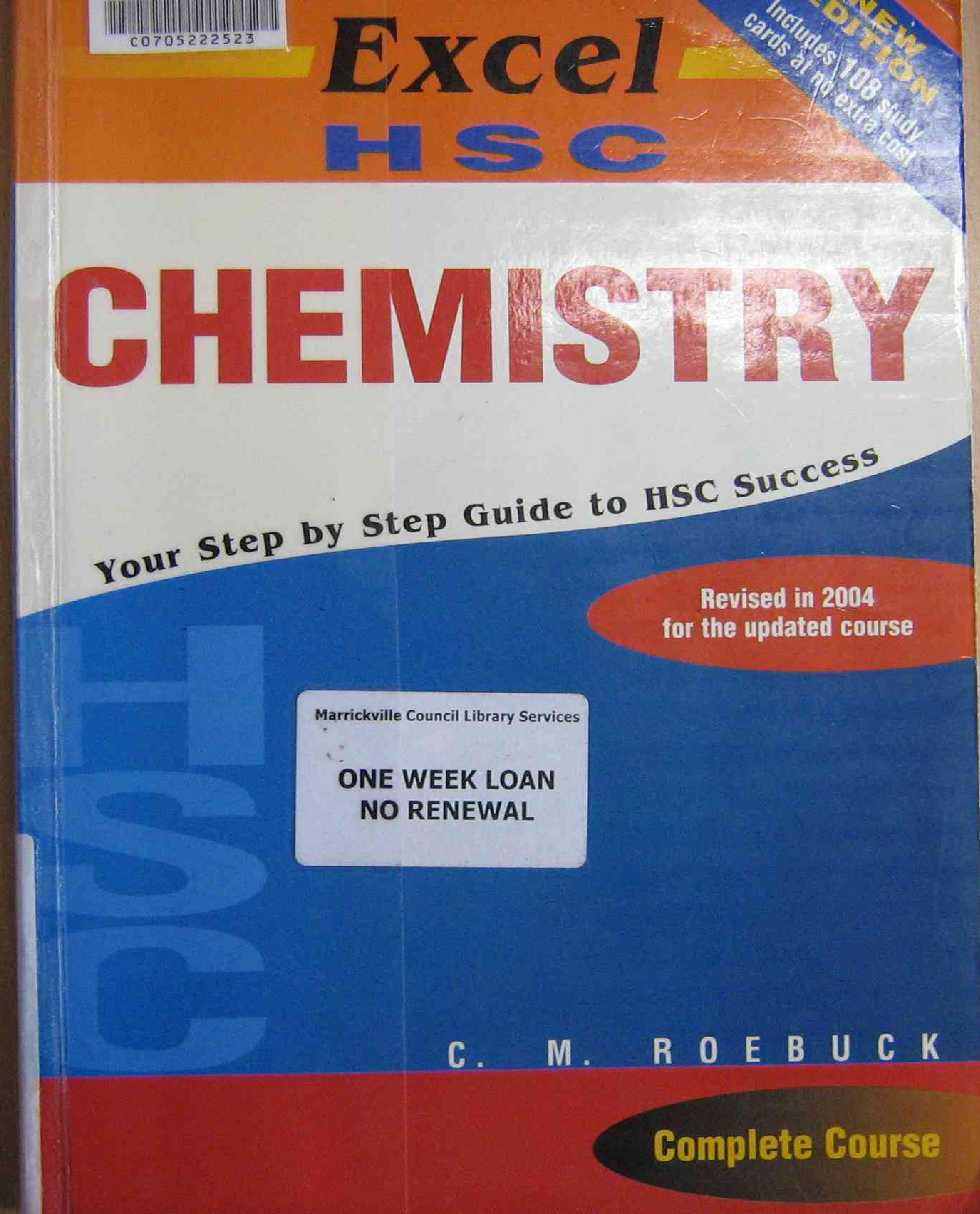

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CHEMISTRY

Your Step by Step Guide to HSC Success

Revised in 2004
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C. M. ROEBUCK

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CHEMISTRY

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BSc DipEd

PASCAL

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Students:
All care has been taken in the preparation of this study guide, but please check with your teacher or the Board of Studies about the exact requirements of the course you are studying as they can change from year to year.

Contents

Introduction

How to use this book

The main objective of this book is to improve your Chemistry results by providing a logical study base. It is structured to complement the new Stage 6 HSC Chemistry syllabus and is divided into the three compulsory core topics:

- The Identification and Production of Materials
- The Acidic Environment
- Chemical Monitoring and Management

and the five option topics, of which you are expected to choose one option:

- Industrial Chemistry
- Shipwrecks and Salvage
- The Biochemistry of Movement
- Forensic Chemistry
- The Chemistry of Art

To assist you with your revision this study guide contains —

- clearly explained essential concepts
- tables and diagrams to help you study
- revision exercises for each chapter
- a selection of worked examples
- assignments linked to the syllabus outcomes to improve your chemistry skills
- fully explained first-hand investigations
- a concise end of chapter summary
- a revision test per chapter
- a practice examination covering all four chapters
- a glossary to help you learn key terms
- Excel icons to help you locate essential information and to aid revision

✓ Essential knowledge and formula

● Keywords and terms

▨ First-hand investigations and practical work

The HSC Examination

Good examination technique is necessary if you are to maximise your marks.

Section I

Part A

Consists of 15 multiple choice questions. Since 15 marks are allocated, you should allow $1\frac{1}{2}$ minutes per question, or about 25 minutes for the section. Multiple choice questions are not multiple *guess* questions.

Sample question

In the reaction

$$Cu(s) + 2AgNO_3(aq) \rightarrow 2Ag(s) + Cu(NO_3)_2(aq)$$

(A) copper is reduced
(B) silver ions are reduced
(C) nitrate ions are oxidised
(D) silver ions are the reduction product

In all cases CAREFULLY READ THE QUESTION. Eliminate the more obvious distractors, e.g. nitrate ion is a spectator ion.

Write half-cell equations, e.g.

$$Cu \rightarrow Cu^{2+} \text{ and } 2Ag^+ \rightarrow 2Ag$$

if you are doubtful. From these it is easily seen that copper is oxidised and silver ions are reduced, so the answer is (B).

Part B

Consists of 11 questions, totalling 60 marks, with the average mark in the 5–6 range. Again allow $1\frac{1}{2}$ minutes per mark allocated, which is 90 minutes for Part B.

- Write your answers neatly and legibly IN THE SPACE PROVIDED.
- Point form can be used.
- Always show your working.
- If asked to draw a diagram, draw in pencil and fully label in ink. Use all the space provided.
- Include units for all numerical answers.

Sample question [6 marks]

A galvanic cell was constructed by a student using two half-cells. One half-cell consisted of iron metal and iron (II) sulfate solution, and the other half-cell copper metal and a copper (II) sulfate solution.

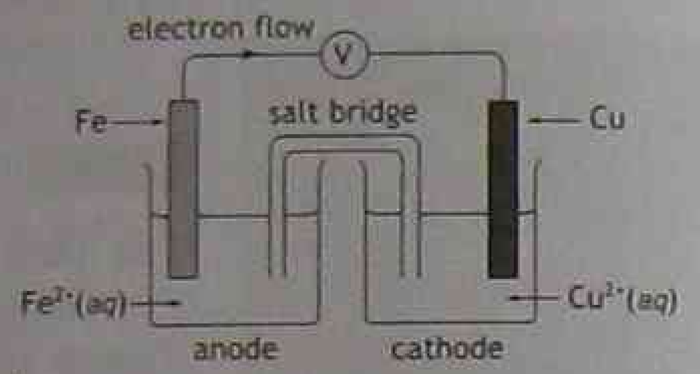
(a) Draw a diagram of the galvanic cell, labelling the anode and the cathode, and indicate the direction of electron flow.

(b) Using the relevant parts of the Chemical Data Sheet, calculate the theoretical voltage for the cell.

(c) The actual voltage the student obtained from the cell was 0.2 V less than the theoretical value. Give TWO reasons that could account for the difference between the two values in the voltage.

Answer

(a)



(b) Data:

$$Fe^{2+} + 2e^- \rightleftharpoons Fe(s) \qquad E^\circ = -0.41 \text{ V}$$

$$Cu^{2+} + 2e^- \rightleftharpoons Cu(s) \qquad E^\circ = +0.36 \text{ V}$$

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{cathode} - E^\circ_{anode} \\ &= +0.36 \text{ V} - (-0.41 \text{ V}) \\ &= +0.76 \text{ V} \end{aligned}$$

(c) For the theoretical value, the cell solutions are 1 M and the cell temperature is 25°C. If the molarity of the solutions is not 1 M and the temperature not 25°C, then there would be a difference between the two voltages.

Section II

Options [25 marks]

- Time allocated = 43 minutes. Only one option is to be answered. Answer the option you have prepared. Usually 4–6 questions will be asked in the section.
- Read the questions carefully.
- If you are asked to 'state and explain', do not simply repeat the question in different words.
- If you are asked 'state what you would observe', simply to state what chemical substances are formed in a reaction would not be satisfactory.
- In the times given for the sections in this exam, 10 minutes have been allowed to read over your answers at the finish.

REMEMBER — Chemistry is a practical subject, so revise all your experiments.

How to study

Everybody studies differently and as you go along you will work out the most effective way for you to get the best out of your study. However, there are a number of proven study techniques which will help.

- Establish a regular place to study, which is quiet, organised and comfortable.
- Timetable your study to give equal time to each subject.
- Study for 50 minutes then have a 10 minute break.
- Make a regular time for studying.
- Keep healthy — eat well, exercise, get plenty of sleep and save time for relaxation.
- Summarise your notes and work your way through your Excel Chemistry study guide.
- Constant repetition improves your ability to retain information.
- Do practice questions, exercises and exams, as these are some of the best ways to prepare for the exam.

Other methods which may work for you are:

- group study — explaining a concept to someone else is excellent reinforcement for you
- be tested orally on your work by a relative or friend.

How to approach exams

Here are some useful hints for answering exam and test questions.

- Read through the entire exam paper carefully.
- Work out how long you need to spend on each section. You should calculate this based on how many marks each section is worth. Don't forget to allow 5–10 minutes for checking at the end.
- Do not spend too much time on multiple choice questions.
- Read each question carefully and underline keywords.
- Attempt every question even if you are short of time as the first few marks are the 'easy' marks.
- Use the Periodic Table supplied to
  - check valencies
  - check activity of metals in their groups
  - check the atomic number and hence the number of protons and electrons in an element.
- Answer the question exactly as it is asked —
  - you may be asked to write several types of formula, for example, empirical CH_2O; molecular $C_2H_4O_2$; or Lewis  $H:\overset{\overset{H}{..}}{\underset{\underset{H}{..}}{C}}:H$
  - you may be asked to write several types of balanced equations, for example formula equations:

    $$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g);$$

    ionic equations:

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

  - include states in these equations
  - charges must balance in ionic equations
  - include thermochemical matter and states in enthalpy equations.
- Write your answers in the correct place and order on your answer sheet.
- If diagrams are to be drawn, draw a reasonably sized diagram neatly in pencil and label it in ink.
- Make sure you understand basic chemical concepts, for example, why metals conduct electricity.
- Be able to explain forces which hold particles together.
- Practice drawing relevant Lewis electron dot diagrams and hence state shapes of the molecules.
- Draw and interpret any graphs carefully.
- Read carefully through any relevant experiments noting any underlying principles and the purpose of the practical work.

Chemistry skills

Chemistry applies mathematics to its measurements, data and its reading of instruments, all of which must meet acceptable levels of accuracy.

Scientific notation

Scientific notation is a means of writing very large or very small numbers in a clear, concise and unambiguous way. A number is written in scientific notation by writing it as a number between 1 and 10 multiplied by the appropriate power of ten. To do this you should move the decimal point so that only one digit remains to the left of it. The number is then multiplied by a power of ten. If you moved the decimal point three places to the left multiplied by ten to the power of three, 10^3. If you moved the decimal point three places to the right it must be multiplied by ten to the power of minus three, 10^{-3}.

Example	Number	Number written in scientific notation
	1896	1.896×10^3
	0.00593	5.93×10^{-3}

Significant figures

When using and interpreting numbers it is important to calculate your final answer to the required number of significant figures.

Make sure that you do not include decimal places just because they appear on your calculator.

Example

$$\text{Density} = \frac{\text{mass}}{\text{volume}} = \frac{18.79\ \text{g}}{3.06\ \text{cc}}$$

from experimental data
the result should be 6.14 g cm^{-3}

Your calculator would give you a result of 6.1372549 and would include figures that were not meaningful for your experimental measurements.

Scientific Notation for Significant Figures

With a large number such as 25 400 cm it is possible to misinterpret the number or make a mistake, but by using scientific notation the experimenter can show the degree of precision which has been attained.

2.54×10^4 cm (3 significant figures)
2.540×10^4 cm (4 significant figures)
2.5400×10^4 cm (5 significant figures)

When adding or subtracting significant figures, the same number of decimal points that are present in the least precise measurement are retained in the answer.

When multiplying or dividing significant figures, the answer carries the same number of significant figures as are present in the factor with the least number of significant figures.

Example 1 73.01 g + 4.357 g = 77.37

Example 2 $\frac{3.7 \times 14.1}{274.6} = 0.19$

Errors

In chemical calculations and first-hand investigations it is possible for a number of different factors to introduce errors into your results. In your course you will be using data from many sources. It is important to be aware of the degree of uncertainty that may be present in measurements taken during experiments.

Errors
- Systematic (mainly instrumental)
- Random (unpredictable, for example, bad eyesight, varying room temperature)
- $\text{Relative error} = \frac{\text{absolute error}}{\text{true value}}$

Example measurement = 4.32 ± 0.06 cm

$$\text{relative error} = \frac{0.06}{4.36} = 0.014$$

% relative error = 1.4%

Qualitative or quantitative analysis

When collecting or carrying out experiments to obtain data, you will need to determine whether qualitative (what substances are present) or quantitative (how much of a substance is present) analytical procedures are required. For example, do you need to find out if iron is present as an impurity in a sample of brass or do you need to find out the percentage of iron that is present in the brass?

Destructive or non-destructive testing

Before testing material in a first-hand investigation you must know whether the material, for example, brass, is to be tested in a non-destructive manner such as by finding out physical properties like density or whether it can be tested destructively, such as dissolving a weighed sample in nitric acid to determine the copper content.

Prefixes commonly used in Chemistry

Multiplying by	Prefix	Symbol
10^6	mega	M
10^3	kilo	k
10^2	hecto	h
10	deka	da
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n

The International System (SI) of Units

An international system of units is used when scientific measurements are made. The base units used in Chemistry are given in the table below.

Derived units are built from these fundamental units. For example, the commonly used unit for the volume of liquids is the litre (L) and its volume is 1/1000 of a cubic metre.

Base or fundamental units

Quantity	Quantity symbol (written in italics)	Unit	Unit symbol (written in roman letters)
Mass	m	kilogram	kg
Length	l	metre	m
Time	t	second	s
Amount of substance	n	mole	mol
Temperature	T	kelvin	K
Volume	V	litre	L

Graphing skills

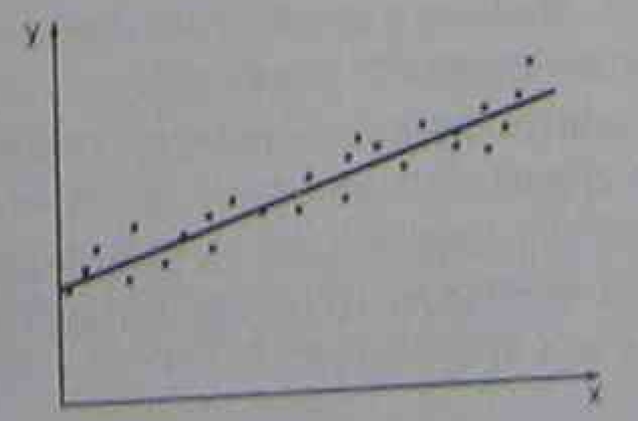
During your Chemistry course and in exams, you will be required to interpret and draw graphs. Graphs are a very useful method of conveying information clearly and accurately if they are used correctly.

Here are some basic rules for using graphs.

(a) **Variables.** The independent variable is plotted along the x-axis (horizontal axis). The dependant variable is plotted on the y-axis (vertical axis). Axes must be labelled and units of measurement indicated.

(b) **Scales** must be
  (i) as large as possible
  (ii) on a linear scale, unless using semi-log graph paper.

(c) **Points** must be
  (i) accurately plotted
  (ii) line of best fit should be used



  (iii) in some cases a curve of best fit is suitable, for example, solubility curves
  (iv) extrapolation should be avoided since predictions are often inaccurate.

(d) Statistics are often presented as bar charts, pie charts or computer generated graphs.

The Scientific Method

The Scientific Method is the logical way in which a scientist goes about trying to solve a problem. Chemistry uses a step by step process to gain and refine information and to solve chemical problems.

1. **Observations.** Make observations about the problem you are investigating, using all your senses – sight, smell, touch, taste and hearing.
2. **Classification.** Consider your observations and identify any patterns you may have noticed. Define the problem based on your observations.
3. **Hypothesis.** Make an educated guess at a possible solution to your problem.
4. **Test the hypothesis.** Design a first-hand investigation to test your hypothesis.
5. **Results.** Collect and record the results of your first-hand investigation.
6. **Analysis.** Analyse and think critically about your results to see if they have supported your hypothesis.
7. **Conclusions.** If your results support your hypothesis, finish by writing up your conclusions. If your results do not support your hypothesis you must formulate a new hypothesis and work through the same process to test your new hypothesis.

Note: If a hypothesis is tested over a long period of time and is found to apply in all cases it becomes known as a law, for example, Avogadro's Law.

Practical skills

Chemistry is a practical subject and many examination questions will relate to practical work. Also many of the syllabus outcomes focus on your ability to plan, carry out and analyse first-hand investigations. You should read the practical work below carefully and make sure you understand all the skills associated with first-hand investigations.

During your experimental work you will not only learn a great deal of chemistry, but also develop correct techniques for planning, conducting and writing up first-hand investigations, and in handling chemicals and equipment carefully and safely.

First-hand investigations

Planning first-hand investigations

Planning, or designing, your own first-hand investigations is something you will be required to do as part of your Chemistry course. Here are some points to help you.

Begin by thinking about these questions.

- What do you need to find out?
- How can you design a question, or questions, which will help you reach a suitable conclusion? (These questions will probably guide you in forming your hypothesis.)
- What type of data will you need to collect to answer your questions?
- What equipment will you need to carry out your first-hand investigation?
- What types of errors and problems are you likely to encounter as part of your experimental procedure and how can you design your first-hand investigation to minimise errors?
- What safety procedures do you need to follow to avoid accident or injury?
- How can you write up your experiment, using diagrams, graphs, tables, and a step by step written explanation, to best illustrate your procedure, results and conclusion?

Once you have considered these questions (and any others you think of), write out a step by step plan for your first-hand investigation.

It is important that your first-hand investigation is a controlled experiment. This means that you must have identified all **variables** and use a **control**.

Variables

All experiments have variables. A variable is an environmental factor or condition, for example, temperature, or the solubility of a salt. These variables may be **independent** or **dependent**. The independent variable is the factor or condition being tested by the experiment. It is the one you have control over in your experiment. The dependent variable is the factor that responds to the change in the independent variable. You have no control over this variable.

Note: In graphs, the independent variable is plotted on the x-axis (horizontal axis) and the dependent variable is plotted on the y-axis (verical axis).

Control

To make sure your experiment tests your hypothesis fairly you will need to use a control. This means that all the variables are kept constant except the one you are investigating. By doing this you can make sure that any changes are due to that one variable and nothing else.

Performing your first-hand investigation

Once you have planned your first-hand investigation you will be required to carry it out, either on your own or as part of a small team. You should work through the procedure carefully. The purpose of most first-hand investigations is to gather first-hand data. To ensure that your data is correct, you will need to be careful when taking all measurements so they are as accurate as possible.

If you experience problems with your experiment you may need to make adjustments to the procedure to eliminate errors. For example, you may be carrying out a heat of combustion experiment using a spirit lamp. A draft may be blowing the flame around so that you must organise a shield. It is important to be able to 'think on your feet'.

If possible, repeat the first-hand investigation to check your results.

Carry out your first-hand investigation to minimise hazards and save resources. After your experiment you must clean up thoroughly. Remember 'a good chemist is a clean chemist'. Dispose of waste material as recommended.

Take note of the safety practices listed on page xv and follow them carefully.

Transfer of solutions

When transferring a solution from a beaker into a filter funnel use a glass rod across the pouring lip of the beaker to direct the flow of solution.

Measurement of volume

Each item of glassware has its specific use depending on the accuracy required.

- Beakers with calibration marks on the side can be used for approximate dilutions.
- Measuring cylinders are used for greater accuracy. Readings are taken from the bottom of the meniscus and at eye level.
- Volumetric flasks are used to make up standard solutions.
- Pipettes are used to transfer a specific volume of solution. A small amount of the liquid should be allowed to remain in the pipette after draining into the receiving vessel, for example, a conical flask.
- A burette is a graduated tube with a tap at the lower end and a zero mark at the top. It is widely used in titration work.

Filtration

Filtration through a filter paper supported in a funnel is widely used to separate a precipitated solid from a liquid. After the paper is correctly folded, it is opened out to form a cone with three thicknesses of paper on one side and one on the other. This cone is placed in a filter funnel and dampened using a wash bottle to hold it in place. When washing the precipitate to remove traces of the filtrate use small washes several times.

Igniting a precipitate

The precipitate, after being dried in an oven at about 120°C, should be folded into a 'parcel' and placed in a clean, dry crucible. The crucible and lid assembly should have been previously weighed. The crucible is first placed at an angle on a pipe clay triangle with the lid covering about three-quarters of the opening until the paper is carbonised. Using metal tongs, the crucible is placed upright with the lid on and is heated, cooled in a desiccator and weighed until constant mass is reached.

Weighing using an electronic balance

No chemical reagents should be placed directly on the pan. No hot objects should be weighed on the balance.

Distillation

A liquid can be separated from dissolved solids or another liquid with a higher boiling point (at least 10°C difference) by distillation. During distillation the thermometer (placed to measure the vapour temperature) will record a constant temperature (that of the liquid being distilled). The cold water supplied to the condenser must flow in at the lower end and out at the upper end. To stop 'bumping' during boiling, a few pieces of 'porous pot', for example, a broken crucible, should be added to the flask before distillation is started.

Safety practices

Many chemical procedures can be dangerous if not carried out correctly. Sometimes the substances being handled are corrosive or toxic. To avoid accidents there are some very effective safety procedures which must be followed.

- Protective clothing and footwear must be worn.
- Safety glasses should be worn during experiments.
- Long hair should be suitably fastened.
- Every student should know where to find the fire extinguishers and fire blanket.
- All accidents, breakages and faulty equipment should be reported immediately to the teacher.
- All spills should be wiped up immediately.
- Any labels on hazardous chemicals should be noted and their use in school laboratories avoided.
- When storing flammable substances in schools and colleges, a large metal cupboard with spring loaded lockable doors should be used. A flammable warning sticker should be attached. This cupboard should be kept in a permanently ventilated storeroom. A fire extinguisher should be present.
- Students should work in a fume cupboard when heating flammable liquids. Use hot plates rather than bunsen burners.
- A water bath should be present if a bunsen burner is used.
- Inhaling fumes of organic compounds should be avoided.
- Organic wastes should be placed in a residue bottle for later collection and safe disposal.

Labelling of Hazardous Chemicals

Hazardous chemicals are identified by a system of codes and symbols which appear clearly displayed on containers of chemicals.

Hazard Classifications

Class 1. Explosive

Class 2. Gases
2a Flammable

2b. Non flammable
2c. Toxic

Class 3. Liquids
3a. Extremely flammable Fp < –18°C
3b. Highly flammable Fp > –18°C < +23°C
3c. Flammable Fp > +23°C < +61°C

Class 4. Flammable solids
4a. Flammable
4b. Spontaneously combustible
4c. Dangerous when wet

Class 5. Oxidising agent

Class 6. Toxic
NR = Not regulated

6n. Harmful

Class 7. Radioactive
NA = Not available

Class 8. Corrosive

8i. Irritant

Writing up first-hand investigations

You will learn the preferred method for writing up first-hand investigations in your Chemistry classes, but here are some important points to consider.

Keep accurate records of the data you collect, and any other relevant observations, while you are *conducting the first-hand investigation*. It is easy to make mistakes if you leave this until after the experiment is completed.

Make your language clear and concise when writing up your first-hand investigation. Remember that you are communicating your procedure, results and conclusions to someone else so it must be easy to understand. Also, it is most likely that you will need to refer back yourself to the first-hand investigation at a later date.

Your write-up should use a number of different methods for conveying information — prose explanation, bullet points, tables, graphs, diagrams and flow charts.

Your write-up should include:

1. The name of the first-hand investigation.
2. The date it was carried out.
3. The names of the students carrying out the first-hand investigation.
4. The aim of the first-hand investigation (what you were trying to find out).
5. The method and equipment used (describe these clearly and concisely).
6. The results (include numerical results and other observations).
7. Chemical equations and mathematical calculations relating to the data.
8. Your conclusions (including any problems you experienced, improvements to the procedure, patterns in your results, comparison of your results with expected outcomes and a concluding statement which refers back to the aim).

Assessing and collecting information from secondary sources

As well as collecting information from first-hand investigations, you will also be required to supplement this data with information from secondary sources.

Information skills

Finding information

Printed material (from libraries) — text books, study guides and reference books, science magazines and journals, newspaper articles.

Electronic — the Internet and CDs.

Visual — photographs, drawings, video and film.

Audio — radio, lectures, tapes and CDs.

Using and understanding information

Defining your research task and deciding where to look.

Locating the required information.

Selecting and evaluating the most suitable pieces of information.

Organising the information and combining information from different sources.

Presenting the information in an appropriate and easy to understand manner.

1 — The Production of Materials

Contents

Introduction

Because of the enormous and continuing increase in human population over the past several centuries, there has been a significant growth in average energy consumption and a subsequent depletion of non-renewable resources such as fossil fuels. To meet these and other unforeseen human demands during the past century, there has been a substantial and expanding growth in scientific knowledge and the application of technological skills to a range of new materials.

This chapter deals with such developments in energy production and other applied sciences.

Some initial points to note are:

- Fossil fuels are not only a major energy source, especially for transportation and power production, but also provide the raw materials, such as ethene, for a wide range of petrochemical products.
- In this 'plastic age', the main use of ethene is to produce polyethylene (50%) polyvinyl chloride (PVC, 15%) and polystyrene or styrofoam (10%).
- Scientists continue to research and develop new biomass fuels, usually by fermentation processes. The biopolymer cellulose, for example, contains the basic carbon chain structure and will help reduce our dependence on non-renewable fossil fuels as they become even more severely depleted.
- The discovery of the first electrical battery provided a powerful tool for chemists. Chemical or galvanic cells have been manufactured and sold to fill a large number of everyday electrical needs, from motor vehicle batteries to hearing aids.
- An electrochemical method called electrolysis is used by the mining industry to win and refine a range of important metals. Electroplating is also widely used in industry as a coating, either to improve the appearance of metals or to protect them from corrosion.
- Nuclear reactors provide an alternative source of energy to fossil fuels. Nuclear chemistry based on this technology provides a range of radioisotopes for use in industry, diagnostic and therapeutic medicine, agriculture and many other fields. Although natural radioactivity has existed throughout the history of the Earth, the planet is now old enough to have allowed the originally intense natural radioactivity to almost disappear.

Carbon chemistry

1.1 Naming of carbon compounds

The systematic naming of carbon compounds is in two parts:

(a) Stem

A **stem** to show the number of carbon atoms.

C_1	meth-	C_6	hex-
C_2	eth-	C_7	hept-
C_3	prop-	C_8	oct-
C_4	but-	C_9	non-
C_5	pent-	C_{10}	dec-

(b) Ending

An **ending** to show the grouping of atoms or functional group.

For hydrocarbons with

single bonds	-ane
a double bond	-ene
a triple bond	-yne

Hydrocarbons are compounds which are made up of hydrogen atoms and carbon atoms only.

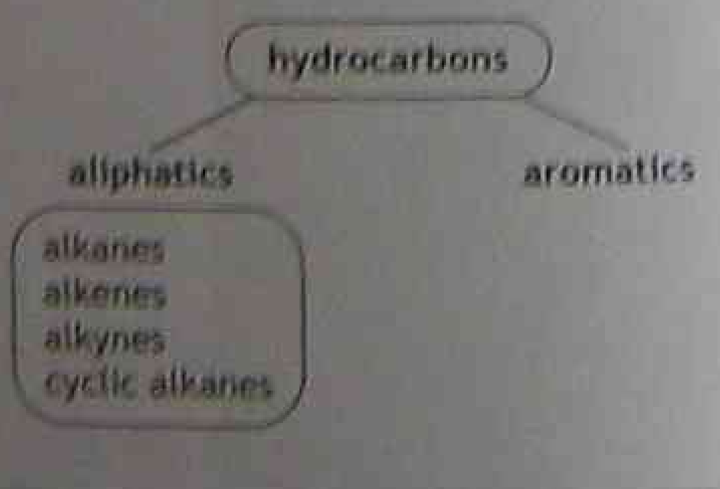


Figure 1.1 Types of hydrocarbons

Functional group: an atom or group of atoms which gives a homologous series its characteristic chemical properties.

Homologous series: a series in which all the members have the same functional group and the same general molecular formula. Members differ by a $-CH_2$ group.

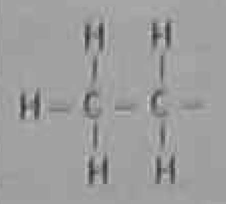
Alkanes

1. Saturated hydrocarbons.
2. Same homologous series.
3. General molecular formula C_nH_{2n+2}.
4. Found in natural gases (C_1–C_4) and liquid petroleum (C_5–C_{17}).
5. Functional group is alkyl group.
6. Contain single C–C bonds only.

Branched-chain hydrocarbons

Alkyl groups are alkane chains minus a hydrogen atom. The -ane of the parent hydrocarbon is dropped and the -yl is added.

Table 1.1 Alkyl groups

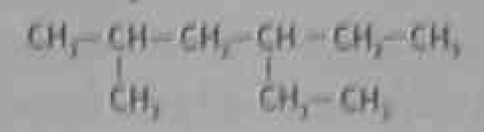
No. of carbon atoms	Structural formula		Alkyl group name
	Full	Condensed	
One		CH_3-	methyl
Two		CH_3CH_2-	ethyl

Rules for naming branched-chain alkanes

1. Find the longest chain of carbon atoms in the molecule.
2. Name any branch (side) chains as the alkyl groups.
3. Number the side chains from the end of the parent chain which will give them the lowest number.
4. When there is more than one side chain, they are listed alphabetically.
5. If the same side chain occurs more than once, prefixes di-, tri-, tetra- are used.

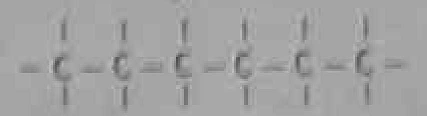
Example 1

To name the compound drawn below:



$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-\underset{\displaystyle CH_2-CH_3}{\underset{|}{CH}}-CH_2-CH_3$$

Step 1. Draw the longest carbon chain.



Step 2. Use the chain like a surname.

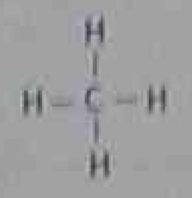
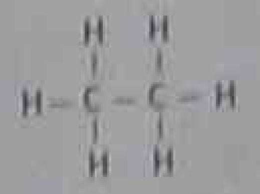
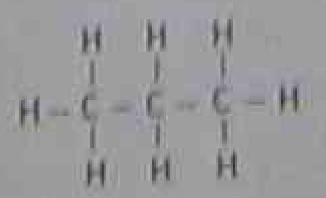
..... hexane

Step 3. Name side chain in alphabetical order.

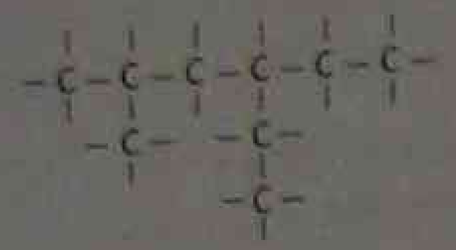
ethyl-methyl

Step 4. Number from the end of the skeleton to give the lowest number for side chains. Naming of branches is alphabetical before numerical.

Table 1.2 The alkanes (first 3 members)

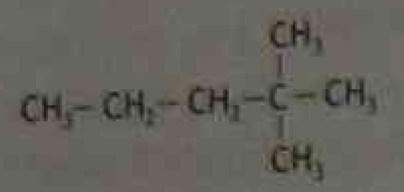
Name	Molecular formula	Structural formula	State (SLC*)	Uses as fuels
Methane	CH_4		gas	natural gas (78%)
Ethane	C_2H_6		gas	natural gas (small %)
Propane	C_3H_8		gas	LPG (butane and propane)

* SLC – standard laboratory conditions (25°C/100 kPa)



(Answer: 4-ethyl-2-methylhexane)

Example 2

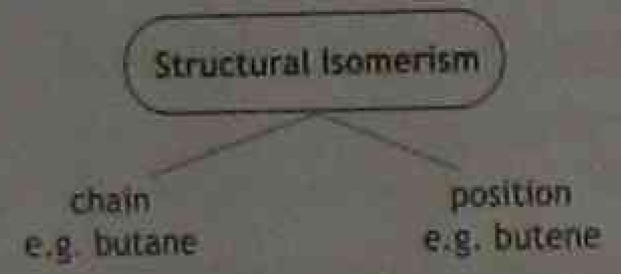


$$CH_3-CH_2-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3$$

When same-name side chains are involved, use prefixes, di-, tri-... The compound above is called 2, 2-dimethylpentane.

Isomerism in alkanes

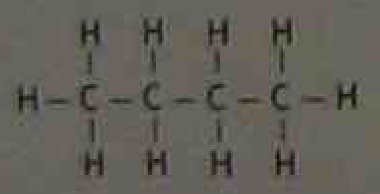
Isomers are compounds which have the same molecular, but different structural, formula.



Isomers of butane

Molecular formula C_4H_{10}

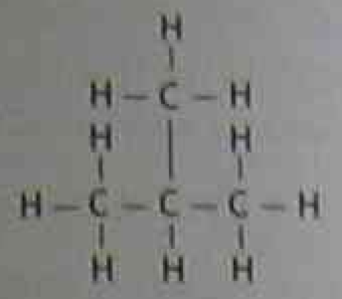
Straight chain

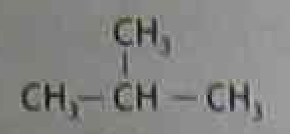


$CH_3-CH_2-CH_2-CH_3$

butane

Branched chain





$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_3$$

2-methylpropane

Alkenes

Unsaturated hydrocarbons.

General molecular formula C_nH_{2n}.

Functional group C = C.

Models

Model kits should be used regularly to show that carbon-carbon covalent bonds may be

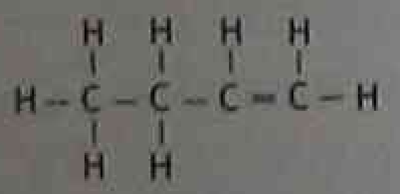
	single:	C – C
	double:	C = C
or	triple:	C ≡ C

Other elements can join these structures, the commonest being hydrogen, oxygen, nitrogen, sulfur and the halogens.

After propene, different isomers are possible by shifting the position of the double bond, so the double bond must be numbered.

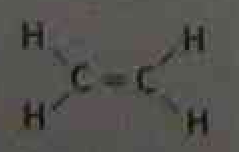
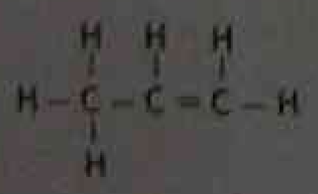
1-butene

C_4H_8



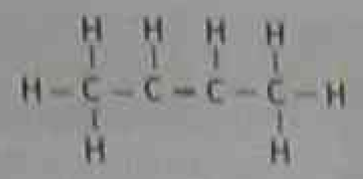
gas

Table 1.3 The alkenes

Name	Molecular formula	Structural formula	State (SLC) 25 °C/100 kPa	Uses
Ethene	C_2H_4		gas	making plastics (e.g. polyethylene), alcohol, antifreeze (ethylene glycol)
Propene	C_3H_6		gas	making plastics (e.g. polypropylene)

2-butene

C_4H_8



gas

Position isomers

Same homologous series.

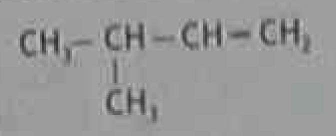
Different position of functional group, e.g. alkenes C = C bond. Owing to isomerism, additional naming rules are needed.

Rules for naming alkenes

1. Choose the longest consecutive chain of carbon atoms that includes the double bond, and name it as the parent alkene.
2. Number the chain from the end that gives the double bond its smaller number.
3. Name and number the alkyl groups as with the alkanes.

Example

When side chains are present.
Name the compound drawn below:



$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH=CH_2$$

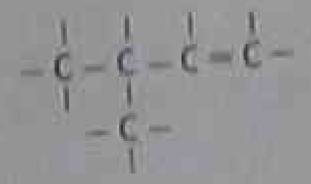
Step 1. Draw the longest carbon chain that contains the double bond.

$$-\overset{4}{C}-\overset{3}{C}-\overset{2}{C}=\overset{1}{C}-$$

Step 2. Use the chain as a surname. Number the chain.

..........1-butene

Step 3. Name and number any side chains, using the same numbering system as for the double bond.



3-methyl-1-butene

Haloalkanes

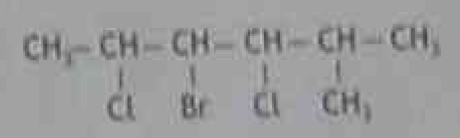
Compounds in which one or more hydrogen atoms of alkanes have been replaced by halogen atoms (F, Cl, Br, I) are called haloalkanes.

Rules for naming haloalkanes

1. Prefixes bromo-, chloro-, fluoro- and iodo- are used with the parent hydrocarbon.
2. The carbon chain is numbered so that the halogen atom has the smallest possible number.
3. In the case of polyhalogen compounds:
    (a) If only one type of halogen atom is present, each is numbered, and di-, tri-, etc are used.
    (b) If more than one type of halogen atom is present, they are listed alphabetically as in 1.
4. Since the halogen atoms are functional groups, they are numbered in preference to any side chains.

Example

To name the compound below.



$$CH_3-\underset{\underset{\displaystyle Cl}{|}}{CH}-\underset{\underset{\displaystyle Br}{|}}{CH}-\underset{\underset{\displaystyle Cl}{|}}{CH}-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$$

Step 1. Find the longest straight carbon chain.

....................hexane

Step 2. Number from the end that will make the halogens the lower.

Step 3. Arrange halo atoms in alphabetical order.

Step 4. Name and number any side chains present.

The name of the compound is 3-bromo-2,4-dichloro-5-methylhexane.

1.2 Classification of organic reactions

Substitution

This is the replacement of one atom or group by another:

$$P-Q + R \rightarrow P-R + Q$$

Substitution reactions occur with the chlorination of alkanes in the presence of ultraviolet light. A mixture of CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 can be formed.

Addition

It is possible to add atoms or groups of atoms to alkenes or alkynes. The reaction occurs at a double bond or at a triple bond.

$$-\overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}}- \;+\; P-Q \;\rightarrow\; -\overset{P}{\underset{|}{C}}-\overset{Q}{\underset{|}{C}}-$$

Here one bond breaks and the reagent adds onto the molecule.

Elimination

This is the reverse of addition. A small molecule breaks off and a double bond is formed.

$$-\overset{P}{\underset{|}{C}}-\overset{Q}{\underset{|}{C}}- \;\rightarrow\; -\overset{|}{C}=\overset{|}{C}- \;+\; P-Q$$

Condensation

Two molecules react, forming a new compound and a small molecule, usually water.

$P + Q \rightarrow R + H_2O$

organic acid + alkanol → ester + water

Hydrolysis

This is the opposite of condensation. The action of water on a molecule results in two new products:

$R + H_2O \rightarrow P + Q$

ester + water → organic acid + alkanol

The equilibrium can be shifted by adding acids or bases.

Polymerisation

Polymerisation, to form a long-chain molecule or polymer from monomers, can be

(i) addition, e.g. in alkenes, or

(ii) condensation, when a small molecule is eliminated, e.g. nylon-66.

1.3 Common aliphatic reactions involving ethylene

Ethylene, because of the high reactivity of its double bond, is readily transformed into many useful products as seen in the flowchart below:

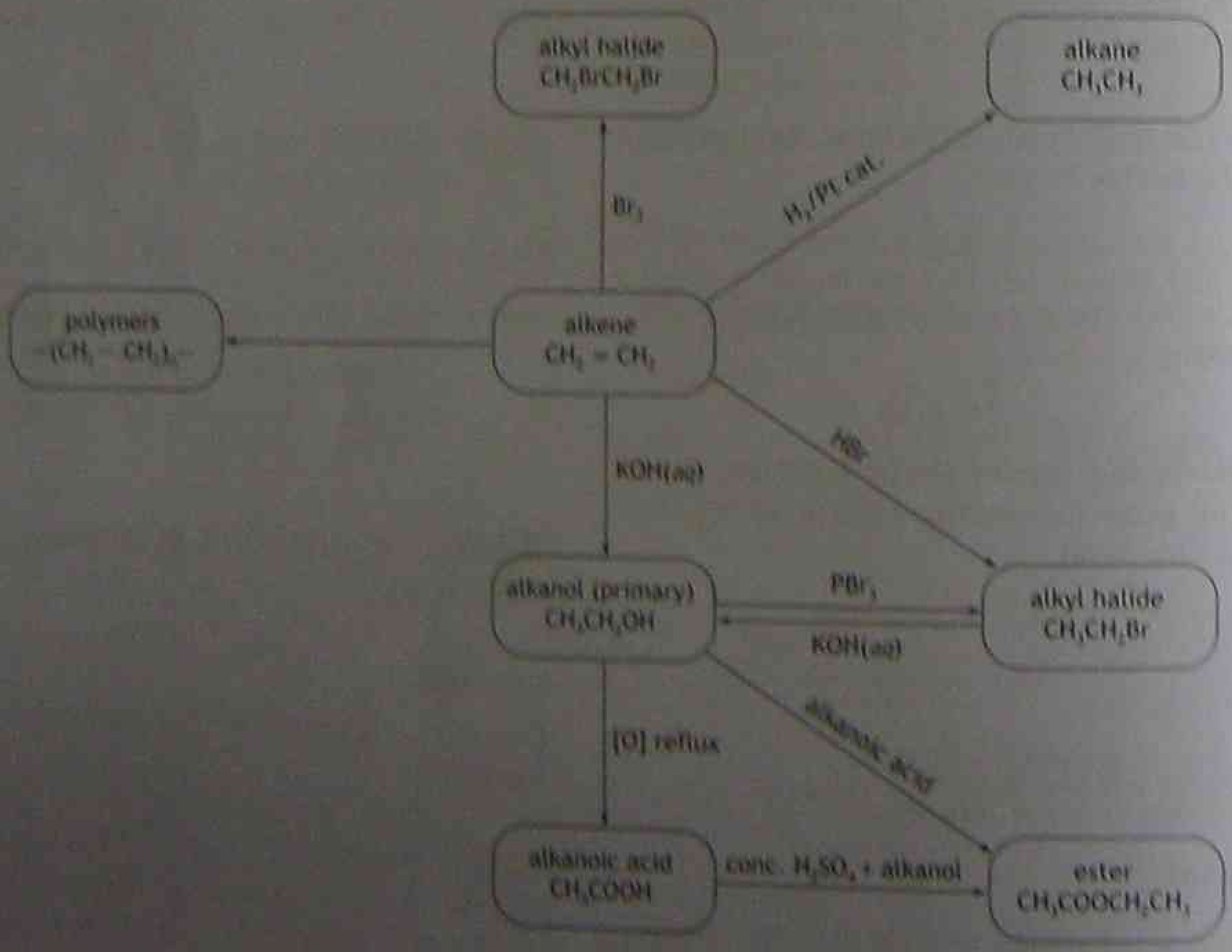
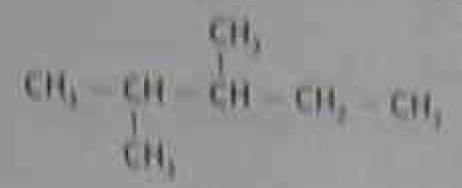


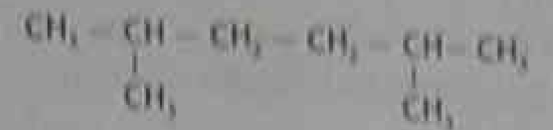
Figure 1.4 Flow chart of common aliphatic reactions

Problems on carbon chemistry

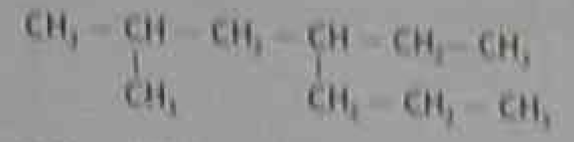
1. Write names for the following structural formulae:

(a) 

$CH_3-\underset{CH_3}{CH}-\overset{CH_3}{CH}-CH_2-CH_3$

(b) 

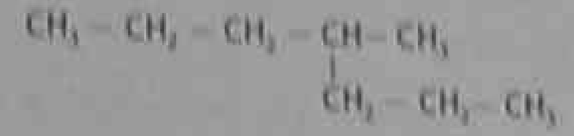
$CH_3-\underset{CH_3}{CH}-CH_2-CH_2-\underset{CH_3}{CH}-CH_3$

(c) 

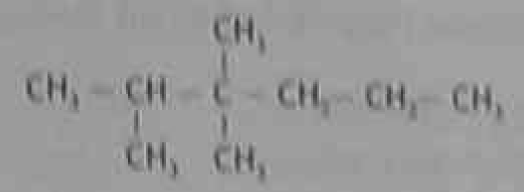
$CH_3-\underset{CH_3}{CH}-CH_2-\underset{CH_2-CH_2-CH_3}{CH}-CH_2-CH_3$

(d) $CH_3-(CH_2)_8-CH_3$

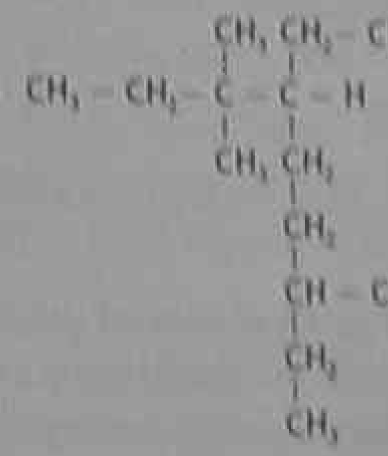
(e) $(CH_3)_3-CH$

(f) 

$CH_3-CH_2-CH_2-\underset{CH_2-CH_2-CH_3}{CH}-CH_3$

(g) 

$CH_3-\underset{CH_3}{CH}-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_2-CH_3$

(h) 

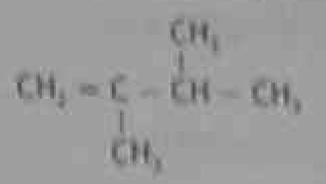
$CH_3-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_2-CH_3}{\underset{\substack{CH_2\\|\\CH_2\\|\\CH-CH_3\\|\\CH_2\\|\\CH_3}}{C}}-H$

2. Write structural formulae for:
   (a) 2,2-dimethylpropane
   (b) 2,2,4-trimethylhexane
   (c) 2-methylpentane
   (d) 2,3,3-trimethylhexane
   (e) 2,3,5-trimethylhexane
   (f) 3-methylpentane
   (g) 5-propyl-2,4-dimethylnonane

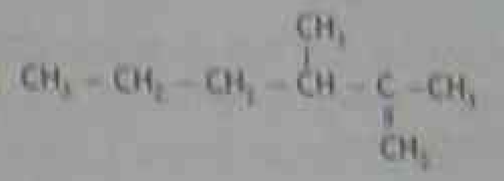
3. Explain why the following names are incorrect. Draw the structural formula and name each correctly:
   (a) 1,3-dimethylbutane
   (b) 4-methylpentane
   (c) 4,4-dimethylhexane

4. Draw and name the structural isomers of C_6H_{14}.

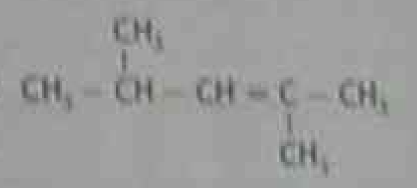
5. Name the following compounds:

(a) 

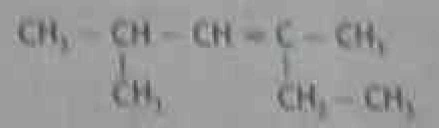
$CH_2=\underset{CH_3}{C}-\overset{CH_3}{CH}-CH_3$

(b) 

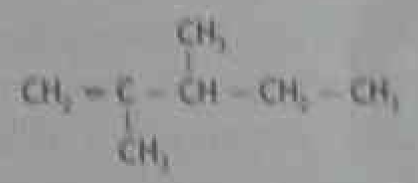
$CH_3-CH_2-CH_2-\overset{CH_3}{CH}-\underset{\substack{\|\\CH_2}}{C}-CH_3$

(c) 

$CH_3-\overset{CH_3}{CH}-CH=\underset{CH_3}{C}-CH_3$

(d) 

$CH_3-\underset{CH_3}{CH}-CH=\underset{CH_2-CH_3}{C}-CH_3$

(e) 

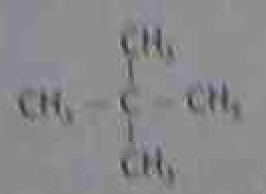
$CH_2=\underset{CH_3}{C}-\overset{CH_3}{CH}-CH_2-CH_3$

(f) 

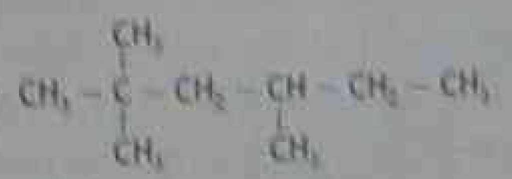
$CH_3-CH=CH-\underset{CH_3}{CH}-CH_2-CH_3$

Answers to problems on carbon chemistry

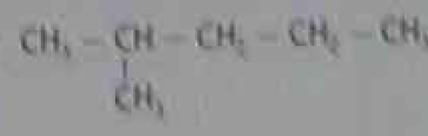
1. (a) 2,3-dimethylpentane
   (b) 2,5-dimethylhexane
   (c) 4-ethyl-2-methylheptane
   (d) decane
   (e) 2-methylpropane
   (f) 4-methylheptane
   (g) 2,3,3-trimethylhexane
   (h) 4-ethyl-3,3,7-trimethylnonane

2. (a) 

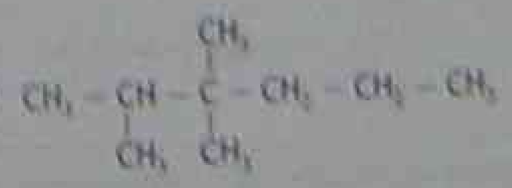
$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$

(b) 

$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\underset{CH_3}{CH}-CH_2-CH_3$

(c) 

$CH_3-\underset{CH_3}{CH}-CH_2-CH_2-CH_3$

(d) 

$CH_3-\underset{CH_3}{CH}-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_2-CH_3$

(e) 

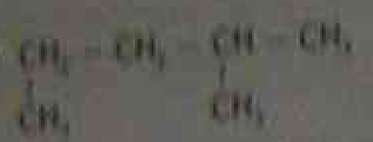
$CH_3-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-\underset{CH_3}{CH}-CH_3$

(f)

$$CH_3-CH_2-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-CH_2-CH_3$$

(g)

$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_2-CH_2-CH_3}{|}}{CH}-CH_2-CH_2-CH_2-CH_3$$

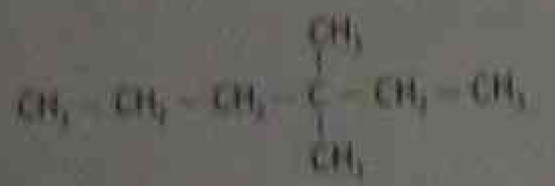
3. (a)

$$\underset{\underset{CH_3}{|}}{CH_2}-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

The longest chain is pentane, so name is 2-methylpentane.

