
	2.0
	2.1
	2,3
$R{-}C{\equiv}C{-}H$	2.6
$R{-}CH_2{-}Hal$	3.2–3.7
$R{-}O{-}CH_3$	3.8
$R{-}O{-}H$	4.5*
$RHC{=}CH_2$	4.9
$RHC{=}CH_2$	5.9
	7*
	7.3
	9.7*
	11.5*

*Sensitive to solvent, substituents, concentration

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