(b)

$$CH_3-CH_2-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3$$

Number from end closest to the side chain, so compound is 2-methylpentane.

(c)

$$CH_3-CH_2-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-CH_3$$

Number from the end that gives side chains the smallest number, so compound is 3,3-dimethylhexane.

4. Structural isomers of C_6H_{14}

$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$

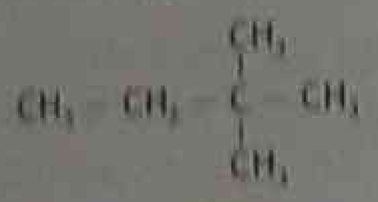
hexane (straight chain)


$$CH_3-CH_2-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3$$

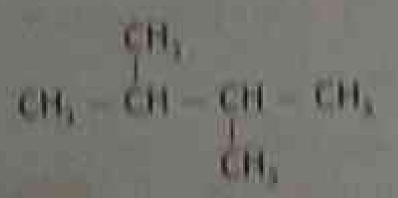
2-methylpentane (single-branched chain)


$$CH_3-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_3$$

3-methylpentane (single-branched chain)


$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

2,2-dimethylbutane (double-branched chain)


$$CH_3-\overset{\overset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-CH_3$$

2,3-dimethylbutane (double-branched chain)

5. (a) 2,3-dimethylbut-1-ene
(b) 2,3-dimethylhex-1-ene
(c) 2,4-dimethylpent-2-ene
(d) 3,5-dimethylhex-3-ene
(e) 2,3-dimethylpent-1-ene
(f) 4-methylhex-2-ene

1.4 The industrial source of ethylene

Ethylene


Because of the reactivity of its double bond, ethylene is used in the manufacture of polyethylene and many key intermediate products.

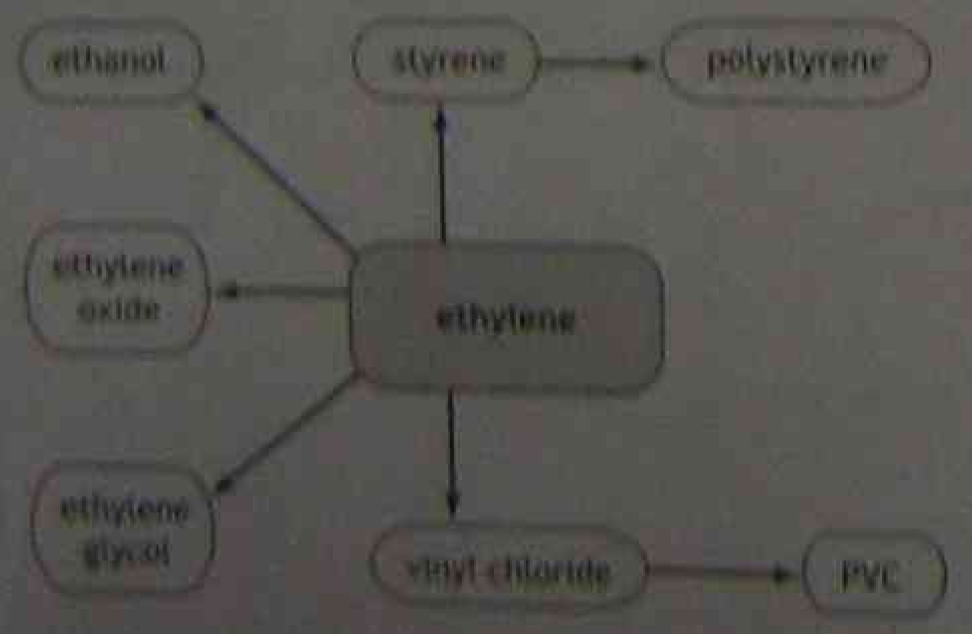


Figure 1.5 Some petroleum products manufactured from ethylene

Ethylene is produced either from *natural gas* or *crude oil*, which are mixtures of hydrocarbons (mostly alkanes); petroleum refineries use both chemical and physical changes to produce ethylene.

Thermal cracking

The main method used to produce unsaturated hydrocarbons such as ethene (ethylene) is by the thermal cracking of suitable feedstock. Typical feedstocks are:

(a) Ethane and propane from natural gas.

(b) Ethene can also be produced from the fractional distillation of crude oil using naphtha or gas oil fractions. The type of feedstock used determines and alters the plant conditions needed to yield the desired product. Examples of chemical reactions which occur during the thermal cracking process are as follows:

(i) $\underset{\text{ethane}}{C_2H_6(g)} \rightleftharpoons \underset{\text{ethylene}}{C_2H_4(g)} + H_2(g) \quad \Delta H = +138\ \text{kJ mol}^{-1}$

Hydrogen is a useful by-product that is used to manufacture fertiliser and harden margarine.

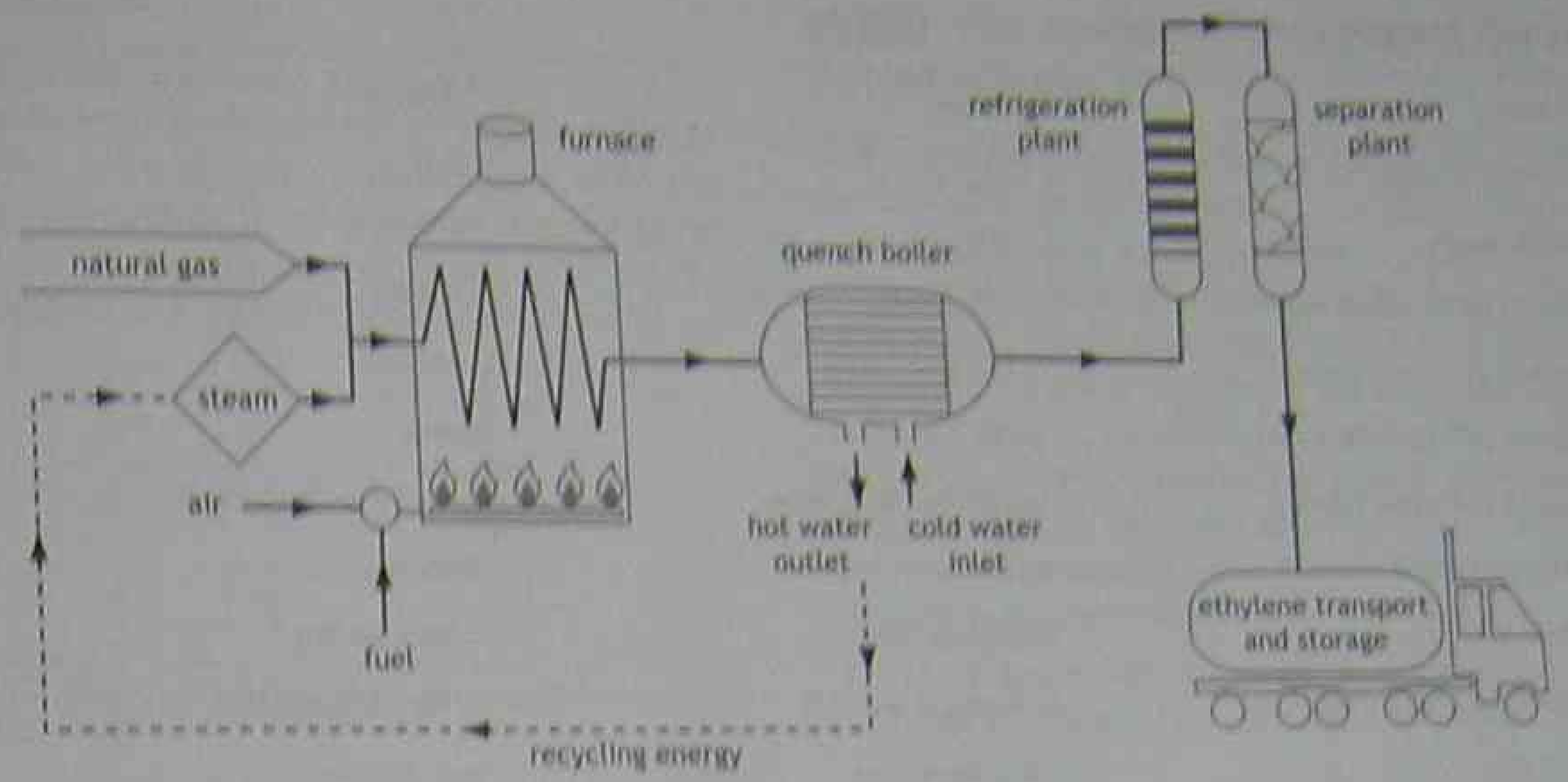


Figure 1.6 Thermal cracking flow chart

(ii) $\underset{\text{propane}}{C_3H_8(g)} \rightleftharpoons \underset{\text{ethylene}}{C_2H_4(g)} + \underset{\text{methane}}{CH_4(g)} \quad \Delta H = +81\ \text{kJ mol}^{-1}$

Any methane produced is mixed with natural gas.

Since both reactions are endothermic, high temperatures (reduced by the use of catalysts) will result in a high equilibrium yield of ethene.

Ethylene is used as a starting point in the production of synthetic organic compounds including insecticides, refrigerants, explosives and pharmaceuticals, as well as the products shown in Figure 1.5.

The cracking of alkanes to produce lighter fractions is now carried out by the *catalytic cracking* process. By using *zeolite catalysts*, cracking can be carried out at 400–500°C. Zeolites are a naturally occurring group of substances containing a mixture of aluminium and silicon oxides.

1.5 Differences between alkanes and alkenes

The *alkanes* comprise most of the compounds in crude oil.

Their general molecular formula is C_nH_{2n+2}

The formula of each successive member of the series increases by a $-CH_2$ group, so its overall mass increases by 14. The alkanes form a *homologous series* with similar chemical properties and physical properties that change gradually with increasing molar mass. Carbon forms no more than four bonds in any of its compounds, so the alkanes which bond to four other atoms from each carbon atom are called saturated hydrocarbons.

Note: Both alkanes and alkenes show their non-polar nature by being insoluble in the polar solvent water since the forces between water molecules are relatively strong. Alkanes and alkenes will dissolve in other hydrocarbons and similar compounds since they all have dispersion forces as their sole intermolecular force. The size of the intermolecular force depends on the size of the molecule and thus increases with increasing molecular size.

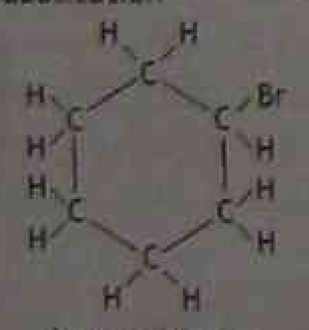
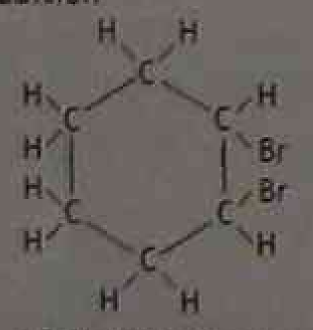
A simple distinguishing test

A simple test to distinguish between an alkene and the corresponding alkane depends on the greater reactivity of alkenes. The test is usually demonstrated in the laboratory using cyclohexane and cyclohexene, since they are both liquids at room temperature and pressure (RTP).

Table 1.5 Properties of alkanes and alkenes

Property	Alkanes	Alkenes
General formula	C_nH_{2n+2}	C_nH_{2n}
Family name	– ane	– ene
Melting point (1st member)	–183°C	–169°C
Boiling point (1st member)	–162°C	–104°C
State at RTP (members 1-4)	gases	gases
State at RTP (remainder)	low BP liquids or solids	low BP liquids or solids
Solubility in water	insoluble	insoluble
Organic solvents	mainly soluble	mainly soluble
Combustion with excess O_2	to form CO_2 and H_2O	to form CO_2 and H_2O
Reactivity	fairly unreactive	very reactive
Characterisitic reaction	substitution	addition
First member	CH_4	$CH_2 = CH_2$
Name	methane	ethylene
Bonding	single C – C bonds	one double C = C bond at least

Table 1.6 Differences between alkene and alkane on the basis of cyclohexane and cyclohexene laboratory tests

Reagent	Cyclohexane  C_6H_{12}	Cyclohexene  C_6H_{10}
Bromine water	brown colour of Br_2 remains with slow fading in ultraviolet light	brown colour of Br_2 is decolourised instantly
Type of reaction	substitution  bromocyclohexane	addition  1,2-dibromocyclohexane
Equation	$CH_3CH_3(g) + Br_2(l) \rightarrow$ ethane $CH_2BrCH_3(l) + HBr(g)$ bromoethane	$H_2C{=}CH_2(g) + Br_2(l) \rightarrow$ ethene $CH_2BrCH_2Br(l)$ 1,2-dibromoethane

Combustion of alkanes and alkenes

When sufficient oxygen is present, the products of combustion are carbon dioxide and water. Reactions are exothermic.

Example 1

$$\underset{\text{ethane}}{CH_3CH_3(g)} + 3\tfrac{1}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$$

Example 2

$$\underset{\text{ethylene}}{H_2C{=}CH_2(g)} + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(l)$$

1.6 Classification of plastics

Plastics are manufactured materials that may contain some or all combinations of carbon with oxygen, hydrogen, nitrogen and other organic and inorganic elements. These combinations, although solid in the finished state, are fluid at some stage of manufacture and are capable of being formed into various shapes by the application of heat and pressure, or both. Although they form large and varied groups, plastics can be defined under two major classifications:

(a) Thermosets

These are set into a permanent shape when heat and pressure are applied to them. Reheating will not soften these materials. The simple building block on which synthetic plastics are based is called a single unit or 'monomer'. When monomers are combined into long chain-like structures, the new structures are called 'polymers'. If the polymer strands are cross-linked, then the material is described as thermosetting plastic, e.g. bakelite.

(b) Thermoplastics

Thermoplastics become soft when exposed to sufficient heat and harden on cooling. These properties are retained, no matter how often the process is repeated. If the polymer chains remain unlinked, then the material is said to be thermoplastic, e.g. polyethylene.

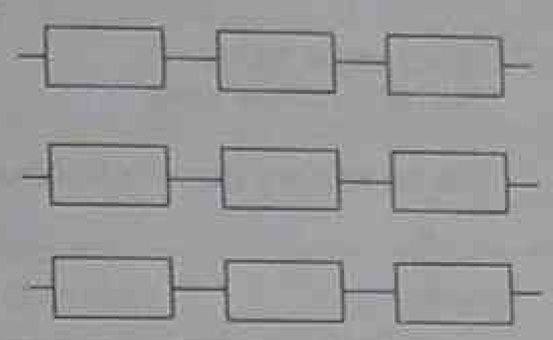


Figure 1.7 Strands of a thermoplastic. No cross-linking between polymer strands

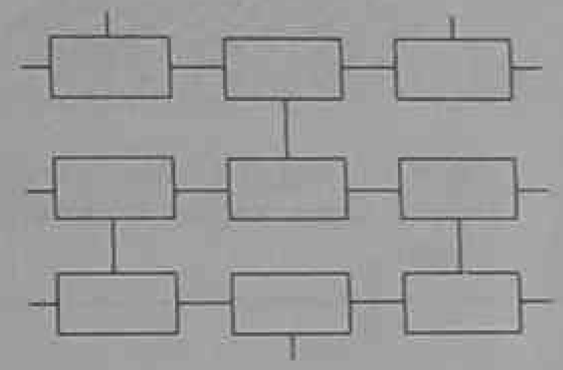


Figure 1.8 Thermosetting network. Chains are cross-linked by covalent bonds.

Polymerisation is the process by which the many small molecules join together. Different processes involving changeable conditions of temperature, pressure and a variety of catalysts are used to produce different polymers. The reaction can occur simply by adding many monomer units to each other and is called 'addition polymerisation', e.g. the thermoplastics polyethene, polystyrene, polyvinyl chloride and polyacrylonitrile.

Differences between plastics depends on the following:

- The monomer used.
- How many molecules are joined together (molecular weight).
- Whether the polymer molecule has a straight or branched chain.
- If other molecules are in the chain (copolymer).
- What additives are present.
- The degree of crystallinity in solid polymers.

Note: The molecular weight distribution of a polymer affects its properties and also the way in which it behaves during processing.

1.7 The commercial preparation of polyethylene

Chain growth polymerisation is started by adding an 'initiator' to the monomer. The most common type of initiator is a substance which, when added in small quantities, is decomposed by heat or light to produce a free radical (symbol $R^\bullet$). Free radicals are formed when a covalent bond is broken and a bonding electron is left on each part of the broken molecule. Free radicals are easily formed in peroxides since the O–O bond is weak. Dibutyl peroxide is commonly used as an initiator in chain-growth polymerisation.

Ethylene feedstocks are used by a petrochemical complex to produce two main types of polyethylene:

(a) Low density polyethylene production (LDPE)

Production requires a temperature range of 100–300°C and a very high pressure of 1500–3000 atmospheres. An organic peroxide or oxygen is used as the initiator for the reaction.

$$CH_2{=}CH_2 + R^\bullet \rightarrow -{}^\bullet CH_2{-}CH_2{-}R$$

$$CH_2{=}CH_2 + -{}^\bullet CH_2{-}CH_2{-}R \rightarrow -{}^\bullet CH_2{-}CH_2{-}CH_2{-}CH_2{-}R$$

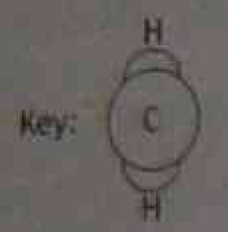
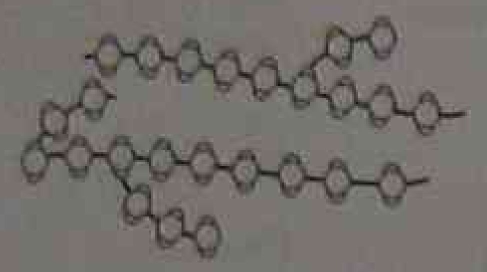
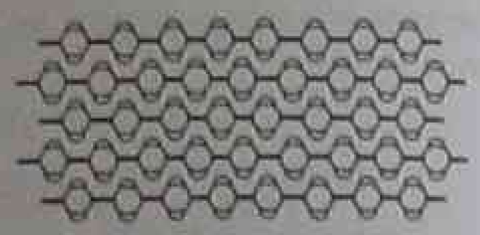
The product of this reaction is polyethylene $-[-CH_2-CH_2-]_n$. Low density polyethylene has molecular chains which can have many short branches (2–4C). These disrupt the close regular packing of the linear chains and also results in fewer of the long linear chains in the molecule. Low density polyethylene is a tough, flexible, translucent semicrystalline plastic. A high purity product is obtained.

(b) High density polyethylene (HDPE)

The polymerisation is carried out using special aluminium-based metal oxide catalysts, called *metallocene catalysts*, at atmospheric pressure and a temperature of about 300°C. The molecules have fewer side chains, so the long chains are almost linear and the molecules can pack closer on cooling to produce a more dense and crystalline material. Crystalline regions provide strength to the polymer. Some impurities are present (due to the catalyst).

Table 1.7 is an example of two polymers made from the same monomer, but having different properties due to the configuration of their molecules.

Table 1.7 Properties of two polymers prepared from the same monomer

Property	LDPE	HDPE
Flexibility	more flexible used for sandwich bags, cling wrap, motor vehicle covers	more rigid used for freezer bags
Strength	not as strong (irregular packing)	strong (regular packing) suitable for water pipes
Heat resistance		useful above 100°C can use for water pipes
Transparency	good (more amorphous, i.e. non-crystalline regions)	less transparent (more crystalline)
Density	low, so lighter	higher
Schematic of chains Key: 	 chains with short branches (2 – 4C) in amorphous regions. Packing is irregular and non-crystalline.	 chains are long and linear in crystalline regions. Closer packing is therefore possible.

1.8 Source and domestic use of some commercially significant polymers

To extend the range of plastics, additives are used to alter properties of polymers, e.g. to decrease flammability, as indicated below:

(a) **Plasticisers** which render the finished material more flexible by weakening the attractions between the polymer chains. These additives stop polyvinyl chloride (PVC) from becoming brittle over time.

(b) **Fillers** which are added to modify a particular property, e.g. as a reinforcing agent to improve strength, such as fibre glass. Fillers also add bulk and reduce cost.

(c) **Dyes and pigments** which are used as decoration.

(d) **Stabilisers** which are incorporated to reduce damage to plastic from exposure to the environment, e.g. ultraviolet stabilisers which absorb sunlight and prevent long chains from being broken. A number of plastics, e.g. polystyrene, react with oxygen in the air, so antioxidants are added to stop the chain breaking.

Copolymers

To extend the range of polymers produced by chain growth, more than one monomer may be incorporated. This is called *copolymerisation.*

Example 1

The monomers styrene, butadiene and acrylonitrile may be incorporated to form an ABS copolymer. This is used to make telephone cases.

Example 2

About 60% of the world's rubber is made by the copolymerisation of butadiene and styrene.

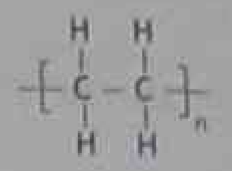
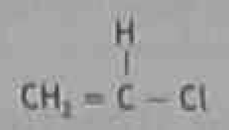
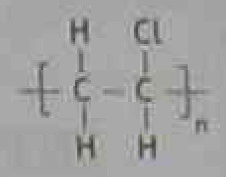
Reinforced plastics

The addition of fibres to most polymer materials results in greatly increased stiffness and strength to the plastic, e.g. glass, carbon and 'Kevlar', which is a brand name for a polyamide containing aromatic rings. Carbon is widely used in the manufacture of tennis racquet handles and golf club shafts. 'Fibre-glass' is added to the styrene-polyester polymers used to make canoes, boats and surf skis.

Shaping Plastics

Once polymers are synthesised they can be processed in different ways to provide a wide range of shapes and structures.

Table 1.8 Commercially significant polymers

Name	Monomer	Polymer	Properties
Ethylene	$CH_2 = CH_2$	 $-\!\left[\begin{matrix} H & & H \\ \vert & & \vert \\ C & - & C \\ \vert & & \vert \\ H & & H \end{matrix}\right]\!-_n$ polyethylene	LDPE light, flexible, translucent HDPE strong, stiffer, high resistance to chemicals and corrosion
Chloroethylene (c.n. vinyl chloride)	 $\begin{matrix} & & H & & \\ & & \vert & & \\ CH_2 & = & C & - & Cl \end{matrix}$	 $-\!\left[\begin{matrix} H & & Cl \\ \vert & & \vert \\ C & - & C \\ \vert & & \vert \\ H & & H \end{matrix}\right]\!-_n$ polyvinyl chloride	since PVC is not weather-resistant, it is only used as electrical conduit indoors or as underground water pipes
Styrene (c.n. vinyl benzene) accepted systematic name	 $\begin{matrix} & & H & & \\ & & \vert & & \\ CH_2 & = & C & - & C_6H_5 \end{matrix}$	 $-\!\left[\begin{matrix} H & & H \\ \vert & & \vert \\ C & - & C \\ \vert & & \vert \\ H & & C_6H_5 \end{matrix}\right]\!-_n$	easily formed to produce good thermal, sound and insulation properties, transparent sheets and pipes

Fibres

(a) **Cold drawing** is the process which produces fibres by stretching a liquid polymer into a long, thin filament. The polymer chains form a more crystalline structure which leads to increased strength, e.g. nylon fibres.

(b) **Extrusion**, in which small granules of polymer are melted and then forced through a nozzle to produce a continuous length of fibre, e.g. terylene fibre.

Sheets, tubes and pipes

These can also be produced by *extrusion*. In this process, thermoplastic raw material in powdered or granulated form is fed into a heated cylinder. A plunger or screw mechanism compacts the plastic mass in the cylinder where it melts and is then shaped by being forced through a die.

To make hollow objects such as bottles by extrusion, *blow moulding* is used.

Injection moulding

An injection unit forces the material into a mould, to produce a wide variety of shapes with great accuracy.

Calendering

A molten mass of polymer is passed through *heated rollers* to form a *sheet* that is used to produce semi-finished goods such as coverings, flooring and plastic wrappings.

Foam

Many polymers, e.g. polystyrene, polyethylene and polyvinyl chloride are *foamed* to *reduce their density*. In the foaming process, a gas is introduced into the polymer, either by mixing compressed air or gas into the melted polymer mass, or by adding a 'blowing agent', e.g. sodium hydrogen carbonate ($NaHCO_3$), to the plastic raw material. When the hot melt is formed, $NaHCO_3$ decomposes to produce CO_2 which forms bubbles in the foam. Expanded polymers such as this can be used for foam insulation, drinking cups and egg boxes.

1.9 Reactions of some condensation polymers

Condensation polymerisation

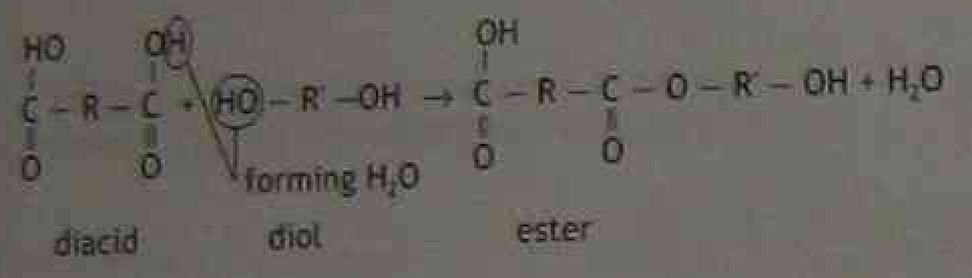
This process involves a reaction between two functional groups where a small molecule, usually water, is eliminated and the two functional groups are linked together. An example of a condensation copolymer is the formation of 'terylene', which is a polyester polymer which makes useful textile fibres.

Table 1.9 Source and domestic uses of some polymers

Source	Raw materials	Monomer	Polymer	Uses
Crude oil	ethylene	ethylene	polyethylene	LDPE: cling wrap, sandwich bags, motor vehicle covers HDPE: milk bottles, garbage cans, kitchenware
Crude oil salt	ethene chlorine	vinyl chloride	polyvinyl chloride (PVC)	plastic plumbing features, toys, upholstery, floor tiles, rainwear
Crude oil	propene ammonia	acrylonitrile	polyacrylonitrile	Orlon fibre, carpet, acrylic sweaters
Crude oil	ethene benzene	styrene	polystyrene easily formed	surf boards, wall tiles, foam insulation, most of fridge cabinets and insulation

Example 1

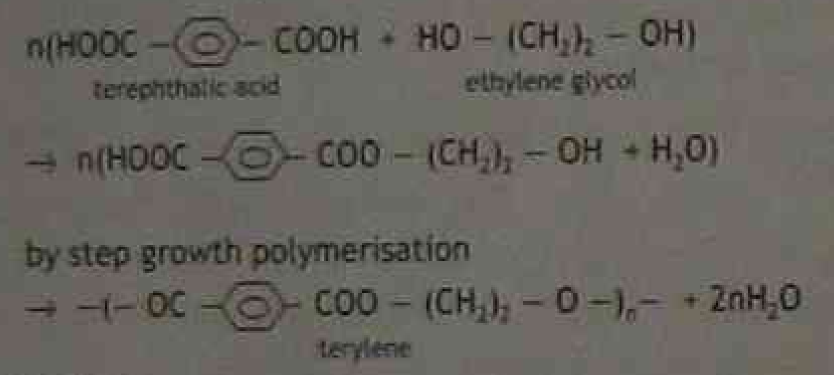
General reaction between a dicarboxylic acid and a diol



$$\underset{\text{diacid}}{\overset{HO}{\underset{\underset{O}{\|}}{C}}-R-\overset{OH}{\underset{\underset{O}{\|}}{C}}} + \underset{\text{diol}}{HO-R'-OH} \rightarrow \underset{\text{ester}}{\overset{OH}{\underset{\underset{O}{\|}}{C}}-R-\underset{\underset{O}{\|}}{C}-O-R'-OH} + H_2O$$

forming H_2O

Formation of terylene



$$n(\underset{\text{terephthalic acid}}{HOOC-\bigcirc-COOH} + \underset{\text{ethylene glycol}}{HO-(CH_2)_2-OH})$$

$$\rightarrow n(HOOC-\bigcirc-COO-(CH_2)_2-OH + H_2O)$$

by step growth polymerisation

$$\rightarrow \underset{\text{terylene}}{-(-OC-\bigcirc-COO-(CH_2)_2-O-)_n-} + 2nH_2O$$

Example 2

General reaction between a dicarboxylic acid and a diamine

$$n(HOOC-R-COOH + H_2N-R-NH_2)$$

$$\rightarrow n(HOOC-R-CONH-R-NH_2 + H_2O)$$

Formation of nylon-66

$$n(\underset{\text{hexanedioic acid}}{HOOC-(CH_2)_4-COOH} + \underset{\text{1,6-hexanediamine}}{H_2N-(CH_2)_6-NH_2})$$

$$\rightarrow n(HOOC-(CH_2)_4-CONH-(CH_2)_6-NH_2) + H_2O)$$

by step growth polymerisation

$$\rightarrow \underset{\text{nylon-66}}{-(-OC-(CH_2)_4-CONH-(CH_2)_6-NH_2-)_n-} + 2nH_2O$$

Example 3

Biopolymers of the monomer glucose (starch and cellulose) are also examples of condensation polymers where two -OH functional groups from the two glucose monomers are linked and a molecule of water is eliminated.

Note: In Examples 1 and 2, the functional groups are different. In Example 3, the functional groups are the same.

1.10 The structure of the biopolymers starch and cellulose

Starch

Starches are polymers of glucose, that is, starch molecules consist of many hundreds of glucose molecules joined together.

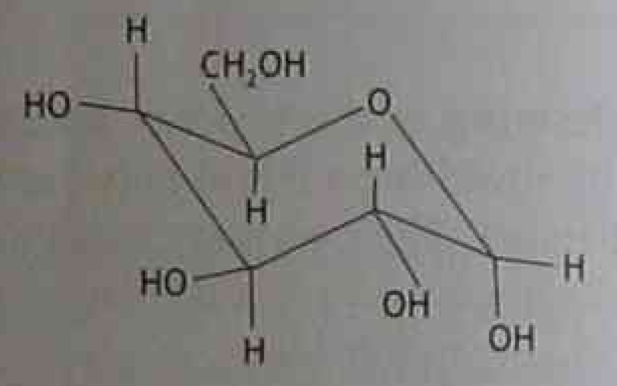


Figure 1.9 Glucose

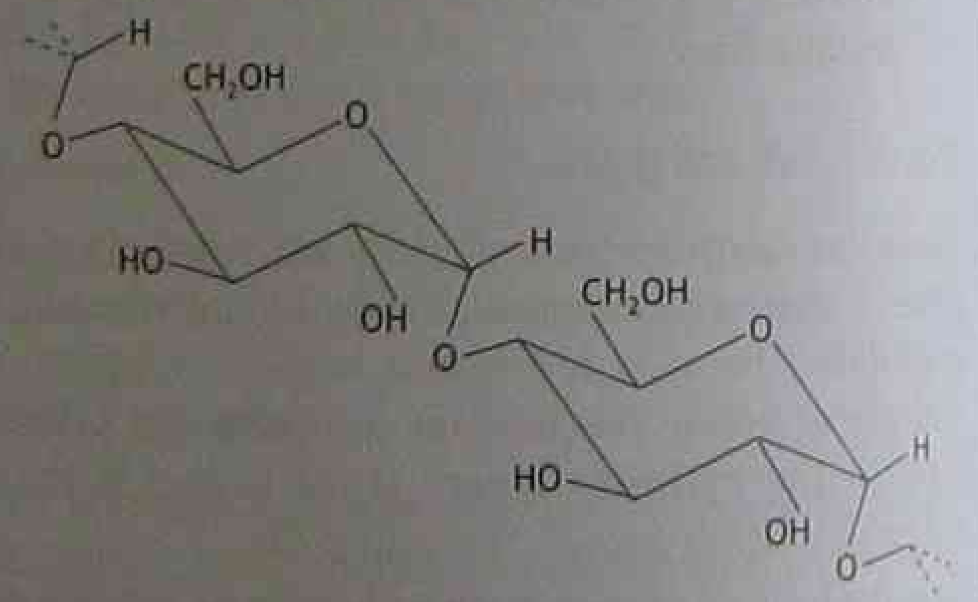
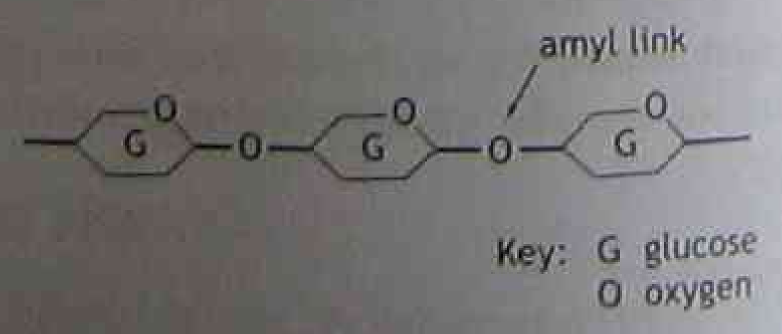


Figure 1.10 Amylose. A type of starch



Key: G glucose
O oxygen

Figure 1.11(a) Schematic starch structure

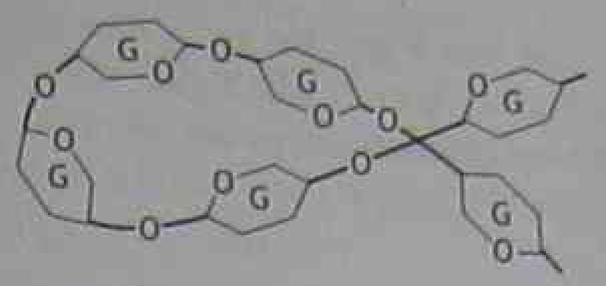


Figure 1.11(b) Schematic starch structure (helical coil)

Cellulose

Cellulose is also a polymer of glucose. It is made by plants from glucose produced during photosynthesis.

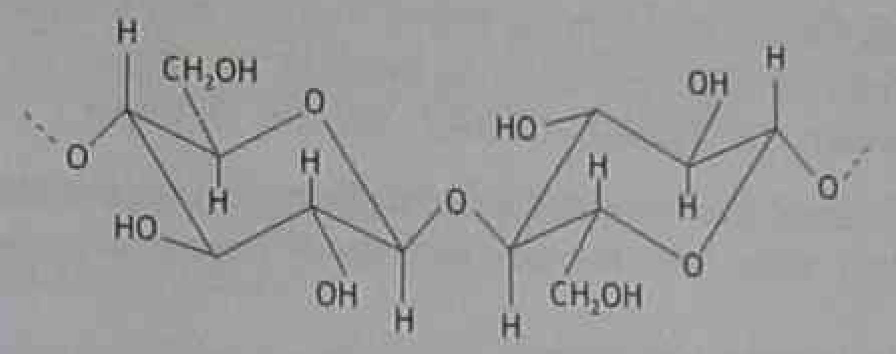
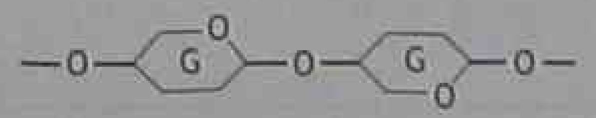


Figure 1.12 Cellulose. The way in which the glucose molecules are joined together in cellulose is different from the way that they are joined in starches.

Cellulose forms linear polymers which contain much longer chains than starches. Cotton is nearly pure cellulose. Wood is a mixture of lignin and cellulose. Cellulose is extracted by dissolving the lignin in sodium sulfite solution.

The cellulose molecules form long chains which produce parallel arrays held together by hydrogen bonding between the many -OH groups on the adjacent chains. The twisted bundles form rope-like structures.



Key: G glucose unit
O oxygen

Figure 1.13 Schematic cellulose structure

Cellulose, the most readily available organic material, is used extensively in paper making and is also readily recycled.

1.11 Rayon – an industrially produced biopolymer

Cellulose which has been extracted from lignin can be used for making synthetic fibres such as rayon. The development of a process to make rayon, a type of artificial silk, was one of the early success stories in polymer chemistry.

Viscose rayon is made from regenerated cellulose normally obtained from wood pulp or cotton. Purified cellulose is treated with sodium hydroxide solution before being shredded and 'aged'. It forms a viscose solution when it is reacted with carbon disulfide and sodium hydroxide. The solution is forced into an acid solution through holes in a spinneret. The fibres are then wound onto a spool.

Other solvents such as those containing the complex ion of copper, $Cu(NH_3)_4^{2+}$, can be used to dissolve the cellulose. In this case, when the solution is squirted into the acid bath, Cu^{2+} and NH_4^+ ions form and the cellulose precipitates as rayon fibres.

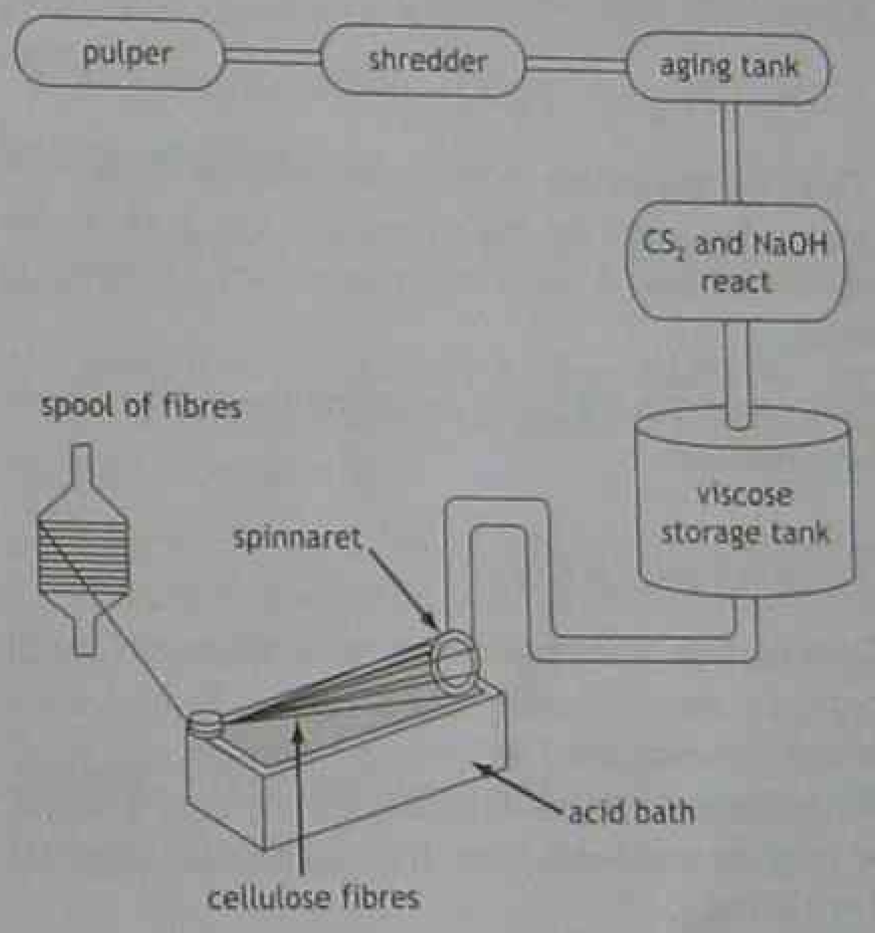


Figure 1.14 The manufacture of viscose rayon

1.12 Reversible reactions between ethanol and ethylene

Industrial ethanol

The preparation of ethanol from ethene (ethylene) involves the addition of water to ethene and is a typical addition reaction. Ethanal and ethanoic acid can then be made from ethanol by oxidation.

(a) Sulfuric acid method

Ethylene is first absorbed by concentrated sulfuric acid to form a mixture of ethyl hydrogen sulfate and diethyl sulfate.

$$CH_2{=}CH_2 + H_2SO_4 \rightarrow \underset{\text{ethyl hydrogen sulfate}}{CH_3CH_2SO_4H}$$

$$CH_3CH_2SO_4H + CH_2{=}CH_2 \rightarrow \underset{\text{diethyl sulfate}}{(CH_3CH_2)_2SO_4}$$

On dilution with water, hydrolysis occurs and ethanol is produced.

$$CH_3CH_2SO_4H + H_2O \rightarrow CH_3CH_2OH + H_2SO_4$$

$$(CH_3CH_2)_2SO_4 + 2H_2O \rightarrow \underset{\text{ethanol}}{2CH_3CH_2OH} + H_2SO_4$$

(b) Direct catalytic hydration method

Ethylene and steam are passed over a solid phosphoric acid catalyst.

$$CH_2{=}CH_2(g) + H_2O(g) \xrightleftharpoons{\text{catalyst}} CH_3CH_2OH(g)$$

This is a reversible exothermic reaction with high yields favoured by high pressure and high steam concentration. A working temperature of 300°C is used.

This process is gradually replacing the older sulfuric acid method.

(c) Dehydration of ethanol

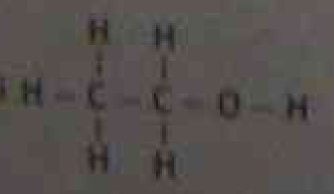
Dehydration (the elimination of a water molecule) requires an acid catalyst. Ethanol is heated with either concentrated sulfuric or phosphoric acid. Water formed can be absorbed by the acid catalyst or may be removed from the reaction mixture by distillation.

$$CH_3CH_2OH(g) \xrightarrow[\text{180°C}]{H_2SO_4\text{ catalyst}} C_2H_4(g) + H_2O(l)$$

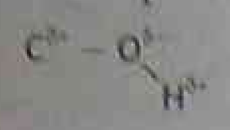
Note: The acid-catalysed hydration of alkenes to yield alkanols is reversible with this reaction. Large amounts of water favour ethanol formation, but when water is removed, the formation of ethene is favoured. The mechanism described for the hydration of ethene also applies to the dehydration of ethanol.

1.13 Physical properties of ethanol

Bond polarity

The structural formula of ethanol is 

Since oxygen has a greater attraction for bonding electrons than carbon or hydrogen, the C–O and O–H bonds of ethanol are polar.



This results in the lower alkanols such as ethanol being miscible (soluble) in water which is also a polar.

However, as the non-polar carbon chain becomes longer, the importance of dispersion forces increases. When these forces become much larger than the hydrogen bonding between the alkanol and water, the alkanol becomes insoluble in water.

Ethanol is an excellent solvent since it is miscible not only with water but also with many organic liquids.

Hydrogen bonding

Hydrogen bonding strengthens intermolecular forces. It occurs in molecular substances where a hydrogen atom is covalently bonded to an atom of oxygen, nitrogen or fluorine (which are all strongly electro-negative).

Where hydrogen bonding occurs in organic compounds such as the lower alkanols, e.g. methanol and ethanol, the effect of dispersion forces is negligible.

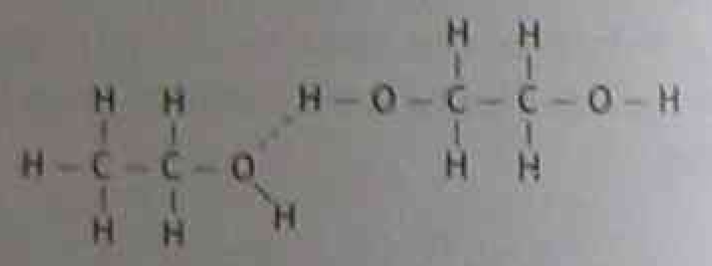


Figure 1.15 Hydrogen bonding in ethanol (BP 78°C)

Bond polarity and hydrogen bonding make ethanol soluble in water in all proportions.

1.14 The alkanols

Alkanols (c.n. alcohols) contain carbon, hydrogen and oxygen atoms. General molecular formula is $C_nH_{2n+2}O$ or $C_nH_{2n+1}OH$. Functional group is the hydroxyl group –OH. In naming the -e from the parent alkane is replaced by -ol.

Rules for naming alkanols

1. Choose the longest consecutive chain of carbon atoms which contains the –OH group.
2. Number the chain from the end that gives the –OH group its smallest number.
3. Name and number the alkyl groups, as with the alkenes.

Isomerism in alkanols

After ethanol, different isomers are possible owing to position isomerism. After propanol, both position and branched chain isomerism can occur.

Chemical properties

(a) Combustion

Alcohols burn readily in air and are exothermic. For example:

$$\underset{\text{1-propanol}}{CH_3–CH_2–CH_2–OH(l)} + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$$

(b) Reaction with sodium metal

This is a very important reaction for alcohols since it shows that one hydrogen atom, the one in the –OH group, is bonded differently from the other hydrogen atoms in the alcohol molecule.

$$2ROH(l) + 2Na(s) \rightarrow 2RONa(s) + H_2(g)$$

1.15 Commercial uses of ethanol

Solvents

(a) **Pharmaceutical products** such as rubbing compounds, lotion, colognes, perfumes, and as an antiseptic for swabbing the skin.

(b) **Food products and medicines** such as food colourings, essences, cough mixtures and syrups.

(c) **Industrial alcohol** (denatured by 'bittering' agents) which is used in large quantities in varnishes and plastics.

(d) **Cleaning fluids for home use**, e.g. methylated spirits as a glass cleaner.

Petrol as a fuel

We are dependent on fossil fuel petroleum for about 80% of the world's demand for transportation fuels, especially its major derivative, petrol. This is due to present economic conditions. The development of major non-fossil alternative fuels depends on the price of crude oil and when the over-supply of oil ends.

Petrol additives

The addition of ethanol to petrol reduces air pollution by:

(i) using it as a substitute for lead additives, e.g. tetraethyl lead, which are added to boost octane performance; and

(ii) adding oxygen to petrol which cuts the amount of carbon monoxide in motor vehicle exhausts if the carburettor is well tuned.

1.16 Alternative fuels and by-products

Biomass fuels

'Biomass' includes wood and other plant matter (e.g. rice straw and sugar cane bagasse), animal wastes and urban organic refuse. Almost all crop plants produce large amounts of biomass. With few

Table 1.10 The alkanols

Name	Molecular formula	Structural formula	State (SLC)	Uses
Methanol (c.n. methyl alcohol)	CH_3OH	$CH_3–OH$	liquid	denatures ethanol
Ethanol (c.n. ethyl alcohol)	C_2H_5OH	$CH_3–CH_2–OH$	liquid	beer (3 – 5%) wine (10 – 15%) spirits (40 – 50%)

Methanol is extremely poisonous, and can cause blindness and death if drunk. Methylated spirits is a mixture containing 95% ethanol and 5% methanol. It is denatured by the addition of a blue dye and another substance which gives it a foul taste. This is to stop people from drinking it.

exceptions such as sugar cane bagasse, high transportation costs do not justify their use as fuel.

The natural process of photosynthesis makes it possible to develop 'biomass' fuels, so that in the future, dependence on 'fossil' fuels can be reduced as they become scarcer, more difficult to recover and hence more expensive. Some arguments against the use of biomass material in the production of alternative fuels point out that there will be an increased use of old growth forest as a source of materials. This could lead to an increased need for land clearing and farming to produce more biomass material. This will cause increased problems of soil erosion, salination, overuse of water resources and increased use of fertilisers and pesticides.

Genetically modified crops could provide some help in the commercial production of biomass fuels of the future, but this has still to be proved.

Commercial production of ethanol fuel

In Australia, sugar cane and wheat have been used to produce ethanol by a process of fermentation using yeast. Yeast is a fungus which can multiply in the absence of oxygen by using enzymes, e.g. zymase, to catalyse the decomposition of a sugar such as sucrose or maltose. In the case of glucose:

$$C_6H_{12}O_6(aq) \xrightarrow{enzymes} 2CH_3CH_2OH(aq) + 2CO_2(g)$$

The alcohol content of the sugar solution cannot rise above 15% in the fermentation process since above that level the yeast cells would be poisoned.

Ethanol produced by the fermentation process can be used in existing motor vehicles.

Although the cost of ethanol produced in this way is almost double the cost of petrol, a fuel called 'Petranol' is sold in Queensland which contains about 10% ethanol. Ethanol yields two-thirds of the energy of petrol. It has been estimated that the available land for crop production would provide for only 10% of Australia's fuel needs.

Current work on alternative fuel technologies include the following:

- China is planning an ethanol fuel production plant in Tangshan capable of producing 50 million litres of ethanol annually. Rice straw will be used as the raw material; this could reduce the current 'burn off' of the rice stalks by farmers to prepare for the next planting, which causes large-scale air pollution in the region. A proprietary process has been developed for freeing sugars in the cellulosic plant material by acid hydrolysis.

  Cellulose → cellobiose → two molecules of glucose from each molecule of cellobiose

  One tonne of rice straw can produce 350 litres of ethanol.

  Once the sugars have been produced, yeast fermentation is carried out to convert them into ethanol.
- An American company (BCI) owns a commercial biomass-to-ethanol production plant that uses sugar cane stalks as the raw material. The process uses a genetically engineered bacterium to liberate the sugars in the cellulose.
- Another US company is building a biogas model to determine if garbage and raw sewage wastes can be used to produce ethanol economically. Biogas could be used to replace natural gas once it becomes an economical and environmentally viable resource. At present, it is produced in limited amounts from organic materials such as agricultural products, cellulose and refuse.

Dimethyl ether (DME) is a new fuel that is produced from natural gas. In the longer term, it too will be produced from biogas and provide a viable alternative to diesel fuel.

Main users of alternative fuels

- Brazil: 30% of the fuel used in 6 million Brazilian motor vehicles has 25% ethanol in the petrol.
- South Africa: 40% of the synthetic gasoline fuel used is derived by catalytic synthesis from coal.

The liquor industry

Fermentation

Natural sugars can undergo fermentation reactions using the enzymes present in yeast to catalyse the reaction and produce ethanol and carbon dioxide.

A simple practical experiment can be carried out by fermenting a carton of fruit juice, using dried yeast, in a large stoppered flask with a delivery tube leading into limewater. The production of carbon dioxide will at first turn the limewater milky. After about two days, the strained mixture can be placed in a distillation flask and a boiling chip added. The apparatus is then set up as in Figure 1.17, and the ethanol fraction (95% ethanol: 5% water) called 'rectified spirits' is collected at 78°C.

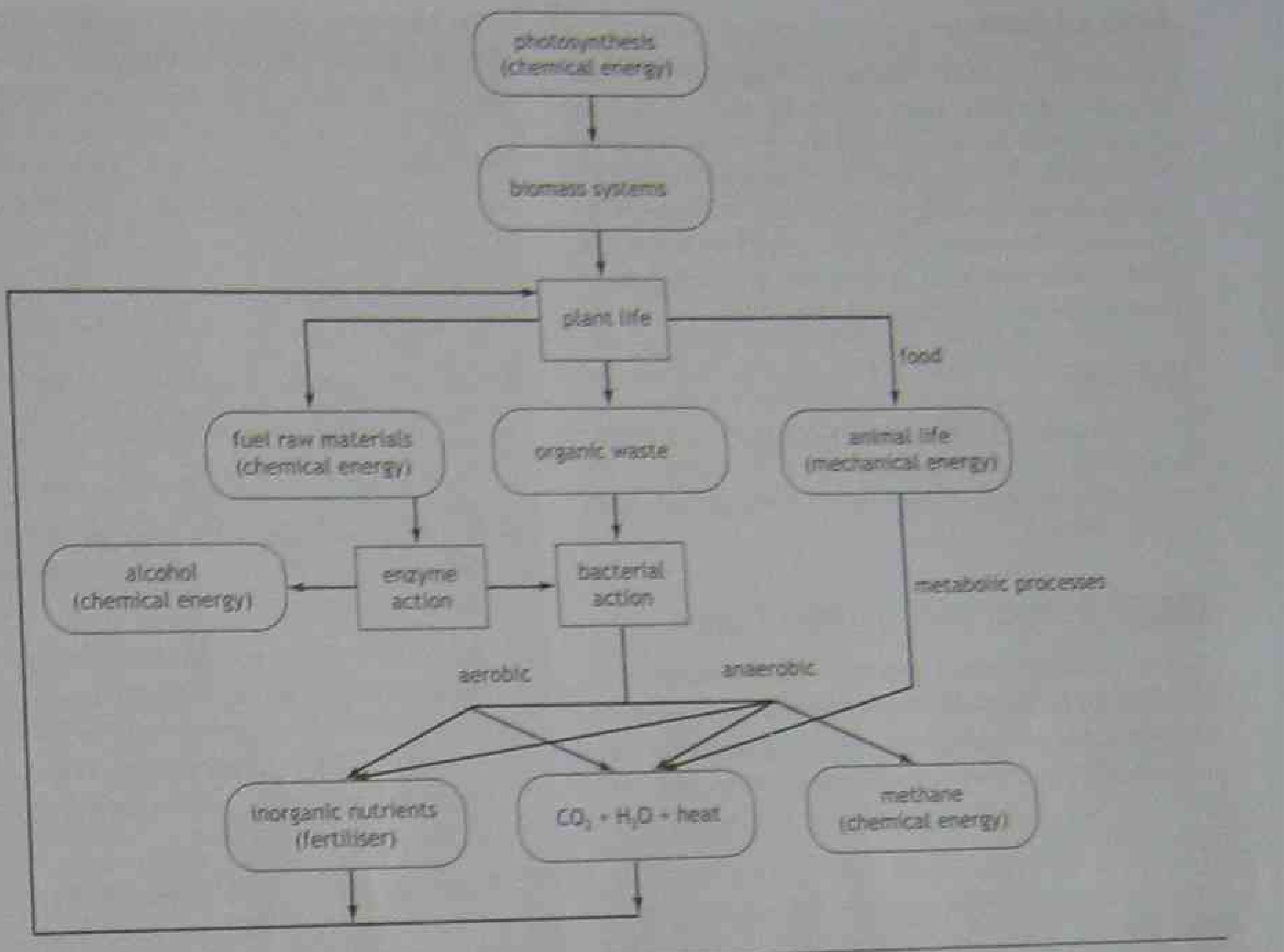


Figure 1.16 Energy from plants

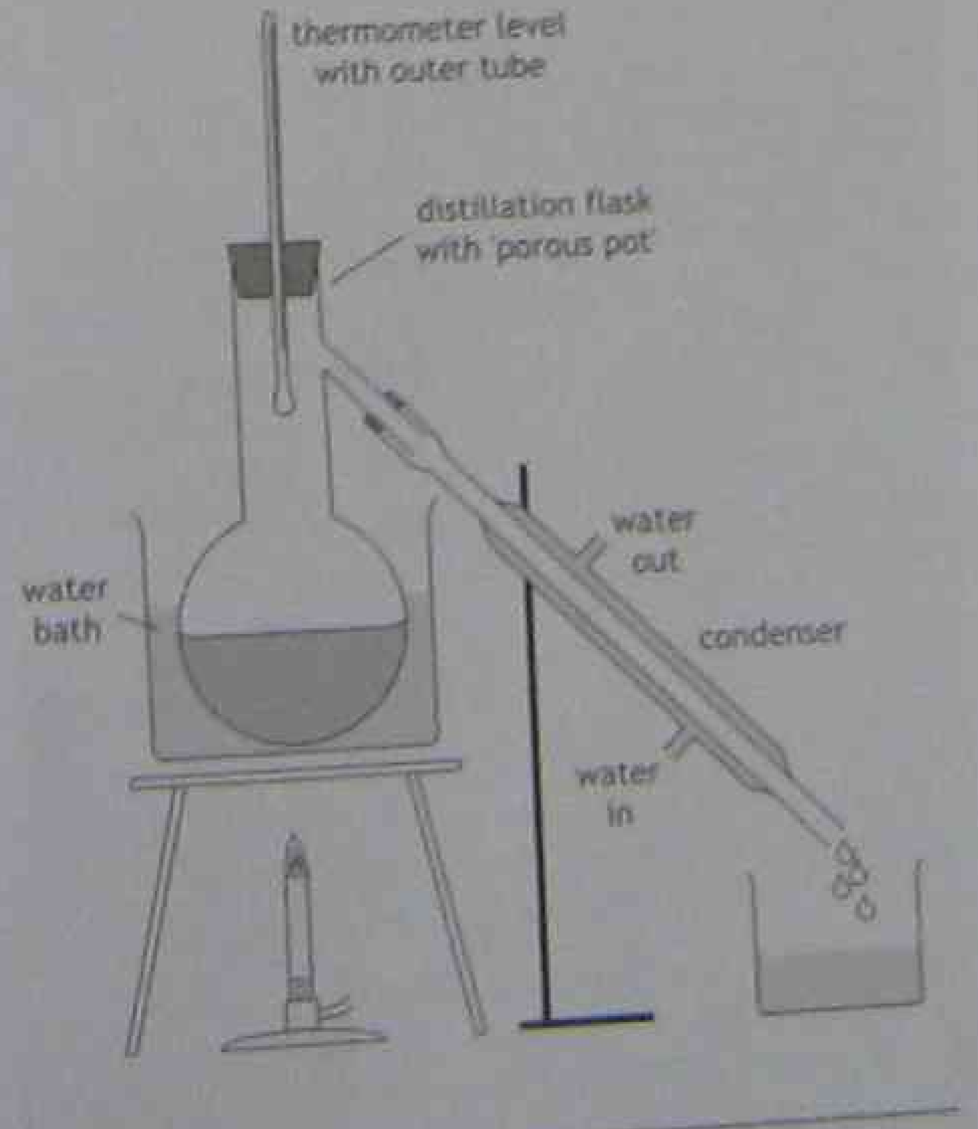


Figure 1.17 Ethanol prepared by fermentation then distillation. Simple distillation apparatus

Equation:

$$\underset{glucose}{C_6H_{12}O_6(aq)} \xrightarrow[zymase]{enzymes} \underset{ethanol}{2CH_3CH_2OH(aq)} + 2CO_2(g)$$

Since the alcohol content of the fermenting liquor cannot rise above 15%, drinks with higher alcohol content, e.g. whisky, are produced by distillation of the dilute solutions.

At present, because of the relatively low price of petroleum, only 5% of the world's ethanol is being prepared by fermentation.

Beers

Beer is produced by allowing barley to sprout and produce the enzyme diastase which coverts the starch to maltose. Yeast provides both the enzyme maltase (maltose → glucose) and the enzyme zymase (glucose → ethanol). After about a week in fermentation tanks, the beer is transferred to and allowed to mature in conditioning tanks, and then is bottled before completion.

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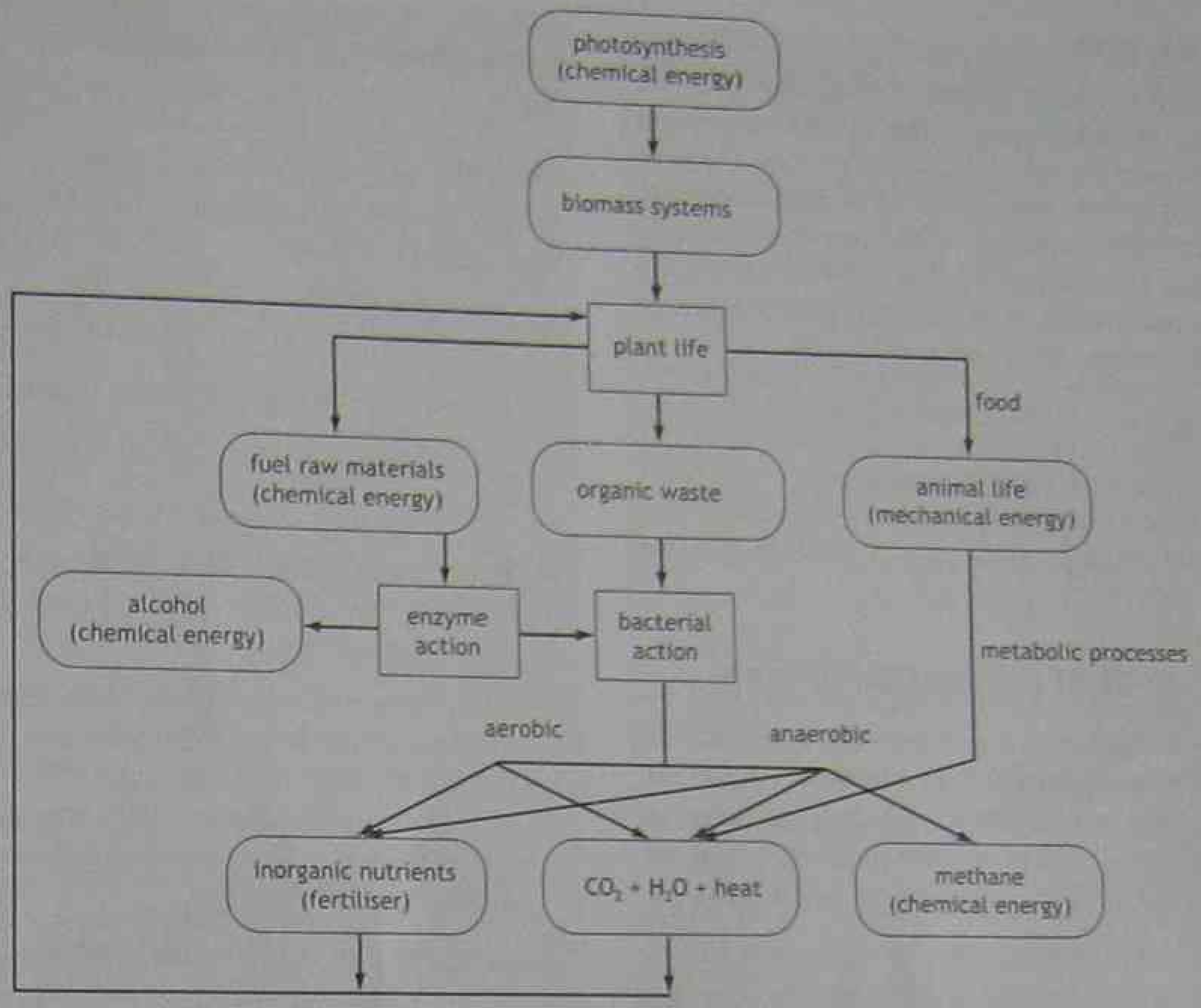
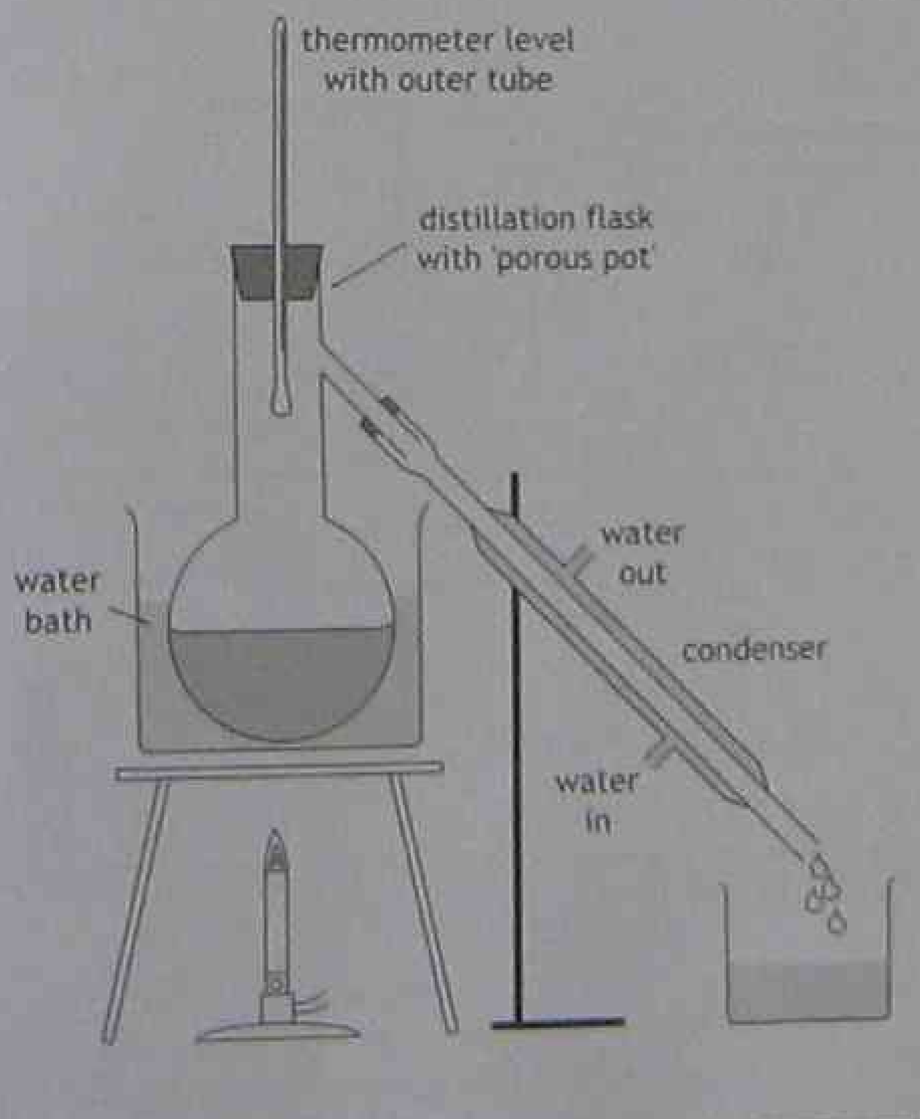


Figure 1.16 Energy from plants



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Wines and Spirits

Wines and spirits are produced by the fermentation of grape and other juice sugars by zymase present in wine-yeast strains. For sparkling wines, the juice is bottles before completion of fermentation; the carbon dioxide produced in the bottle dissolves in the wine. Distillation of wine produces *brandy*, a 100% proof spirit in which the ethanol/water mixture contains 49.2% ethanol by mass.

By-products

Residual products from this process include dried barley husks (cattle food), extract of excess yeast produced during fermentation (Vegemite) and carbon dioxide.

1.17 Heat of combustion of fuels

The molar heat of combustion of a substance is equal to the enthalpy change when one mole of that substance reacts completely with oxygen. Below is a worked experiment to determine the heat of combustion of ethanol using standardised apparatus.

Activity 1.1

Inquiry

To determine the amount of heat released when one mole of ethanol is burnt in air.

Pre-lab

The heat of combustion of a substance is the heat change which takes place when one mole of the substance is completely burnt.

When a known mass of ethanol burns, the heat released can be used to raise the temperature of a container of water. By measuring this temperature increase, the amount of heat released and hence the heat of combustion of ethanol can be calculated.

Materials

- Copper boiling can containing about 100 mL of water (or a 500 mL Pyrex conical flask).
- 1 x thermometer (0°C–50°C, graduated to 0.1°C).
- Retort stand and clamp.
- 10 mL of ethanol in a 'spirit burner' (a small screw top bottle containing a wick can be used).
- 10 mL of propanone (acetone) in a 'spirit burner'.
- Electronic balance.

Standardisation of apparatus

PART A

Method

In a draught-free position, standardise the apparatus as follows:

1. Record the initial temperature of water in the can.
2. Record the mass of the burner + propanone.
3. Set up apparatus as in Figure 1.18.
4. Centre the wick of the burner and light it.
5. Stir the water GENTLY with the thermometer ensuring that the thermometer does not touch the bottom of the can.
6. Raise the temperature by about 10°C and record the final temperature, extinguish the flame and IMMEDIATELY weigh the burner. Do not delay here as warm propanone is very volatile. Record the final mass of the burner and the remaining propanone.
7. Place the can in cold water. While the can is cooling ready for the next procedure, calculate the energy in kilojoules (kJ) needed to raise the temperature of the apparatus.

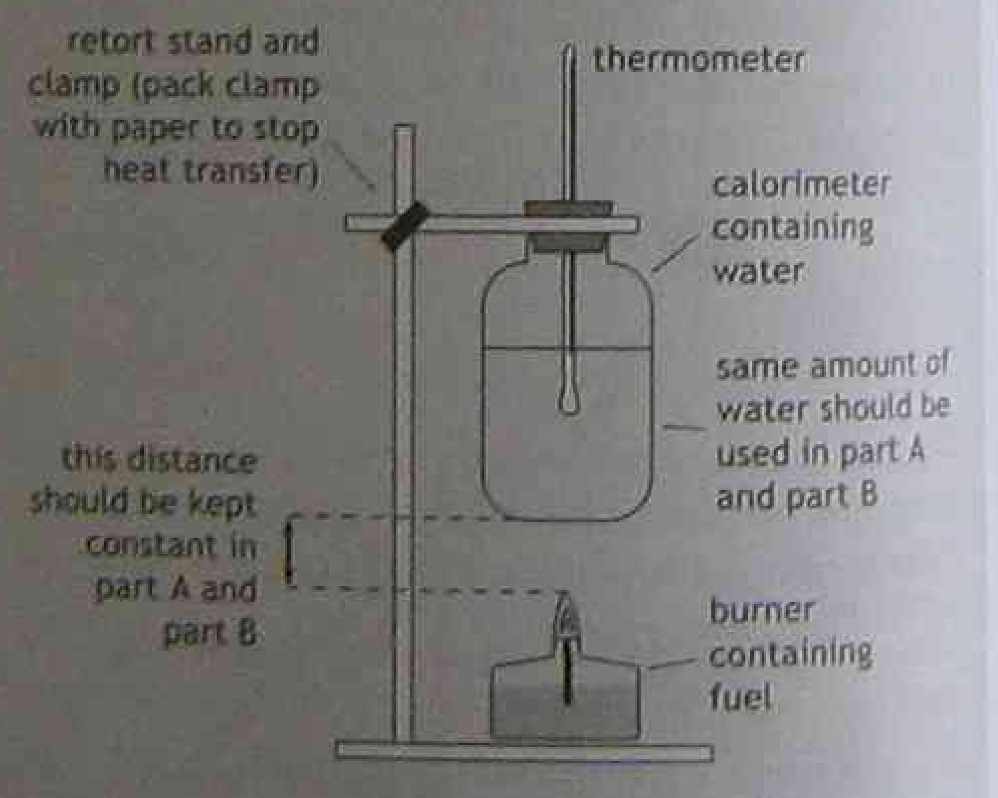
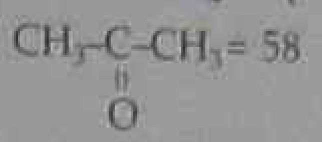


Figure 1.18 Calorimeter

Results

Initial mass of burner + propanone	19.41 g
Final mass of burner + propanone	18.96 g
Mass of propanone burnt	0.45 g
Initial temperature of water	24.5°C
Final temperature of water	34.8°C
Rise in temperature of water	10.3°C
Heat of combustion of propanone (from data)	$-\Delta_c H^\circ = 1790$ kJ mol^{-1}
Heat of combustion for 1 g of propanone	30.86 kJ

Molar mass of 
$CH_3{-}\underset{\overset{\|}{O}}{C}{-}CH_3 = 58$

0.45 g of propanone produces 13.89 kJ of heat energy, so the apparatus is raised 10.3°C by 13.89 kJ of heat energy.

The apparatus is raised through 1°C by the release of 1.35 kJ.

PART B

Method

Repeat method set out in Part A.

Results

Initial mass of burner with ethanol	19.38 g
Final mass of burner with ethanol	18.92 g
Mass of ethanol burnt	0.46 g
Initial temperature of water	24.5°C
Final temperature of water	34.5°C
Rise in temperature of water	10.0°C

By experiment, a mass of 0.46 g of ethanol produces 10.0°C rise. Since at 1°C rise in the apparatus is caused by 1.35 kJ of heat energy (from standardisation) then a 10°C temperature rise results from a release of 13.5 kJ.

For one mole of ethanol, the heat energy released is 1350 kJ. Molar mass of $CH_3CH_2OH = 46$.

Energy released when one mole of ethanol burns in air is 1350 kJ $\quad -\Delta_c H^\circ = 1350$ kJ mol^{-1}

Post-lab

1. Write a thermochemical equation to show the combustion of ethanol.
2. Compare the class average value with the value from the data for the combustion of ethanol ($-\Delta_c H^\circ = 1367$ kJ mol^{-1})
3. Is there any significant variation between the experiment and the recorded value?
4. Suggest likely sources of error in your experiment and also improvements that could be made.

Activity 1.2

Inquiry

To determine and compare the heats of combustion of methanol, 1-propanol and 1-butanol with previously standardised ethanol.

Method

The experiment is carried out as in Activity 1.1 using the heat of combustion of ethanol to calculate the heat of combustion of the other alkanols. With such simple equipment only a fraction of the total heat will be absorbed. The success of the experiment depends on, as far as possible, this fraction being the same for all the alkanols tested.

Precaution

- The vessel being used as the calorimeter must contain the same amount of water and be at the same initial temperature for each alkanol.
- The distance between the calorimeter and the flame of the spirit burner must remain the same.
- The burner must be centred each time.
- The apparatus must be shielded from drafts.

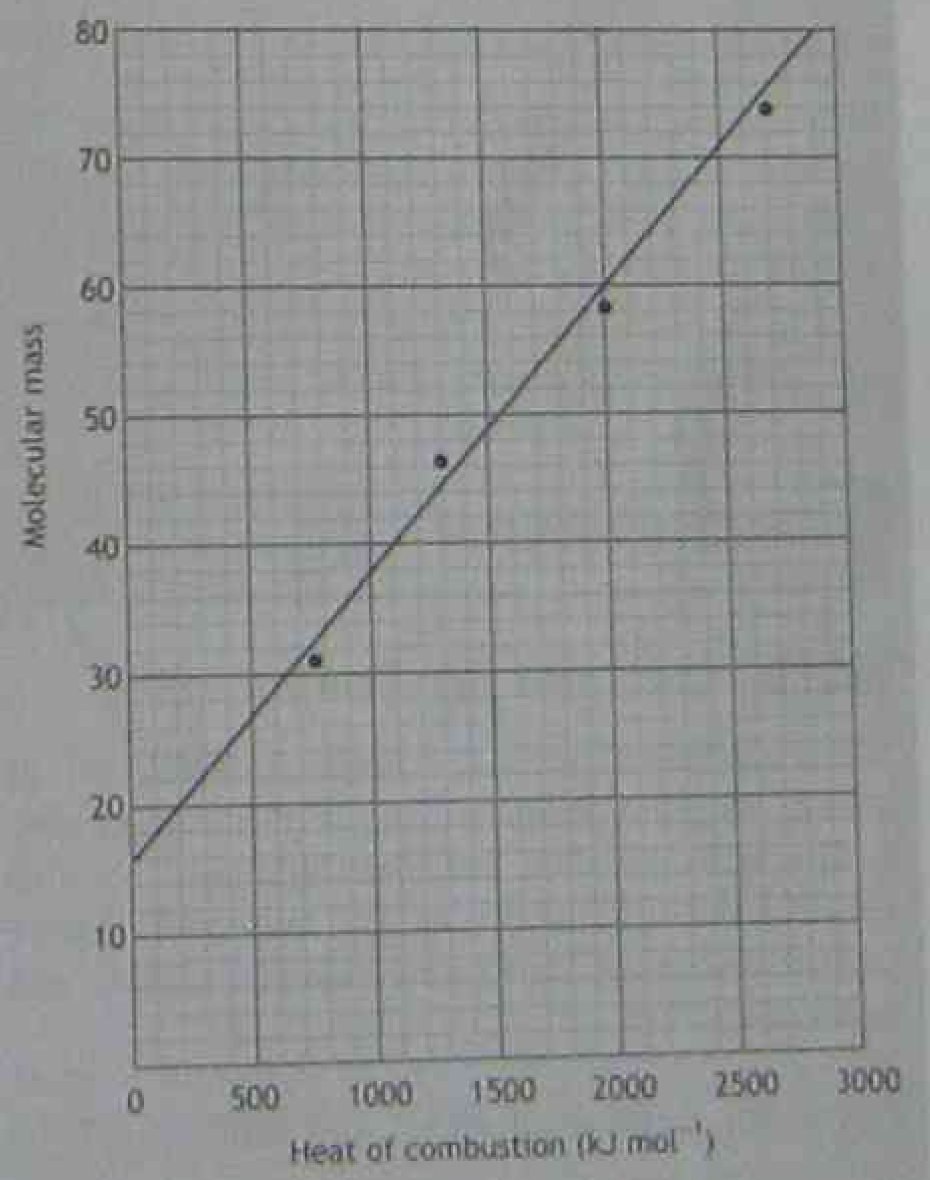


Figure 1.19 Graph of experimental results. A line of best fit has been drawn to connect the experimental points. Difference between neighbouring molecules is $-CH_2-$. From the graph, a difference in mass of 14 ($-CH_2-$) is equal to 650 kJ mol^{-1}.

Table 1.11 Experimental results

Alcohol	Temperature of water (°C)			Mass of burner and alcohol (g)		
	Initial	Final	Difference	Initial	Final	Difference
Methanol	22.4	32.4	10.0	19.60	19.00	0.60
Ethanol	22.8	32.8	10.0	19.15	18.69	0.46
1-Propanol	23.0	33.0	10.0	19.85	19.45	0.40
1-Butanol	23.6	33.6	10.0	19.50	19.13	0.37

Alcohol	Formula	Molecular mass	Mass to raise temperature by 1°C (g)	Mass to raise temperature by 1°C (moles)	Molar heat of combustion (kJ mol^{-1})	Actual
Methanol	CH_3OH	32	0.060	0.00188	720	726
Ethanol (Act. 1.1)	C_2H_5OH	46	0.046	0.0010	1350 (Act. 1.1)	1367
1-Propanol	C_3H_7OH	60	0.040	0.00067	2025	2021
1-Butanol	C_4H_9OH	74	0.037	0.00050	2700	2676

It would be relatively simple to extrapolate the graph to find the value for 1-pentanol (3331 kJ mol^{-1}). In the case of higher alkanols such as 1-octanol, a simple calculation can be used (720 – 650) + (8 x 650) = 5270 kJ mol^{-1} (by experiment). The value from the SI Chemical Data is 5294 kJ mol^{-1}.

Electrochemistry

1.10 Reactions involving metals

Electrochemical cells are important sources of energy. Another important use of electrochemistry is the electro-refining and electroplating of metals to produce or enhance useful materials. These processes involve reactions between metals and non-metals.

Reactions between metals and non-metals

At the beginning of the twentieth century when the theories of atomic structure and bonding were developed, the changes that occur within atoms taking part in oxidation-reduction reactions were also investigated.

Consider the oxidation of magnesium to magnesium oxide and the changes in the electron configurations that occur:

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

It is easier to understand the electron transfers that take place if the equations are written as half-equations

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

$$O_2 + 4e^- \rightarrow 2O^{2-}$$

Many other non-metals were found to be capable of removing electrons from magnesium atoms.

Example

(a) $Mg(s) + Cl_2(g) \rightarrow Mg^{2+}(aq) + 2Cl^-(aq)$
(b) $Mg(s) + S(l) \rightarrow Mg^{2+}(aq) + S^{2-}(aq)$

This led to an extension of reduction-oxidation or redox reactions to include reactions with substances other than oxygen.

Oxidation is defined as the loss of electrons from a substance. *Reduction* is defined as the gain of electrons by a substance. An *oxidising agent* or *oxidant* is defined as an electron acceptor and a *reducing agent* or *reductant* as an electron donor. The oxidation number of a element in a molecule is the charge that the atom would have if the molecule were completely ionic. The oxidation number of an element is a zero.

Redox reactions are reactions where electrons are transferred. The reaction is made up of two half-reactions, one for oxidation and one for reduction.

Table 1.12 Characteristics of redox reactions

Process	No. of electrons	Oxidation no.
Oxidation	decreases	increases
Reduction	increases	decreases
Oxidant	increases	decreases
Reductant	decreases	increases

In the following example, the metal will be the electron donor, so it will be a reductant. The non-metal will be the electron acceptor so it will be an oxidant. The reductant (reducing agent) is itself oxidised. The oxidant (oxidising agent) is itself reduced.

Example

The reaction with the metal silver and the non-metal bromine is:

(i) $Ag \rightarrow Ag^+ + e^-$ (oxidation)
(ii) $Br_2 + 2e^- \rightarrow 2Br^-$ (reduction)

To balance the electrons, we must multiply the half-reaction (i) by 2:

(iii) $2Ag \rightarrow 2Ag^+ + 2e^-$

Add (ii) and (iii):

$$2Ag(g) + Br_2(aq) \rightarrow 2Ag^+(aq) + 2Br^-(aq)$$

In this reaction, Ag is the reductant and Br_2 the oxidant.

Note:

Ionic equations must be balanced both atomically and electrically.

1. Write the half-equations including the electrons.
2. Adjust equations if needed so that the electrons are balanced.
3. Add the half-equations. The electrons should then cancel.

Reactions to extract metals from ores

Industry uses a number of reactions to extract metals from their ores. Most ores consist of the sulfides or oxides of metals.

Example

The extraction of iron in a blast furnace. At first, coke is converted to carbon monoxide, which is used to convert the iron oxide (haematite), Fe_2O_3 to iron.

Formation of carbon monoxide:

$$2C(s) + O_2(g) \rightarrow 2CO(g)$$

In this reaction, carbon is the reductant.

$$Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(l) + 3CO_2(g)$$

In this reaction the metal oxide is reduced to the metal, so Fe_2O_3 is the **oxidant** and carbon monoxide is the **reductant**.

Summary of major points in reactions of metals

Table 1.13 The activity series

Reductant		Oxidant
K	⇌	$K^+ + e^-$
Ba	⇌	$Ba^{2+} + 2e^-$
Ca	⇌	$Ca^{2+} + 2e^-$
Na	⇌	$Na^+ + e^-$
Mg	⇌	$Mg^{2+} + 2e^-$
Al *	⇌	$Al^{3+} + 3e^-$
Zn	⇌	$Zn^{2+} + 2e^-$
Fe	⇌	$Fe^{2+} + 2e^-$
Sn	⇌	$Sn^{2+} + 2e^-$
Pb	⇌	$Pb^{2+} + 2e^-$
(H_2)**	⇌	$2H^+ + 2e^-$
Cu	⇌	$Cu^{2+} + 2e^-$
Ag	⇌	$Ag^+ + e^-$
Hg	⇌	$Hg^{2+} + 2e^-$

Increasing strengths as reductants ↑

Increasing strengths as oxidants ↓

*Note 1. Because of its thin protective skin of aluminium oxide, **aluminium** is often difficult to dissolve in replacement acids. In laboratories that analyse aluminium and aluminium alloys, a small amount of hydrogen peroxide is added to hydrochloric acid to facilitate the reaction.

Note 2. Replacement acids are acids in which the hydrogen ion can oxidise reactive metals. These are the inorganic acids, hydrochloric acid and dilute sulfuric acid, and some organic acids such as ethanoic acid.

**Note 3. Hydrogen is included in Table 1.13 because metals above it in the series can reduce the H^+ ions of replacement acids, liberating $H_2(g)$, whereas those metals below it do not react with replacement acids.

1. The higher a metal is in the activity series, the more powerful it is as a reductant. It follows that the most powerful reductant, potassium, will be the metal most readily oxidised to form potassium ions.
2. Conversely, the lower a metal is in the activity series, the more difficult it is to oxidise.
3. Any metal in the activity series will displace any metal below it from a solution of its salts. The further apart the metals are, the more vigorous will be the reaction.

Example

If zinc is placed in copper sulfate solution, zinc sulfate is formed and copper is deposited.

Displacement of a metal from a solution of its salt by another metal

From Table 1.13 we can see that the reducing strength of metals decreases as we go from K → Hg. Hence, any metal in the table will reduce the ion of any metal below it. Using the activity series we can predict whether reactions will occur.

Practical work

The reactions of selected metals with ions of other metals in solution should be observed.

Example

If a piece of iron wire is dipped into a solution of copper sulfate, will a reaction take place?

Since iron is higher than copper in the activity series, the following half-equations can be written:

(i) $Fe \rightarrow Fe^{2+} + 2e^-$ (oxidation)

(ii) $Cu^{2+} + 2e^- \rightarrow Cu$ (reduction)

Adding (i) and (ii):

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

If such a reaction were left overnight, the blue colour of the copper sulfate would disappear and copper would be deposited. Iron is the reductant and copper the oxidant.

This simple reaction is used for copper recovery in mining processes.

1.19 Reactions where metal atoms show different oxidation states

Oxidation number is very useful in dealing with elements whose compounds show a variety of oxidation states (e.g. transition metals).

The oxidation number is the charge, real or imaginary, that an atom would have if it occurred as an ion in a compound.

Iron is a typical transition metal, showing more than one oxidation state. Another example is titanium which has oxidation states of +2, +3 and +4.

Other metals, which are not transition metals, may occur in more than one oxidation state, for example, tin (+2 and +4).

Rules for assigning oxidation numbers

1. In uncombined elements, each atom has an oxidation number (O.N.) of zero. For example, Na and Cl_2 have an oxidation number of 0.
2. The oxidation number of a monatomic ion is equal to the charge on that ion. For example, Na^+ (O.N. = +1), Fe^{3+} (O.N. +3), S^{2-}(O.N. = −2) and Cl^- (O.N. = −1).
3. Oxygen has an oxidation number of −2 in compounds.

   [Peroxides and superoxides are the exceptions. For example, H_2O_2 (O.N. = −1) and KO_2 (containing O_2^- ion).]
4. Hydrogen has an oxidation number of +1 in compounds.

   [Ionic hydrides are the exception where the O.N. = −1. For example, NaH (O.N. = −1).]
5. The sum of the oxidation numbers of all atoms
   - (a) in a neutral molecule is zero, and
   - (b) in a polyatomic ion,

   is equal to the charge on the ion.

Example 1

In the compound $FeCl_3$, the O.N. for iron is +3.

In the compound $FeCl_2$, the O.N. for iron is +2.

Example 2

Find the O.N. for manganese in the following compounds:

(i)	$MnCl_2$	+2
(ii)	$MnCl_3$	+3
(iii)	$KMnO_4$	+7 [1 + Mn + (−8)]

Example 3

Write half-equations for the reaction which takes place when iron (II) nitrate has bromine added to it. Write the balanced equation for the reaction and state the oxidant and the reductant.

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

(ii) $Br_2 + 2e^- \rightarrow 2Br^-$ (reduction)

Multiply (i) by 2:

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

Add (ii) and (iii):

$$2Fe^{2+}(aq) + Br_2(l) \rightarrow 2Fe^{3+}(aq) + 2Br^-(aq)$$

Br_2 is the oxidant; Fe^{2+} is the reductant.

1.20 The use of redox reactions to generate electricity

The Daniell Cell

Professor John Daniell produced the first practical depolarising cell in 1836 to overcome a polarising effect observed in existing primary cells that drastically reduced current. He adopted a two-fluid (or two-cell) approach that was taken up and improved on by later researchers.

The Daniell cell is divided into two half-cells:

(a) The electron donor half-cell, where loss of electrons (oxidation) occurs, which is called the anode.

Anode half-cell reaction:

$Zn \rightarrow Zn^{2+} + 2e^-$

(b) The electron acceptor half-cell, where electrons are gained (reduction), which is called the cathode.

Cathode half-cell reaction:

$Cu^{2+} + 2e^- \rightarrow Cu$

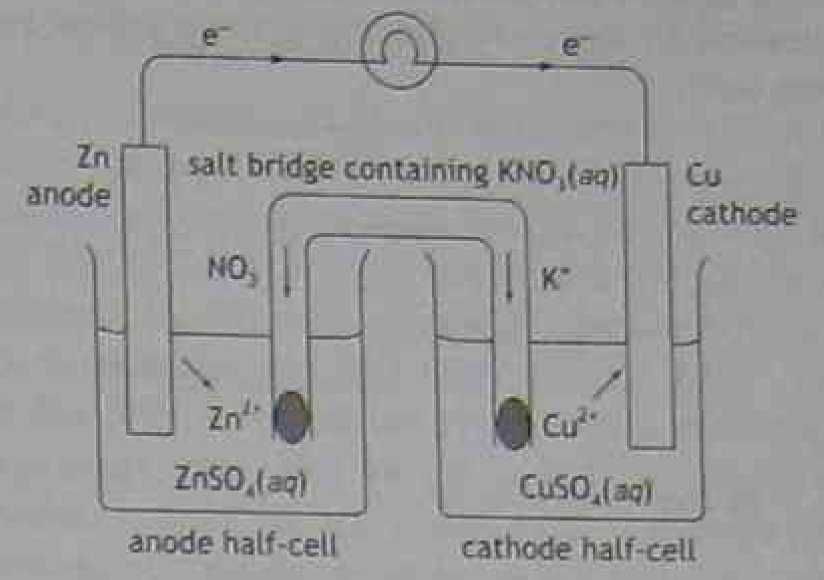


Figure 1.20 The Daniell cell

The half-cells are connected by an external wire which forces electrons, released by the anode, to travel by an external circuit to the cathode rather than through the solution.

A salt bridge, usually filled with KNO_3, between the two half-cells, completes the circuit and enables ions to move. The salt bridge may be an inverted U-tube of KNO_3 with cotton wool plugs at the ends, or strips of filter paper soaked in the salt. The movement of ions through the salt bridge balances the charges due to the electron flow in the external circuit.

The overall cell reaction is obtained by adding the anode and cathode half-cell reactions. The electrons must be balanced.

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

The potential difference or electromotive force (emf) of a galvanic cell depends on the nature of the electrodes and the electrolyte. It does not depend on the size of the cell.

Practical work

Construct a Daniell cell.

Electrode potentials

In electrochemical cells, also called galvanic or voltaic cells, chemicals interact spontaneously to produce an electric current.

Every half-reaction has its own redox potential as shown in Table 1.14. These have been obtained by measurement of the potential difference produced when the half-cell, under stated conditions, is coupled with a hydrogen reference electrode (Figure 1.21). By convention, the redox potentials are listed in the table as standard reduction potentials and the standard hydrogen electrode is given a potential of zero volts.

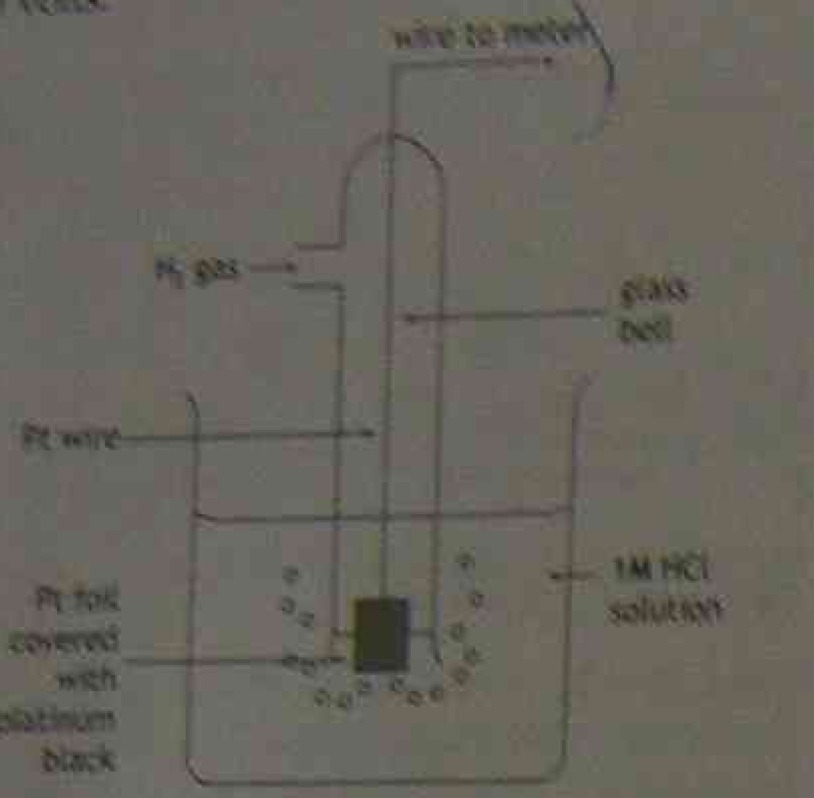


Figure 1.21 Standard hydrogen electrode. The reference electrode consists of a platinum electrode in a solution which contains **1M** (H^+) ions through which hydrogen gas is bubbled at a pressure of 101.3 kPa and a temperature of 298 K.

Note: Standard state conditions for operating a voltaic cell include **1M** concentrations for reactants and products that are in solution and 101.3 kPa pressure for those that are gases. The temperature of the cell would be taken as 298 K (25°C). For the Daniell cell (Figure 1.20), $Zn/Zn^{2+}//Cu^{2+}/Cu$ if the cell is operating under standard state conditions then the emf of the cell is called the standard emf, E° volts. If the cell is not operating under standard state conditions then it has an emf of E volts.

When coupled with another half-cell, the total potential across the cell will be due to the electrode of the other half-cell.

Case 1

If the metal in Figure 1.22 is zinc, the potential difference will be 0.76 V. This means that the reaction

$$Zn \rightarrow Zn^{2+} + 2e^-$$

has a greater tendency to occur than the reaction

$$H_2(g) \rightarrow 2H^+ + 2e^-$$

By convention, the redox potentials in the table are listed as reduction potentials, for example,

$$Zn^{2+} + 2e^- \rightarrow Zn \qquad E^\circ = -0.76 \text{ V}$$

Since oxidation is the reverse of reduction, we ca reverse the equation and also the sign of the E value. We then have two half-equations:

(i) $Zn \rightarrow Zn^{2+} + 2e^-$ (oxidation) $E^\circ = +0.76$ V

(ii) $2H^+ + 2e^- \rightarrow H_2(g)$ (reduction) $E^\circ = 0$ V

Cell reaction

$$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g) \qquad E^\circ_{cell} = 0.76 \text{ V}$$

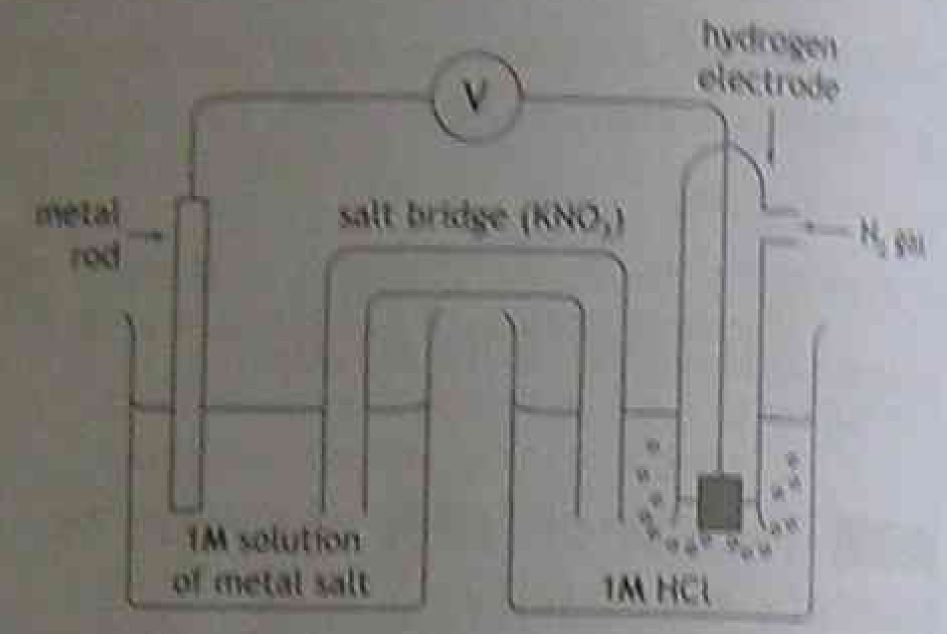


Figure 1.22 A metal electrode coupled with a hydrogen reference electrode

Note 1. The voltage of an electrochemical cell

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

Note 2. If in determining the cell reaction the half-cell equations are balanced, the E° value for each half-cell remains the same.

Case 2

If the metal used in Figure 1.22 is silver, the reduction potential for $Ag^+ + e^- \rightarrow Ag$ is $E^\circ = +0.8$ V.

This shows that the tendency for Ag^+ ions to be reduced to Ag in the half-cell is greater then the tendency for H^+ ions to be reduced to H_2 in the reference cell.

We then have two half equations:

(i) $H_2(g) \rightarrow 2H^+ + 2e^-$ $E^\circ = 0.0$ V

(ii) $Ag^+ + e^- \rightarrow Ag$ $E^\circ = +0.8$ V

Then 2 × (ii) + (i) gives cell reaction

$$H_2(g) + 2Ag^+(aq) \rightarrow 2H^+(aq) + 2Ag(s)$$

$$E^\circ_{cell} = +0.8 \text{ V}$$

1.21 Calculation of a cell voltage

So far we have calculated E°_{cell} using hydrogen as one of the electrodes. In the following example we will use two metal electrodes, zinc and silver.

Example

(a) Draw a diagram for the $Zn/Zn^{2+}//Ag^+/Ag$ cell.

(b) Find the overall reaction and the emf for the cell.

Step 1. Inspect the half-cell equations and their E° from Table 1.14.

Step 2. Write the half-equation which has the more positive E° as the reduction reaction.

(i) $Ag^+(aq) + e^- \rightarrow Ag(s)$ $E^\circ = +0.80$ V

Step 3. Reverse the direction of the other equation and change the sign of E° so that it becomes the oxidation reaction.

(ii) $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $E^\circ = +0.76$ V

Step 4. The E°_{cell} can now be calculated by adding $E^\circ_{oxidation}$ and $E^\circ_{reduction}$

Step 5. Balance the half-cell equations for electrons, 2 × (i) + (ii) gives

Cell reaction

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

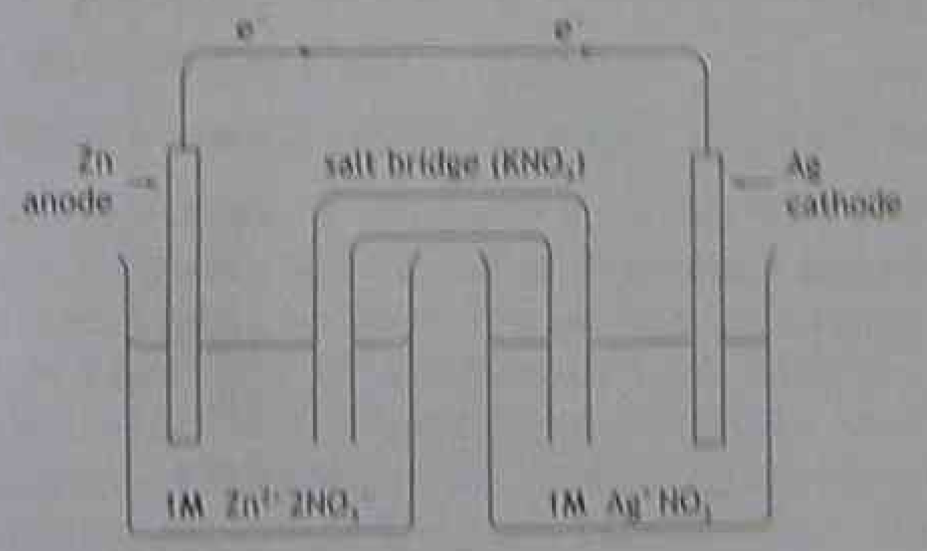


Figure 1.23 $Zn/Zn^{2+}//Ag^+/Ag$ cell

For the cell to operate as a galvanic cell, there must be:

(a) two half-cell reactions (one oxidising and one reducing);

(b) an ion path; and

(c) an electron path.

Note: The emf generated depends on the nature of the half-cell reactions, the concentration of the electrolytes and the temperature.

A comparison of the oxidising strengths of metals using cell voltages

Instead of drawing diagrams to represent cells, it is simpler to represent them in a symbolic way. The Daniell cell, in Figure 1.20, can be represented as $Zn/Zn^{2+}//Cu^{2+}/Cu$. By convention, the anode is written at the left, with a single line between the two species present (in this case, Zn and Zn^{2+}). The double lines in the middle shows that a salt bridge is present, providing an ion path. The cathode is written at the right and again there is a single line between the species present (in this case Cu^{2+} ions and Cu).

Example

Given the following information:

(a) $Cu/Cu^{2+}//Ag^+/Ag$ cell voltage = 0.45 V

(b) $Zn/Zn^{2+}//Cu^{2+}/Cu$ cell voltage = 1.11 V

(c) $Mg/Mg^{2+}//Cu^{2+}/Cu$ cell voltage = 2.71 V

write the four metals, from weak to strong, as reductants. All ions are at the same concentration.

Calculation

For cell (a) at the anode

$$Cu \rightarrow Cu^{2+} + 2e^-$$

so copper will be a stronger reductant than silver.

For cell (b) at the anode

$$Zn \rightarrow Zn^{2+} + 2e^-$$

so zinc will be a stronger reductant than copper.

For cell (c) at the anode

$$Mg \rightarrow Mg^{2+} + 2e^-$$

so magnesium will also be a stronger reductant than copper.

However the cell voltage of (c) is much higher than that of (b), so magnesium will be a stronger reductant than zinc.

The order from weakest to strongest reductants is silver, copper, zinc, magnesium.

The use of the electrochemical series to predict either the order of reductant strength of metals or the direction of reactions is subject to some restrictions.

1. The order of half-cells close together in the activity series can be changed with concentration change. The ease with which a metal ion can be reduced depends on concentration.

Table 1.14 Some standard reduction potentials at 298K (25°C and 100 kPa), i.e. SLC conditions

Oxidant		Reductant	E°
$K^+ + e^-$	⇌	$K(s)$	−2.92 V
$Ba^{2+} + 2e^-$	⇌	$Ba(s)$	−2.90 V
$Ca^{2+} + 2e^-$	⇌	$Ca(s)$	−2.87 V
$Na^+ + e^-$	⇌	$Na(s)$	−2.71 V
$Mg^{2+} + 2e^-$	⇌	$Mg(s)$	−2.36 V
$Al^{3+} + 3e^-$	⇌	$Al(s)$	−1.66 V
$Mn^{2+} + 2e^-$	⇌	$Mn(s)$	−1.18 V
$H_2O + e^-$	⇌	$\frac{1}{2} H_2(g) + OH^-$	−0.83 V
$Zn^{2+} + 2e^-$	⇌	$Zn(s)$	−0.76 V
$S(s) + 2e^-$	⇌	S^{2-}	−0.48 V
$Fe^{2+} + 2e^-$	⇌	$Fe(s)$	−0.41 V
$Ni^{2+} + 2e^-$	⇌	$Ni(s)$	−0.23 V
$Sn^{2+} + 2e^-$	⇌	$Sn(s)$	−0.14 V
$Pb^{2+} + 2e^-$	⇌	$Pb(s)$	−0.13 V
$CO_2(g) + 4H^+ + 4e^-$	⇌	$HCHO + H_2O$	−0.07 V
$CO_2(g) + 4H^+ + 4e^-$	⇌	$\frac{1}{6} C_6H_{12}O_6$(glucose) $+ H_2O$	−0.01 V
$H^+ + e^-$	⇌	$\frac{1}{2} H_2(g)$	0.00 V
$CO_2(g) + 6H^+ + 6e^-$	⇌	$CH_3OH + H_2O$	0.03 V
$Sn^{4+} + 2e^-$	⇌	Sn^{2+}	0.15 V
$CO_2(g) + 8H^+ + 8e^-$	⇌	$CH_4(g) + 2H_2O$	0.17 V
$HCHO + 2H^+ + 2e^-$	⇌	CH_3OH	0.24 V
$Cu^{2+} + 2e^-$	⇌	$Cu(s)$	0.35 V
$O_2(g) + 2H_2O + 4e^-$	⇌	$4OH^-$	0.40 V
$HCHO + 4H^+ + 4e^-$	⇌	$CH_4(g) + H_2O$	0.41 V
$NiO_2(s) + 2H_2O + 2e^-$	⇌	$Ni(OH)_2(s) + 2OH^-$	0.49 V
$Cu^+ + e^-$	⇌	$Cu(s)$	0.52 V
$I_2(s) + 2e^-$	⇌	$2I^-$	0.54 V
$I_2(aq) + 2e^-$	⇌	$2I^-$	0.62 V
$Fe^{3+} + e^-$	⇌	Fe^{2+}	0.77 V
$Ag^+ + e^-$	⇌	$Ag(s)$	0.80 V
$Br_2(l) + 2e^-$	⇌	$2Br^-$	1.07 V
$Br_2(aq) + 2e^-$	⇌	$2Br^-$	1.09 V
$O_2(g) + 4H^+ + 4e^-$	⇌	$2H_2O$	1.23 V
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	⇌	$2Cr^{3+} + 7H_2O$	1.33 V
$Cl_2(g) + 2e^-$	⇌	$2Cl^-$	1.36 V
$Cl_2(aq) + 2e^-$	⇌	$2Cl^-$	1.40 V
$MnO_4^- + 8H^+ + 5e^-$	⇌	$Mn^{2+} + 4H_2O$	1.51 V
$F_2(g) + 2e^-$	⇌	$2F^-$	2.87 V

Increasing strength as oxidants ↓

Increasing strength as reductants ↑

Note: Unless otherwise indicated, all ionic species are in aqueous solution.

2. The series only applies to reactions in aqueous solution.
3. The emf of a galvanic cell is temperature-dependent.
4. The emf of a galvanic cell depends in some cases on pH.

1.22 Classification of cells

The types of cells we have discussed so far have had metal/metal ion electrodes, for example,

$$Cu/Cu^{2+}//Ag^+/Ag.$$

Another type of electrode involves an inert substance such as platinum or carbon and equimolar amounts of a non-metal and its ion. If the symbol for platinum (Pt) is written on the left of the conducting material the convention is that an oxidising process will occur.

Example

$$Pt(s)/I_2(s)/I^-(aq)//Fe^{2+}(aq)/Fe^{3+}(aq)/Pt(s)$$

The half-equation with the most positive E° will be the reduction reaction:

(i) $Fe^{3+} + e^- \rightarrow Fe^{2+}$, $E° = +0.77$ V (reduction)

(ii) $2I^-(aq) \rightarrow I_2(s) + 2e^-$, $E° = -0.54$ V (oxidation)

Overall reaction 2 x (i) + (ii) gives

$$2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(s),\ E°_{cell} = 0.23\ V$$

Another type of electrode involves an inert substance such as platinum or carbon, and ions of different oxidation states. This can be seen in Figure 1.24 where Fe^{2+}/Fe^{3+} solutions are used. Hydrogen electrodes are also used. They involve an inert platinum electrode and, for example, hydrogen or chlorine gas at SLC. The gas is bubbled into a 1 M HCl solution.

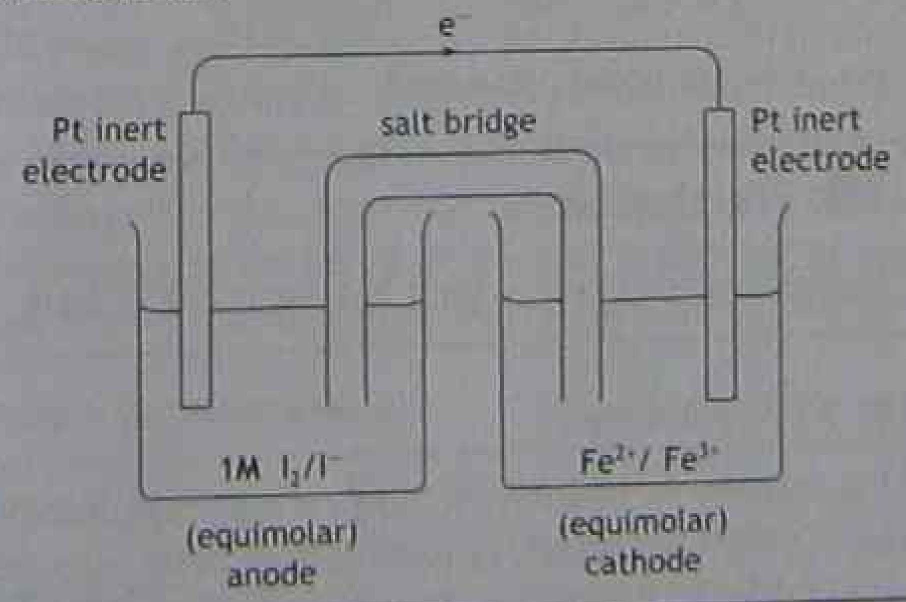


Figure 1.24 Cell with inert electrodes

The hydrogen electrode has already been mentioned as the standard reference electrode. Another reference electrode, used in pH meters, is the calomel electrode.

The pH meter measures the potential difference between a reference half-cell (the calomel electrode) and a half-cell (the glass electrode) whose potential changes as the $[H^+]$ varies.

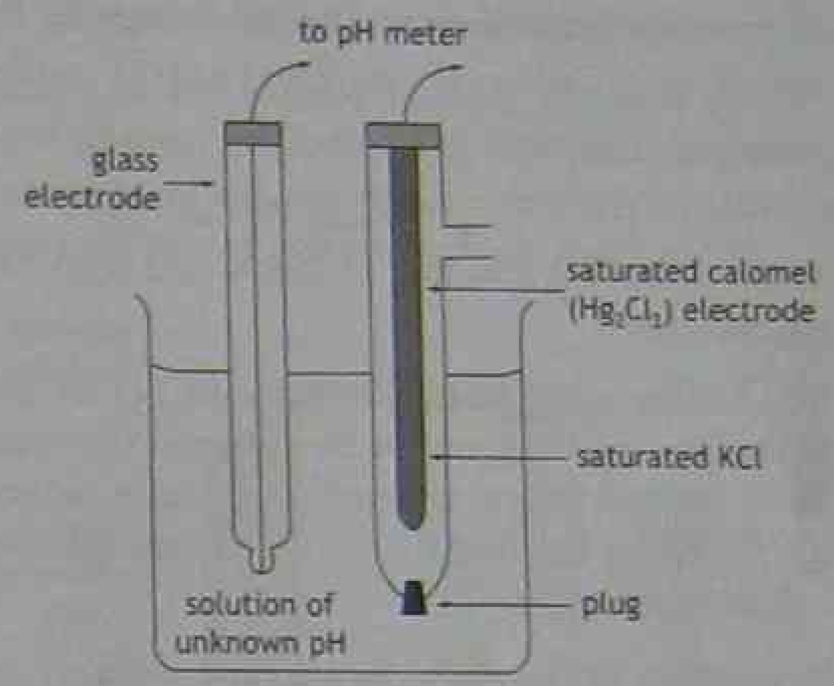


Figure 1.25 Electrodes used in a pH meter

The half-cell reaction for the calomel electrode is

$$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^- \qquad E° = 0.28\ V$$

The KCl solution is 1M.

How to predict reactions tendencies

Without actually performing the experiments, students can determine whether a redox reaction can take place by referring to Table 1.14.

$$E°_{cell} = E°_{cathode} - E°_{anode}$$

If a piece of copper metal is placed in a solution of silver nitrate, the silver is deposited and the copper metal goes into solution as Cu^{2+} ions.

Half-cell equations:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad E° = +0.34\ V$$

$$Ag^+(aq) + e^- \rightarrow Ag(s) \qquad E° = +0.8\ V$$

We already know that the cell with the most positive E° is the reduction reaction, so $Ag^+ + e^- \rightarrow Ag$ is the reduction reaction and $Cu \rightarrow Cu^{2+} + 2e^-$ is the oxidation reaction.

After balancing the electrons in the half-equations the reaction is

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

This means that we can predict that when we place a strip of copper metal in a solution of silver nitrate, a reaction will occur. It also allows us to predict that if a strip of silver is placed in copper sulfate solution, no reaction will occur.

This reasoning can be extended to cell reactions:

- *A cell reaction can only take place if the cell emf has a positive value.* This indicates a spontaneous reaction. If a cell shows a negative value, the reverse reaction will occur. The cell voltage for the cell, $Cu(s)/Cu^{2+}(aq)//Ag^{+}(aq)/Ag(s)$, under standard conditions is 0.8 V – 0.34 V = 0.46 V

  $(i.e.\ E^{\circ}_{cathode} - E^{\circ}_{anode} = E^{\circ}_{cell})$

  This cell should function at 298 K and with 1M electrolytes.
- The farther apart the half-equations are on the table, the larger the emf of the cell, and the more likely the reaction is to occur. In practice, where the cell emf is less than 0.2 V, a significant reaction will not take place.
- In practice, electrochemical cells are unlikely to operate under standard conditions. The emf generated depends on the temperature and on the concentration of reactants and products in the cell. In general, if the concentration of reactants increases relative to products, the cell reaction becomes more spontaneous and the emf increases. As the cell operates, the reactants are used up and more by-products form. This will cause the emf to decrease.
- Predictions of cell emf must fit in with *Le Chatelier's Principle* which states that if an equilibrium system is subjected to change, that system will react in a way to oppose that change. Consider the $Cu/Cu^{2+}//Ag^{+}/Ag$ cell which is not operating under standard conditions. At the anode, as the concentration of the Cu^{2+} ions increases, the tendency of $Cu \rightarrow Cu^{2+}$ decreases and the voltage drops.

  At the cathode, if the $[Ag^{+}]$ is increased, Ag will be deposited at a faster rate, so the voltage will increase. By applying Le Chatelier's Principle, it can be seen that forward tendencies are increased by making the $[Cu^{2+}]$ as small as possible at the anode and by making the $[Ag^{+}]$ as large as possible at the cathode.
- It should be realised that a positive emf does not ensure that a redox reaction will occur to any significant extent.

Some commercial cells

The Leclanché cell

The Daniell cell was very difficult to use because the electrolytes but, in 1890, Leclanché developed 'dry cell' which we now use with very litt modification in torches, pocket radios, toys a some calculators. It delivers about 1.5 V.

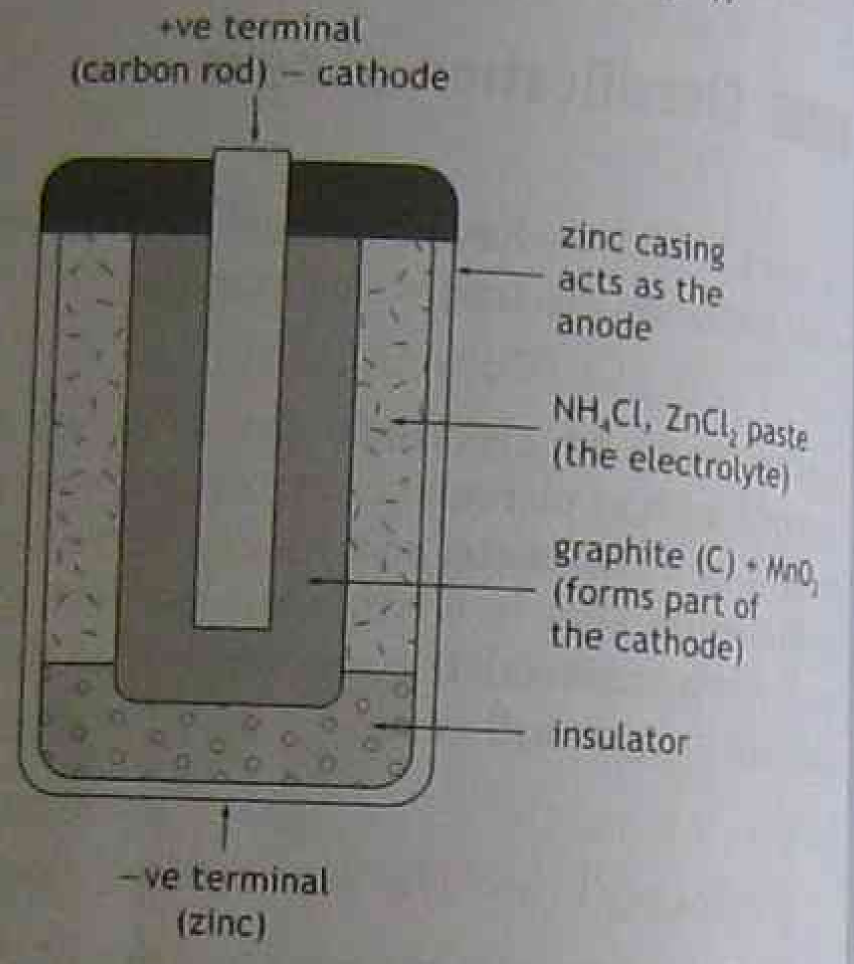


Figure 1.26 Structure of a Leclanché dry cell

Half-cell reactions:

(i) Oxidation reaction at the anode (-ve)

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^{-}$$

(ii) Cathode reaction (+ve)

$$2MnO_2(s) + 2H^{+}(aq) + 2e^{-} \rightarrow Mn_2O_3(s) + H_2O(l)$$

NH_4^{+} ions provide H^{+} ions needed for cathode process.

$$NH_4^{+}(aq) \rightleftharpoons NH_3(aq) + H^{+}(aq)$$

Overall,

$$Zn(s) + 2H^{+}(aq) + 2MnO_2(s) \rightarrow Zn^{2+}(aq) + Mn_2O_3(s) + H_2O(l)$$

This cell cannot be recharged.

Practical work

Examine a 'dry cell' which has been cut in half.

The alkaline battery

This battery is used with 'high drain' appliances such as tape recorders, requiring high total capacity (see Table 1.15) but its size means that it is not suitable for use in watches and calculators. The electrolyte paste contains potassium hydroxide and is similar in appearance to that in the Leclanché cell.

The alkaline cell can deliver higher currents than the Leclanché cell because the reactions occur more rapidly in the alkaline (KOH) electrolyte paste. It is therefore preferred for use in appliances requiring high currents, such as electronic photographic flash units. It is more expensive than the conventional dry cell but can last up to ten times longer. At present it is the leading type for commercial use. Alkaline batteries are non-hazardous and can be thrown away as waste.

Table 1.15 The alkaline cell

Name	Anode reaction	Cathode reaction	Uses
Manganese dioxide cell (primary)	$Zn + 2OH^{-} \rightarrow ZnO + H_2O + 2e^{-}$	$MnO_2 + 2H_2O + e^{-} \rightarrow Mn(OH)_3 + OH^{-}$	shavers, tape recorders

Lithium batteries

(a) Lithium/thionyl chloride cell

The porous carbon cathode is saturated with the electrolyte material [a solution of lithium aluminium chloride ($LiAlCl_4$) in thionyl chloride ($SOCl_2$)]. Because lithium reacts strongly with water, only non-aqueous electrolytes can be used for this cell.

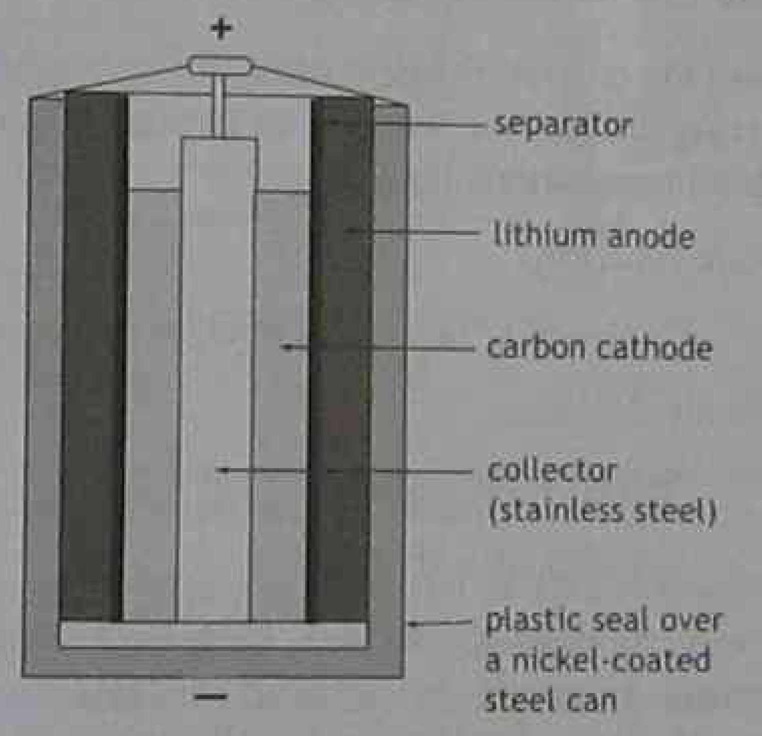


Figure 1.27 Lithium/thionyl chloride cell

Lithium/thionyl chloride batteries were originally developed for military use where their long shelf life (10 years) was necessary. One application is to provide power for an array of motion and environmental sensors used to monitor nuclear materials extracted during the dismantling of weapons systems. Technologies are being developed to provide power sources for remote or portable sensors under demanding environmental conditions, e.g. operating in a temperature range of –55°C to 150°C.

The power source must also provide high voltage per cell, be available in various sizes and shapes, and be able to deliver a good cost/performance ratio. To achieve the safest and most reliable operation of the system, the characteristics of the battery are carefully matched to the conditions of a particular activity.

(b) Lithium 'button' and pacemaker cells

Table 1.16 and Figures 1.28 and 1.29 give details of two typical miniaturised lithium-ion cells in common use as power sources for implanted cardiac pacemakers and small electronic instruments.

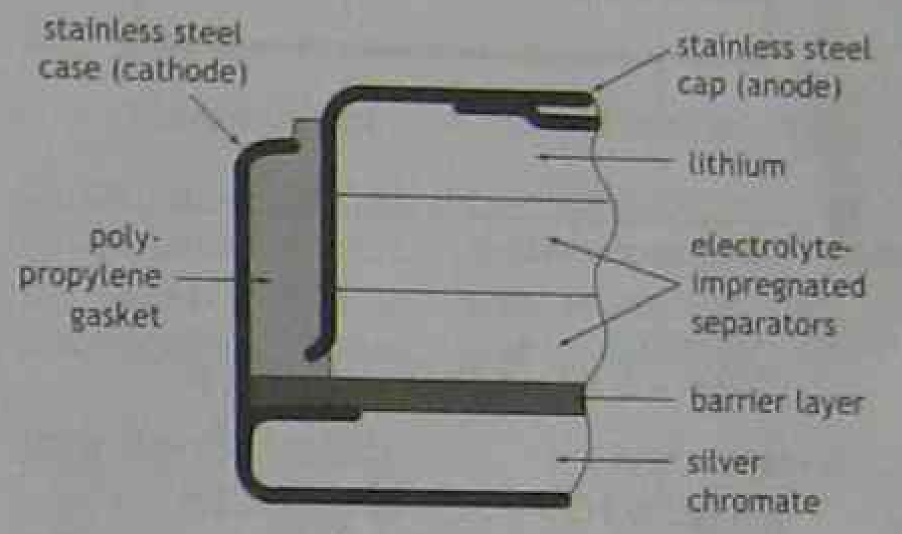


Figure 1.28 Cross-section of a typical lithium-silver chromate button cell

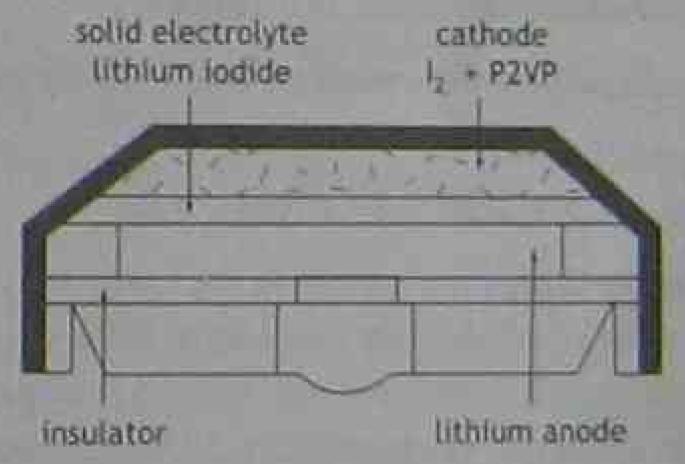


Figure 1.29 Lithium-iodide solid-state cell

Alkaline 'button' cells

(a) Mercury cell (primary)

Many other dry cells are available such as the mercury (II) oxide (button) cell used as a power source for hearing aids, electronic watches, two-way radios and microphones. Mercury (II) oxide is the cathode and powdered zinc is the anode. Potassium hydroxide is the electrolyte in a porous carrier.

These small cells can provide large amounts of electricity at a constant voltage over a long period of time. Mercury is, however, toxic to the human nervous system. All batteries including button batteries which contain mercuric oxide should be recycled if at all possible. A single cell delivers 1.2 V.

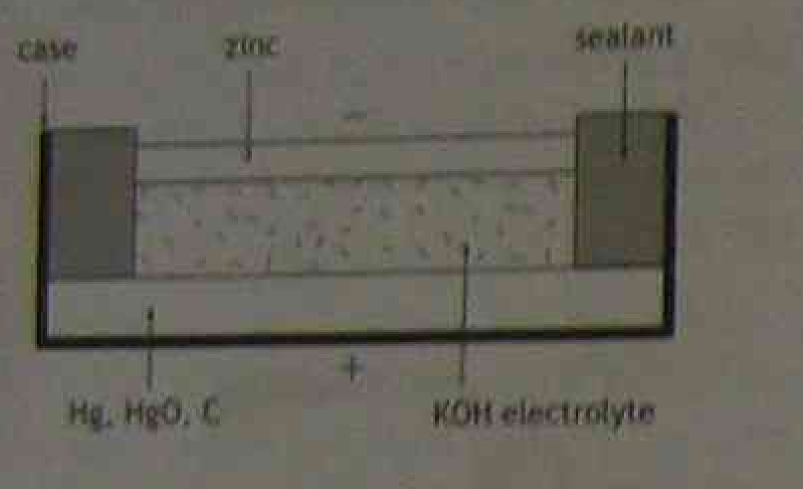


Figure 1.30 A mercury cell

Anode reaction

$$Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^-$$

Cathode reaction

$$HgO + H_2O + 2e^- \rightarrow Hg + 2OH^-$$

Cell reaction

$$Zn(s) + HgO(s) \rightarrow ZnO(s) + Hg(s)$$

(b) Silver oxide/cadmium cell (primary)

These cells are used in watches and hearing aids.

Anode reaction

$$Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$$

Cathode reaction

$$Ag_2O + H_2O + 2e^- \rightarrow 2Ag + 2OH^-$$

Cell reaction

$$Cd(s) + Ag_2O(s) + H_2O(l) \rightarrow Cd(OH)_2(s) + 2Ag(s)$$

(c) Silver oxide/zinc cells

These cells use powdered zinc anodes and potassium hydroxide as the electrolyte and are also used in watches and hearing aids. A small cell delivers 1.5 V.

Table 1.16 Some lithium cells

Name	Cell reaction	Uses
Lithium-silver chromate (primary)	$2Li(s) + Ag_2CrO_4(s) \rightarrow 2Ag(s) + Li_2CrO_4(s)$	cardiac pacemaker
Solid state cell Lithium iodide (primary)	$Li(s) + \frac{1}{2}I_2(s) \rightarrow LiI(s)$	cardiac pacemaker, electric watches, pocket calculators

Secondary or rechargeable batteries

The lead-acid accumulator (motor vehicle battery)

This is a storage or secondary battery and can be recharged. It is made up of a series of cells, each of which can deliver about 2 V. A six-volt battery will therefore contain three cells connected in series.

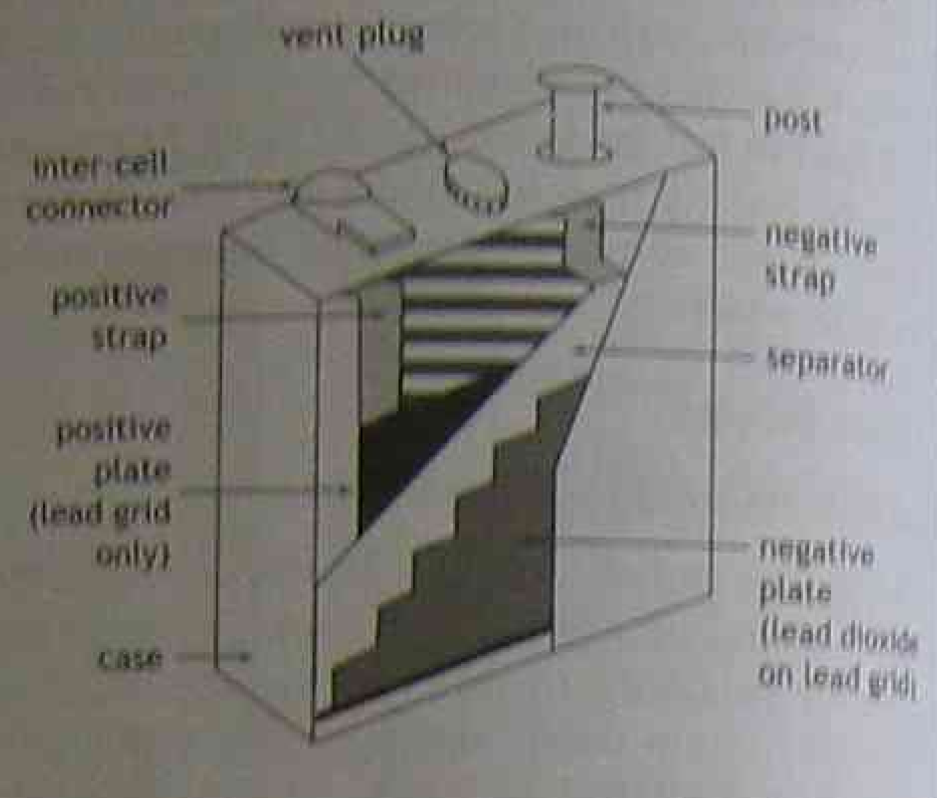


Figure 1.31 The lead-acid accumulator

When the current is being used, for example, when starting the motor vehicle or for headlights, the following reactions take place:

Anode reaction

$$Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$$

Cathode reaction

$$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^-$$
$$\rightarrow PbSO_4(s) + 2H_2O(l)$$

As the cell delivers current, both lead plates then become covered with lead sulfate and the concentration of sulfuric acid falls. When the motor vehicle generator forces current back into the battery, the above reactions are reversed. The cell can be charged and discharged many times.

Disadvantages

- The weight of the battery, especially when being used in golf buggies and carts.
- It requires six hours to recharge.
- The electrolyte must be checked regularly using a hydrometer.
- Irreversible changes in the solids (Pb at the +ve pole; PbO_2 at the −ve pole) can cause permanent damage to the battery.

Disposal

This group includes most motor vehicle and motor cycle batteries. The cases are made of 12% antimonial lead for hardening. They should be recycled.

Practical work

Examine an old motor vehicle battery with the casing removed.

The Vanadium redox battery

This durable battery was developed for use in **electric vehicles**. The battery operates on stored charge contained in vanadium chemical solutions.

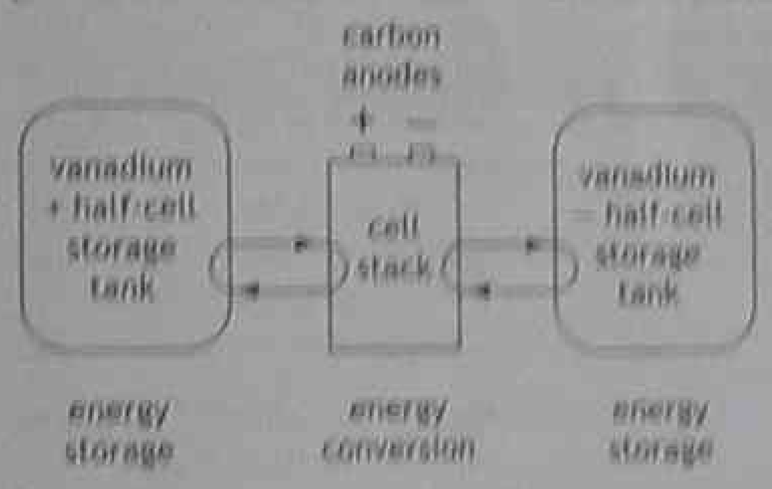


Figure 1.32 The vanadium redox battery

The battery's capacity is stored in two electrolytes which flow into a cell unit. The charged electrolytes are V(+5) and V(+2) salts. During discharge they change to V(+4) and V(+3) salts. The electrolytes are separated in the cell by an ion-selective membrane.

The battery stores charge in the vanadium chemical solutions. The vehicle draws its power from this stored energy. When the solution needs recharging, it is drained from the vehicle's storage tank and placed in recharging tanks. The electric vehicle is then supplied with another fully charged battery solution so that the recharge/refuel process takes less than 10 minutes. The vehicle needs only two sets of solution for continuous use plus a recharging station for the battery solutions.

Nickel-cadmium rechargeable battery

These batteries are widely used in cellular phones, portable hand tools and toys. Nickel-cadmium (Ni-Cd) batteries contain regulated amounts of cadmium which should be recycled or disposed of as hazardous waste.

The electrodes are made of nickel powder sintered onto a steel plate. Anode plates are impregnated with nickel salts and cathode plates with cadmium salts. The electrolyte is potassium hydroxide. A single cell delivers 1.3 V.

Half-cell reactions

Anode

$$Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$$

Cathode

$$Ni(OH)_3 + e^- \rightarrow Ni(OH)_2 + OH^-$$

Cell reaction

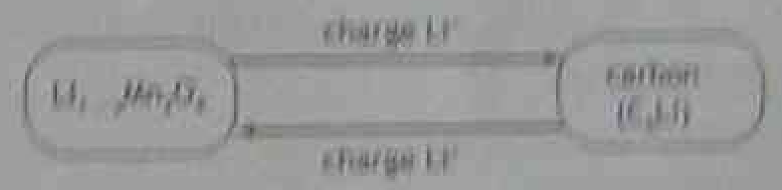
$$Cd + 2Ni(OH)_3 \rightarrow Cd(OH)_2 + 2Ni(OH)_2$$

Larger Ni-Cd batteries are finding increasing use as an alternative to the lead-acid accumulator. The cells are lighter, stronger and more resistant to electrochemical abuse, e.g. short-circuiting.

New developments

Lithium ion batteries

Only lithium ions are involved in charge/discharge reactions.



The unit cells are made in flat shapes that can be connected in series and parallel to reach required voltages. Lithium ion batteries are smaller and lighter than Ni-Cd batteries, can operate at higher temperatures and have an average discharge voltage of 3.7 V.

Table 1.17 Some expected uses of lithium ion batteries

Non-military uses	Military and space uses
Cellular phones	Backpack radio battery
Laptop computers	Missile launch battery
Portable radios	Marine battery (submersible)
Two-way radios	Satellite batteries
Electric vehicles	

New Gratzel type nano-crystalline organic photovoltaic devices

The working principle of the nano-crystalline, dye-sensitised solar cell (nc-DSC) depends on the following working cycle:

- Dye excitation.
- Electron injection into porous nano-crystalline titanium oxide, nc-TiO_2.
- Fast reduction of the oxidised dye by a redox couple.

This type of cell is based on the principle of the regenerative photoelectrochemical process. The active layer is nc-TiO_2. A monomolecular layer of dye on the nc-TiO_2 surface absorbs the incoming light. The device is completed by a counter-electrode which is made up of a platinum catalyst and an inorganic solvent-based electrolyte containing the redox couple iodide/triiodide.

For low power devices, e.g. calculators and solar-powered watches, an nc-DSC plastic cell is used. For high power outdoor use, a sealing and interconnection technique is used. Introduction of the new nc-DSC cell will depend on low-cost production, efficient marketing and device stability.

Fuel cells

Fuel cells differ from electrochemical cells in several ways.

1. They do not store reactants, products or electrolytes.
2. They obtain electricity direct from the redox reaction.
3. They supply energy at a constant rate as reactants enter and products leave the cell.
4. The electrodes do not undergo permanent change.
5. The reactants are usually gases.
6. Their energy/mass ratio is much higher than for electrochemical cells.

The most successful of these fuel cells developed so far is the hydrogen/oxygen cell (Figure 1.33). If an alkaline electrolyte such as potassium hydroxide is used:

Anode reaction

(i) $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$

Cathode reaction

(ii) $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

2 × (i) + (ii) gives **cell reaction**

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

Latest fuel cells being developed are methanol-fille with a special catalyst on a highly efficient me made from non-conductive silicon.

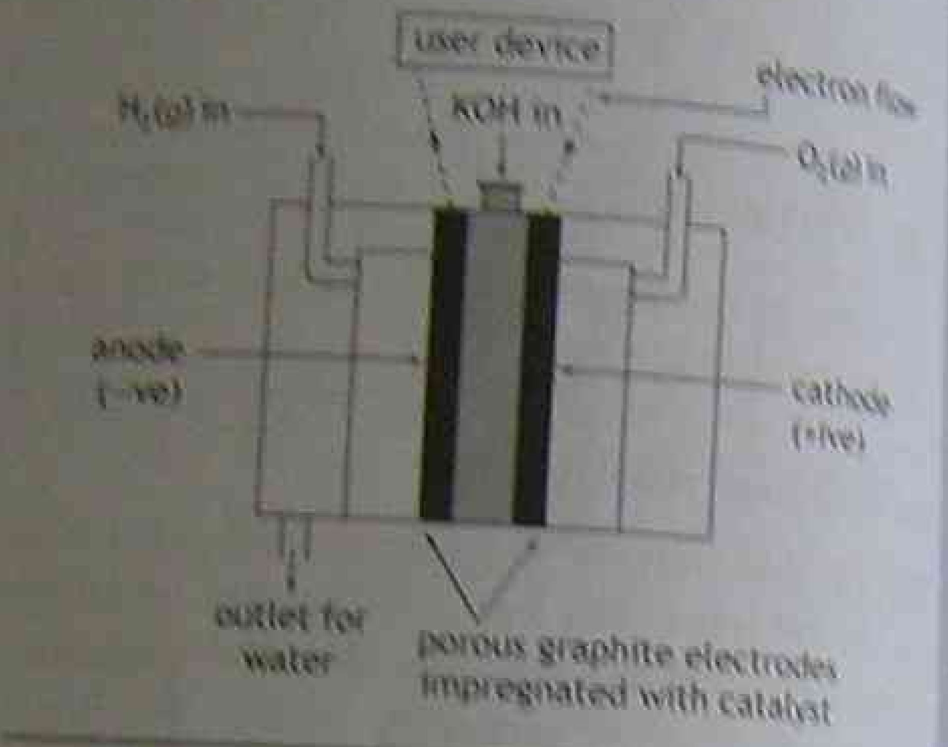


Figure 1.33 A simplified hydrogen-oxygen fuel cell

Problems on oxidation and reduction

1. For each of the following reactions,
   (i) write the half-reaction and state which reaction is the oxidation and which is the reduction reaction, and
   (ii) write a balanced ionic equation for the reaction and state which substance is the reductant and which substance is the oxidant:
      (a) calcium + oxygen
      (b) iron + sulfur
      (c) zinc + bromine
      (d) silver + iodine
      (e) aluminium + sulfur
2. Write balanced equations and state the oxidant and reductant in each case for the following metal extraction processes:
   (a) The extraction of lead from its ore, galena (lead sulfide).
   (b) The extraction of zinc from its ore, sphalerite (zinc sulfide).

3. Use balanced half-equations in writing the following ionic equations. In each case, state which equation is the oxidising reaction and which is the reducing reaction. State which substance is the oxidant and which substance is the reductant:
   (a) Zinc + sulfuric acid
   (b) Magnesium + hydrochloric acid
   (c) Zinc + acetic acid
   (d) Calcium + hydrochloric acid

4. In each of the following equations,
   (a) copper + silver nitrate
   (b) aluminium + lead nitrate
   (c) silver + copper nitrate
   (d) zinc + lead nitrate
   (e) silver + zinc nitrate
   If you think that no reaction occurs write NR; if you think that a reaction does occur
      (i) write the balanced ionic equation using half-reactions, and
      (ii) state in each case which metal ion is the oxidant and which metal is the reductant.

5. Which is (a) the strongest, and (b) the weakest, reductant in the following list of metals?
   Cu, Pb, Fe, Ag, Zn

6. Which is (a) the strongest, and (b) the weakest, oxidant in the following list of metal ions?
   Cu^{2+}, Pb^{2+}, Fe^{2+}, Ag^+, Zn^{2+}

7. State the oxidation number of the underlined elements in each of the following:
   (a) Compounds
      CrO_3, HNO_3, $FeSO_4$, $HClO_4$, $KMnO_4$
   (b) Ions
      CrO_4^{2-}, AsO_4^{3-}, HCO_3^-, $S_2O_3^{2-}$, $Xe_2O_7^{2-}$

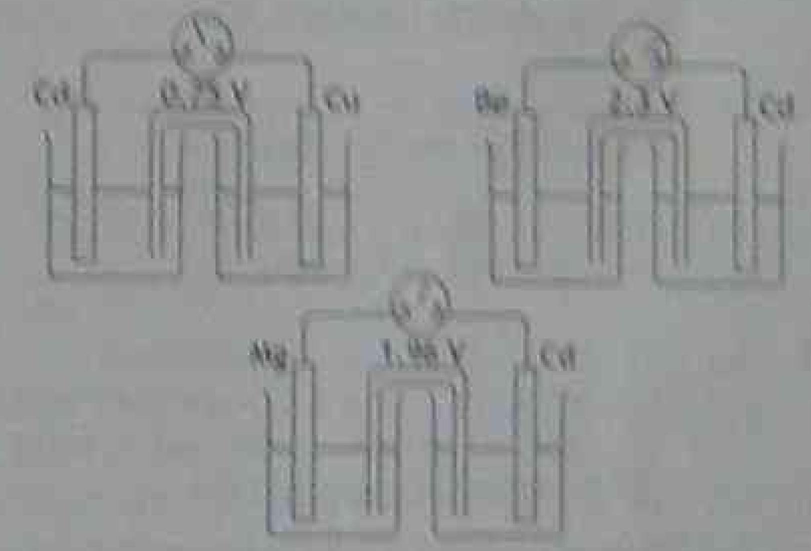
8. Write balanced redox equations for each of the following reactions by using ion-electron half-equations:
   (a) copper + chlorine
   (b) iodine + hydrogen sulfide to produce iodide ions + sulfur + H^+ ions
   (c) copper + conc. nitric acid

9. In each of the reactions in Problem 9, state: (i) the oxidant, and (ii) the reductant.

10. State which of the reactions below are redox reactions:
   (a) $PI_3 + 3H_2O \rightarrow H_3PO_3 + 3HI$
   (b) $Sn + Cu^{2+} \rightarrow Sn^{2+} + Cu$
   (c) $CaCO_3 \rightarrow CaO + CO_2$
   (d) $NaOH + HCl \rightarrow NaCl + H_2O$
   (e) Zn + dil. $H_2SO_4 \rightarrow ZnSO_4 + H_2$

11. (a) Draw a cell represented by $Cu/Cu^{2+}//Ag^+/Ag$
   Label the anode, the cathode and the direction of electron flow in the connecting wire.
   (b) Write
      (i) the anode reaction;
      (ii) the cathode reaction; and hence
      (ii) the cell reaction.

12.



Three electrochemical cells are shown above, with the emf given for each cell. All ions are at the same concentration. Give the metals in order of their strength as reducing agents (most powerful → least powerful reductants).

Answers to problems on oxidation and reduction

1. (a) (i) $Ca \rightarrow Ca^{2+} + 2e^-$ (oxidation)
   $O_2 + 4e^- \rightarrow 2O^{2-}$ (reduction)
   (ii) $2Ca(s) + O_2(g) \rightarrow 2Ca^{2+}(aq) + 2O^{2-}(aq)$
   [oxidant O_2, reductant Ca]

   (b) (i) $Fe \rightarrow Fe^{2+} + 2e^-$ (oxidation)
   $S + 2e^- \rightarrow S^{2-}$ (reduction)
   (ii) $Fe(s) + S(s) \rightarrow Fe^{2+}(aq) + S^{2-}(aq)$
   [oxidant S, reductant Fe]

   (c) (i) $Zn \rightarrow Zn^{2+} + 2e^-$ (oxidation)
   $Br_2 + 2e^- \rightarrow 2Br^-$ (reduction)
   (ii) $Zn(s) + Br_2(aq) \rightarrow Zn^{2+}(aq) + 2Br^-(aq)$
   [oxidant Br_2, reductant Zn]

   (d) (i) $Ag \rightarrow Ag^+ + e^-$ (oxidation)
   $I_2 + 2e^- \rightarrow 2I^-$ (reduction)
   $(1) \times 2 = (3)$: $2Ag \rightarrow 2Ag^+ + 2e^-$
   (ii) Adding (2) and (3) we get
   $2Ag(s) + I_2(aq) \rightarrow 2Ag^+(aq) + 2I^-(aq)$
   [oxidant I_2, reductant Ag]

   (e) (i) (1) $Al \rightarrow Al^{3+} + 3e^-$ (oxidation)
   (2) $S + 2e^- \rightarrow S^{2-}$ (reduction)
   $(1) \times 2 = (3)$: $2Al \rightarrow 2Al^{3+} + 6e^-$
   $(2) \times 3 = (4)$: $3S + 6e^- \rightarrow 3S^{2-}$
   (ii) Adding (3) and (4) we get
   $2Al(s) + 3S(s) \rightarrow 2Al^{3+}(aq) + 3S^{2-}(aq)$
   [oxidant S, reductant Al]

2. (a) $PbS(s) + O_2(g) \rightarrow Pb(s) + SO_2(g)$
   [oxidant Pb^{2+} and O_2, reductant S^{2-}]

   (b) $2ZnS(s) + 2O_2(g) \rightarrow 2ZnO(s) + SO_2(g)$
   [oxidant Zn^{2+} and O_2, reductant S^{2-}]

3. (a) (i) $Zn \rightarrow Zn^{2+} + 2e^-$ (oxidation)
   (ii) $2H^+ + 2e^- \rightarrow H_2$ (reduction)
   $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$
   [oxidant H^+, reductant Zn]

   (b) (i) $Mg \rightarrow Mg^{2+} + 2e^-$ (oxidation)
   (ii) $2H^+ + 2e^- \rightarrow H_2$ (reduction)
   $Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$
   [oxidant H^+, reductant Mg]

   (c) (i) $Zn \rightarrow Zn^{2+} + 2e^-$ (oxidation)
   (ii) $2H^+ + 2e^- \rightarrow H_2$ (reduction)
   $Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$
   [oxidant H^+, reductant Zn]

   (d) (i) $Ca \rightarrow Ca^{2+} + 2e^-$ (oxidation)
   (ii) $2H^+ + 2e^- \rightarrow H_2$ (reduction)
   $Ca(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2(g)$
   [oxidant H^+, reductant Ca]

4. (a) (i) $Cu \rightarrow Cu^{2+} + 2e^-$
   (ii) $Ag^+ + e^- \rightarrow Ag$
   (ii) × 2: $2Ag^+ + 2e^- \rightarrow 2Ag$
   $Cu(s) + 2Ag^+(aq) \rightarrow 2Ag(s) + Cu^{2+}(aq)$
   [oxidant Ag^+, reductant Cu]

   (b) (i) $Al \rightarrow Al^{3+} + 3e^-$
   (ii) $Pb^{2+} + 2e^- \rightarrow Pb$
   (i) × 2: $2Al \rightarrow 2Al^{3+} + 6e^-$
   (ii) × 3: $3Pb^{2+} + 6e^- \rightarrow 3Pb$
   $2Al(s) + 3Pb^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Pb(s)$
   [oxidant Pb^{2+}, reductant Al]

   (c) N.R.

   (d) (i) $Zn \rightarrow Zn^{2+} + 2e^-$
   (ii) $Pb^{2+} + 2e^- \rightarrow Pb$
   $Zn(s) + Pb^{2+}(aq) \rightarrow Zn^{2+}(aq) + Pb(s)$
   [oxidant Pb^{2+}, reductant Zn]

   (e) N.R.

5. (a) Zn (b) Ag

6. (a) Ag^+ (b) Zn^{2+}

7. (a) Cr +6; N +5; Fe +2; Cl +7; Mn +7
   (b) Cr +6; As +5; C +4; S +2; Xe +4

8. (a) (i) $Cu \rightarrow Cu^{2+} + 2e^-$
   (ii) $Cl_2 + 2e^- \rightarrow 2Cl^-$
   $Cu(s) + Cl_2(g) \rightarrow Cu^{2+}(aq) + 2Cl^-(aq)$

   (b) (i) $H_2S \rightarrow 2H^+ + S + 2e^-$
   (ii) $I_2 + 2e^- \rightarrow 2I^-$
   $H_2S(aq) + I_2(aq) \rightarrow 2H^+(aq) + S(s) + 2I^-(aq)$

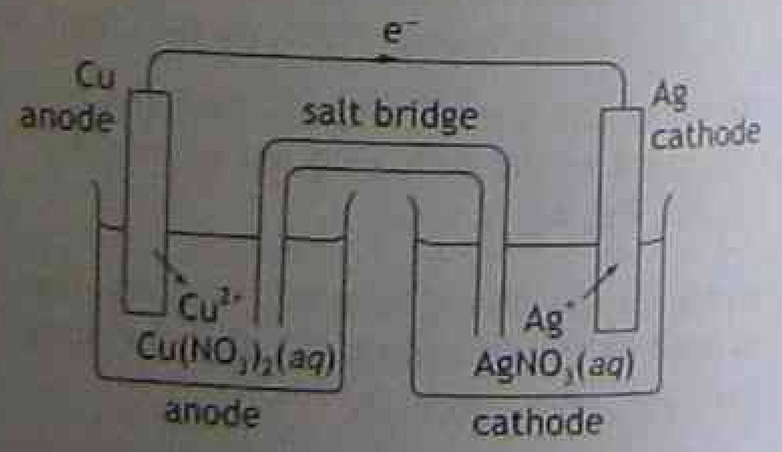
   (c) (i) $Cu \rightarrow Cu^{2+} + 2e^-$
   (ii) $NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$
   (ii) × 2: $2NO_3^- + 4H^+ + 2e^- \rightarrow 2NO_2 + 2H_2O$
   $Cu(s) + 2NO_3^-(aq) + 4H^+(aq)$
   $\rightarrow Cu^{2+}(aq) + 2NO_2(g) + 2H_2O(l)$

9.

	oxidant	reductant
(a)	Cl_2	Cu
(b)	I_2	S^{2-}
(c)	NO_3^-	Cu

10. (b) and (e) are redox reactions.

11. (a)



   (b) (i) Anode reaction: $Cu \rightarrow Cu^{2+} + 2e^-$
   (ii) Cathode reaction: $Ag^+ + e^- \rightarrow Ag$
   (ii) × 2: $2Ag^+ + 2e^- \rightarrow 2Ag$
   (iii) Cell reaction:
   $Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$

12. Order of increasing strength as reductants: beryllium, magnesium, cadmium, copper.

Nuclear chemistry

The term **nuclear chemistry** is now used to refer to the reactions in the nucleus of an atom in which particles or ionising radiations are emitted, or in which the nucleus is bombarded by particles and radiations and captures them.

1.23 Some nuclear reaction equations

Conditions under which a nucleus is unstable

An unstable nucleus will release particles and/or energy to become more stable. This nucleus is *radioactive* and the stabilising process is called *radioactive decay*.

Reasons for instability of the nucleus

(a) Too many neutrons for the number of protons present

In this case a neutron in the nucleus changes to a proton and an electron.

$$^{1}_{0}n \rightarrow {}^{1}_{1}p + {}^{0}_{-1}e$$

Example

$$^{214}_{82}Pb \xrightarrow{\text{decay}} {}^{214}_{83}Bi + {}^{0}_{-1}e$$

Note:

1. The element has changed from Pb → Bi because the atomic number has changed.
2. The symbol β^- can be used in equations instead of ${}^{0}_{-1}e$.

Exercise 1

Complete the following nuclear equation:

(i) $^{228}_{88}Ra \xrightarrow{\beta^- \text{ decay}}$

(ii) $^{210}_{81}Tl \xrightarrow{\beta^- \text{ decay}}$

(iii) $^{233}_{91}Pa \xrightarrow{\beta^- \text{ decay}}$

(b) Too many protons for the number of neutrons

In this case the proton changes into (i) a neutron and (ii) a positron (a positively charged electron) called a beta (β^+) particle or e^+ (${}^{0}_{1}e$).

$$^{1}_{1}p \rightarrow {}^{1}_{0}n + {}^{0}_{1}e$$

Example

$$^{22}_{11}Na \xrightarrow{\text{decay}} {}^{22}_{10}Ne + {}^{0}_{1}e$$

Exercise 2

Complete the following nuclear equation:

$^{11}_{6}C \xrightarrow{\beta^+ \text{ decay}}$

(c) Too many protons and neutrons (the nucleus is too heavy)

In this case the nucleus loses mass by emitting an alpha (α) particle which consists of two protons and two neutrons. It is positively charged and can also be called a helium nucleus (${}^{4}_{2}He$); this symbol represents the alpha particle in equations.

Example

$$^{222}_{86}Rn \xrightarrow{\alpha \text{ decay}} {}^{218}_{84}Po + {}^{4}_{2}He$$

Exercise 3

Complete the following nuclear equations:

(i) $^{230}_{90}Th \xrightarrow{\alpha \text{ decay}}$

(ii) $^{210}_{83}Bi \xrightarrow{\alpha \text{ decay}}$

(iii) $^{235}_{92}U \xrightarrow{\alpha \text{ decay}}$

Exercise 4

Starting with ${}^{238}_{92}U$ and ending with ${}^{226}_{88}Ra$, look up the four missing isotopes and complete the radioactive decay scheme.

Note: Energy in the form of gamma (γ) rays is often released by an atom undergoing radioactive decay. This can be included in a nuclear equation by writing 'energy' or 'γ' as a reaction product.

Answers to exercises

Exercise 1

(i) $^{228}_{88}Ra \xrightarrow{\beta^- \text{ decay}} {}^{228}_{89}Ac + {}^{0}_{-1}e$

(ii) $^{210}_{81}Tl \xrightarrow{\beta^- \text{ decay}} {}^{210}_{82}Pb + {}^{0}_{-1}e$

(iii) $^{233}_{91}Pa \xrightarrow{\beta^- \text{ decay}} {}^{233}_{92}U + {}^{0}_{-1}e$

Exercise 2

$${}^{11}_{6}C \xrightarrow{\beta^+ \text{ decay}} {}^{11}_{5}B + {}^{0}_{1}e$$

Exercise 3

(i) $${}^{230}_{90}Th \xrightarrow{\alpha \text{ decay}} {}^{226}_{88}Ra + {}^{4}_{2}He$$

(ii) $${}^{210}_{83}Bi \xrightarrow{\alpha \text{ decay}} {}^{206}_{81}Tl + {}^{4}_{2}He$$

(iii) $${}^{235}_{92}U \xrightarrow{\alpha \text{ decay}} {}^{231}_{90}Th + {}^{4}_{2}He$$

Exercise 4

$${}^{238}_{92}U \xrightarrow{\alpha \text{ decay}} {}^{234}_{90}Th \xrightarrow{\beta^- \text{ decay}} {}^{234}_{91}Pa \xrightarrow{\beta^- \text{ decay}}$$

$${}^{234}_{92}U \xrightarrow{\alpha \text{ decay}} {}^{230}_{90}Th \xrightarrow{\alpha \text{ decay}} {}^{226}_{88}Ra$$

1.24 Nuclear fuel processing and waste disposal

The nuclear fuel cycle

Most but not all nuclear reactors require uranium 'enriched' in U-235 as their fuel. The enrichment process is one step in a chain of processes from crude uranium ore (see Figure 1.37).

At present there are three types of enrichment in commercial use or under consideration:

(a) Gaseous diffusion

(b) Centrifuge enrichment

(c) Two types of laser enrichment technologies.

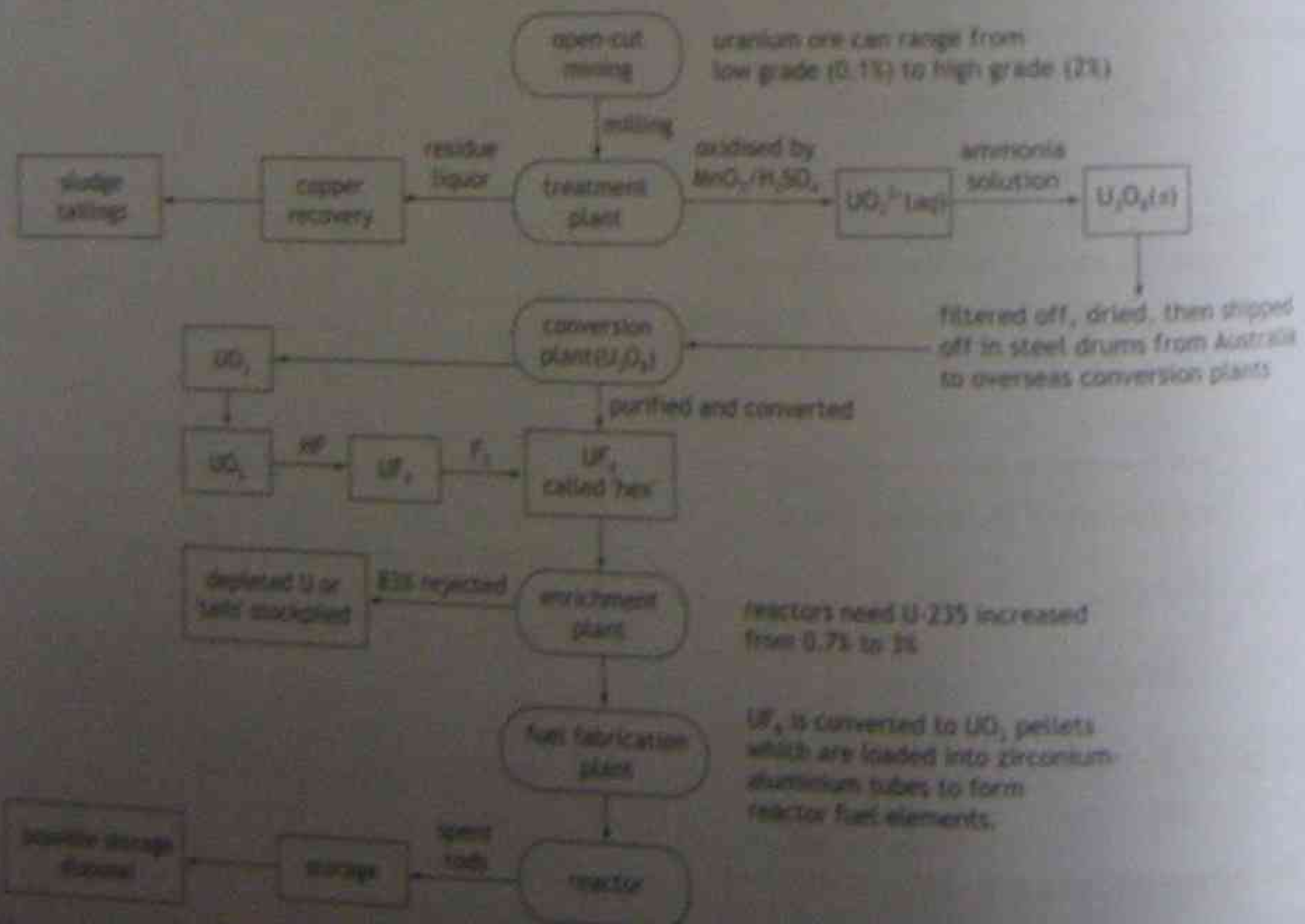
Of these, (a) and (b) are both widely used, but laser enrichment is still at the developmental stage. A laser-based selective photo-ionisation process was developed in Australia, but as yet this has not been commercialised.

Uranium found in nature consists largely of two isotopes U-235 (0.7%) and U-238 (approx. 99.3%). These isotopes differ in their mass with U-235 containing 143 neutrons and U-238 containing 146 neutrons in its nucleus. All enrichment processes are based on this mass difference.

After completion of enrichmentto the uranium hexafluoride stage, the UF_6 is turned into UO_2 pellets which are assembled into fuel rods. Examples of typical reaction products are

$${}^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{144}_{56}Ba + {}^{89}_{36}Kr + 3{}^{1}_{0}n + \text{energy}$$

$${}^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{141}_{56}Ba + {}^{92}_{36}Kr + 3{}^{1}_{0}n + 170 \text{ MeV}$$



Disposal and storage

Stockpiled 'tails'

This material cannot be used in current types of reactors. It can only be utilised in fast breeder reactors and is stored as UF_6(s) in steel containers. About 0.025% U-235 remains in it. Fast breeder reactor programs have ceased for the time being.

Storage and possible waste disposal

Several methods have been used for the disposal of dry radioactive wastes produced after the evaporation of liquid.

(a) Deep burial of drums of wastes in mines where hopefully no earthquake activity will occur. These sites should also be free from ground water and be remote from population centres.

(b) Drums of wastes have been dumped by Belgium, the Netherlands, Switzerland and the UK in deep parts of the oceans where any escaping material would be diluted by seawater.

(c) The use of solids to contain the high level radioactive wastes. Such a solid must be chemically stable, resistant to pressure, irradiation damage, structural change and especially to high temperatures and have a low susceptibility to leaching. It must be able to incorporate a wide range of waste elements. The solid must contain the waste for almost a million years to allow radioactivity to reduce to former levels.

Some of the solids tried were borosilicate glasses in a vitrification process. The Australian contribution 'Synroc', developed by Professor Ted Ringwood and the Australian Nuclear Science and Technology Organisation (ANSTO), has proved to be a better solid than glass since it resists high temperatures and can therefore be buried deeper and with a higher waste loading than glass. It also has better leaching qualities.

'Synroc' is a synthetic rock made up of three minerals, hollandite ($BaAlTi_6O_{16}$), perovskite ($CaTiO_3$) and zirconolite ($CaZiTi_2O_7$). The three minerals are closely related to naturally occurring minerals and found to retain radioactive elements for millions of years by chemically bonding them into the crystal structures.

1.25 Nuclear reactors

The fission process

Most atoms are stable, but U-235 is an unstable atom and is therefore radioactive. If a U-235 atom is bombarded with a neutron it will split in two and a few neutrons will fly off. If the free neutrons can be controlled so that they hit successive atoms, the process becomes a chain reaction. When the U-235 atom is split, the free neutrons travel at very high speeds and must be quickly slowed down by passing them through 'heavy water' (water made from deuterium and oxygen).

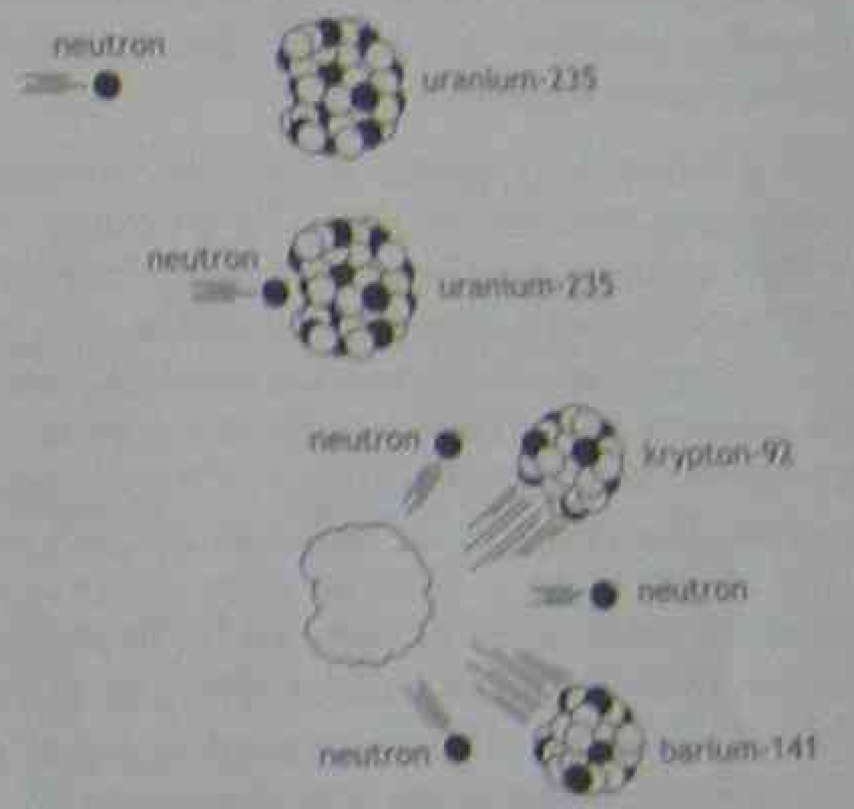


Figure 1.35 Schematic diagram of the fission of the U-235 nucleus

Uses of nuclear reactors

Nuclear reactors are used for a number of commercial purposes. These include:

(a) the production of thermal heat to drive electric power turbines;

(b) the production of specific radioisotopes for use mainly in industry and diagnostic or therapeutic nuclear medicine; and

(c) the provision of a range of scientific research facilities (e.g. for X-ray diffraction studies).

Some nuclear reactors are dedicated to the production of weapons grade plutonium, but this is expected to reduce as more nations sign on to the Nuclear Non-proliferation Treaty.

The High Flux Australian Reactor (HIFAR)

In Australia, the 10 MW materials and testing reactor HIFAR, operated by ANSTO at the Lucas

Heights Research Centre near Sydney, works on this principle. This is achieved by immersing the uranium fuel elements in a heavy water tank which also acts as a cooling system.

The core of the reactor is contained in an aluminium tank that is almost filled with 'heavy water'. The tank is enclosed in inner and outer steel tanks, the outer tank being packed with lead. The whole reactor is encased in a 1.5 m thick concrete biological shield which absorbs residual neutrons and ionising radiations. The reactor and its operating and research facilities are housed in a steel containment building in which the air is monitored continuously for radioactivity. The building is maintained at negative pressure. In addition, there is a multi-layered safety system in place.

The reactor is powered by 25 fuel elements containing enriched uranium. Each element is a hollow aluminium cylinder containing four inner cylinders made of a zirconium-aluminium alloy and enriched uranium. The aluminium cladding protects the uranium alloy from corrosion and stops fission products from contaminating the heavy water coolant. The efficiency of each fuel element as a neutron-producer is reduced after about eight months so they must be replaced. Each element weighs about 6 kg and contains 170 g of U-235. Lead-shielded fuel flasks are used to insert or remove fuel elements safely from the reactor.

1.26 Isotopes, radiation and radioactivity

Transuranic elements

The initial attempts to convert the largest naturally occurring element, uranium (U-235), into heavier elements by neutron bombardment resulted in nuclear fission. The nucleus was split in two. This event ultimately led to the Manhattan Project.

The first transuranic element (element 93) was found in 1940 at Berkeley in California; it was named neptunium (Np). In 1941 element 94 was formed by bombarding uranium with hydrogen nuclei using a cyclotron (a type of particle accelerator). This element was named plutonium (Pu). The formation of larger nuclei from smaller ones is called nuclear fusion. Research teams headed by Glenn Seaborg led the world in making transuranic elements for the next decade. In 1944, elements 95 (americium) and 96 (curium) were produced by bombarding plutonium. Elemen (californium) was followed by discoveries elements 99–103. Element 104 is cal unnilquadium (Unq) and element 105 unnilpentium (Unp). Elements up to 109 have be reported, but they are so short-lived that they not considered to be important. Nuclear reac were used to produce the following elements:

Equations:

$$^{238}_{92}U + ^{1}_{0}n \longrightarrow ^{239}_{92}U + g \longrightarrow ^{239}_{93}Np + ^{0}_{-1}e$$

$$^{239}_{94}U + ^{4}_{2}He \longrightarrow ^{242}_{96}Cm + ^{1}_{0}n$$

$$^{15}_{7}N + ^{249}_{98}Cf \longrightarrow ^{260}_{105}Unp + 4^{1}_{0}n$$

Plutonium-241. This element is formed fro uranium-238 in nuclear reactors by bombardme with neutrons followed by beta-decay in severa steps.

Detailed steps:

Step 1. $^{238}_{92}U$ + neutron $\longrightarrow$ $^{239}_{92}U$

Step 2. $^{239}_{92}U$ by beta decay $\longrightarrow$ $^{239}_{93}Np$

Step 3. $^{239}_{93}Np$ by beta decay $\longrightarrow$ $^{239}_{94}Pu$

Step 4. $^{239}_{94}Pu$ + neutron $\longrightarrow$ $^{240}_{94}Pu$

Step 5. $^{240}_{94}Pu$ + neutron $\longrightarrow$ $^{241}_{94}Pu$ This will decay emitting a beta particle forming $^{241}_{95}Am$.

Note: $^{241}_{94}Pu$ has a half-life of 14 years. $^{241}_{95}Am$ has a half-life of 432 years and is used in smoke detectors.

Isotopes

The nucleus of an atom consists of two subatomic particles, the proton and the neutron. These particles are called nucleons. Atoms of the same element have the same number of protons (atomic number). Atoms of a given element can have different mass numbers (p + n) and are called isotopes.

> Isotopes are atoms with the same atomic number but a different mass number. They therefore contain a different number of neutrons.

Many naturally-occurring elements have two or more isotopes, e.g. three neon isotopes contain 10, 11 or 12 neutrons. The symbol $^{21}_{10}Ne$ shows the particular isotope of neon which contains 11 neutrons.

$^{\text{mass no}}_{\text{atomic no}}X$

is the **comprehensive symbol** for element X.

Different isotopes of the same element are chemically similar because the chemical properties of atoms are determined by the electrons and not the nuclei. There are 82 stable elements with a total of 275 isotopes.

Natural radioactivity

Natural sources of atmospheric radioactivity include:

- cosmic rays from the sun;
- radioactive substances found in rocks and minerals.

Becquerel in 1896 found that uranium ore gives off invisible rays which can penetrate the light-proof covering of a photographic plate and affect the film. Substances which give off these invisible rays are called radioactive. Radioactivity is the spontaneous breakdown of an unstable atomic nucleus, releasing rays and often particles. Polonium, radon, radium, actinium and protactinium have natural radioactive nuclides. Members of the actinide series after uranium include artificially produced radioactive nuclides.

Table 1.18 Nuclear radiation products

Radiation	Type	Penetration
α particle	He nucleus ($^{4}_{2}He$)	least (about 5 cm of air)
β particle	high speed electron ($^{0}_{-1}e$)	greater (about 5 m of air)
γ radiation	short-wave electromagnetic radiation	greatest (at least 2 cm of Pb)

Radioisotopes

> *Radioisotopes* differ from other isotopes of an element because their nuclei are unstable and they emit radioactive particles which usually result in the formation of another element.

Radioactive decay

The half-life of a radioisotope is the time it takes for half the atoms originally present to decay.

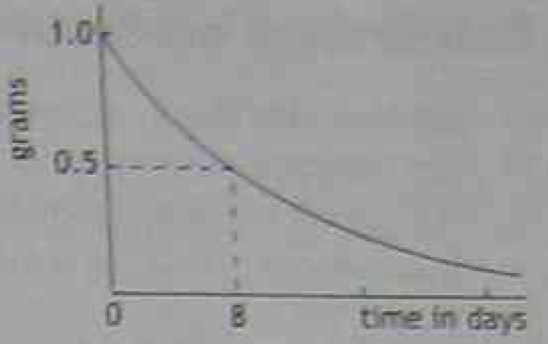


Figure 1.36 Decay curve for iodine-131

Table 1.19 Examples of radioisotopes

Name	Symbol	Half-life	Mode of decay
Uranium-238	$^{238}_{92}U$	4.5 × 10⁹ years	α
Plutonium-239	$^{239}_{94}Pu$	24 000 years	α
Carbon-14	$^{14}_{6}C$	5740 years	β
Strontium-90	$^{90}_{38}Sr$	28 years	β
Cobalt-60	$^{60}_{27}Co$	5.27 years	β
Iodine-131	$^{131}_{53}I$	8 days	β
Bismuth-210	$^{210}_{83}Bi$	5 days	β

Gamma radiation is also emitted in most cases. Two conditions for radioactive isotopes to form:

(a) Too high a ratio of neutrons to protons. A neutron changes to a proton and an electron (β particle) is emitted.

$$n \rightarrow p + e^{-}$$

Example — $^{3}_{1}H$ is tritium, a radioactive isotope of hydrogen.

$$^{3}_{1}H \longrightarrow ^{3}_{2}He + ^{0}_{-1}e$$

(b) The nucleus is too large (where mass number is >209). An α particle will be emitted.

Example

$$^{235}_{92}U \longrightarrow ^{231}_{90}Th + ^{4}_{2}He \quad (\alpha \text{ particle})$$

In writing nuclear equations, the atomic numbers and mass numbers must balance.

Many radioisotopes are made by neutron irradiation of stable isotopes in a nuclear reactor.

Example

$$^{59}_{27}Co + ^{1}_{0}n \longrightarrow ^{60}_{27}Co$$

Cobalt-60 decays to produce β and γ radiation.

$$^{60}_{27}Co \longrightarrow ^{60}_{28}Ni + ^{0}_{-1}e + \gamma$$

1.27 Radioisotope production

The most common method of radioisotope production is by neutron activation in a nuclear reactor. This involves the capture of a neutron by the nucleus of an atom resulting in an excess of neutrons (neutron-rich).

They may be manufactured in a cyclotron (particle accelerator) in which protons are introduced to the nucleus, resulting in a deficiency of neutrons (proton-rich). The cyclotrons use high voltages and electric fields to accelerate hydrogen atoms through a vacuum chamber. When they collide with the target substance they produce radioactivity. It can be more difficult to make a radioisotope in a cyclotron than in a reactor. The Australian government has recently agreed to a new nuclear research and radioisotope production reactor to be installed and operated by ANSTO at the Lucas Heights Science and Technology Centre.

The most frequently used medical radioisotope, technetium-99*m*, evolves by radioactive decay from a precursor radioisotope molybdenum-99 (half-life 66 hours) produced in the reactor. Because of its longer half-life, appropriately large activities of the ^{99}Mo/^{99m}Tc 'generator' can then be transported to nuclear medicine departments around the country for immediate diagnostic use.

Technetium-99*m* (6-hour half-life) can also be produced by cyclotrons directly. However, the very high cost of the rare form of molybdenum needed for use as the target material in the cyclotron, and the need for the transport of much larger quantities of radioactivity around the country, makes this product more expensive than the reactor product.

1.28 Radioisotopes in medicine

There are three main uses of radioisotopes in medicine:

(a) Diagnostic

In nuclear medicine radioisotopes, combined with suitable chemical 'carriers', are used to target and provide essential diagnostic information on the functioning of specific organs.

(b) Therapeutic

Radiotherapy using radiation from a radioactive source is used to treat cancer by weakening or destroying diseased cells. This is possible since rapidly dividing cells are very sensitive to radiation damage. Some cancerous growths can be controlled by radiation from a cobalt-60 source. *Internal radiotherapy* can also be carried out using a small radioactive source (usually a gamma or beta emitter) by implanting it into the target area (e.g. head, breast). Iridium-192 is a frequently used implant.

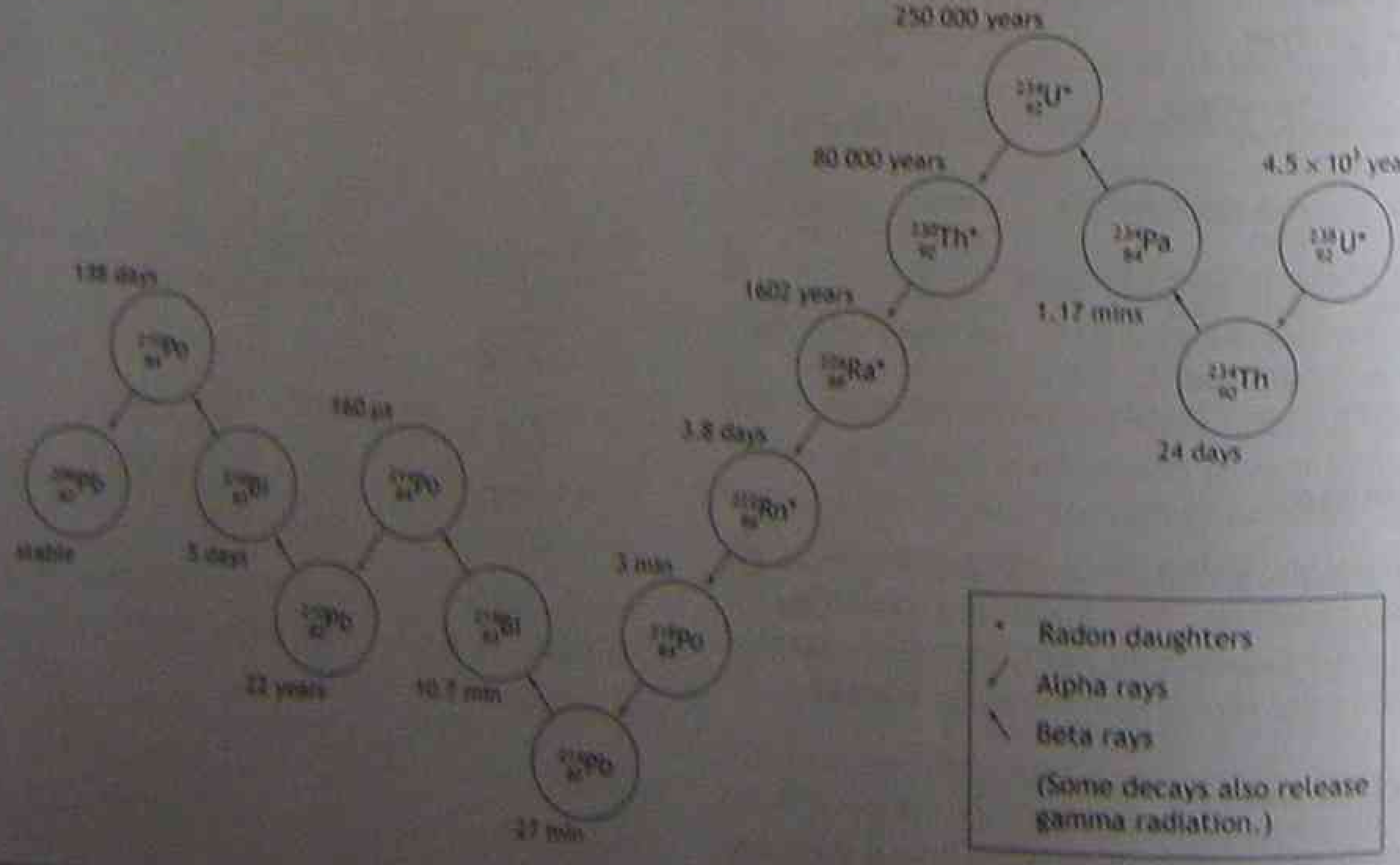


Figure 1.37 Uranium radioactive decay series

(c) Biomedicine

Because they are easily detected in low concentrations, radioisotopes can be used to label molecules of biological samples on which pathologists can carry out *radioimmuno assays*.

Diagnostic radiopharmaceuticals

These are used to examine, for example, the functioning of organs such as the liver, heart or kidneys. The amount of radiopharmaceutical given to the patient is the minimum needed to obtain the information before it undergoes radioactive decay. The selected radiopharmaceutical must emit gamma rays of sufficient energy to escape from the body and have a half-life short enough for it to decay away soon after imaging is completed. Iodine-131 based radiopharmaceuticals are used for therapy in cases of thyroid cancer. Another, based on phosphorus-32, can be used to control the number of red blood cells.

The radioisotope most widely used in nuclear medicine is technetium-99*m*, 'milked' from the artificially produced ^{99}Mo/5 generator, which comprises a lead pot enclosing a glass tube containing the radioisotope supplied by Australian Radioisotopes (ARI) from its laboratories at the Lucas Heights Science and Technology Centre. The molybdenum-99 progressively decays to technetium-99*m*. When it is received at the point of use, the technetium is washed out of its container with saline solution. After about two weeks, the generator is returned to ARI for recharging.

As a producer of radioisotopes the cyclotron complements the neutron-rich reactor products but does not replace them. In other words, reactor-produced radioisotopes have different uses to the equally important 'proton-rich' cyclotron radioisotopes.

Selection of radioisotopes in nuclear medicine

In nuclear medicine, a radioisotope is administered to a patient either to aid the diagnosis of disease or for the treatment of disease.

Table 1.20 Selection of the isotope depends on its use

For diagnosis	For treatment
A short half-life (hours) depending on the length of the investigation.	A half-life which will not cause extended hospital stay due to excessive radiation.
Must not emit alpha or beta particle radiation since these particles would be trapped in the patient's tissues and not be detected externally.	Must emit alpha and beta radiation to penetrate the lesion being treated.
Must emit gamma radiation of an energy which will allow its position in the body to be reliably assessed.	Must emit gamma radiation to assess that the appropriate target region of the body has been reached.

The characteristics of technetium-99m

Technetium-99*m* has the following almost ideal characteristics for a nuclear medicine scan:

- It has a half-life of six hours which enables metabolic processes to be examined yet minimises the radiation dose to the patient.
- It decays by an 'isomeric' process which emits gamma rays and low energy electrons. Since there is no high energy beta emission, the radiation dose to the patient is low.
- The low energy gamma rays easily pass out of the body, so they can be detected by the gamma camera.
- The chemistry of technetium is versatile and can be incorporated into a range of biomolecules (carriers) which concentrate in specific organs.

1.29 Radioisotopes in industry

Modern industry uses radioisotopes in a variety of ways to improve productivity and/or gain specific information.

Industrial gamma radiography

Gamma rays are produced by a small pellet of radioactive material, e.g. cobalt-60 or iridium-192, in a sealed titanium capsule. The capsule is placed on one side of the object being radiographed and photographic film is placed on the other. Like X-rays, gamma rays show flaws in metal castings or welded joints. Because of ease to transport and since no power is needed, gamma radiography is especially useful in remote areas, e.g. to check welds in natural gas or oil pipelines.

Gauging

The radiation that comes from a radioactive source has its intensity reduced by matter placed between source and detector. Detectors can be used to measure this reduction without contact with the material being gauged. This method can be used to measure the thickness of plastic film, the detector signal strength being used to control the plastic film thickness.

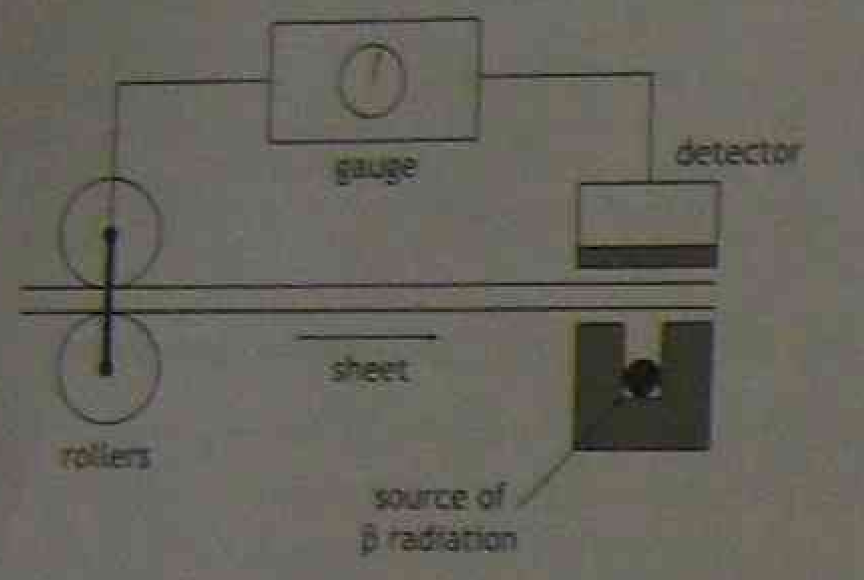


Figure 1.38 Thickness control gauge

Gamma sterilisation

This technique is used for sterilising medical products, e.g. disposable syringes, gloves, sutures and instruments, many of which would be damaged by heat sterilisation. Cobalt-60, an energetic gamma emitter, is widely used. It is produced in nuclear reactors and has a half-life of 5.27 years.

Raw wool for export can also be treated by this method to kill parasites. Food preservation also benefits from gamma irradiation treatment. More than 50 foods have received extended shelf lives and the risk of food-born diseases has been reduced.

Environmental studies

Radioisotopes provide an ultrasensitive analytical technique for studying the age, movement and depletion of water resources.

All water originally contained minute radioisotopes of hydrogen and carbon. Surface water may seep underground into porous rocks and sand. The Great Artesian Basin is the largest underground water resource in Australia. After water goes underground the radioisotopes are no longer replenished from cosmic rays so they decay. The radioisotope of hydrogen (tritium) has a half-life of 12 years, while carbon-14 has a half-life of 5740 years.

Table 1.21 Examples of other reactor radioisotopes

Radiation	Element	Half-life	Use
α	chromium-51	27.7 days	to label red blood cells
β^-, α	iodine-131	8 days	widely used in functional imaging and therapeutic applications for the thyroid gland
β^-, α	potassium-42	22 hours	determination of exchanged potassium in blood flow
β^-, α	sodium-24	15 hours	studies of body electrolytes
γ	ytterbium-169	3 days	brain scan

Table 1.22 Examples of other cyclotron radioisotopes

Radiation	Element	Half-life	Use
γ	gallium-67	3.3 days	tumour-seeking agent
γ	krypton-81m	13 seconds	lung ventilation studies
Positron emitters	carbon-11 nitrogen-13 oxygen-13	ultra short-lived	used in position emission tomography (PET) for studying brain physiology and pathology for epilepsy and dementia

Table 1.23 Naturally occurring radioisotopes for studying water resources

Isotope	Use
Chlorine-36	to measure sources of chlorine and the age of water (up to 2 million years)
Carbon-14	to measure the age of water (up to 50 000 years)
Tritium	to measure the age of groundwater (up to 30 years)

By measuring the minute amounts of these radioisotopes taken from various bores, the 'age' of each sample can be determined and used to determine the rate and direction of flow. For example, water found at the south-western extremity of the Great Artesian Basin entered the Basin in Central Queensland about half a million years ago and has been travelling in a south-westerly direction ever since at a rate of a few metres per year.

Information about the age of water in underground bores can be used to indicate if groundwater is being used faster than the rate of replenishment.

Tracing/mixing uses

Since very small quantities of radioactive material can be easily detected, if it is added to sewage from ocean outfalls, the radioactivù4y can be traced to study sewage dispersion. The half-life of the tracer isotope chosen should be just long enough to obtain the required information so that no long-term residual radiation remains. Flow rates of large rivers can also be measured in this way.

The tandem accelerator

ANSTO's tandem particle accelerator at the Lucas Heights Science and Technology Centre produces an ion beam which is accelerated by an electrostatic field. Electrons are stripped by a carbon foil stripper from the outer orbits of the ions so that they become positively charged. On leaving the accelerator, they finally enter the target room where they can be measured directly to determine the amount of rare isotope in the original samples.

Archeometry

Archeometry is the term used to describe a range of scientific techniques, including radioisotopic dating and other nuclear techniques, to resolve problems posed by archaeologists.

Radiocarbon dating

This is a method for determining the age of objects up to 50 000 years old that contain matter which was once living. Natural carbon consists mainly of the stable isotope carbon-12, some carbon-13 and a small proportion of carbon-14. Carbon-14 has a half-life of 5740 years and is produced by the action of cosmic rays on atmospheric nitrogen. All living organisms absorb carbon from atmospheric carbon dioxide until their death. The once constant carbon-14:carbon-12 ratio then decreases as carbon-14 decays.

To determine the ^{14}C in this ratio, measurements with a tandem accelerator enable a fast analysis of submilligram carbon specimens, e.g. for dating Aboriginal artefacts and middens.

Smoke detectors

Americium-241 is a reactor radioisotope that evolves as a decay product of plutonium-241. It has a half life of 432 years and emits alpha particles during radioactive decay to become neptunium-237; it also emits low energy gamma rays.

The alpha particles are absorbed in the detector and gamma radiation is lower than normal background radiation. The alpha particles ionise oxygen and nitrogen particles in the air in the detector's ionising chamber. When smoke enters the detector, the alpha radiation is absorbed by smoke particles so the rate of ionisation of the air falls and an alarm is triggered.

Safety requirements for smoke detectors in Australia

Domestic smoke detectors must be labelled with the following information:

- The words 'Warning – radioactive material'
- Trefoil symbol

(this is the usual symbol)

- Identity and amount of radioactive material in the source (each detector uses less than 37 kBq of americium-241 which is a minute amount)
- The words 'return to supplier or Department of Health for disposal'.

1.30 Detection of radioactivity

Radiation effects

Becquerel discovered radioactivity because of the effects of radiation on photographic plates. The radiation affects *photographic film* like ordinary light — the greater the extent of exposure to radiation, the darker the area of the developed negative. *Radiographers* and other radiation workers wear *film badges* which are later developed to record the extent of their exposure to radiation over a given period.

The Geiger counter

This instrument is used to detect and measure radioactivity in a particular area. Its operation is based on the ionisation of matter by radiation. The ions and electrons produced permit conduction of an electrical current. (See Figure 1.39)

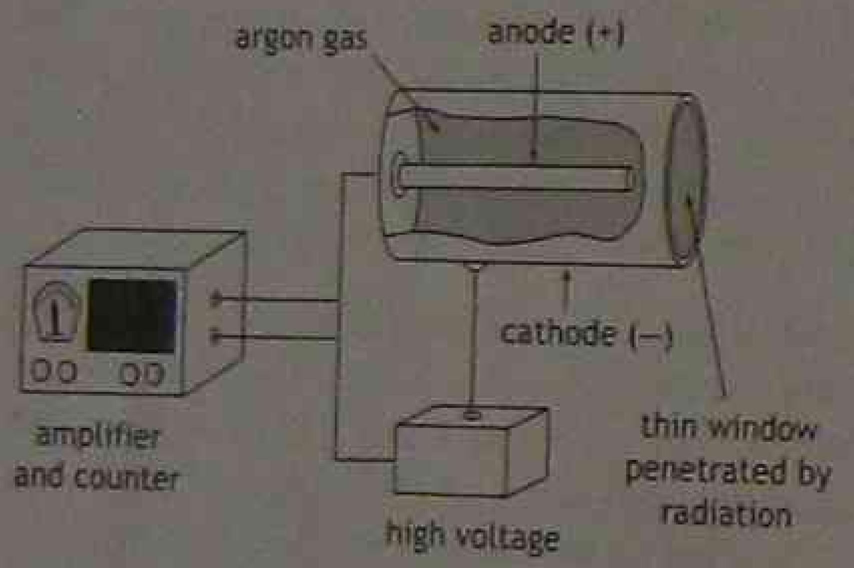


Figure 1.39 A simple diagram of a Geiger counter

Note: School sources are used as a practical means of training students in the basic concepts of radiation.

- **Cobalt-60:** a gamma-emitting radioisotope. Gamma radiation is long range and has high penetration. Dense substances, e.g. lead, are used as a shield.
- **Strontium-90:** a beta-emitting radioisotope. Beta radiation is shorter in range and less penetrating than γ radiation. It can be stopped by a thin sh of aluminium.
- **Americium-241:** an alpha-emitting isotope. Alp radiation can be stopped by a thin sheet of pap and the radiation cannot penetrate the skin.

The scintillation counter

Certain substances that are electronically excited b radiation, fluoresce (give off light) as electro return to their lower energy state. A scintillatio counter measures the fluorescence and hence t radiation causing it.

The gamma camera

Nuclear medicine techniques use radioactive tracer which emit gamma rays from within the body. The are detected by a gamma camera which can vie organs from many angles. The camera builds up a image based on the points from which radiation i emitted. This image is then enhanced on a compute and viewed by a physician on a monitor fo indications of abnormalities.

A distinct advantage of nuclear imaging over X-ra methods is that both bone and soft tissue can b successfully imaged.

Positron Emission Tomography (PET)

This technique can be expensive because it emplo ultra short-lived positron-emitting radioisotope e.g. oxygen-15, nitrogen-13 and carbon-11, produce at a nearby cyclotron. In a PET study, the patient i surrounded by a ring of stationary radiatio detectors.

Single photon emission computer technolog

This latest development in nuclear medicine is als referred to as SPECT. To produce 3-D images, th classical gamma cameras are rotated around th patient. The advantages are a reduced overall co and convenience since longer-lived radioisotopes, e.g. technetium-99*m* with a half life of six hours, can be used so that an on-site cyclotron is not needed.

Table 1.24 Some artificially-produced radioisotopes

Radiation	Isotope	Use
β^-, γ	gold-198 (half-life 2.7 days)	to trace factory waste causing ocean pollution and to trace sand movement in river beds
γ	technetium-99*m*	to study sewage and liquid waste movements
α, γ	americium-241	smoke detector
α, γ	americium-241 (+Be)	thickness gauge in the glass industry

Units of measurement of radioactivity

In material, the becquerel (Bq) is the unit radioactivity present with reference to the number of nuclear disintegrations per second (1 Bq = 1 disintegration/s). Older units include the curie which was the activity of 1 g of radium-226 and is equivalent to 3.7×10^{10} Bq.

In humans, the amount of ionising radiation absorbed in tissue is expressed in grays (Gy), where 1 Gy = 1 J kg^{-1}. Since neutrons and alpha particles cause more damage per gray than gamma or beta radiation, another unit, the sievert (Sv) is used when setting radiological protection standards. One gray of beta or gramma radiation has one sievert of biological effect, one gray of alpha particles has a 20 Sv effect, and one gray of neutrons is equivalent to around 10 Sv. A typical background radiation for Australians is 2 mSv/year. In underground uranium mines, such as Olympic Dam in South Australia, the individual workers' doses are by law kept below 10 mSv/year.

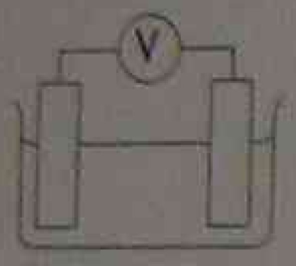
Test on Chapter 1 - The production of materials

Part A

Questions 1–5 are 1 mark multiple choice questions

1. The compound which contains four carbon atoms is
   (A) methyl propane
   (B) 1-bromopropane
   (C) propanol
   (D) propanoic acid

2. The diagram represents a simple galvanic cell in which two metals are placed in a liquid. The metals are connected by a voltmeter. Which of the following combinations would give the highest voltmeter reading?



	Metals	Liquid
(A)	Silver and copper	Water
(B)	Magnesium and lead	Ethanol
(C)	Zinc and tin	Hydrochloric acid
(D)	Both iron	Copper sulfate (aq)

3. Ethene can be converted to ethanol. This type of reaction is called
   (A) polymerisation
   (B) dehydration
   (C) hydration
   (D) esterification

4. Consider the following nuclear reaction:
   ${}^{242}_{94}\mathrm{Pu} \longrightarrow {}^{238}_{92}\mathrm{U} + \mathrm{X}$. What is the identity of X?
   (A) ${}^{0}_{-1}\mathrm{e}$
   (B) ${}^{4}_{2}\mathrm{He}$
   (C) ${}^{1}_{0}\mathrm{n}$
   (D) γ radiation

5. Three metallic elements (X, Y and Z) were tested to determine their relative activities:
   (i) Each metal was first added to a 3 M HCl solution.
   (ii) X and Y were added separately to an aqueous solution of Z^+ ions.
   (iii) Y and Z were added separately to an aqueous solution of X^{2+} ions.

   The observed results are summarised in the following table.

Metal	X	Y	Z
3M HCl	dissolved, gas produced	dissolved, gas produced	no reaction
Z^+ soln.	dissolved, solid formed	dissolved, solid formed	not tested
X^{2+} soln.	not tested	dissolved, solid formed	no reaction

If the three metals were arranged from least to most reactive, the order would be
(A) X, Y, Z
(B) Y, Z, X
(C) Z, Y, X
(D) Z, X, Y

Part B

Extended questions

6. [4 marks]
Use the following data:

$$PbO_2(s) + SO_4^{2-} + 4H^+ + 2e \rightarrow PbSO_4(s) + 2H_2O \qquad E^\circ = +1.6\ V$$

$$PbSO_4(s) + 2e \leftrightarrow Pb(s) + SO_4^{2-} \qquad E^\circ = -0.35\ V$$

(a) In the lead acid battery (car battery), one electrode consists of lead and the other electrode consists of lead (IV) oxide. Which electrode is the anode and which is the cathode?
(b) (i) What is the equation for the overall reaction which generates the current?
(ii) What is the standard electrode potential for the cell?
(c) The cells in a new battery have a higher voltage than the standard electrode potential. Explain.
(d) What happens to the voltage when the battery is used and finally goes flat?

7. [6 marks]
The nickel–cadmium battery is a rechargeable battery for which the following half-cells are relevant.

$$NiO_2(s) + H_2O + 2e^- \Leftrightarrow Ni(OH)_2(s) + 2OH^- \qquad E^\circ = +0.49\ V$$

$$Cd(OH)_2(s) + 2e^- \Leftrightarrow Cd(s) + 2OH^- \qquad E^\circ = -0.76\ V$$

(a) At which electrode does oxidation occur?
(b) Which half-cell is the anode and which is the cathode in the Ni–Cd battery?
(c) Use half-cell reactions to obtain the overall equation for the cell reaction.
(d) What is the E° for the cell reaction?
(e) Give the direction of the electron flow for the cell.

8. [6 marks]
(a) Explain briefly why ethene is more reactive than ethane.
(b) Name the process used to produce ethene from suitable feedstocks such as ethane.
(c) Name and give two uses for the polymer formed from the monomer ethene.
(d) Write balanced chemical reactions to show the role of ethene in the production of TWO substances.

9. [6 marks]
A galvanic cell was constructed by a student using two half-cells. One half-cell contained an iron rod dipping into an iron (II) nitrate solution. The other half-cell contained a copper strip dipping into a copper (II) sulfate solution. A salt bridge was used and a voltmeter completed the circuit.
(a) Draw a diagram of the cell and label
(i) anode,
(ii) cathode,
(iii) the direction of electron flow, and
(iv) salt bridge.
(b) Using standard half-cell potentials, calculate the theoretical voltage of the cell.
(c) The student measured the cell voltage of the constructed cell and found it to be 0.6 V. Suggest a possible reason for the difference between the experimental and theoretical voltage values.

10. [7 marks]
(a) The radioisotope ${}^{244}_{94}\mathrm{Pu}$ can be used as a nuclear fuel. What is meant by the terms
(i) isotope, and
(ii) radioisotope.
(iii) Name and describe the use of one other radioisotope in industry.
(iv) Write an equation for the alpha-decay of ${}^{244}_{94}\mathrm{Pu}$.
(b) High concentrations of caesium-137 were found over much of Europe after the Chernobyl nuclear power plant explosion. Write a balanced nuclear equation for the decay of caesium-137 by beta emission.
(c) Radioisotopes are used in medicine for either diagnosis or treatment. Explain briefly why radioisotopes used for diagnosis should not emit alpha or beta radiation whereas those used for treatment should.

Answers for test 1 - The production of materials

Part A

Multiple choice questions (1 mark)

1. A
2. C
3. C
4. B
5. D

Part B

Extended questions

6. [4 marks]
(a) Lead is oxidised at the anode. PbO_2 is reduced at the cathode.
(b) (i) $Pb(s) + 4H^+(aq) + 2SO_4^{2-}(aq) + PbO_2(s) \rightarrow 2PbSO_4(s) + 2H_2O(l)$
(ii) +1.69 – (–0.35) = 2.04 V
(c) The concentration of the sulfuric acid is greater than the standard state of 1 mol L^{-1}
(d) It falls to zero volts when flat.

7. [6 marks]
(a) At the anode.
(b) NiO_2 is reduced at the cathode and Cd is oxidised at the anode.
(c)

$$Cd + 2OH^- \Leftrightarrow Cd(OH)_2 + 2e^- \qquad E^\circ = +0.76\ V$$

$$NiO_2(s) + H_2O + 2e^- \Leftrightarrow Ni(OH)_2(s) + 2OH^- \qquad E^\circ = +0.49\ V$$

$$NiO_2(s) + H_2O + Cd(s) \Leftrightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$$

(d) $E^\circ_{cell} = +1.25\ V$
(e) Electrons go from Cd to NiO_2

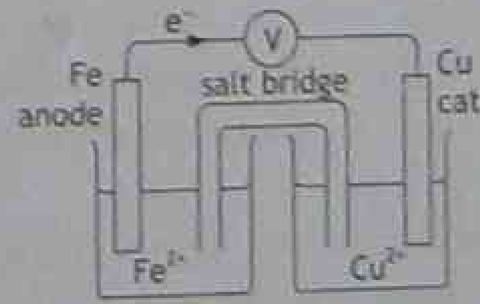
8. [6 marks]
(a) Ethene contains a double bond as its functional group and readily undergoes addition reactions.
(b) Thermal cracking.
(c) The polymer is called polyethene or polyethylene and is used as cling wrap, sandwich bags (LDPE), and milk bottles, garbage cans (HDPE).
(d)

$$\underset{}{CH_2{=}CH_2(g)} + H_2(g) \xrightarrow{catalyst} \underset{\text{ethane}}{CH_3{-}CH_3(g)}$$

$$CH_2{=}CH_2(g) + H_2O(g) \xrightarrow{catalyst} \underset{\text{ethanol}}{CH_3CH_2OH}$$

Other reactions could include the addition reactions of ethene with HCl or Cl_2.

9. [6 marks]
(a)



(b)

$$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s) \quad -0.41\ V$$

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \quad +0.35\ V$$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$= +0.35\ V - (-0.41\ V) = 0.76\ V$$

(c) Solutions of electrolytes not 1 M; temperature not 25°C.

10. [7 marks]

(a) (i) Isotopes are atoms with the same atomic number but different mass numbers.

(ii) Radioisotopes differ from other isotopes of an element because their nuclei are unstable.

(iii) See section on industrial radioisotopes, e.g. americium-241 is used in smoke detectors.

(iv) ${}^{244}_{94}Pu \longrightarrow {}^{4}_{2}He + {}^{240}_{92}U$

(b) ${}^{137}_{55}Cs \longrightarrow {}^{137}_{56}Ba + {}^{0}_{-1}e$

(c) Radioisotopes used for diagnosis should not em alpha or beta radiation since these partic would be trapped in the patient's tissues and n be detected externally. Radioisotopes used fo treatment should emit alpha and beta radiatio to penetrate the lesion being treated.

Total marks = 33 × 3 + 1 = 100%

2 — The Acidic Environment

The metabolic processes of organisms are carried out in both acidic and alkaline environments. Concerns have arisen from the increased release of acidic and basic substances into the environment and their impact on living organisms. An awareness of properties of acids and bases is important for the safer handling of materials.

Contents

2.1 Historical indicators of acids and bases

We encounter a wide variety of acids and bases in everyday living. Early chemists knew that acids had a sour taste, could dissolve many metals and could change the colour of certain vegetable dyes. They also knew that bases had a bitter taste and that soluble bases called alkalis could also change the colour of some dyes.

Early identification of indicators depended on observations that the colour of some flowers depended on the type of soil they were growing in. Hydrangeas, for example, will produce blue flowers in acid soils and pink flowers in alkaline soils.

Litmus, a dye extracted from lichens, has been us for many centuries, since it appears red in ac solutions and blue in alkaline solutions. When us litmus paper to test solutions, a drop of the solu should be added to a small piece of red paper an a small piece of blue paper. If there is no chang then the solution is neutral. If both pieces are bl it is alkaline, but if both pieces are red, the solu is acidic.

Several coloured plant materials show the propert of changing colour like litmus, for example, re cabbage water or alcoholic extracts made from so coloured flower petals such as blue morning glo or red coral tree flowers.

2.2 Classification and properties of acidic oxides

Group IV

GROUP IV	Carbon dioxide (CO_2)	Silicon dioxide (SiO_2)
Structure	covalent molecular	covalent network
Physical properties	gas at room temperature	solid at room temperature
Effect on living things	essential as a source of carbon for photosynthesis	
Effect on atmosphere	the rate of emission of CO_2 and other greenhouse gases is increasing; in the case of CO_2 this is mainly due to fossil-fuel burning and deforestation	
Chemical properties	soluble in water forming an acidic solution containing H_2CO_3 ($K_a = 4.3 \times 10^{-7}$), this accounts for the acidity of carbonated water; reacts with hydroxide ions to form carbonates and hydrogen carbonates in solution	almost insoluble (K_a = about 10^{-10}) forms a wide range of silicates with the hydroxide ion

Group V

GROUP V	**Acidic oxides of nitrogen** nitrogen dioxide (NO_2), dinitrogen trioxide (N_2O_3), dinitrogen pentoxide (N_2O_5)	**Acidic oxides of phosphorus** phosphorus (III) oxide (P_2O_3), phosphorus (IV) oxide (P_4O_{10})
Structure	covalent molecular	covalent molecular
Effect on atmosphere	NO_2 is a serious atmospheric pollutant in photochemical smog formation in cities	
Chemical properties	both the stated oxides of nitrogen are water soluble N_2O_3 is the anhydride of nitrous acid HNO_2 (weak acid) N_2O_5 is the anhydride of nitric acid HNO_3 (strong acid)	both oxides of phosphorus are water soluble; P_2O_3 is the anhydride of orthophosphorous acid H_3PO_3; P_4O_{10} is the anhydride of orthophosphoric acid H_3PO_4
Acid properties of the oxides	N_2O_5 is strongly acidic; N_2O_3 is weakly acidic	P_2O_3 is weakly acidic (weaker than N_2O_3); P_4O_{10} is strongly acidic

Note: The acidic nature of the oxides of Group V decreases down the group.

Group VI

GROUP VI	Sulfur dioxide (SO_2)	Sulfur trioxide (SO_3)
Structure	covalent molecular	covalent molecular
Physical properties	SO_2 is a gas at room temperature	SO_3 is a solid at room temperature (melting point 62°C)
Effect on atmosphere	increases in the amount of sulfur dioxide in the atmosphere have led to 'acid rain', particularly in cities in the Northern Hemisphere	
Chemical properties	SO_2 has a low solubility in water and forms sulfurous acid H_2SO_3; it reacts with hydroxide ions to form sulfites and hydrogen sulfites in solution	SO_3 dissolves in water to form H_2SO_4, which is a strong acid; it reacts with hydroxide ions to form sulfates and hydrogen sulfates in solution

Group VII

- With the exception of F_2O, all the oxides are acidic.
- The oxides of chlorine are strong oxidants.
- ClO_2 is used for bleaching in the paper industry and as a germicide. It is also used as an improving agent for flour.

$$2ClO_2 + H_2O \rightarrow HClO_2 + HClO_3$$

- Another oxide of chlorine, Cl_2O_7, dissolves in water to form a powerful oxidising acid called perchloric acid ($HClO_4$).
- The rest of the oxides of Group VII are not important.

2.3 Periodic trends of some oxides

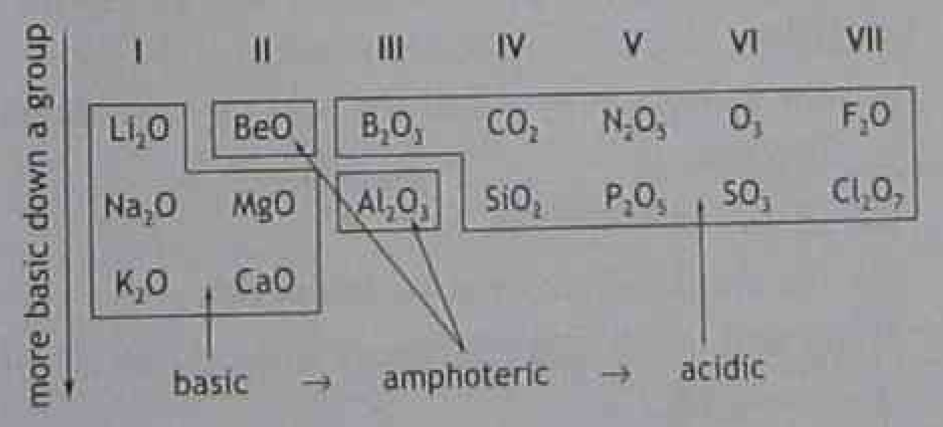


Figure 2.1 Periodic trends of some oxides

Other oxides formed

Peroxides:	H_2O_2, Li_2O_2, Na_2O_2, K_2O_2
Neutral oxides:	CO, N_2O, NO

- Most oxides of metals are bases and, if soluble in water, e.g. Group I oxides and CaO and BaO, they form alkaline solutions. Some insoluble oxides are MgO, CuO, Fe_2O_3 and Ag_2O.
- Some metal oxides are amphoteric and can react with both acids and bases, e.g. Al_2O_3, ZnO, PbO, SnO and Cr_2O_3.

  Example

  $$Al_2O_3(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2O(l)$$

  $$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2NaAl(OH)_4(aq)$$

  Note: Aluminium is a *passivating metal* and forms an inactive Al_2O_3 coating.
- Most oxides of non-metals are acidic, e.g. CO_2, NO_2, P_4O_{10}, SO_2 and SO_3.

  Example

  $$P_4O_{10}(s) + 6H_2O(l) \rightarrow \underset{\text{phosphoric acid}}{4H_3PO_4(aq)}$$

2.4 Disturbing an equilibrium

- If any chemical system at equilibrium is upset, it will re-establish itself.
- Le Châtelier's Principle states that if any chemical system is subjected to a change in concentration or temperature, the system will react in the direction to minimise the effect of the change.

Concentration changes

[R] and [P] are moles per litre of reactants and products. Increase [R] — equilibrium shifts to decrease [R] by consuming some of the added R, for example

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Increase $[H_2]$ — equilibrium shifts to right.

Temperature changes

Increase temperature — equilibrium shifts to minimise the effect of the change for the forward reaction, for example

$$H_2(g) + I_2(g) \rightarrow 2HI(g) \qquad \Delta H = 47.7\ kJ$$

ΔH is positive so heating an endothermic reaction results in equilibrium shift to the right.

Pressure changes in gases

Increase in pressure (or decrease in volume) causes an increase in concentration, for example,

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

Reaction moves to right. (2 moles → 1 mole)

Addition of a noble gas has no effect on the equilibrium.

- Catalysts alter the time taken to reach equilibrium but do not alter the equilibrium position. Catalysts speed up a reaction by lowering the activation energy E_a.

Equilibrium process of CO_2 dissolving in water

- The solubility of carbon dioxide (*g*) in water decreases as the temperature of the water increases.
- The solubility of carbon dioxide in water increases with pressure. Any increase in pressure of the gas means that there is an increase in its concentration. This can be readily observed by decarbonating a fizzy soft drink.

$$\underset{\xrightarrow{\text{increased pressure (conc. } CO_2\text{)}}}{\overset{\xleftarrow{\text{increased temperature}}}{CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)}}$$

Usually when a gas dissolves in a liquid, heat is evolved, so the above reaction is exothermic. As the solution is heated, the equilibrium will move to the left to oppose the change. $CO_2(g)$ will evolve according to Le Châtelier's Principle.

When the pressure (concentration) in increased, at constant temperature, the equilibrium will move to the right to reduce the concentration of CO_2 according to Le Châtelier's Principle.

2.5 Atmospheric gaseous pollution

When present in sufficiently high concentrations, pollutants have a detrimental effect on the community and the environment. When introduced into the atmosphere they are called air pollutants. Many common pollutants such as sulfur dioxide (SO_2), nitrogen monoxide (NO) and nitrogen dioxide (NO_2) are poisonous gases. Many air pollutants are released into the atmosphere in large quantities by natural processes.

Natural pollution due to sulfur dioxide

- About half of the sulfur dioxide in the atmosphere is due to the oxidation of hydrogen sulfide (H_2S) produced during the decay of organic matter.

  Equation:

$$2H_2S(g) + 3O_2(g) \rightarrow 2SO_2(g) + 2H_2O(g)$$

- Volcanic eruptions release sulfur dioxide as well as dust and other gases into the atmosphere.

Artificially produced sulfur dioxide emissions

- Humans can generate both local and global effects on atmospheric pollution. About 40% of sulfur compounds are discharged into the atmosphere around large cities where populations are concentrated.
- About 80% of the SO_2 generated by artificial emissions is a result of the combustion of fossil fuels (coal and oil). The presence of sulfur in fossil fuels is a result of the protein material in the original living matter where, after fossilisation, the free element and compounds of sulfur remained. Australian fuels have a relatively lower sulfur content when compared with fuels from other regions. Fossil-fuelled power plants are the main culprits for the release of SO_2 pollution.
- Smelters release sulfur dioxide in the process of roasting sulfide ores such as those of copper, lead and zinc. This can produce high local SO_2 levels.

  Equation:

$$2ZnS(s) + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g)$$

- Other industries which contribute to SO_2 pollution include
  - (i) the manufacture of sulfuric acid by the contact process,
  - (ii) petroleum refining, and
  - (iii) the manufacture of coke from coal.

  Note: Motor vehicles contribute only about 1% of SO_2 emission.

Effects of SO_2 as a pollutant

- The main effect on humans is irritation of the respiratory system.

  Equation:

$$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$$

- Plants are very sensitive to SO_2. Low concentrations retard the production of chlorophyll while high concentrations result in the formation of sulfuric acid and plant death.

  Equation:

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3 \xrightarrow{+H_2O(l)} H_2SO_4(aq)$$

- Sulfur dioxide can form a 'reducing' smog.

Control of SO_2 pollution

(i) Use low sulfur content fuels.
(ii) Remove sulfur from oils in refineries.
(iii) Remove SO_2 from flue gases of power and other industrial plants.

A manganese compound which can absorb SO_2 and convert it to H_2SO_4 is currently being assessed.

Measurement of pollution

The Environmental Protection Authority (EPA) bases its scale, the Air Pollution Index (API), on the amount of pollutants in the air divided by a weighting factor, e.g. SO_2 is a far worse pollutant than NO. The units for pollutant concentration are in parts per hundred million (pphm). The API is not used throughout the world.

2.6 Acid rain

Because of modern industrial pollution in the atmosphere, there has been in increase in acidity due mostly to the formation of sulfurous and nitric acids. Toxic gases such as sulfur dioxide and oxides of nitrogen are released from motor vehicles and industrial smokestacks.

- Sulfur dioxide can be removed from the air by rain in which it forms a weakly acidic acid solution of sulfurous acid.

  Equation:

$$\underset{\text{sulfur dioxide}}{SO_2(g)} + H_2O(l) \rightleftharpoons \underset{\text{sulfurous acid}}{H_2SO_3(aq)}$$

- Sulfur dioxide can be gradually oxidised to sulfur trioxide which is quickly converted in moist air to sulfuric acid.

  Equation:

$$\underset{\text{sulfur trioxide}}{SO_3(g)} + H_2O(l) \rightarrow \underset{\text{sulfuric acid}}{H_2SO_4(aq)}$$

- Acid rain may also contain nitrous acid and nitric acid formed from oxides of nitrogen.

  Equation:

$$2NO_2(g) + H_2O(l) \rightarrow HNO_3(aq) + HNO_2(aq)$$

Note: The pH of unpolluted rain water is about 5.2 but in a Los Angeles fog, the pH has been known to drop to 2.2.

Effects of acid rain

Acid rain refers to a form of environmental pollution which results in damage to buildings and marble statues in cities. The calcium carbonate present is 'dissolved' by the acid rain, soluble calcium hydrogen carbonate being formed.

$$CaCO_3 + \text{acid rain} \rightarrow Ca(HCO_3)_2 \text{ (soluble)}$$

Even more devastating are the effects of acid rain on forests and the extermination of aquatic life forms from lakes and rivers. Acid rain has a pH below 5.6, while rain from an unpolluted atmosphere has an acidity close to 6.0 due to the reaction of water

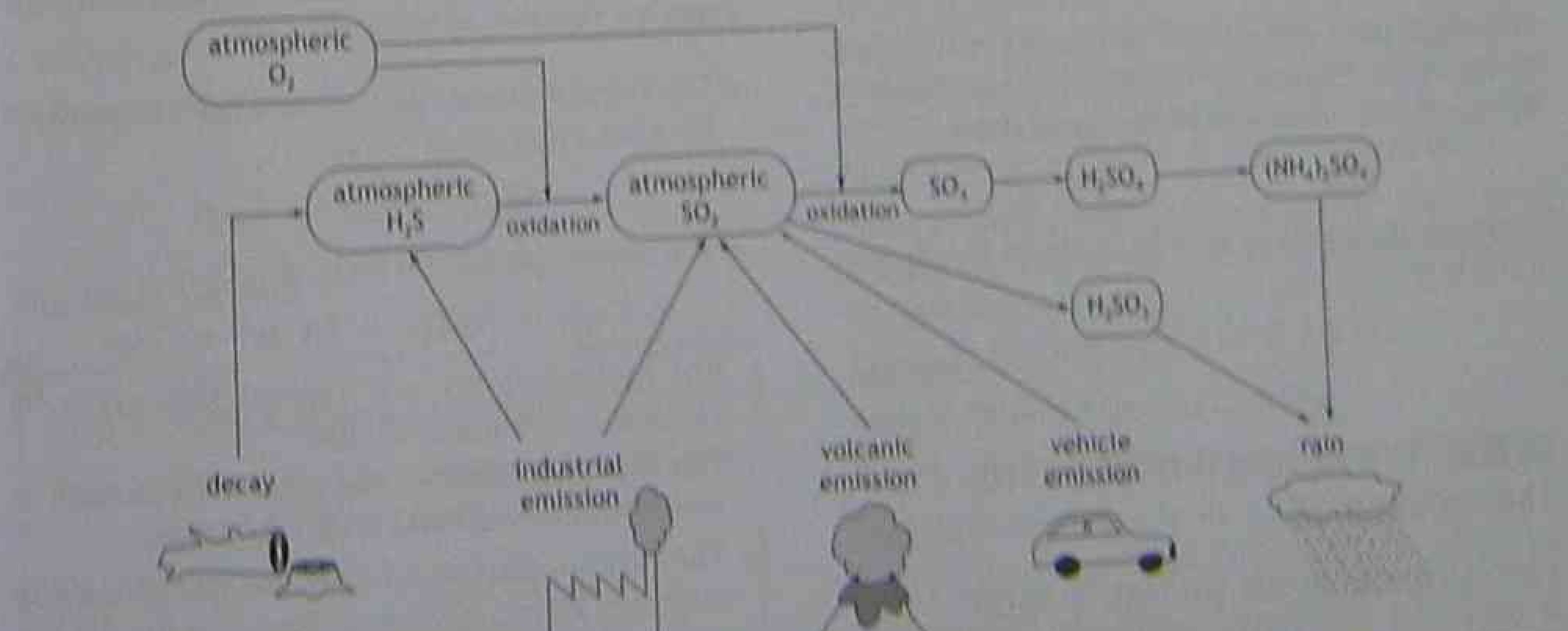


Figure 2.2 The atmospheric sulfur cycle

vapour and carbon dioxide in the atmosphere forming dilute carbonic acid (H_2CO_3).

By upsetting the vital process of photosynthesis, acid rain has resulted in more than 75% of the pine trees in the Black Forest being severely damaged. Acid rain in extreme conditions can also leach aluminium from the soil into ground water and into lakes and rivers. Not only do small concentrations of aluminium poison fish but they also threaten the aquatic life at the bottom of the food chain. Eggs and larvae are particularly vulnerable. The leachant can also poison plant and tree roots.

2.7 Sources which release oxides of nitrogen

Natural sources

The activities of modern human society now discharge into the atmosphere three oxides of nitrogen: dinitrogen monoxide (N_2O), nitrogen monoxide (NO) and nitrogen dioxide (NO_2). The last two are often analysed together as NO_x.

Oxides of nitrogen (NO_x) form naturally when lightning passes through the atmosphere, and are emitted by volcanoes and by some biological processes.

Some chemical reactions which release oxides of nitrogen

These include the burning of fossil fuel and vegetation. Gas-fired power stations and nitric acid manufacture also lead to oxides of nitrogen entering the atmosphere.

Nitrogen monoxide (NO) is formed in internal combustion engines by the direct combination of nitrogen with oxygen at high temperatures:

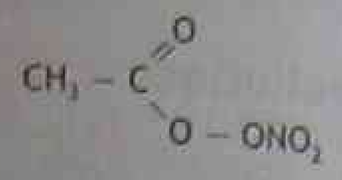
$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$

Nitrogen monoxide is readily oxidised to nitrogen dioxide (NO_2).

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

2.8 The production of photochemical smog

Photochemical smog oxidises in nature and is formed from the primary pollutants, hydrocarbons and oxides of nitrogen discharged by motor vehicles. These react with oxygen in the presence of sunlight to form various harmful secondary pollutants including ozone, aldehydes and peroxyacetyl nitrate (PAN).



In the presence of u.v. light from the sun, nitrogen dioxide decomposes.

$$NO_2(g) \rightarrow NO(g) + O(g)$$

Smog formation needs the following conditions:

- Plenty of sunshine.
- Temperature inversion. Pollutants accumulate in the lower inversion layer.
- The presence of tetraethyl lead $(C_2H_5)_4Pb$. This is used as 'anti-knock' in leaded petrol and deactivated catalytic exhaust devices.

Sydney's climate is conducive to smog formation.

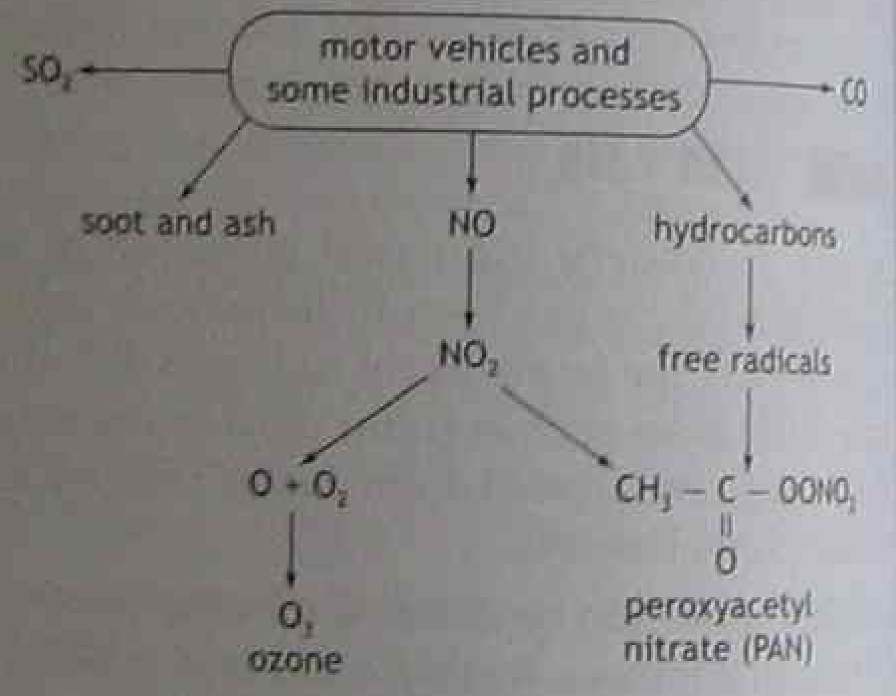


Figure 2.3 Formation of photochemical smog

- The oxygen atoms react with oxygen to produce harmful ozone.

$$O(g) + O_2(g) \rightarrow O_3(g)$$

- The normal photolytic cycle of NO_2 is

$$O_3(g) + NO(g) \rightarrow NO_2(g) + O_2(g)$$

but hydrocarbons can disrupt this cycle by causing competing reactions.

- The ozone accumulates and other irritants such as aldehydes, ketones and PAN are formed.
- The accumulation of pollutants below an inversion layer, i.e. when a layer of warm air lies above a layer of cooler air, aids the development of a photochemical smog.

2.9 Calculations involving mole/volume problems

All thermochemical data should be stated at standard state pressure of 100 kPa (1 bar) and a temperature of 25°C. (Refer to G. Aylward and T. Findlay, *SI Chemical Data*, 5th edition, John Wiley & Sons, 2002.)

The key relationship is that one mole of any gas occupies 24.82 L at 25°C and 100 kPa. One mole of a compound contains its molecular mass.

Step 1. Write a balanced equation.

Step 2. Work out the first part of the problem as a mass/mass type.

Step 3. Use the above relationship of the mole to convert mass of gas to volume of gas.

Example 1

Problem

A student carried out an experiment to decarbonate a bottle of soft drink. The volume of gas released was to be found from the loss in mass which occurred when all the gas was released at 25°C and 100 kPa.

Results

Original mass of stoppered bottle of carbonated drink	= 531.25 g
Final mass of stopper, open bottle and carbonated drink	= 529.80 g
Difference in mass due to loss of CO_2 (molar mass = 44)	= 1.45 g

Calculation

$$\text{Volume of } CO_2 = nCO_2 \times 24\,820 \text{ mL}$$
$$= 0.0330 \times 24\,820 \text{ mL}$$
$$= 819 \text{ mL}$$

The Mole Method

Step 1. Write a balanced equation.

Step 2. Find the moles of known substance (the one for which information is given).

Step 3. Determine the mole ratio.

$$\text{mole ratio} = \frac{\text{moles of unknown}}{\text{moles of known}}$$

Step 4. Find the moles of unknown by multiplying the moles of known (Step 2) by the mole ratio (Step 3).

Step 5. Answer the question by converting moles of known into the units asked for.

In performing the calculations in Steps 2 and 5, there is a choice of equations:

$$n = \frac{N}{N_A},\ n = \frac{m}{M},$$

$$n = \frac{V}{MV} \text{ (gases only)}, n = CV \text{ (solutions)}$$

Example 2

Problem

What volume of hydrogen gas is produced when 6.5 g of magnesium metal is dissolved in excess hydrochloric acid under standard conditions (25°C and 100 kPa).

Step 1. Write equation

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

Step 2. Moles of known substance $n = \frac{m}{M}$

(molar mass for Mg = 24.3).

$$n = \frac{6.5}{24.3} = 0.267 \text{ mol.}$$

Step 3. From equation, number of moles of H_2 = 0.267 mol.

Step 4. Volume of H_2 at 25°C and 100kPa

$$= V = n \times MV$$
$$= 0.267 \times 24.82$$
$$= 6.63 \text{ L}$$

In many problems where the quantities of two substances are given, the limiting reagent is often unknown. To solve such problems, the limiting reagent must first be identified and then used as the known substance in the '5 step mole method'.

Note: It is important to understand that the limiting reagent depends on the mole ratio, not just on which one has less mass.

Method

Step 1. Write a balanced equation.

Step 2. Find the moles of both known quantities.

Step 3. Find (a) the mole ratio of the quantities from Step 2; and (b) the mole ratio from the balanced equation. By comparing the actual mole ratio with the one from the equation, the limiting reagent can be identified.

Step 4. Use the limiting reagent as your known to find the moles of unknown substance (as in previous questions).

Step 5. Answer the question as before.

Example 3

Problem

What volume of carbon dioxide is produced at 25°C and 100 kPa when 20 g of calcium carbonate is heated (atomic mass: Ca = 40, C = 12, O = 16)?

Step 1. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

Step 2. $nCaCO_3 \rightarrow nCO_2$

$$\frac{\text{mass } CaCO_3}{\text{formula mass } CaCO_3} = \frac{\text{vol. } CO_2}{\text{molar volume}}$$

$$\frac{20}{100} = \frac{\text{vol. } CO_2}{24.82}$$

Step 3. Volume $CO_2 = \frac{20}{100} \times 24.82\text{ L} = 4.96\text{ L}$

Example 4

Problem

0.22 g of a gas is found to occupy 0.124 L at 25°C and 100 kPa. Find the molar mass of the gas.

Step 1. Formulate a ratio.

0.22 grams occupies 0.112 litres at 25°C and 100 kPa

M grams occupies 22.4 litres at 25°C and 100 kPa, $\frac{M}{0.22} = \frac{24.82}{0.124}$

Step 2. Solve for M.

$M = 44$

Molar mass of the gas is 44.

Limiting reagent problems

In a chemical equation, the numbers in front of any chemical formula can only tell us what happens when the reactants are mixed in the correct molar ratio so that they will both be completely used up in the reaction. Usually more of one of the reactants than is needed is present. This is called the excess reagent. The other reagent which is completely used up is called the limiting reagent. The limiting reagent depends on the mole ratio, not on the masses of the reactants present. For example, if we place a large piece of zinc in a small amount of hydrochloric acid so that after the reaction some zinc is left, then the zinc will be in excess and the limiting reagent will be the hydrochloric acid.

When quantities of both reactants are given, the limiting reagent must first be identified. It is then used as the known solution in solving the problem.

(a) Mass/mass limiting reagent problems

- Write a balanced equation.
- Find out which reagent is in excess.
- Use the limiting reagent to calculate the mass of the product.

Example 1

Problem

A solution containing 100 g of hydrochloric acid is added to 100 g of zinc. Find the mass of zinc chloride formed.

Equation:

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

From the balanced equation two moles of HCl react with one mole of Zn, so $\frac{100}{36.5}$ moles of HCl is added to $\frac{100}{65.4}$ moles of Zn.

2.74 moles of HCl are added to 1.529 moles of Zn. From equation, for all the Zn to react, 1.529 × two moles of HCl is needed, i.e. 3.058 moles of HCl.

Since only 2.7 moles of HCl is present, then zinc is in excess and 1.37 mole $ZnCl_2$ is formed.

Grams of $ZnCl_2 = 1.37 \times 136.4$ g

Therefore, 186.9 grams of $ZnCl_2$ are formed.

(b) Mass/volume problems with a limiting reagent

Example 2

Problem

A solution containing 100 g of hydrochloric acid is added to 100 g of zinc. find the volume of hydrogen gas evolved under standard conditions of 25°C and 100 kPa.

From Example 1, the limiting reagent is HCl.

2 mol HCl → 24.82 L of H_2 at 25°C and 100 kPa

2.74 mol HCl → y L of H_2

$$\frac{y}{24.82} = \frac{2.74}{2}$$

$$y = \frac{2.74\text{¥}24.82}{2} = 34.0\text{ L}$$

34.0 litres of H_2 are produced at 25°C and 100 kPa.

Limiting reagent problems may also be solved by finding the number of moles of both known quantities and then comparing this mole ratio with that from the balanced equation.

Problems on finding mass/volume using the mole method

1. 3.9 g of zinc was completely dissolved in dilute hydrochloric acid and the gas was collected at 25°C and 100 kPa. Find the volume of hydrogen produced.

2. Sulfur dioxide is produced according to the equation:
   $4FeS(s) + 7O_2(g) \rightarrow 2Fe_2O_3(s) + 4SO_2(g)$
   For every 1.0 kg of FeS_2 which reacts, calculate:
   (a) the volume of oxygen needed at 25°C and 100 kPa.
   (b) the volume of sulfur dioxide produced at 25°C and 100 kPa.

3. Ammonia (*g*) can be prepared in the laboratory by reacting ammonium sulfate with calcium hydroxide according to the following equation:
   $(NH_4)_2SO_4(s) + Ca(OH)_2(aq)$
   $\rightarrow CaSO_4(s) + 2NH_3(g) + 2H_2O(l)$
   Calculate the volume in millilitres of ammonia produced at 25°C and 100 kPa from 1.98 g of ammonium sulfate.

4. A student prepared oxygen (*g*) by carefully heating 5.2 g of potassium chlorate and collecting the gas formed at 25°C and 100 kPa:
   $2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$
   What was the volume of oxygen produced?

5. Calcium phosphide (Ca_3P_2) reacts with water to produce phosphine gas (PH_3) and calcium hydroxide solution. Calculate the volume of phosphine gas, measured in millilitres at 25°C and 100 kPa produced at 45.5 g of calcium phosphide.

Answers to problems on finding mass/volume using the mole method

1. $Zn + 2HCl \rightarrow ZnCl_2 + H_2$
   $\frac{3.9}{65.4}$ mol Zn → x mol H_2
   0.06 mol Zn → x mol H_2 so $x = 0.06$ mol
   1 mol H_2 = 2 g
   $x = 2 \times 0.06 = 0.12$ g of H_2
   1 mol H_2 occupies 24.82 L at 25°C and 100 kPa
   0.06 mol occupies y L at 25°C and 100 kPa
   $y = 0.06 \times 24.82\text{ L} = 1.49\text{ L}$
   So 1.49 L of H_2 was produced.

2. (a) 1 kg = 1000 g
   4 mol FeS reacts with 7 mol O_2
   $\frac{1000}{87.92}$ mol FeS reacts with x mol O_2
   $\frac{4}{11.374} = \frac{7}{x}$ so $x = \frac{7 \times 11.374}{4} = 19.90$ mol O_2
   1 mol O_2 occupies 24.82 L at 25°C and 100 kPa
   19.90 mol O_2 occupies y L at 25°C and 100 kPa
   $y = 24.82 \times 19.90\text{ L} = 494\text{ L}$
   So 494 L of O_2 was used.

   (b) 4 mol FeS → 4 mol SO_2
   $\frac{1000}{120.1} \rightarrow x$ mol SO_2
   $\frac{4}{11.374} = \frac{4}{x}$ so $x = \frac{4 \times 11.374}{4} = 11.374$ mol SO_2
   At STP, 1mol SO_2 occupies 24.82 L at 25°C and 100 kPa
   11.374 mol SO_2 occupies y L
   $y = 11.374 \times 24.82 = 282.3\text{ L}$
   So 282.3 L of SO_2 was produced.

3. 1 mol $(NH_4)_2SO_4(s) \rightarrow$ 2 mol $NH_3(g)$
   $\frac{1.98}{132.08} = \frac{x}{2}$
   $x = 0.015 \times 2 = 0.03$ mol
   Amount of $NH_3 = 0.03 \times 17 = 0.51$ g
   1 mol $NH_3(g)$ occupies 24.82 L at 25°C and 100 kPa
   0.03 mol occupies y L
   $y = 0.03 \times 24.82 = 0.745\text{ L} = 745\text{ mL}$
   So 745 mL of $NH_3(g)$ was produced at 25°C and 100 kPa.

4. 2 mol $KClO_3(s) \rightarrow$ 3 mol $O_2(g)$
   $\frac{5.2}{122.55} \times 0.5 = \frac{x}{3}$
   $x = \frac{0.0424 \times 3}{2} = 0.0636$ mol
   Amount of $O_2 = 0.0636 \times 32 = 2.04$ g
   So 2.04 g of O_2 was produced.
   2.04 g of O_2 occupies $\frac{2.04 \times 24.82}{32} = 1.58$ L of O_2

5. Equation:
   $Ca_3P_2(s) + 6H_2O(l) \rightarrow 2PH_3(g) + 3Ca(OH)_2(aq)$
   1 mol $Ca_3P_2 \rightarrow$ 2 mol PH_3
   $\frac{45.5}{182.18} = \frac{x}{2}$ ($x = 0.500$ mol)
   $x = 0.500 \times 33.99 = 17.00$ g
   1 mol $PH_3(g)$ occupies 24.82 L at 25°C and 100 kPa
   0.500 mol $PH_3(g)$ occupies $0.500 \times 24.82\text{ L} = 12.41\text{ L}$
   So 1241 mL of $PH_3(g)$ was produced.

2.10 Natural and manufactured acids

Natural acids

These include the following:

(a) Acetic acid (ethanoic acid). Vinegar of 0.5 – 1.0 M solution of acetic acid.

(b) Citric acid found in lemons and other citrus fruit. It is used by soft drink manufacturers to give an acid taste.

(c) Ascorbic acid (Vitamin C) found in fruit and vegetables.

(d) Tartaric acid found in grapes.

(e) Dilute hydrochloric acid (0.1 M) found in gastric juices.

Manufactured acids

These include the following:

(a) Sulfuric acid, which is the most widely used industrial acid. It is usually manufactured by the contact process.

$$S + O_2 \rightarrow SO_2 + \tfrac{1}{2}O_2 \xrightarrow[V_2O_5\ (\text{cat.})]{400^\circ C} SO_3 + H_2O \rightarrow H_2SO_4$$

(b) Hydrochloric acid, made by

$$NaCl(s) + H_2SO_4(l) \rightarrow NaHSO_4(aq) + HCl(g)$$

$$HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

Note: Hydrochloric acid occurs naturally in the stomach and is also manufactured. It is used widely by builders for brick cleaning.

2.11 Acids as proton donors

Acids in aqueous solutions are called *proton (H^+) donors.*

$$H^+ + H_2O \rightleftharpoons H_3O^+$$

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

or $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

The forward reaction shows acetic (ethanoic) acid acting as an acid by releasing hydrogen ions.

For water

$[H^+]\,[OH^-] = K[H_2O] = K_w$. K_w is called the ionic product of water, and equals 1×10^{-14} at 25°C.

Pure water is a neutral solution.

$[H^+] = [OH^-] = 10^{-7}$ M at 25°C.

Acidic solutions, e.g. CH_3COOH, HCl, produce ex H^+ ions in aqueous solutions so $[H^+] > [OH^-]$.

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

For pure water pH = 7 at 25°C.

As the $[H^+]$ increases the pH will decrease.

Concentration of acids

In a concentrated acid there is a large amount acid/unit volume, e.g. 10 M HCl is a concentrate acid, 0.1 M HCl is a dilute acid.

Strength of acids

This is *not* the same as concentration. The strength vary between strong and weak according to the extent that the acids ionise in solution and a indicated by dissociation constants. A *strong* aci dissociates completely into hydrogen ions and anions in aqueous solutions.

Example 1

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

The equilibrium constant $K = \dfrac{[H^+][Cl^-]}{[HCl]}$

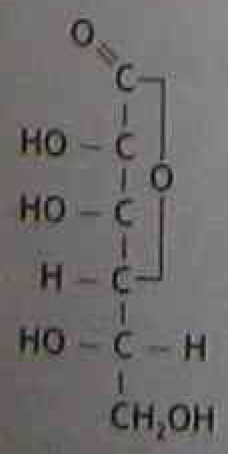
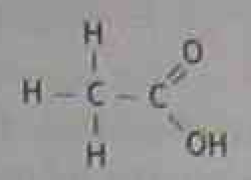
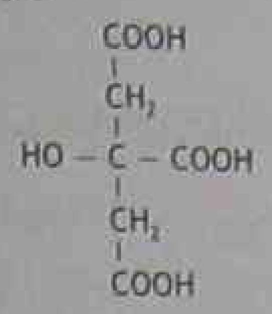
If the [HCl] is almost zero, then K is too large t measure.

A *weak acid* does not dissociate completely i aqueous solution. The weaker the acid, the smalle is the dissociation constant.

Note: If we compare the pH of a 0.1 M solution o HCl and a 0.1 M solution of CH_3COOH (K_a = 1.8 × 10^{-5}) we find that the pH of 0.1 M HCl = 1, but the pH of 0.1 M CH_3COOH = 2.87. Equal concentrations of acids do *not* have equal pH values.

Relative strengths of weak acids (exension work)

Table 2.1 Some weak acids in water at 25°C

Acid	Formula	K_a
Ascorbic (vitamin C)	$C_6H_7O_6$ 	$K_{a_1} = 8.0 \times 10^{-5}$ $K_{a_2} = 1.62 \times 10^{-12}$
Acetic (ethanoic)	CH_3COOH 	1.8×10^{-5}
Citric (hydrate $C_6H_8O_7 \cdot H_2O$)	$C_6H_8O_7$ 	$K_{a_1} = 7.1 \times 10^{-4}$ $K_{a_2} = 1.68 \times 10^{-5}$ $K_{a_3} = 8.4 \times 10^{-6}$

continued next page

Note 1: Polyprotic acids, e.g. citric acid, have more than one ionisable proton. These acids have more than one dissociation constant, K_{a_1}, K_{a_2}, K_{a_3}.

Note 2: In multiprotic acids the value of K_{a_1} is always the highest since it is more difficult to remove a hydrogen ion from a negatively charged substance than from a neutral molecule.

2.12 Changes in conductivity of weak acids with dilution

The conductivity of a strong acid, e.g. HCl, increases approximately in proportion to concentration. The conductivity of a weak acid, e.g. acetic acid, does not vary linearly with the acid concentration. This happens because the percentage of acid ionised various with the acid concentration (see Section 2.13).

Example

$$\text{Percentage ionised} = \frac{\text{concentration ionised}}{\text{original concentration}} \times \frac{100}{1}$$

Dilution

By applying Le Chatelier's Principle to the case of equilibrium in solution, the effect of diluting the solution in water is similar to changing the volume of gaseous equilibria. Dilution causes the reaction to shift in the direction that produces the larger number of particles. For example, the dilution of a 1 M solution of acetic acid by a factor of 10 (to a 0.1 M solution) results in an increase in the percentage of molecules ionised by about a factor of 3.

2.13 Ionisation constants for weak acids (extension work)

- *Strong acids* (HCl, HNO_3, H_2SO_4) are completely dissociated ($K_a = \infty$) in aqueous solution.
- *Weak acids* have a small K_a and are partially dissociated in aqueous solution, e.g. CH_3COOH. At 25°C, $K_a = 1.8 \times 10^{-5}$. The higher the K_a, the stronger is the acid.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

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

or $HA \rightleftharpoons H^+ + A^-$

- Relationship to pH

$$\text{pH} = -\log[H^+]$$

$$\text{acid strength} \longrightarrow K_a = \frac{[H^+]\,[A^-]}{[HA] \longleftarrow \text{undissociated acid concentration}}$$

Any one unknown can be calculated from this relationship.

Table 2.2 Ionisation constants for some common weak acids at 25°C

Acid	Formula	K_a at 25°C
*Sulfurous acid	H_2SO_3	1.5×10^{-2}
Hydrogen sulfate ion	HSO_4^-	1.2×10^{-2}
*Phosphoric acid	H_3PO_4	7.5×10^{-3}
Hydrofluoric acid	HF	7.0×10^{-4}
Benzoic acid	C_6H_5COOH	6.5×10^{-5}
Acetic acid	CH_3COOH	1.8×10^{-5}
*Carbonic acid	H_2CO_3	4.2×10^{-7}
Hypochlorous acid	HClO	3.5×10^{-8}
Hydrocyanic acid	HCN	4.0×10^{-10}

* First stage

Example 1

Consider the weak acid, ethanoic acid (acetic acid)

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

Because water is the solvent,

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

$$= 1.8 \times 10^{-5} \text{ at } 25^\circ C$$

Note: The stronger the acid, the weaker is its conjugate base.

Example 2

Given the molarity of a 0.001 **M** solution of acetic acid and that its K_a is 1.0×10^{-5} at the temperature of reaction, find

(a) the hydrogen ion concentration, and

(b) the pH of the solution.

Step 1. Write the expression for K_a.

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1 \times 10^{-5}$$

Step 2. Find the relationship between the $[H^+]$ and its conjugate base. Let *x* be the degree of dissociation.
For each mole of hydrogen ions there is one mole of acetate ions, so

$$\underset{x}{[H^+]} = \underset{x}{[CH_3COO^-]}$$

Step 3. Rewrite the K_a expression

$$K_a = 1 \times 10^{-5} = \frac{[H^+]^2}{0.001}$$

(Assume that undissociated acid = molarity. In fact it is molarity − *x*.)

Step 4. Calculate $[H^+]$ and hence pH.

$[H^+]^2 = 10^{-8}$

(a) $[H^+] = 10^{-4}$

(b) pH = 4

Example 3

A student carried out an experiment to find K_a for ethanoic acid (acetic acid) given an exactly 0.1 **M** solution of CH_3COOH and Universal Indicator paper (or a pH meter). The 0.1 **M** solution was tested with the UI paper and the pH recorded. Using volumetric flasks, the 0.1 **M** solution was diluted to produce a 0.01 **M** and a 0.001 **M** solution of CH_3COOH.

The results were as follows:

	Acid concentration	pH
1.	0.1	3.0
2.	0.01	3.5
3.	0.001	4.0

(a) Write an equation to show the ionisation of ethanoic acid in water.

(b) Write an expression for the equilibrium cons K_a for the reaction.

(c) Use the student's experimental results evaluate K_a.

(d) Would you expect the pH of the 0.1 M solu to increase or decrease if a few millilitres of 1 M CH_3COONH_4 were added? Explain.

Answers:

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

(b) $$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{[H^+]^2}{[CH_3COOH]}$$

(c) $$K_{a_1} = \frac{[10^{-3}]^2}{10^{-1}} = 1 \times 10^{-5};\ K_{a_2} = \frac{[10^{-3.5}]^2}{10^{-2}} = 1 \times 10^{-5};$$

$$K_{a_3} = \frac{[10^{-4}]^2}{10^{-3}} = 1 \times 10^{-5}$$

$$K_a = 1 \times 10^{-5}$$

(d) The addition of CH_3COONH_4 increased the $[CH_3COO^-]$ so, according to Le Chatelier's Principle, the equilibrium would shift to form more CH_3COOH. This causes the $[H^+]$ to decrease so that the pH will increase.

pH and pKw

- Water is a weak electrolyte that ionises slightly to form H^+ and OH^- ions.
- K_w is the ionic product of water at 25°C. $K_w = [H^+][OH^-] = 1 \times 10^{-14}$.
- $pK_w = pH + pOH$. pH is calculated from $pH = -\log_{10}[H^+]$. In a neutral solution $[H^+] = [OH^-]$ or pH = pOH = 7. If pH > 7 solution is basic, pH = 7 neutral, pH < 7 acidic.
- Strong acids and bases are completely ionised in solution.
- Weak acids such as organic acids are partly ionised in solution.

2.14 The pH scale

As we become more environmentally aware, the acid/base properties of water are seen to be extremely important. The pollution of our beaches river systems and wetlands has aroused considerable concern.

Not only the suitability of an aquatic environment for support of plant and animal life, but also the rate of corrosion of man-made metallic structures, are very much dependent on the acidity or basicity of the water. The degree of this depends then on the $[H^+]$ and $[OH^-]$ in the water and this is commonly expressed in terms of pH and pOH.

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

In a *neutral* solution,

$[H^+] = [OH^-] = 1 \times 10^{-7}$, so pH = pOH = 7.

Since $[H^+][OH^-] = 1 \times 10^{-14}$, taking negative logs, pH + pOH = 14.

pH is < 7 in acidic solutions

and > 7 in basic solutions

Remember that pH is a measure of the $[H^+]$ at equilibrium for substances that do not ionise completely.

The pH scale operates for the convenience of the chemist. If we consider the range to be at one end equal to 1 **M** HCl and the other end to be equal to 1 **M** NaOH, we can see that strong acids can have a pH of < 0 and strong alkalis can have a pH of > 14.

Table 2.3 pH and pOH for some solutions

Solution	pH	pOH
1 M HCl	0	14
0.1 M HCl	1	13
Gastric juice	2	12
Coca cola	3	11
Wine	4	10
Coffee	5	9
Tap water	6	8
Pure water	7	7
Blood	7.4	6.6
Sea water	8.5	5.5
Detergents	10–11	4–5
0.1 M NaOH	13	1
1 M NaOH	14	0

2.15 Indicators and their pH range

Indicators can be used to determine the acidic or basic nature of a substance over a range that can be determined by an indicator colour. Chemists have introduced a scale which can be used to measure how acid or alkaline a solution is. It is called the pH scale and ranges from 1 **M** HCl having a pH = 0 to 1 **M** NaOH having a pH = 14, so that it operates for the convenience of the chemist. pH = 7 is neutral whereas values below that level are acidic and above are alkaline. Universal Indicator, which is a mixed selection of indicators changing over different pH ranges, can be used in liquid or paper form. A colour chart matching colour to pH present is provided.

Indicators are dyes that change colour if their pH is changed

Practical work should include indicators commonly used in titrations, such as methyl orange, bromothymol blue and phenolphthalein. Universal Indicator is a range of indicator blends. A natural universal indicator can be made by boiling a small amount of chopped red cabbage and straining off the red liquid.

The remarkable properties of this indicator called cyanidin is the variety of colours it produces over a pH range of 1–12. The usual acid-base indicators are weak acids HA whose conjugate bases A^- undergo structural changes that result in colour changes.

$$\underset{\text{colour I}}{HA} \rightleftharpoons H^+ + \underset{\text{colour II}}{A^-}$$

Cyanidin belongs to a group of substances called bioflavinoids which are widely distributed in plants.

Activity 2.1

Add cabbage water to a number of solutions where pH has been measured by a pH meter or Universal Indicator paper.

Substance tested	Colour	pH
0.1 M HCl	deep cherry red	1.5
0.2 M acetic acid (vinegar)	cerise	2.6
5% NaH_2PO_4	purple	4.2
Tap water	blue	5.5 – 7.0
5% $NaHCO_3$	aquamarine	8.0
5% Na_2HPO_4	emerald green	9.0
5% Na_2CO_3	light lime	10.9
5% NaOH	brilliant yellow	12.0

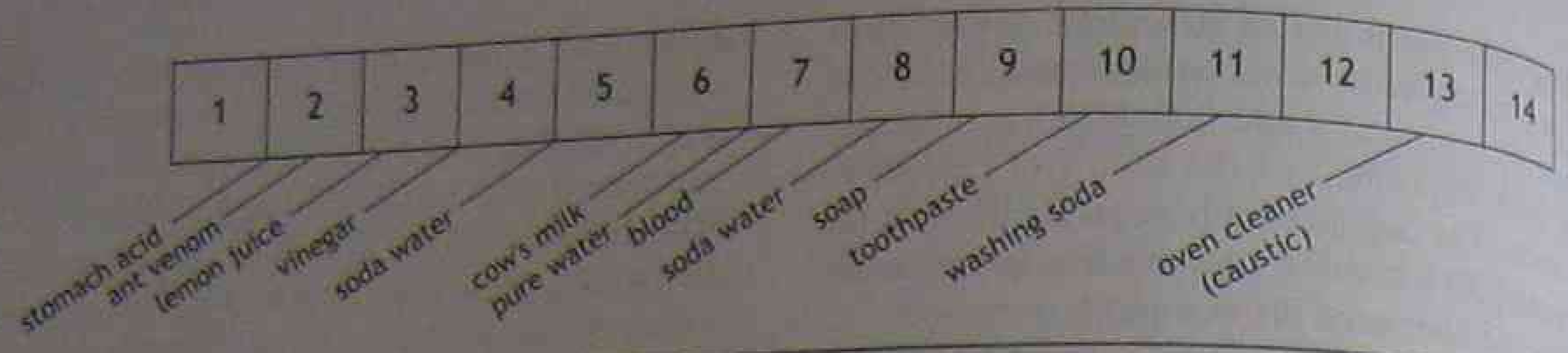


Figure 2.4 pH values of some common substances

Table 2.4 Indicators

Indicator	Colour on acid side	Colour on basic side	pH range of colour change
Methyl orange	red	yellow	3.2 – 4.4
Methyl red	red	yellow	4.8 – 6.0
Bromothymol blue	yellow	blue	6.0 – 7.6
Phenolphthalein	colourless	pink	8.2 – 10
Litmus	red	blue	unsuitable for titration

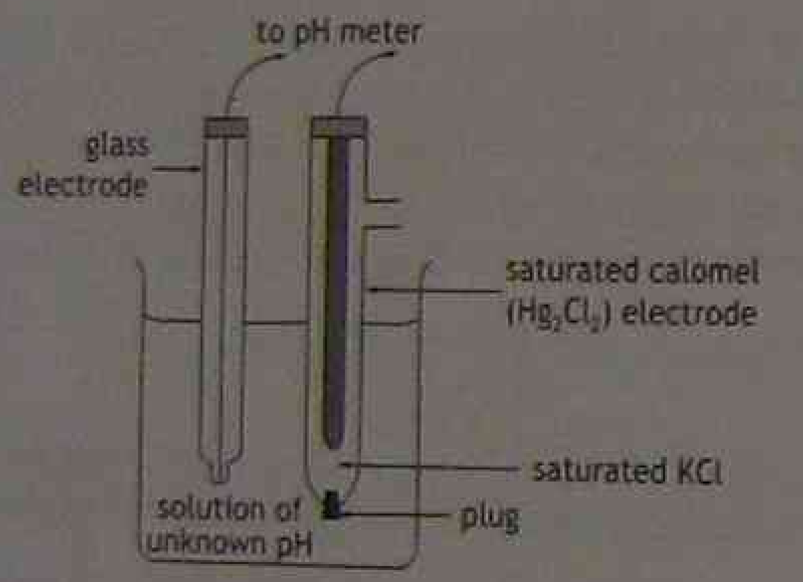


Figure 2.5 Electrodes used in a pH meter (Enclosed probe types of electrodes are also used, e.g. for determining pH of soils.)

2.16 Calculations involving pH

Strong acids and bases are said to be completely ionised in water, so it is relatively easy to calculate their pH and pOH from known molarities.

Example 1

Find the pH of a 0.001 **M** solution of HCl at SLC.

$$HCl \rightarrow H^+ + Cl^-$$

so for each mole of HCl, one mole of H^+ ions will be produced.

$[H^+] = 0.001$ **M** $= 10^{-3}$ M

From the definition of pH, negative logs are taken so that pH = 3.

Hence pOH = 14 − 3 = 11.

Example 2

Find the pH of a 0.005 **M** solution of barium hydroxide.

Note: In finding the pH of alkalis, the pOH is first found using the $[OH^-]$, then 14 − pOH = pH.

$$Ba(OH)_2 \rightarrow Ba^{2+} + 2OH^-$$

so for each mole of $Ba(OH)_2$, two moles of OH^- ions will be produced.

$[OH^-] = 2 \times 0.005 = 0.01$ **M** $= 1 \times 10^{-2}$ M

pOH = 2, pH = 12

Example 3

(a) For 20 mL of a 0.1 **M** solution of HCl find:
  (i) the pH, and
  (ii) the number of moles of hydrogen ions present.

(b) If 5 mL of 0.1 **M** NaOH is then added to the HCl, find
  (i) the number of moles of H^+ ions left,
  (ii) the concentration of the H^+ ion, and hence
  (iii) the new pH.

Answers:

(a) (i) $[H^+] = 10^{-1}$, so pH = 1.0

(ii) No. of moles of H^+

$$= 10^{-1} \times \frac{20}{1000} = 2 \times 10^{-3} \text{ mol}$$

(b) No. of moles of OH^- ions added

$$= 0.1 \times \frac{5}{1000} = 0.5 \times 10^{-3}$$

(i) No. of moles of H^+ left
$= 2 \times 10^{-3} - 0.5 \times 10^{-3}$
$= 1.5 \times 10^{-3}$ mol

(ii) Conc. $= \text{No. of moles} \times \frac{1000}{V}$

(the new volume $V = 20 + 5$ mL)

$$= 1.5 \times 10^{-3} \times \frac{1000}{25} = 0.06 \text{ M}$$

$$\text{or concentration} = \frac{\text{No. of moles}}{\text{volume of soln. in L}}$$

$$= \frac{1.5 \times 10^{-3}}{2.5 \times 10^{-2}} = 0.06 \text{ M}$$

(iii) Hence pH = 1.22

Example 4

Calculate the pH of a barium hydroxide solution containing 0.0856 g of barium hydroxide in a litre of solution.

Step 1. Find the molarity of the $Ba(OH)_2$ solution.
171.35 g of $Ba(OH)_2$ in 1 L is a 1 **M** solution.
0.0856 g of $Ba(OH)_2$ in 1 L is a 5×10^{-4} **M** solution.

Step 2. Find the concentration of $[OH^-]$.
$[OH^-] = 2 \times 5 \times 10^{-4}$ **M** $= 1 \times 10^{-3}$ M

Step 3. Find pOH, hence pH.
pOH = 3, so pH = 14 − 3 = 11

Problems on acids and bases

1. Find the concentration of the solution in mol L^{-1} when the pH is
   (a) 2.0 (b) 3.26
   (c) 4.57 (d) 6.58
   (e) 8.32 (f) 7.89

2. Find
   (i) the pH and
   (ii) the pOH
   of the following solutions:

$[H^+]$ in mol L^{-1} is	(a) 1.1×10^{-2} (b) 0.00067 (c) 4.8×10^{-3}
$[OH^-]$ in mol L^{-1} is	(d) 3.3×10^{-6} (e) 0.0053 (f) 6.7×10^{-4}

3. Calculate the value for the pH of a solution containing 0.39 g of potassium hydroxide dissolved in 250 mL of water.

Answers to problems on acids and bases

1. (a) 0.01 or 1×10^{-2}
   (b) 5.50×10^{-4}
   (c) 2.69×10^{-5}
   (d) 2.63×10^{-7}
   (e) 4.79×10^{-9}
   (f) 1.29×10^{-8}

2. (a) 1.96; 12.04
   (b) 3.17; 10.83
   (c) 2.32; 11.68
   (d) 8.52; 5.48
   (e) 11.72; 2.28
   (f) 10.83; 3.17

3. 56 g L^{-1} = 1 M KOH,
   so molarity of KOH solution = 0.0279 M.
   pOH = 1.56, so pH = 12.44.

2.17 Some applications of pH

Swimming pools

'Chlorination' in swimming pools depends on keeping the pH of the water close to 7.2. Hypochlorite ions are added as calcium and sodium salts and form an equilibrium with hypochlorous acid.

$$\mathrm{HClO} \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{ClO^-}(aq)$$

$$\xleftarrow[\text{green algal scum}]{\text{pH 7.4 (alkaline)}} \qquad \xrightarrow[\text{eye problems}]{\text{pH 7.0 (acidic)}}$$

Food preservation

A low pH (less than 4) will prevent the development of some dangerous pathogens in food. In pickled onions, for example, vinegar (pH 2.8) is used. Benzoic acid also preserves food by inhibiting the growth of bacteria, and is used particularly in soft drinks where the pH is less than 4.5. Sulfur dioxide is the most effective inhibitor of the deterioration of dried fruits and fruit juices.

Control of pH in soils

In high rainfall areas around the Australian coastal strip, the pH of soils is about 5.5–6.5. Further inland, where the rainfall is less, soils have a higher pH at about 7.5–8. An interesting activity would be to check soils from your area for pH.

Plants grow in a narrow pH range and different species prefer a different pH value for the soil. Azaleas, for example, will only grow in an 'acid' soil. To increase the pH of soil, powdered limestone ($CaCO_3$) is often used, making it more 'basic'. To decrease the pH of the soil, ammonium sulfate is often used.

Variation of pH in the human digestive system

Catalytic enzymes function in a narrow pH range.

Because of the low pH of gastric juices in the stomach, antacids are used to reduce the acidity. Some brands use a mixture of calcium carbonate and magnesium carbonate. Others use a mixture of magnesium hydroxide and aluminium hydroxide. (See Figure 2.6.)

Cosmetic applications of pH

During recent years, the topic of pH has been introduced into hair shampoo advertisements.

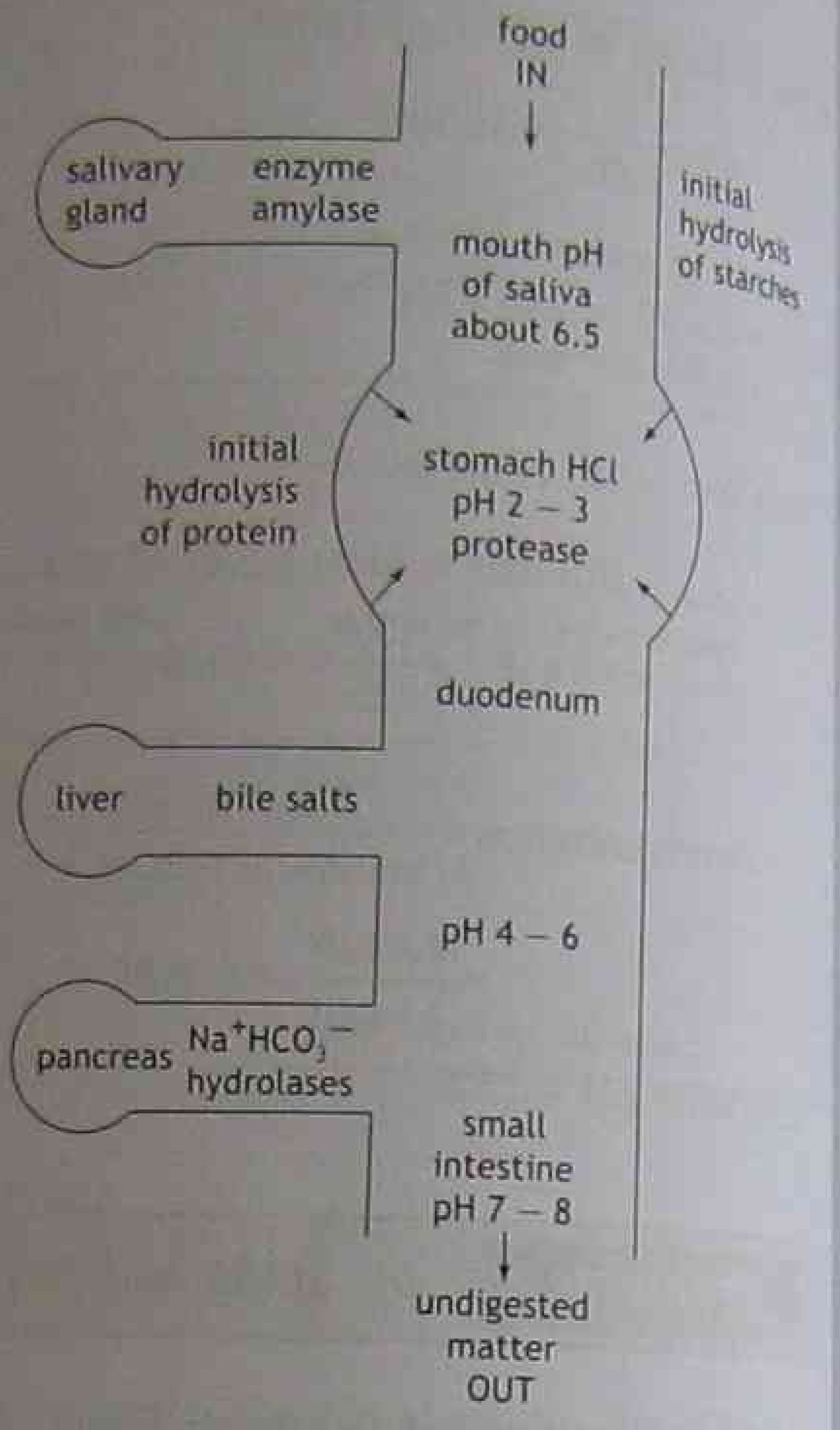


Figure 2.6 pH in the human digestive tract

Claims that pH control not only improves the cleansing of hair but also makes it shinier, bouncier and stronger are found in these advertisements. Most shampoos have a pH range of 4–7.5 for humans. Conditioners lie in the range of 2.6–4.8, all being acidic. Perhaps your class would like to test a variety of shampoos and conditioners using pH paper.

The cleansing power of a shampoo refers to its ability to remove grease, dirt and foreign material from the hair and scalp. A good shampoo should not remove all oils since this could cause scalp diseases.

Human skin has a natural acid layer on its surface with a pH range of 3–5. This is why conditioners are used after shampoos to restore the pH balance.

Shampoos can have the pH adjusted for special reasons. For example, for small children the pH is kept near 7 so that it will not cause eye irritation. Dog shampoos are much more alkaline with a pH as high as 8.7.

Many other substances such as antiperspirants and deodorants, mouthwashes, toothpastes and soaps all have a controlled pH.

2.18 Theories of acids and bases

The fact that all acids and all bases show certain characteristic chemical properties suggest that each class must show an essential feature. In 1779, *Antoine Lavoisier* proposed that acids were oxygen-containing substances.

However, careful studies by *Joseph Gay-Lussac* with hydrogen cyanide and *Sir Humphry Davy* wih hydrochloric acid showed that neither of the acids contained oxygen, so Lavoisier's theory was incorrect. Davy suggested that hydrogen was the one element present in all acids. It was subsequently shown that both acids and bases conduct electrical currents.

To explain this conduction, the Swedish chemist *Svante Arrhenius* proposed a theory in 1887 of 'electrolytic dissociation'. According to his theory:

- An acid is a substance which dissolves in water to produce hydrogen ions as the only positive ion in solution.
- A water soluble base is a substance which produces hydroxide ions as its only negative ion in solution.

Example

Acids	Ions produced
HCl CH_3COOH	H^+; Cl^- H^+; CH_3COO^-
Alkalis	**Ions produced**
NaOH KOH	Na^+; OH^- K^+; OH^-

This theory only applies to aqueous solutions.

In 1923, *Brønsted* and *Lowry* independently proposed that in all solvents:

- An acid is a substance which when in solution donates a proton (H^+ ion).
- A base is a substance which when in solution accepts a proton.

Since an acid is a proton donor, it must contain hydrogen atoms. Acidic solutions are formed when an acid transfers a proton to a water molecule.

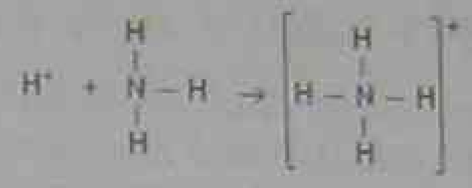
Example

$$\mathrm{HCl}(aq) + \mathrm{H_2O}(l) \rightarrow \mathrm{Cl^-}(aq) + \underset{\text{hydronium ion}}{[\mathrm{H_3O}]^+(aq)}$$

Since the proton is transferred from an acid to a base, acids and bases must exist in pairs which are called conjugate pairs. An acid-base reaction is therefore the transfer of a proton from an acid to a base.

Lewis proposed a definition of a base that emphasises the shared electron pair: an acid is an electron-pair acceptor and a base is an electron pair donor.

Example



$$H^+ + NH_3 \rightarrow [NH_4]^+$$

A Brønsted-Lowry base (a proton acceptor) is also a Lewis base (an electron-pair donor).

Acid - base pairs

$$\overbrace{\text{acid} + \underbrace{\mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+}}_{\text{conjugate pair}} + \text{base}}^{\text{conjugate pair}}$$

Example

$$\overbrace{\mathrm{HCN}(g) + \underbrace{\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq)}_{\text{conjugate pair}} + \mathrm{CN^-}(aq)}^{\text{conjugate pair}}$$

acid I + base II   acid II + base I

In the reaction, HCN loses a proton to form its conjugate base CN^- while H_2O gains a proton to form its conjugate acid H_3O^+ for the forward reaction.

Strength of acids and bases

The strength of an acid is measured by the concentration of H^+ ions or more precisely $[H_3O]^+$ ions in solution. Since many acid-base reactions are examples of equilibrium reactions in aqueous solutions, the concentration of H^+ ions produced is determined by the value of the equilibrium constant for that reaction.

Table 2.5 Conjugate pairs

Strength	Acid	Base
Strong (fully ionised in water)	H_2SO_4 HCl	HSO_4^- Cl^-
Weak (partly ionised in water)	CH_3COOH H_2CO_3 HSO_4^- NH_4^+	CH_3COO^- HCO_3^- SO_4^{2-} NH_3
Very weak	H_2O	OH^-

HCl is a strong acid. Its conjugate base is the Cl^- ion which is so weak that it is neutral when dissolved in water.

$$\underset{\text{acid I}}{CH_3COOH(aq)} + \underset{\text{base II}}{H_2O(l)} \rightleftharpoons \underset{\text{acid II}}{H_3O^+(aq)} + \underset{\text{base I}}{CH_3COO^-(aq)}$$

This reaction will go from left to right if acid I is stronger than acid II. If acid II is stronger than acid I then the reverse is the case.

In the Brønsted-Lowry Theory, acids can be ions as well as molecules.

Example

$$\underset{\text{acid I}}{HCO_3^-} + \underset{\text{base II}}{OH^-} \rightleftharpoons \underset{\text{acid II}}{H_2O} + \underset{\text{base I}}{CO_3^{2-}}$$

hydrogen carbonate ion

2.19 Amphiprotic ions and molecules

Amphiprotic ions

An amphiprotic ion is one which can act either as a base or as an acid, depending on which reaction takes place.

Example 1

$$\underset{\text{acid I}}{HCO_3^-} + \underset{\text{base II}}{H_2O} \rightleftharpoons \underset{\text{acid II}}{H_3O^+} + \underset{\text{base I}}{CO_3^{2-}}$$

Example 2

$$\underset{\text{base I}}{HCO_3^-} + \underset{\text{acid II}}{H_3O^+} \rightleftharpoons \underset{\text{base II}}{H_2O} + \underset{\text{acid I}}{H_2CO_3^{2-}}$$

Since the HCO_3^- ion is both the conjugate acid of the base CO_3^{2-} and the conjugate base of the acid H_2CO_3, it is said to be amphiprotic.

Amphiprotic molecule

Water as a base:
conjugate acid/base pair: H_3O^+/H_2O

$$\underset{\text{acid I}}{H_2SO_4} + \underset{\text{base II}}{H_2O} \rightleftharpoons \underset{\text{acid II}}{H_3O^+} + \underset{\text{base I}}{HSO_4^-}$$

Water as an acid:
conjugate acid/base pair: H_2O/OH^-

$$\underset{\text{base I}}{NH_3} + \underset{\text{acid II}}{H_2O} \rightleftharpoons \underset{\text{acid I}}{OH^-} + \underset{\text{base II}}{NH_4^+}$$

Bases

Bases are substances which can accept protons. They may be molecules, for example, NH_3 or ions, for example, OH^-, CO_3^{2-}.

2.20 The pH of various salts

Only a few common salts are neutral and the Brønsted-Lowry Theory can be used to explain the different pH values.

Note: To predict the pH for salts of weak acids/weak bases, the K_a and K_b must be known.

Salts formed from a strong base/weak acid

Example

Sodium acetate

The anion CH_3COO^- is a conjugate base so, in water

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

The free OH^- ions increase the pH to > 7, so aqueous solutions of sodium acetate are alkaline.

Salts formed from a strong acid/weak base

Example

Ammonium chloride

The cation is the conjugate acid of a weak base, NH_3, so in water

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$$

Since H^+ ions have been produced, the pH will be < 7, so solutions of ammonium chloride are acidic.

Salts formed from a strong acid/strong base

Example

Sodium chloride

No hydrolysis occurs, so pH = 7.

Salts formed from a weak acid/weak base

Example

Ammonium acetate

Both anion and cation will react with water

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

$$NH_4^+ + H_2O \rightleftharpoons H_3O^+ + NH_3$$

Since both anions and cations OH^- and H^+ are present, and in this case $K_a = K_b$, then the salt will have a pH = 7.

2.21 Volumetric analysis and titration

Volumetric analysis involves determining the volume of a solution of accurately known concentration (the standard solution)which is to react quantitatively with the solution being determined.

To be useful in volumetric analysis, a reaction should fulfil the following conditions:

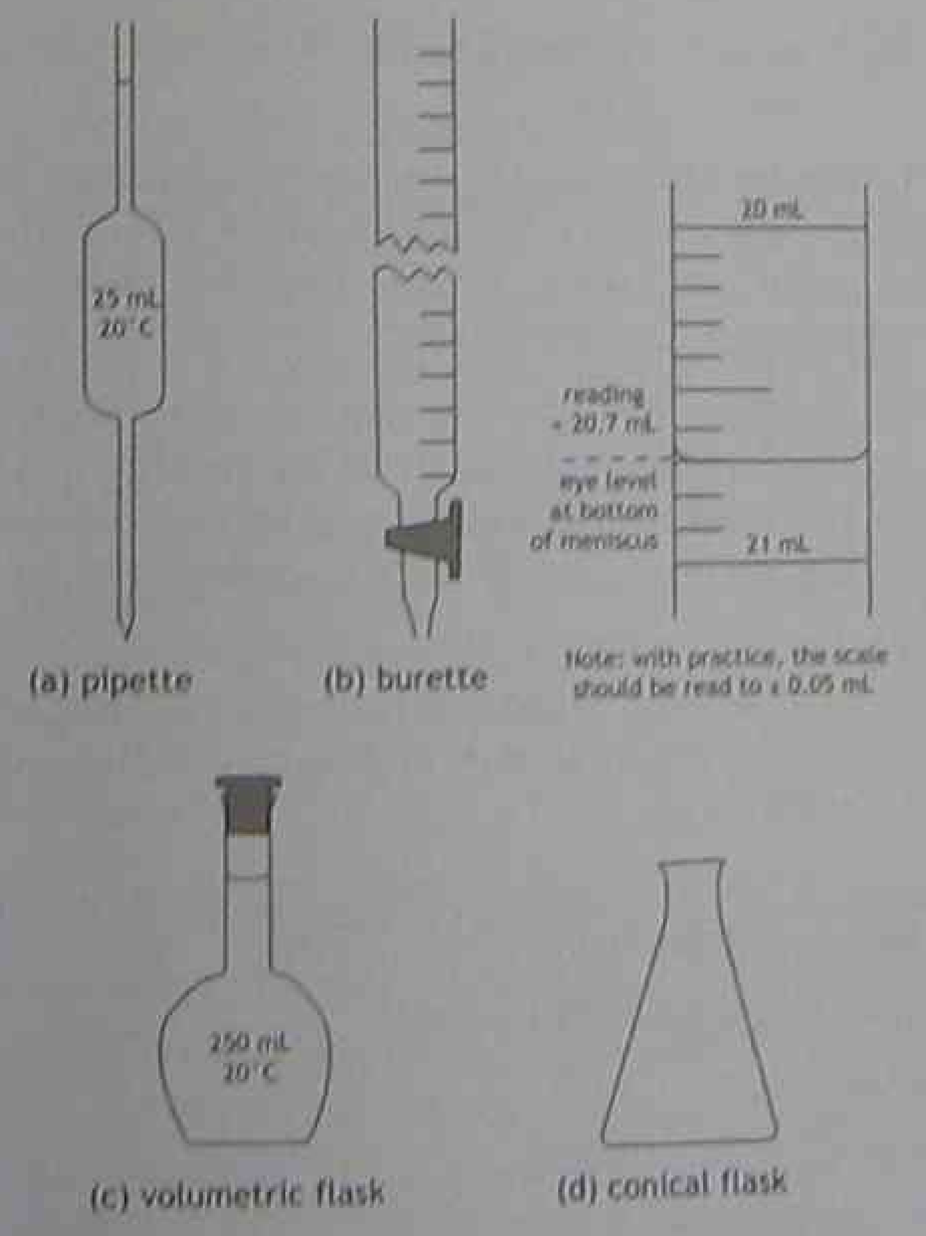
1. The reaction should be rapid.
2. The reaction should be in keeping with a chemical equation.
3. There must be a marked change at the equivalence point.
4. An indicator, or some other method, must be able to detect the change.

The procedure for carrying out a volumetric analysis is called titration.

Titration

In a titration, one reactant is placed in a conical flask and the other solution is delivered in a measured amount from a burette.

In determining the end point in titrations, an appropriate indicator must be used.



(a) pipette (b) burette

Note: with practice, the scale should be read to ± 0.05 mL

(c) volumetric flask (d) conical flask

Figure 2.7 Equipment used in titration. The volumetric and conical flasks are receiving vessels and are rinsed with distilled water.

Example 1

Bromothymol blue changes colour around a pH of 7 and can be used in strong acid/strong base titrations.

$$H_3O^+ + \underset{\text{blue}}{In^-} \rightarrow \underset{\text{yellow}}{HIn} + H_2O$$

Example 2

Phenolphthalein changes colour around a pH of 9 and can be used in weak acid/strong base titrations.

$$\underset{\text{colourless}}{HIn} + OH^- \rightarrow H_2O + \underset{\text{pink}}{In^-}$$

Example 3

Methyl orange changes colour around a pH of 4 and can be used in strong acid/weak base titrations.

Colour change: red → yellow

Because of the importance of practical work in volumetric analysis, the following 'worked' experiment has been included.

Figure 2.8 How to titrate

Experiment 1

The percentage of acetic acid in vinegar

The concentration of an unknown acid or basic solution can be found by titration with a solution of known concentration. The equivalence, or end-point of the titration, is marked by the colour change of a suitable indicator.

Special pieces of equipment are shown in Figure 2.7 and the method of titration is shown in Figure 2.8.

The pipette and burette are transfer vessels and must be rinsed before use with the solution you are going to transfer.

Aim:

To find the percentage of acetic (ethanoic acid) in white vinegar.

Method:

1. Rinse the burette with the 0.20 **M** sodium hydroxide solution. Fill the burette and record the volume reading.
2. Rinse the pipette with vinegar. Pipette a 10.00 mL vinegar sample into each of the conical flasks.
3. Add about 20 mL of distilled water to the flask to add to the volume.
4. Add 2 drops of the phenolphthalein indicator solution.
5. Titrate vinegar with the standard solution of sodium hydroxide, swirling and washing down the sides frequently with distilled water from the wash bottle. Add the sodium hydroxide dropwise when the endpoint is close. Titrate to the first pink permanent endpoint. Read the burette and record the result.
6. Repeat the titration until results agree to 0.1 mL (0.05 mL if possible).

Results:

Reading	1st titration	2nd titration
Final reading	30.9 mL NaOH	30.9 mL
Initial reading	0.0 mL NaOH	0.2 mL
Volume used	30.9 mL NaOH	30.7 mL
Average volume used		30.8 mL

Calculation:

Write a balanced equation for the reaction of NaOH and acetic acid.

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$

Mole ratio of NaOH : CH_3COOH = 1 : 1

No. of moles of NaOH $= 0.2 \times \frac{30.8}{1000} = 6.16 \times 10^{-3}$

No. of moles of $CH_3COOH = 6.16 \times 10^{-3}$

Molarity of $CH_3COOH = 6.16 \times 10^{-3} \times \frac{1000}{10} = 0.616$ **M**

No. of moles of CH_3COOH in 100 grams of vinegar $= 6.16 \times 10^{-2}$

Molar mass $CH_3COOH = 60.06$

Therefore, no. of grams of CH_3COOH in 100 grams of sample $= 6.16 \times 10^{-2} \times 60 = 3.7$ g.

(Assume that the densities of vinegar and water are the same – so 100 mL of vinegar weighs 100 grams)

So $\%CH_3COOH$ in vinegar = 3.70%

Note: Burettes filled with NaOH must be rinsed with water immediately after use.

2.22 Standardisation of solutions of acids and bases

Standardising solutions

This is carried out by using a *primary standard* which is a solid.

A primary standard has certain requirements:

(a) It should be easy to purify, dry and store in pure state.

(b) It should be unaffected by moisture in the air when it is being weighted.

(c) It should have a reasonably high molar mass so that weighing errors can be minimised.

(d) It should be readily soluble in water or a required solvent.

To standardise sodium hydroxide which cannot be used as a primary standard (since it absorbs moisture and carbon dioxide from the air), two methods are frequently used:

(a) Anhydrous Na_2CO_3 is used as the primary standard to determine the exact molarity of an HCl solution. The standardised HCl is then used in a titration with an NaOH solution.

(b) A solid organic acid, usually oxalic acid or benzoic acid, is used as the primary standard. This method is detailed in the following experiment.

Experiment 2

Titration, using a solid standard

Aim:

To standardise approximately 0.1 **M** NaOH using oxalic acid ($COOH.COOH.2H_2O$).

Method:

1. Weigh out accurately a sample of AR (analytical reagent purity) oxalic acid (0.15–0.2 g) onto a watch glass and transfer carefully (using a filter funnel and a camel-hair brush) into the titration flask. Rinse the watch glass into the flask using the wash bottle.
2. Add about 20 mL of water and swirl to dissolve the sample. Add 2–3 drops of indicator (phenolphthalein).
3. Fill the burette with the approx. 0.1 **M** NaOH and titrate to the first permanent pink colour, after recording the initial reading.
4. Record the final burette reading.
5. Repeat until the results agree to 0.1 mL.
6. Calculate the exact molarity of the NaOH.

Results:

Readings	1st titration	2nd titration	3rd titration
2nd reading of burette	20.0 mL	20.2 mL	20.0 mL
1st reading of burette	0.0 mL	0.1 mL	0.1 mL
Volume of NaOH used	20.0 mL	20.1 mL	19.9 mL
Average volume of NaOH used			20.0 mL
No. of grams of oxalic acid			0.15 g

Calculation:

When the molar mass of oxalic acid is calculated, the water of crystallisation must be included. Oxalic acid is a diprotic acid, so one mole of it will react with two moles of NaOH.

Write a balanced equation.

$$2NaOH + COOH.COOH \rightarrow COONa.COONa + 2H_2O$$

Mole ratio = 2 : 1

No. of moles of oxalic acid $= \frac{0.15}{126} = 1.19 \times 10^{-3}$

No. of moles of NaOH $= 2.38 \times 10^{-3}$

Molarity of NaOH $= 2.38 \times 10^{-3} \times \frac{1000}{20} = 0.12$ M

Remember: Rinse burette and pipette with the solution that will be used in them. Rinse conical flask and volumetric flask with distilled water.

Table 2.6 Choice of indicators

Titration	Indicator used	Salt formed
Weak base/strong acid Na_2CO_3/HCl	methyl orange pH 3.1 – 4.4	in this case NaCl + H_2CO_3 (H_2O + CO_2), acidic
Strong base/strong acid NaOH/HCl	bromothymol blue pH 6.0 – 7.6	NaCl, neutral salt, no hydrolysis, pH = 7
Weak acid/strong base CH_3COOH/NaOH	phenolphthalein pH 8.3 – 10.0	CH_3COONa, basic salt, hydrolysis, $CH_3COO^- + H_2O \rightarrow OH^- + CH_3COOH$, pH > 7
Weak base/strong acid NH_3/HCl	methyl red pH 4.4 – 6.2 or methyl orange	NH_4Cl, acidic salt, pH < 7, $NH_4^+ + H_2O \rightarrow NH_3 + H_3O^+$
Weak base/weak acid	bromothymol blue	pH = 7

2.23 Typical problems in volumetric analysis

In volumetric analysis, one mole of solid is its molar mass in grams. A one molar solution is the molar mass of the solid in grams dissolved in a litre of solution. (Expressed as 1 **M** or 1 $molL^{-1}$)

Various substances are used as primary standards:

(a) Anhydrous sodium carbonate is often used to standardise strong acids such as HCl and H_2SO_4 using methyl orange as indicator. (Methyl orange is not affected by any H_2CO_3 formed.)

(b) Oxalic acid $(COOH)_2.2H_2O$ is used to standardise strong alkalis, for example, NaOH, KOH.

Other organic acids or acid salts used are benzoic acid C_6H_5COOH (solution in alcohol) or potassium hydrogen phthalate ($KHC_8H_4O_4$). In all cases the indicator used is phenolphthalein.

Example 1

How much anhydrous sodium carbonate would you weigh out to make up 500 mL of a 0.01 **M** solution?

Step 1. Find the molar mass of Na_2CO_3, which is 106 g.

Step 2. Find the no. of moles in 500 mL of a 0.01 **M** solution.

$$\text{No. of moles} = \mathbf{M} \times \frac{\text{V mL}}{1000}$$
$$= 0.01 \times \frac{500}{1000}$$
$$= 0.005$$

Step 3. Find the no. of grams.

$$\text{No. of grams} = \text{no. of moles} \times \text{molar mass}$$
$$= 0.0005 \times 106$$
$$= 0.53\text{ g}$$

Example 2

How many (a) moles and (b) grams are there in 100 mL of a 0.01 **M** solution of sodium hydroxide?

Step 1. Find the molar mass of NaOH. It is 40 g.

Step 2. Find the no. of moles present.

$$\text{No. of moles} = \mathbf{M} \times \frac{\text{V mL}}{1000}$$
$$= 0.01 \times \frac{100}{1000}$$
$$= 0.001$$

Step 3. Find the no. of grams.

$$\text{No. of grams} = \text{no. of moles} \times \text{molar mass}$$
$$= 0.04\text{ g}$$

In each of the following problems, find
(a) the moles, and (b) the grams present

Problem 1

500 mL of a 2 **M** solution of anhydrous sodium hydrogen carbonate.

Answer: (a) 1 mole, (b) 84.01 g.

Problem 2

500 mL of a 0.01 **M** solution of anhydrous sodium carbonate.

Answer: (a) 0.005 mole, (b) 5.3 g.

Problem 3

100 mL of a 0.2 **M** solution of anhydrous calcium hydroxide.

Answer: (a) 0.02 mole, (b) 1.48 g.

Example 3

Dilution

How many mL of water must be added to dilute 100 mL of a 0.2 **M** solution of HCl to a 0.01 **M** solution?

$$\mathbf{M}_1\text{V}_1 = \mathbf{M}_2\text{V}_2, \text{ where } \mathbf{M} \text{ is molarity.}$$
$$0.2 \times 100 = 0.01\text{ V}_2, \text{ where V is volume (mL)}$$
$$\text{V}_2 = 2000\text{ mL}$$
$$\text{Amount of water added} = \text{V}_2 - \text{V}_1$$
$$= 2000 - 100 = 1900\text{ mL} = 1.9\text{ L}$$

Example 4

Neutralisation

What volume of 0.1 **M** NaOH will just neutralise 25 mL of 0.08 **M** H_2SO_4?

Step 1. Write word equation

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

Step 2. Find mole ratio.

$$\frac{H_2SO_4}{NaOH} = \frac{1}{2}$$

Step 3. Find the no. of moles of H_2SO_4.

$$= 0.08 \times \frac{25}{1000} \qquad \text{(a)}$$

Step 4. Find the no. of moles of NaOH.

$$= 0.1 \times \frac{x}{1000} \qquad \text{(b)}$$

Step 5. Divide (a) by (b). i.e. $\frac{1}{2} = \frac{0.08 \times 25}{0.1 \times x}$

Step 6. Solve for x. i.e. $x = \frac{0.08 \times 25 \times 2}{0.1} = 40\text{ mL}$

Volume of 0.1 **M** NaOH needed is 40 mL.

Example 5

When one reagent is a solid

Find the molarity of HCl if 24 mL reacts completely with 0.207 g of sodium carbonate.

Step 1. Write equation.

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

Step 2. The number of moles of solid $= \frac{0.207}{106}$

Step 3. Find the mole ratio.
1 mole of Na_2CO_3 uses 2 moles HCl.

Step 4. No. of moles of HCl $= 2 \times \frac{0.207}{106}$

Step 5. Find molarity of HCl.

$$\text{No. of moles} = \mathbf{M} \times \frac{\text{V mL}}{1000}$$
$$\text{Molarity of HCl} = 2 \times \frac{0.207}{106} \times \frac{1000}{24}$$
$$= 0.163\text{ M}$$

Problems on volumetric analysis

1. Find the mass of sodium hydrogen carbonate needed to make up 250 mL of a 0.02 **M** solution.
2. Find the mass of benzoic acid needed to make up 500 mL of a 0.05 **M** solution.
3. Find the mass of COOH–COOH.$2H_2O$ needed to make up 100 mL of a 0.05 **M** solution?
4. How many mL of water must be added to dilute 20 mL of 5 **M** sulfuric acid to 0.1 **M**?
5. What volume of 0.1 **M** NaOH would neutralise 25 mL of 0.05 **M** HCl?
6. What volume of 0.08 **M** sulfuric acid is needed to neutralise 20 mL of 0.05 **M** NaOH?
7. Find the molarity of potassium hydroxide if 47.8 mL of it reacts completely with 0.26 g of oxalic acid $(COOH)_2.2H_2O$.
8. Find the molarity of the potassium hydroxide if 26.3 mL of it reacts with 0.15 g of benzoic acid (C_6H_5COOH) dissolved in ethanol.

Harder problems

9. 0.52 g of calcium carbonate was dissolved in 35 mL of HCl of unknown molarity. After all reaction had ceased and any CO_2 was removed by boiling, the sample was cooled. Methyl red was added and the solution was titrated with 0.1 **M** NaOH. 22.3 mL was needed to reach the endpoint. Find the molarity of the HCl.
10. What volume of 0.02 **M** sulfuric acid would be needed to neutralise a solution made by mixing 20 mL of 0.01 **M** calcium hydroxide and 30 mL of 0.03 **M** sodium hydroxide?

Answers to problems on volumetric analysis

1. $NaHCO_3$; molar mass = 84.
   No. of grams needed = 84 × 0.02 × 250/1000 = 0.42 g
2. C_6H_5COOH; molar mass = 122.
   No. of grams needed = 122 × 0.05 × 500/1000 = 3.05 g
3. COOH.COOH.$2H_2O$; molar mass = 126.
   No. of grams needed = 126 × 0.05 × 100/1000 = 0.63 g
4. $V_2 = 20 \times 5/0.1 = 1000$ mL.
   Water added = 1000 – 20 = 980 mL.
5. Mole ratio NaOH : HCl = 1:1
   $1 = (x \times 0.1)/(25 \times 0.05)$, so $x = 12.5$ mL.
6. Mole ratio H_2SO_4 : NaOH = 1:2
   $\frac{1}{2} = (x \times 0.08)/(20 \times 0.05)$, so $x = 6.25$ mL.
7. Mole ratio KOH : oxalic acid = 2:1
   No. of moles of oxalic acid = 0.26/126 = 2.06×10^{-3}
   Number of moles of KOH = 4.13×10^{-3}
   Number of moles = M × V/1000 = 4.13×10^{-3}
   = M × 47.8/1000
   Molarity of KOH = 0.09 **M**
8. Mole ratio KOH : C_6H_5COOH = 1:1
   Number of moles of $C_6H_5COOH = 1.23 \times 10^{-3}$
   Number of moles of KOH = 1.23×10^{-3}
   Molarity of KOH = $1000 \times 1.23 \times 10^{-3} \div 26.3$
   = 0.047 **M**
9. $CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$
   Mole ratio $CaCO_3$: HCl = 1:2
   To find the number of moles of excess HCl after reaction with $CaCO_3$:
   Mole ratio NaOH : HCl = 1:1
   Number of moles of NaOH = 0.1 × 22.3/1000
   = 2.23×10^{-3}
   Number of moles of HCl = 2.23×10^{-3}
   Number of moles of $CaCO_3$ used = 0.52/100 = 0.0052
   Number of moles of HCl used to react with 0.0052 moles of $CaCO_3$ = 2 × 0.0052 = 0.0104
   Total number of moles of HCl = 0.0126
   = M × 35/1000
   So molarity of HCl = 0.36 **M**.
10. Volume of 0.02 **M** H_2SO_4 used to neutralise 20 mL of 0.01 **M** $Ca(OH)_2$:
    Mole ratio H_2SO_4 : $Ca(OH)_2$ = 1:1
    = $(0.02 \times x)/(0.01 \times 20)$
    Therefore, $x = 10$ mL
    Volume of 0.02 **M** H_2SO_4 used to neutralise 30 mL of 0.03 **M** NaOH:
    Mole ratio H_2SO_4 : NaOH = 1:2
    = $(0.02 \times y)/(30 \times 0.03)$
    Therefore, $y = 22.5$ mL
    Total volume of 0.02 **M** H_2SO_4 = 32.5 mL.

Calculations

Example 1

Find the molarity of a 20.00 mL HCl solution that needs 25.00 mL of a 0.05 **M** Na_2CO_3 for neutralisation using methyl orange as indicator.

Step 1. Write equation.

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

Step 2. Mole ratio $= \frac{Na_2CO_3}{HCl} = \frac{1}{2}$

Step 3. No. of moles = molarity (M) $\times \frac{\text{vol. in mL (V)}}{1000}$

No. of moles of $Na_2CO_3 = 0.050 \times \frac{25.00}{1000}$

No. of moles of $HCl = X \times \frac{20.00}{1000}$

Step 4. Mole ratio $= \frac{1}{2} = \frac{0.050 \times 25.00}{X \times 20.00}$

Step 5. $X = \frac{2 \times 0.050 \times 25.00}{20.00} = 0.125\ M$

So the molarity of HCl is 0.125 **M**.

Example 2

Find the molarity of a solution of NaOH if 20.00 mL of it reacts completely with 0.122 g of benzoic acid (C_6H_5COOH) dissolved in ethanol using phenolphthalein as indicator.

Step 1. Equation:

$$NaOH + C_6H_5COOH \rightarrow C_6H_5COONa + H_2O$$

Step 2. Mole ratio $= \frac{NaOH}{C_6H_5COOH} = \frac{1}{1}$

Step 3. Molar mass of acid = 122

Step 4. No. of moles of benzoic acid

$= \frac{\text{mass}}{\text{molar mass}} = \frac{0.122}{122}$

Step 5. From the mole ratio

No. of moles of NaOH $= \frac{0.122}{122}$

Step 6. No. of moles = molarity $\times \frac{\text{vol. in mL}}{1000}$

$\frac{0.122}{122} = M \times \frac{20.00}{1000} = 0.05\ M$

So molarity of NaOH = 0.050 **M**.

2.24 Titration curves

Accurate acid/base titration curves can be obtained using a pH meter (see Figures 2.9–2.12).

Strong acid/strong base titrations

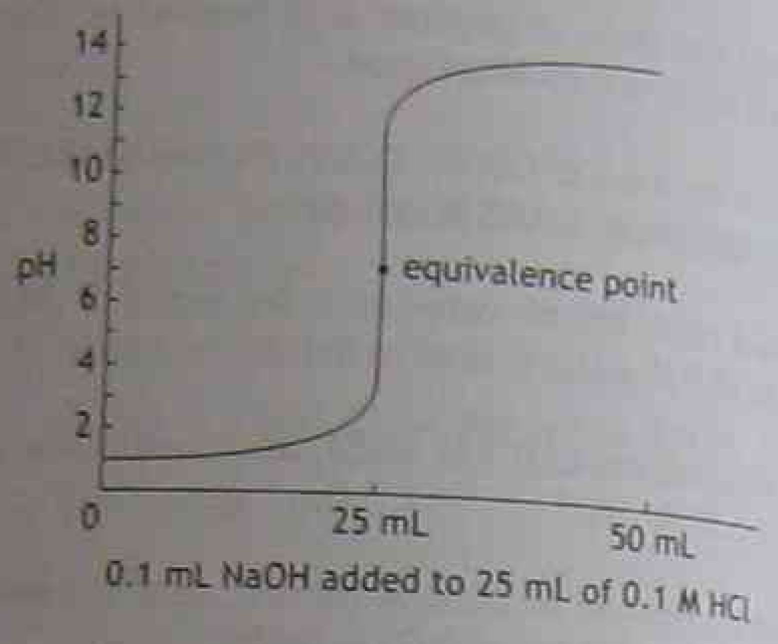


Figure 2.9 Titration of strong acid by strong base

From the graphs of titrations involving a strong acid/strong base (Figures 2.9 and 2.10) it can be seen that any indicator in Table 2.6 could be used.

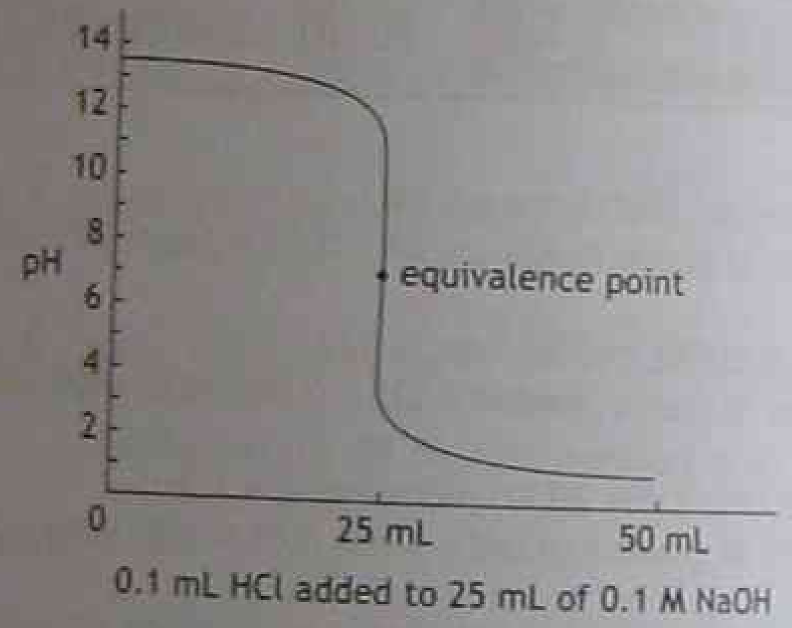


Figure 2.10 Titration of strong base by strong acid

Strong acid/weak base

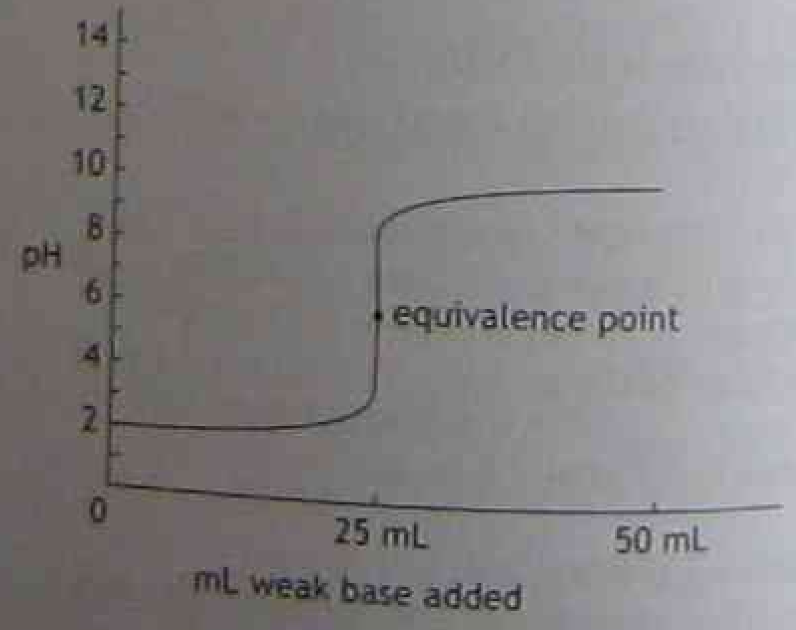


Figure 2.11 Titration of strong acid by weak base

pH range 4.5–8.0, so only methyl red or bromothymol blue are suitable

Weak acid/strong base

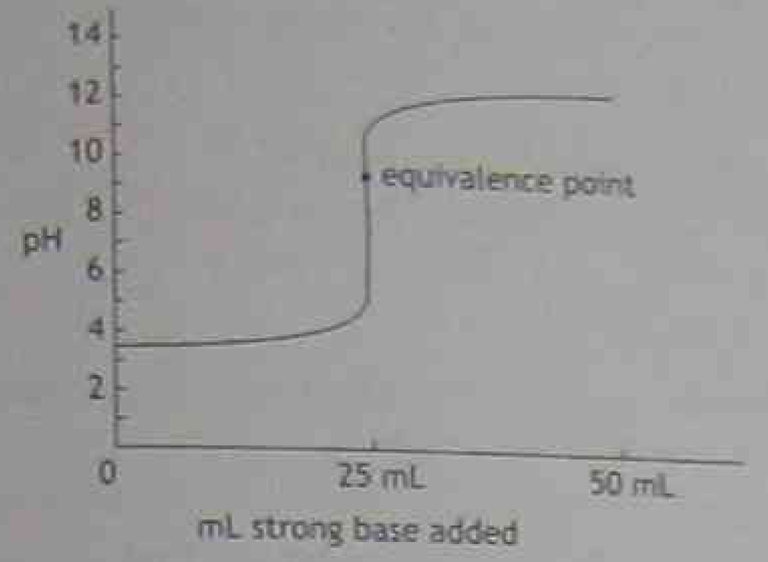


Figure 2.12 Titration of weak acid by strong base

pH range 7–11, so only phenolphthalein can be used.

2.25 Worked experiments in titration on commercial products

The following experiments are aimed at helping you with revision, but it is essential that you also carry out first-hand investigations on a variety of commercial acidic or alkaline substances.

Experiment 3

Analysis of white vinegar

Aim:

To carry out a titration on white vinegar to determine whether consumer laws, that vinegar should contain at least 40.0 g L^{-1} of acetic acid, are being obeyed.

Method:

1. Collect about 20 mL of vinegar and about 150 mL of standardised 0.10 **M** NaOH, using separate clean, dry beakers.
2. Using a graduated pipette, transfer 5.00 mL of vinegar to each of three clean conical flasks labelled A, B and C.
3. Add about 30 mL of distilled water and 2 drops of phenolphthalein to flasks A, B and C. Titrate each in turn with sodium hydroxide from the burette until the first permanent pink colour is reached.
Record the initial and final readings from the burette for each titration.

Results:

(See following table.)

Reading	Conical flask		
	A	B	C
Initial burette (mL)	0.00	0.00	0.00
Final burette (mL)	34.5	33.9	33.9

Calculations:

1. For flasks A, B and C calculate the volume of sodium hydroxide used in each titration and also the average volume.

Reading	Conical flask		
	A	B	C
Volume of NaOH used (mL)	34.5	33.9	33.9
Av. volume of NaOH used (mL)	do not use	33.9	

2. Calculate the average number of moles of NaOH used.

   = litres of solution (average) × molarity
   $= 3.39 \times 10^{-3}$

3. The equation for the reaction is

   $$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

   Calculate the average number of moles of acetic acid used in each titration
   $= 3.39 \times 10^{-3}$

4. Calculate the concentration of the acetic acid solution

   $= \frac{3.39}{5} = 0.678\ M$

5. Calculate the mass of acetic acid present in one litre of vinegar
   $= 40.7\ g\ L^{-1}$ (molar mass $CH_3COOH = 60$)

Discussion:

1. In Step 3 of the Method:
   (a) 'about 30 mL of distilled water' is added to the vinegar. Why is it unnecessary to measure this volume accurately? We only need to know the volume of vinegar present.
   (b) '2 drops of phenolphthalein' are added. Why would a large amount of added phenolphthalein increase the titration volume?

   $$HIn \rightleftharpoons H^+ + In^-$$

   Large amount of H^+ will result in more NaOH being needed for neutralisation.

2. Consumer laws require vinegar to contain at least 40.0 g L^{-1} of acetic acid. Does this brand of vinegar meet these requirements?

   Yes. 40.7 g L^{-1} present.

3. Why must the correct indicator, in this case phenolphthalein, be used? The indicator used must change colour at the equivalence point.

Experiment 4

Analysis of aspirin tablets

Aim:

To carry out a titration using dissolved aspirin tablet to see whether the manufacturer's claim, that each tablet contains a minimum of 300 mg of aspirin, is valid.

Method:

1. Place an aspirin tablet into each of three clean conical flasks labelled A, B and C. To each flask add about 30 mL of distilled water and 5 mL of ethanol.
2. Warm the flasks gently to help the tablets dissolve, then let them cool. (The solution is cloudy due to starch from the tablet.)
3. Add 2 drops of phenolphthalein to flask A, then titrate with the 0.120 **M** sodium hydroxide solution from the burette until the first permanent pink colour is reached. Record the initial and final readings from the burette.
4. Perform similar titrations with flasks B and C, refilling the burette each time.

Results:

Reading	Conical flask		
	A	B	C
Initial burette (mL)	0.00	0.00	0.00
Final burette (mL)	15.50	15.00	15.00

Calculations:

1. Calculate the volume of sodium hydroxide solution used in each titration and also the average volume. Only take the average of concordant titres.

Reading	Conical flask		
	A	B	C
Volume of NaOH used (mL)	do not use	15.00	15.00
Av. volume of NaOH used (mL)	15.00		

2. Calculate the average number of moles of NaOH used
   = litres of solution (average) × molarity
   = 1.80×10^{-3}

3. The equation for the reaction is

$$\underset{\text{aspirin}}{HC_9H_7O_4} + NaOH \rightarrow \underset{\text{Disprin}}{NaC_9H_7O_4} + H_2O$$

   Calculate:

   (a) the number of moles of aspirin present in one tablet
   = 1.80×10^{-3}

   (b) the average mass of aspirin present in one tablet
   = 324 mg (molar mass = 180)

Discussion:

1. The manufacturer's label states that each tablet contains a minimum of 300 mg of aspirin.
   (a) Do your results support this claim? Yes
   (b) Weigh one tablet and calculate what fraction of the tablet is pure aspirin. (0.38 g, 85%)
2. Briefly explain why disprin could not be analysed by titration using sodium hydroxide.
   Disprin is a sodium salt, not an acid.

Experiment 5 (extension work)

Molar heat of neutralisation

Aim:

To describe the molar heat of neutralisation in a stoichiometric reaction

At the stoichiometric point where neither reagent is in excess, neutralisation will have occurred and the rise in temperature can be used to calculate the molar heat of neutralisation. A set of experimentally determined results are included.

Method:

1. Set up two burettes, one containing 1.0 M NaOH solution and the other containing 1.0 M HNO_3 solution. Record the temperatures of each solution (to 0.1°C).
2. Add 4.0 mL of the NaOH into a clean dry styrofoam cup. Add 16.0 mL of nitric acid and stir to mix before recording the highest temperatures reached.
3. Clean and dry cup and repeat Steps 1 and 2 for each of the pairs of NaOH and HNO_3 in the results table. The total volume of any mixture of 20.0 mL.

Results:

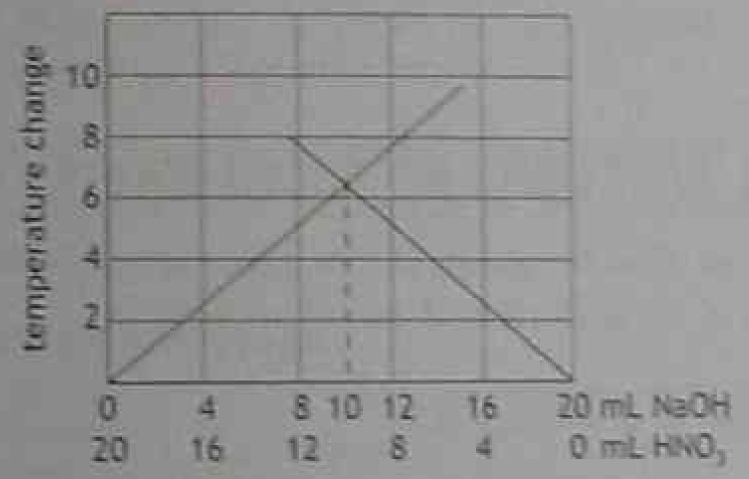
Volume 1.0 **M** NaOH (mL)	4.0	8.0	10.0	12.0	16.0
Temperature 1.0 **M** NaOH (°C)	20.6 →				
Volume 1.0 **M** HNO_3 (mL)	16.0	12.0	10.0	8.0	4.0
Temperature 1.0 **M** HNO_3 (°C)	20.6 →				
Final temperature (°C)	23.4	25.8	27.0	26.2	23.6

Calculations:

1. Calculate the temperature change for each mixture. (If the initial temperatures were not equal, use an average temperature for your calculations.)

Volume 1.0 **M** NaOH (mL)	4.0	8.0	10.0	12.0	16.0
Volume 1.0 **M** HNO_3 (mL)	16.0	12.0	10.0	8.0	4.0
Temperature change (°C)	2.80	5.20	6.20	5.60	3.00

2. Plot these results on the grid provided with temperature change on the vertical axis. (The two end points should be included.)



3. Draw two lines of best fit and measure the coordinates of their point of intersection.

   At point of intersection
   Volume of NaOH = 10.0 mL
   Volume of HNO_3 = 10.0 mL
   Temperature change ΔT = 6.2°C

4. At this intersection point the amount of reaction is greatest because the two reactants are in their correct proportions, i.e. neither is in excess. This is called the *stoichiometric point*. For this stoichiometric point, evaluate

   (a) moles of $NaOH(aq)$ = 0.010 mol
   (b) moles of $HNO_3(aq)$ = 0.010 mol

   Use the mole ratio at the stoichiometric point to write a balanced equation (including states) for this reaction.

   $NaOH(aq) + HNO_3(aq) \rightarrow NaNO_3(aq) + H_2O(l)$

5. Calculate the amount of heat energy produced at the stoichiometric point using
   Heat energy = $M_{H_2O} \times 4.18 \times \Delta T$
   = $20.0 \times 4.18 \times 6.20$
   = 520 J

6. Calculate the enthalpy change for one mole quantities of the two compounds in the reaction.
   $\Delta H = -52 \text{ kJ mol}^{-1}$

7. Write the thermochemical equation for the reaction.
   $NaOH(aq) + HNO_3(aq) \rightarrow NaNO_3(aq) + H_2O(l)$
   $\Delta H = -52 \text{ kJ mol}^{-1}$

Discussion:

The listed value for the enthalpy change in this reaction is −55.8 kJ. Compare this with your value and suggest reasons for any difference.

Heat loss to the surroundings.

2.26 The effect of buffers in a natural system – blood

Many aqueous solutions resist a change in pH on addition of small amounts of an acid or a base. Such solutions are called buffer solutions.

A buffer is a mixture of a weak acid and its conjugate base. Human blood is a complex aqueous medium which is buffered at about 7.4. Death results if the pH falls below 7.0 or rises above 7.8. The blood contains several buffers, including H_2CO_3–HCO_3^-, $H_2PO_4^-$ – HPO_4^{2-} and the complex buffering system involving haemoglobin, a protein present in red blood cells.

Haemoglobin and oxyhaemoglobin (both bases) form their conjugate acids. Oxygen in the blood is carried by the large haemoglobin molecule and our oxygen fixing system depends on the chemical equilibrium

$$\text{haemoglobin} + \text{oxygen} \rightleftharpoons \text{oxyhaemoglobin}$$

Haemoglobin (Hb) is involved in a series of equilibria whose overall result is

$$HbH^+(aq) + O_2(aq) \rightleftharpoons HbO_2(aq) + H^+(aq)$$

Acidosis (pH of blood < 7.4) and alkalosis (pH of blood > 7.4) cause the mechanisms by which haemoglobin transports oxygen in the blood to be disrupted. In acidosis, the equilibrium shifts to the left and the ability to form oxyhaemoglobin (HbO_2) is decreased. The reduced supply of oxygen to body cells causes fatigue and headaches. Acidosis is the more common tendency, because ordinary metabolism produces several acids. Temporary acidosis occurs during strenuous exercise, when energy demands exceed the oxygen available for the complete oxidation of glucose to CO_2. The glucose is converted to the acidic metabolism product lactic acid.

> **Note 1:** The natural buffer system involves haemoglobin and oxyhaemoglobin, which are both bases, with their conjugate acids. An interplay between these acid-base pairs enables CO_2 to be transported in venous blood and released in the lungs.
>
> **Note 2:** Arterial blood coming from the left ventricle is bright red and loaded with oxygen. About 86% of the oxyhaemoglobin is in its 'basic' form and 14% of its 'acidic' form. Venous blood, returning to the right atrium of the heart, is dark blue deoxygenated blood; only about 14% of the haemoglobin is in its 'basic' form and 86% is in its 'acidic' form.

The haemoglobin buffer system can be represented

as $\frac{\text{haemoglobinate}^-}{\text{H}-\text{haemoglobin}}$.

The oxyhaemoglobin buffer system can be represented as $\frac{\text{oxyhaemoglobinate}^-}{\text{H}-\text{oxyhaemoglobin}}$.

The major *extracellular system* in the blood is the bicarbonate system (H_2CO_3/HCO_3^-).

Equilibria

$$H^+(aq) + HCO_3^-(aq) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons H_2O(l) + CO_2(g)$$

To maintain the blood pH at 7.4 requires the H_2CO_3/HCO_3^- ratio to be 1:20. HCO_3^- is an important base in the blood.

When acid is added to the blood

$$HA + HCO_3^- \rightarrow H_2CO_3 + A^-$$

and the ratio will rise. As this happens, CO_2 is expelled more rapidly from the lungs from the decomposition of

$$H_2CO_3(aq) \rightarrow H_2O(l) + CO_2(g)$$

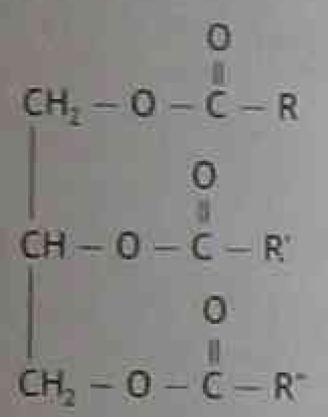
so that as more acid is added to the blood, more of the blood acid H_2CO_3 is decomposed and excreted through the lung as $CO_2(g)$. In this way, relatively large amounts of acid can be added to the blood without changing appreciably the 1:20 ratio of $H_2CO_3 : HCO_3^-$.

2.27 The naturally-occurring esters

Esters are used widely as artificial flavourings, for example, in jellies and in cosmetics. Esters are also excellent solvents and are used in nail-polish removers and in lacquers.

Animal fats and vegetable oils are naturally occurring esters. They are formed from glycerol (1,2,3-propantriol) and a single fatty acid or a mixture of fatty acids. These esters are called triglycerides.

General formula for triglycerides



$$\begin{array}{l} CH_2-O-\overset{O}{\overset{\|}{C}}-R \\ \quad | \\ CH-O-\overset{O}{\overset{\|}{C}}-R' \\ \quad | \\ CH_2-O-\overset{O}{\overset{\|}{C}}-R'' \end{array}$$

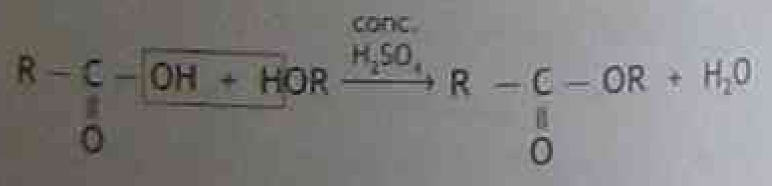
2.28 Artificially produced esters

Esters can also be made in the laboratory by the reaction of an alkanol and an alkanoic acid.

Preparation of artificial esters

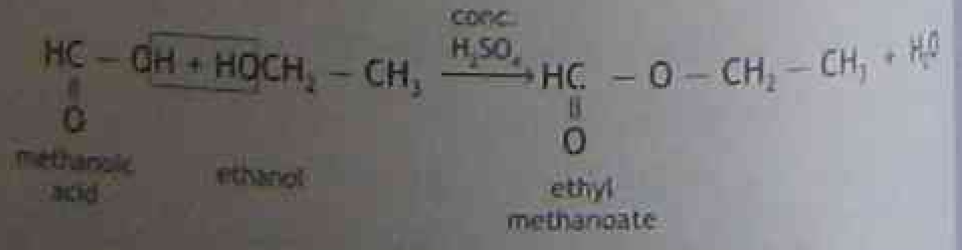
Esters are prepared by the reaction of an alkanoic acid and an alkanol in the presence of concentrated H_2SO_4 which acts as a dehydrating agent and removes water formed.

General equation



$$R-\underset{\underset{O}{\|}}{C}-\boxed{OH + HO}R \xrightarrow{\text{conc. } H_2SO_4} R-\underset{\underset{O}{\|}}{C}-OR + H_2O$$

Example

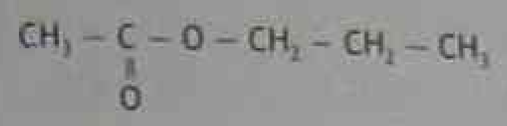


$$HC-\boxed{OH + HO}CH_2-CH_3 \xrightarrow{\text{conc. } H_2SO_4} HC-O-CH_2-CH_3 + H_2O$$

Naming

The 'surname' ending in -oate comes from the acid. The 'first name' is the alkyl group which comes from the alkanol. The acid part of the formula is, however, written first and is followed by the alkyl group.

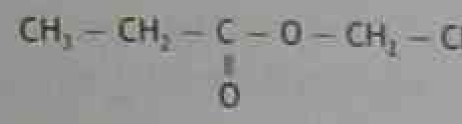
Example 1



$$CH_3-\underset{\underset{O}{\|}}{C}-O-CH_2-CH_2-CH_3$$

is called 1-propyl ethanoate.

Example 2



$$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-O-CH_2-CH_3$$

is called ethyl propanoate.

Distillation and refluxing methods

An esterification reaction is an example of an equilibrium reaction. If the amount of water present is minimised (by use of conc. H_2SO_4) and if an excess of one reactant (alkanol or carboxylic acid) is used, then the reaction will favour the formation of the ester. (In manufacturing esters, the cheaper reactant is used in excess.)

The reaction mixture is often heated in a vessel with a cooling condenser attached to prevent loss of any volatile reactant or product. This process is called refluxing (see Figure 2.13).

The process used to collect the ester varies with the boiling points of the reactants and products (Table 2.7).

Table 2.7 Boiling points

Alkanoic acids	BP (°C)	Alkanols	BP (°C)	Esters	BP (°C)
methanoic acid	100	methanol	65	methyl methanoate	32
ethanoic acid	118	ethanol	78	methyl ethanoate	57
propanoic acid	141	1-propanol	97	ethyl ethanoate	77
butanoic acid	164	1-butanol	117	ethyl propanoate	99
pentanoic acid	186	1-pentanol	138	propyl ethanoate	102
				butyl ethanoate	126.5

When the boiling point of the ester formed is lower than that of the reactants, distillation can follow refluxing, e.g. methyl ethanoate. If the boiling point of the ester is relatively high then, after refluxing, the contents fo the flask may be transferred to a separating funnel and Na_2CO_3 soln is gradually added to remove excess acid. After the layers have separated, the lower (aqueous layer) is discarded. The layer containing the ester is then distilled (see Figure 2.14), e.g. ethyl propanoate (B.P. 99°C).

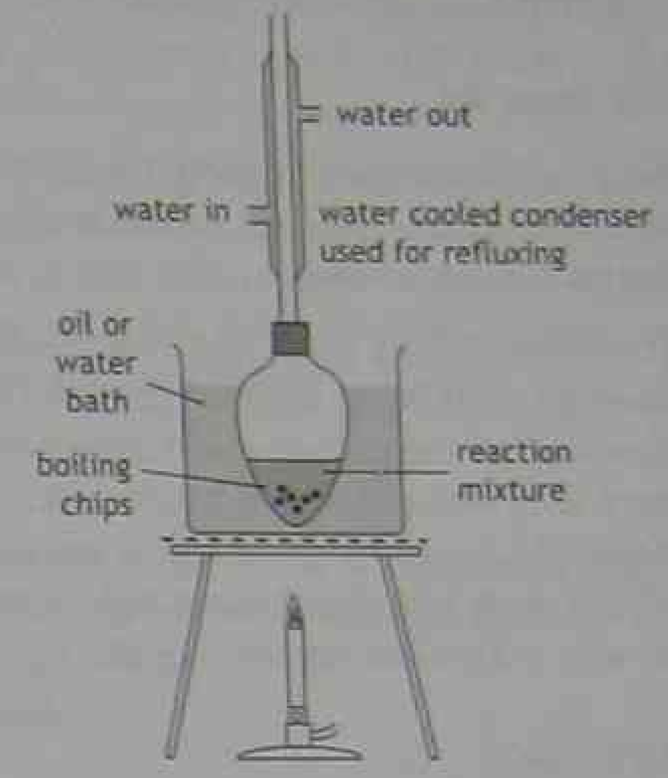


Figure 2.13 Refluxing mixtures

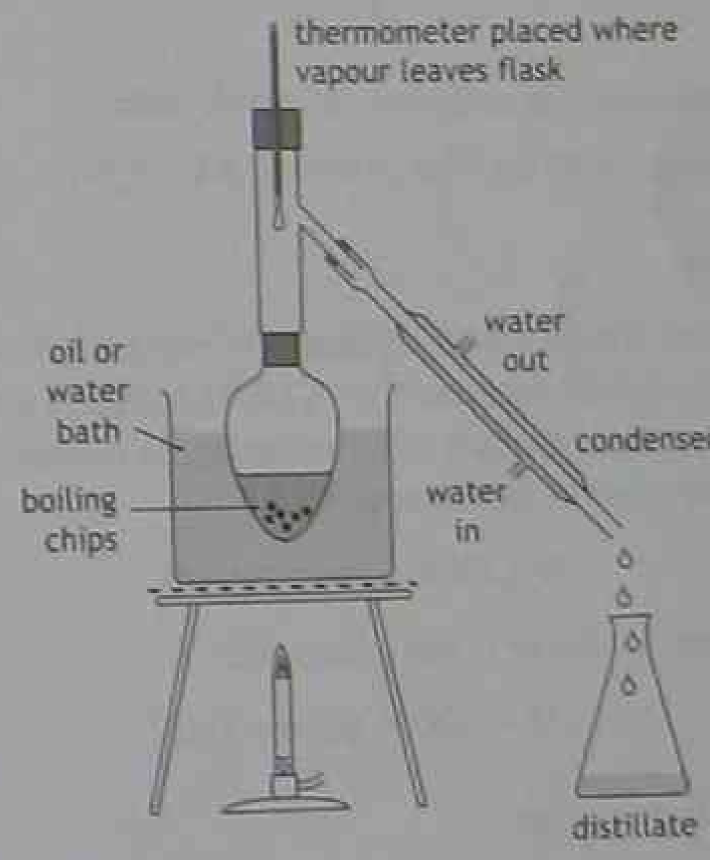


Figure 2.14 Distilling mixtures

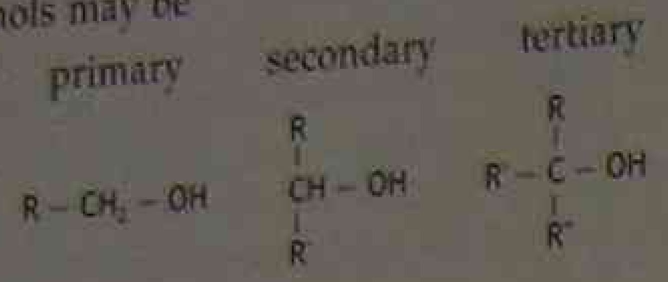
Alkanols (alcohols)

General molecular formula

$C_nH_{2n+2}O$; first member CH_3OH methanol

Alkanols are alcohols which are formed from alkanes. Alcohols refer to a wider group of compounds which all contain an –OH group. For example, cholesterol is an alcohol.

Alkanols may be



$R-CH_2-OH$ $\quad$ $\overset{R}{\underset{R'}{CH}}-OH$ $\quad$ $R'-\overset{R}{\underset{R''}{C}}-OH$

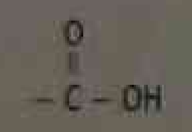
where R– is any alkyl group.

Physical properties

1. Because of hydrogen bonding, the alkanols have much higher boiling points than the corresponding alkanes.
2. The molecules are polar and this results in the lower alkanols being soluble (miscible) in water. However, as the carbon chain becomes longer, since it is non-polar, the higher alkanols are insoluble in water. Ethanol is an excellent solvent since it is miscible not only with water, but also with some organic liquids, e.g. ethers.

Alkanoic acids

If any alkyl group is attached to the functional group



$-\overset{O}{\overset{\|}{C}}-OH$

the substance is called an alkanoic acid.

The general molecular formula is $C_nH_{2n}O_2$.

Naming

The -e of the alkane is replaced by -oic and the word acid is added. Because the –COOH group is always on a terminal carbon, no numbering is needed. The first member is methanoic acid:

H-COOH (formic acid)

The next member is ethanoic acid:

CH_3-COOH (acetic acid)

Physical properties

1. The first four members are water soluble.
2. Because of their hydrogen bonding they have relatively high boiling points.

Relationships between functional groups of alkanols and alkanoic acids

(a) *Oxygen* has a greater attraction for bonding electrons than carbon or hydrogen do, so C–O and O-H bonds of alkanols are *polar*.

Figure 2.15 Comparison of polar –COH group with water

Hydrogen bonding also occurs with alkanols but to a lesser extent than with water.

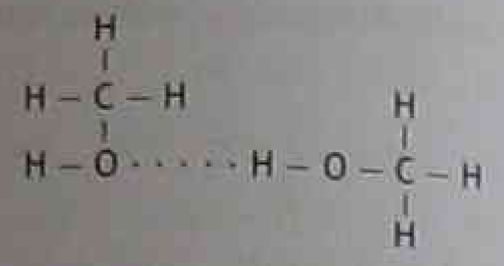
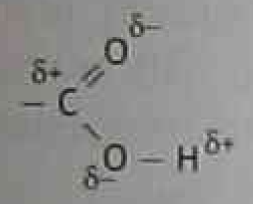


Figure 2.16 Hydrogen bonding in methanol

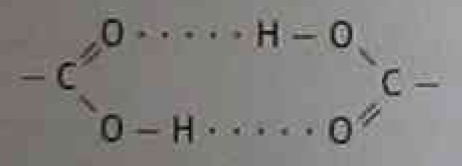
(b) The carboxylic acid group is a planar group with a 120° bond angle separating bonds. The presence of two oxygen atoms on the one carbon atoms leads to a polar carbonyl group.



The high polarity of the –COOH group makes the carboxyl group weakly acidic in water,

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

The presence of a hydrogen atom on one of the oxygen atoms enables hydrogen bonding to occur.



Because of the polar nature of the functional groups of alkanols and alkanoic acids and because of hydrogen bonding, both groups have much higher melting and boiling points than hydrocarbons of comparable molecular mass.

Table 2.8 Formulae and some physical properties of alkanols

Name	BP (°C)	Formula	Solubility in water
methanol	65	CH_3OH	miscible
ethanol	78	CH_3CH_2OH	miscible
1-propanol	97	$CH_3CH_2CH_2OH$	miscible
1-butanol	117	$CH_3CH_2CH_2CH_2OH$	slightly soluble
methanoic acid	100	HCOOH	miscible
ethanoic acid	118	CH_3COOH	miscible
propanoic acid	141	CH_3CH_2COOH	miscible
butanoic acid	164	$CH_3CH_2CH_2COOH$	miscible

Note: Higher acids become immiscible in water.

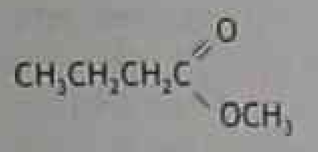
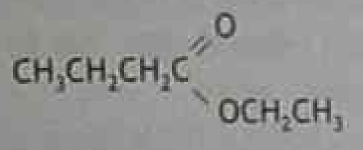
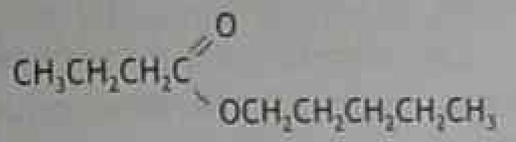
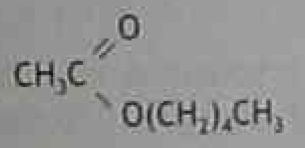
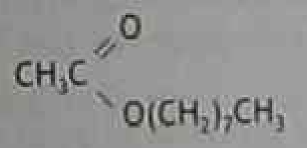
2.29 Some commercial uses of esters

Food flavouring

Esters are usually sweet-smelling substances and many are responsible for the flavour and odour of fruits. Even though there are usually several compounds contributing to the odour and aroma, it is often one ester which is mainly responsible, e.g. 1-pentyl ethanoate has the aroma of bananas.

Many esters used in the commercial manufacture of perfumes and flavourings are made from petroleum.

Table 2.9 Examples of esters and their uses as food flavouring

methyl butanoate	 $CH_3CH_2CH_2C\overset{\nearrow O}{\underset{\searrow OCH_3}{}}$	rum
ethyl butanoate	 $CH_3CH_2CH_2C\overset{\nearrow O}{\underset{\searrow OCH_2CH_3}{}}$	pineapple peach apricot
1-pentyl butanoate	 $CH_3CH_2CH_2C\overset{\nearrow O}{\underset{\searrow OCH_2CH_2CH_2CH_2CH_3}{}}$	apricot
1-pentyl ethanoate	 $CH_3C\overset{\nearrow O}{\underset{\searrow O(CH_2)_4CH_3}{}}$	banana
1-octyl ethanoate	 $CH_3C\overset{\nearrow O}{\underset{\searrow O(CH_2)_7CH_3}{}}$	orange

Food

The main use of glycerol esters (i.e. natural fats and oils) is food, e.g. margarine, fats.

Solvents

Another major use of esters is as solvents, since they dissolve both polar and non-polar organic compounds.

Ethyl and pentyl ethanoate are used, for example, in the manufacture of cellulose lacquers. Ethyl ethanoate is also used as a solvent in the preparation of paints, varnishes (including nail varnish, model aeroplane glue and plastic cement).

Soaps

Soaps are produced by the hydrolysis of long-chain esters found in vegetable oils and fats.

Other uses

Some glycerol esters are used for cosmetics, commercial oils and for making linoleum.

Test on Chapter 2 – The Acidic Environment

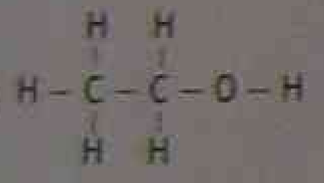
Part A

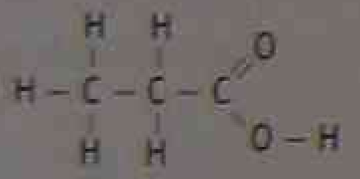
Questions 1–5 are worth 1 mark each

1. Which of the following pairs of solutions when mixed together would form the most effective buffer?
   (A) Hydrochloric acid and sodium chloride.
   (B) Ethanoic acid and ethanol.
   (C) Nitric acid and sodium hydroxide.
   (D) Ammonia solution and ammonium chloride.

2. A paper mill produces waste water which contains 0.20 M NaOH. What volume of HCl solution with a pH = 1 would be needed to bring 5000 L to a pH of 7.
   (A) 1000 L
   (B) 2500 L
   (C) 5000 L
   (D) 10 000 L

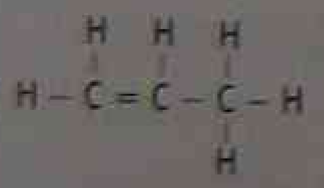
3. A compound has the following properties:
   (i) It is soluble in water.
   (ii) It has no immediate reaction with bromine water.
   (iii) It reacts readily with dilute sodium hydroxide.
   The compound could be

(A)

$\mathrm{H-C-C-O-H}$

(B)

$\mathrm{H-C-C-C(=O)-O-H}$

(C)

$\mathrm{H-C-C-C-H}$

(D)

$\mathrm{H-C=C-C-H}$

4. All three species act as Brønsted-Lowry acids in
   (A) NH_2^-, H_2O, NO_3^-
   (B) $H_2PO_4^-$, SO_4^{2-}, OH^-
   (C) H_2O, HCO_3^-, HPO_4^{2-}
   (D) NO_2^-, OH^-, CH_3COO^-

5. 0.100 mol L^{-1} solutions of four different monoprotic acids were made up. Their pH was measured at 25°C and recorded in the table below:

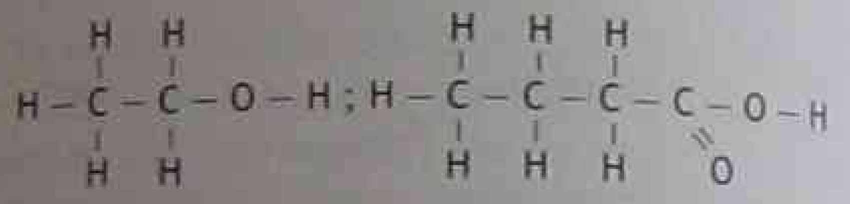
Acids	pH
A	1.0
B	2.2
C	4.0
D	5.2

The strongest acid is
(A) acid A,
(B) acid B,
(C) acid C, or
(D) acid D.

Part B

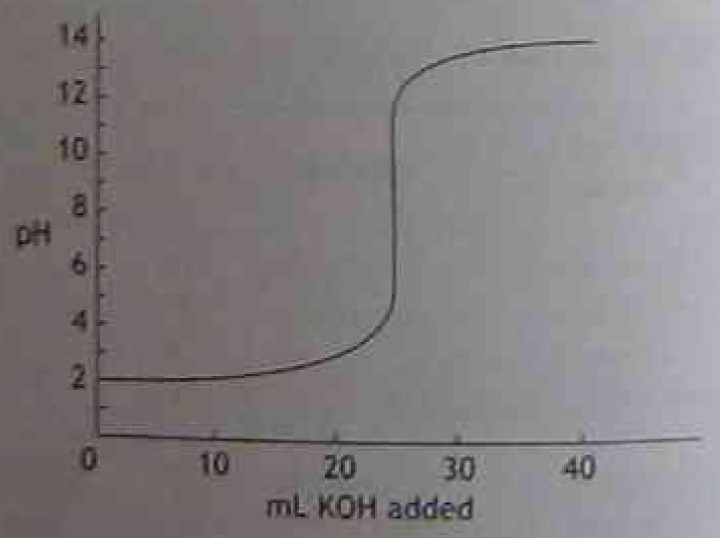
Extended mark questions

6. [6 marks]
   The structure of ethanol (BP 78°C) and butanoic acid (BP 180°C) are given below:


$\mathrm{H-C-C-O-H\ ;\ H-C-C-C-C(=O)-O-H}$

   (a) Explain the difference in their boiling points when compared with ethane (BP −88.6°C) and butane (BP 36°C) respectively.
   (b) When refluxed with a little concentrated H_2SO_4, an ester is formed.
      (i) Why was concentrated H_2SO_4 added?
      (ii) Why was the mixture refluxed?
   (c) Write a balanced chemical equation for the reaction.

7. [7 marks]
   Nitrous acid (HNO_2) solution can be formed by dissolving a mixture of nitrogen (II) oxide and nitrogen (IV) oxide in cold water.
   (a) (i) Write a balanced equation for this reaction.
      (ii) Write an expression for the K_a for nitrous acid.
   (b) Find the pH of a 0.001 M nitrous acid solution, given the value of the acid dissociation constant (K_a) for nitrous acid is 1.0×10^{-5}.
   (c) The graph below was obtained when 20.0 mL of 0.10 M nitrous acid was titrated against potassium hydroxide solution.



   Calculate the concentration of the potassium hydroxide solution.
   (d) Name a suitable indicator for this titration and briefly explain your choice.

8. [6 marks]
   A 1.0 M solution of sodium sulfate has a pH of 1.0.
   (a) Write an ionic equation to represent the hydrolysis reaction of the HSO_4^- (aq) ion.
   (b) Write down the formula of the conjugate base of the HSO_4^- ion.
   (c) Calculate the percentage of the HSO_4^- (aq) ions which undergo hydrolysis.
   (d) HSO_4^- is an amphiprotic ion. Name an amphiprotic molecule and write the formulae for its acid/base pair with the molecule acting as the base.

9. [5 marks]
   (a) Explain briefly using equations when necessary to illustrate your answer, how 'acid rain' can form.
   (b) Briefly explain why 'acid rain' has caused extensive damage to world famous buildings and statues where marble and limestone have been used in their construction.
   (c) Describe a problem affecting the natural environment that is caused by 'acid rain'.

10. [4 marks]
   The citric acid content of orange juice can be determined by titrating a known volume of juice with standardised NaOH using phenolphthalein as indicator. Citric acid ($C_6H_8O_7$) is a triprotic acid.
   (a) A student found that a 25.0 mL sample of orange juice required 28.5 mL of 0.1 M NaOH.
   Find the percentage of mass of the citric acid in the orange juice (assume 1 mL of juice weights 1 g).
   (b) Explain why phenolphthalein is a more suitable indicator than methyl orange for this titration.

Answers for test on Chapter 2 – The Acidic Environment

Part A

Multiple choice (Questions 1–5, worth 1 mark each)

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

* Molarity of HCl = 0.10 M so volume = 2 × 5000 = D

Part B

Extended answers

6. [6 marks]
   (a) Because of the polar nature of the functional group of alkanols and alkanoic acids, and because of hydrogen bonding, both groups have higher melting and boiling points than hydrocarbons of comparable size.
   (b) (i) To act as a catalyst.
      (ii) To prevent the loss of any volatile reactant or product and lower the activation energy.
   (c) $CH_3{-}CH_2{-}OH + CH_3{-}CH_2{-}CH_2{-}COOH$
   $\xrightarrow{\text{conc. } H_2SO_4} \underset{\text{ethyl butanoate}}{CH_3{-}CH_2{-}CH_2{-}COO{-}CH_2{-}CH_3} + H_2O$

7. [7 marks]
   (a) (i) $NO_2(g) + NO(g) + H_2O(l) \rightarrow 2HNO_2(aq)$
   $HNO_2 \rightleftharpoons H^+ + NO_2^-$
      (ii) $K_a = \dfrac{[H^+][NO_2^-]}{[HNO_2]}$
   (b) $K_a = 1.0\times10^{-5} = \dfrac{[H^+]^2}{0.001}$
   $[H^+]^2 = 10^{-8}$, $[H^+] = 10^{-4}$, so pH = 4
   (c) Molarity of KOH $= \dfrac{0.10\times0.020}{0.025} = 0.08$ M
   (d) Phenolphthalein. The equivalence point from the graph is 8, which is in the basic range of pH (strong base/weak acid).

8. [6 marks]
   (a) $HSO_4^-(aq) + H_2O(l) \rightleftharpoons SO_4^{2-}(aq) + H_3O^+(aq)$
   (b) SO_4^{2-}
   (c) pH = 1, so $[H^+] = 10^{-1} = 0.1$ M
   Dissociation $= \dfrac{0.1}{1}\times100 = 10\%$
   (d) $H_2O : H_3O^+/H_2O$ or $NH_3 : NH_4^+/NH_3$

9. [5 marks]
   (a) Sulfur dioxide can be removed from the air by rain in which it forms a weakly acidic solution of sulfurous acid. $SO_2(g) + H_2O(aq) \rightarrow H_2SO_3(aq)$. SO_2 can be oxidised to SO_3 which forms H_2SO_4 in the presence of moisture. $SO_3(g) + H_2O(aq) \rightarrow H_2SO_4(aq)$
   (b) Acid + carbonate → salt + carbon dioxide + water, so marble and limestone are attacked by acid rain and give a soluble salt.
   (c) Run-off from acid rain into lakes and rivers increases their acidity. This can result in the death of aquatic species with eggs and larvae being particularly vulnerable.

10. [4 marks]

(a) No. of moles of NaOH = $\frac{28.5}{1000} \times 0.1$

1 mole of citric acid requires 3 moles of NaOH
so, no. of moles of citric acid = 0.00095
Molar mass of citric acid = 192
mass of citric acid = 0.0095 × 192
= 0.1824 g

% of citric acid = $\frac{0.1824}{25} \times 100 = 0.73\%$

(b) Citric acid is a weak acid and NaOH is a strong base so the equivalence point will be > 7, and phenolphthalein should be used.

Total marks = 33 × 3 + 1 = 100%

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3 — Chemical Monitoring and Management

It is essential to understand the chemical processes involved in interactions in the full range of global environments. Chemists can improve or minimise the environmental problems caused by technology and the increasing human demand for products and services.

Contents

3.1 The work of chemists in monitoring and managing reactions

Chemistry and the needs of human society are strongly linked as the processes of quality control on everyday products are carried out by chemists and laboratory staff. The quality of products may be assessed by knowing

(a) what chemicals are present (*qualitative analysis*), and

(b) how much of each chemical is present (*quantitative analysis*).

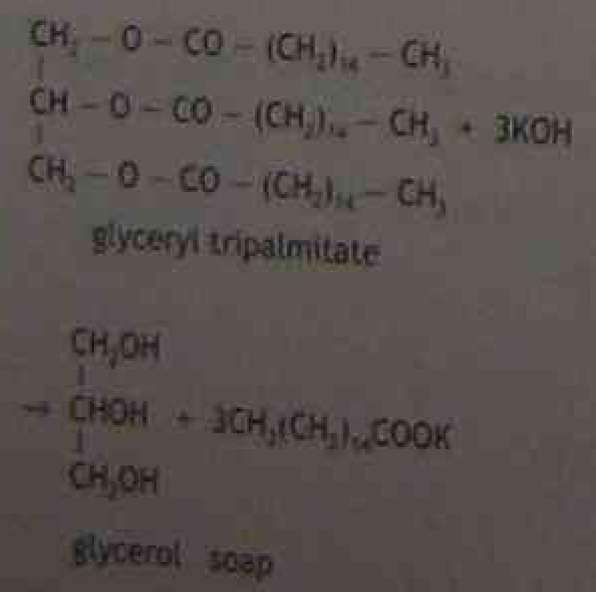
An example of this is well illustrated by examining the production of commercial soaps such as 'Palmolive Gold' made by Colgate-Palmolive Pty Ltd. In this case, *quality control* involves checking the quality of the raw materials and intermediate products as well as ensuring the consistent quality of the final product:

- Packaging materials are tested for weight, thickness and size.
- Raw materials, such as fatty acid blends, are carefully checked since the ratio of palm oil, palm stearin and palm kernel oil determines the type of lather produced when the soap is used. Three checks are carried out:

(a) The *free fatty acid test* which is defined as the volume in mL of standardised 0.1 M KOH needed to neutralise a 5.0 g sample of the fat or oil.

(b) *Saponification value* which gives a measure of the average molar mass of fats and oils used to make the soap and is the number of moles of KOH needed to saponify one gram of the fat or oil.

Example



$$\begin{array}{l} CH_2-O-CO-(CH_2)_{14}-CH_3 \\ | \\ CH-O-CO-(CH_2)_{14}-CH_3 \quad + \quad 3KOH \\ | \\ CH_2-O-CO-(CH_2)_{14}-CH_3 \end{array}$$

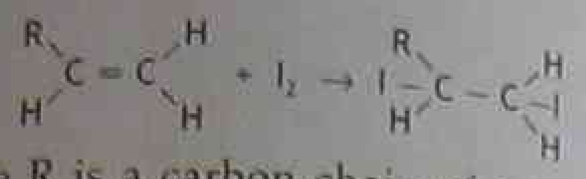
glyceryl tripalmitate

$$\rightarrow \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3CH_3(CH_2)_{14}COOK$$

glycerol soap

(c) The *iodine number* which is the mass in grams of iodine which reacts with 100 g of oil or fat. This is a measure of the degree of unsaturation of the fat or oil.

Example



where R is a carbon chain of 8 to 18 carbon atoms.

Palmolive soaps are made by a two-step process:

Step 1. The initial neutralisation of fatty acids by soda ash.

Step 2. The final saponification of unreacted acids by caustic soda.

Soda ash (Na_2CO_3) is used in the first step because of its low price and minor level of metallic impurities which could have a long-term effect on the soap's perfume and colour stability.

The basic reaction in soap manufacture is that between a fat or oil and an alkali which results in soap and glycerol:

$$C_3H_5(O_2CR)_3 + 3NaOH \rightarrow 3RCO_2Na + C_3H_5(OH)_3$$

where R is the carbon chain which can consist of between 8 and 18 carbon atoms.

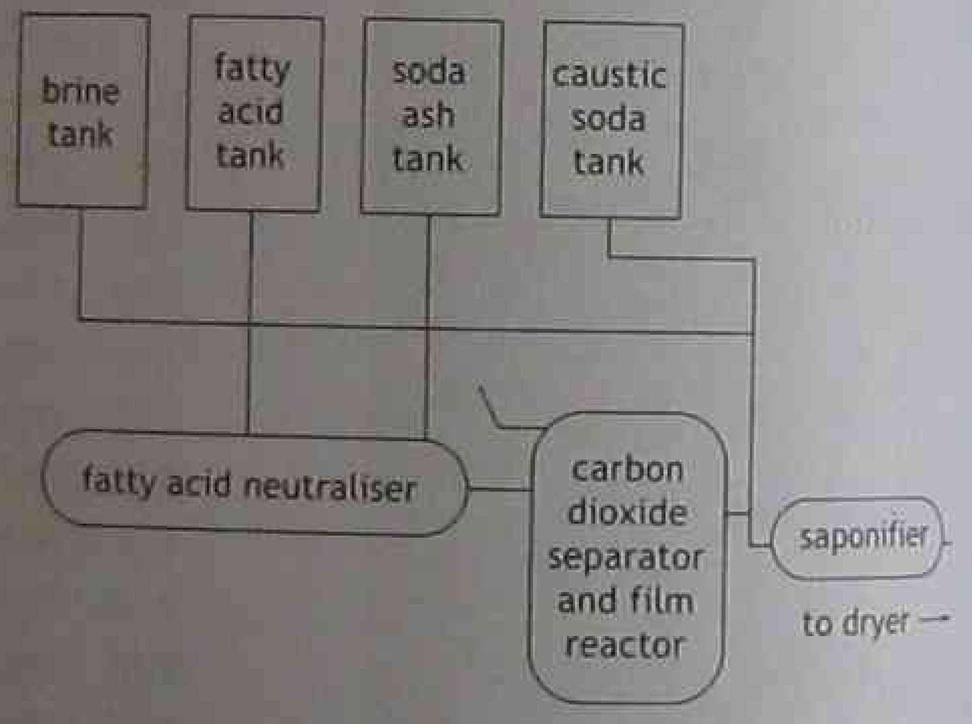


Figure 3.1 Soap manufacture

Intermediate products

Soap is tested to ensure that correct amounts of NaOH are used in the final saponification process. This soap is called 'neat' soap and contains about 65% soap and 35% water with minor levels of impurities. After the soap has been neutralised, it is vacuum-dried to reduce the level of moisture to below 17%. Moisture levels must be tested. Preservatives are added and lastly fragrances, colour and a deodorant ingredient complete the production.

Final product is examined by a *quality inspector* who checks weights, odour and appearance of wrapped and unwrapped soap before it goes to the warehouse. Chemists and other laboratory staff check the product throughout manufacture to ensure that the final product meets the Australian Standard for personal soap.

3.2 A chemical process for managing reaction conditions

The viability of the *Ostwald process* used to manufacture nitric acid from ammonia needs monitoring since reactants can form different products under different conditions. The production of nitric acid depends on the control of kinetic and equilibrium factors and the choice of a suitable catalyst.

At high temperature, NH_3 burns in air to produce mainly nitrogen but not NO.

$$4NH_3(g) + 3O_2(g) \rightarrow 6H_2O(g) + 2N_2(g)$$

$$\Delta H = -1267 \text{ kJ mol}^{-1}$$

However, if conditions are carefully controlled so that

- the optimum temperature is in the range of 820–930°C (depending on pressure),
- a fine wire gauze pad of a 90% platinum/10% rhodium alloy is used as a catalyst for a contact time of below 0.003 seconds, and
- the level of $NH_3(g)$/air mixture is 9–12% (to keep the fraction of NH_3 well below the explosive limit),

then the required high yield of NO can be obtained.

Step 1. Catalytic oxidation of ammonia:

$$4NH_3(g) + 5O_2(g) \rightarrow 6H_2O(g) + 4NO(g)$$
$$\Delta H = -907 \text{ kJ mol}^{-1}$$

Step 2. Oxidation of nitric oxide:

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$
$$\Delta H = -114 \text{ kJ mol}^{-1}$$

Step 3. Absorption of nitrogen dioxide by water:

$$3NO_2(g) + H_2O(l) \rightarrow 2HNO_3(aq) + NO(g)$$

$NO(g)$ reacts with air in the tower to form $NO_2(g)$. Solutions of 45–50% nitric acid are obtained by this process.

3.3 Ammonia and its applications

Table 3.1 Applications of ammonia in industry

Industry	Application of ammonia
Fertiliser	production of $(NH_4)_2SO_4$, $(NH_4)_3PO_4$, NH_4NO_3, where ammonia acts as a base; urea $(NH_2)_2CO$ is made by reaction with CO_2
Chemicals	synthesis of HNO_3, $NaHCO_3$, Na_2CO_3, HCN, N_2H_4
Explosives (5%)	NH_4NO_3
Fibres and plastics (10%)	nylon and other polyamides
Refrigeration (5%)	used for making ice, large scale refrigeration plants, air-conditioning in buildings and plants
Pharmaceuticals	manufacture of drugs, e.g. sulfonamide, anti-malarials, vitamins
Pulp and paper	ammonium hydrogen sulfite enables some hardwoods to be used
Mining and metallurgy (5%)	used in nitriding (bright annealing) steel; in zinc and nickel extraction
Cleaning	in solution as a cleaning agent, e.g. 'cloudy ammonia'

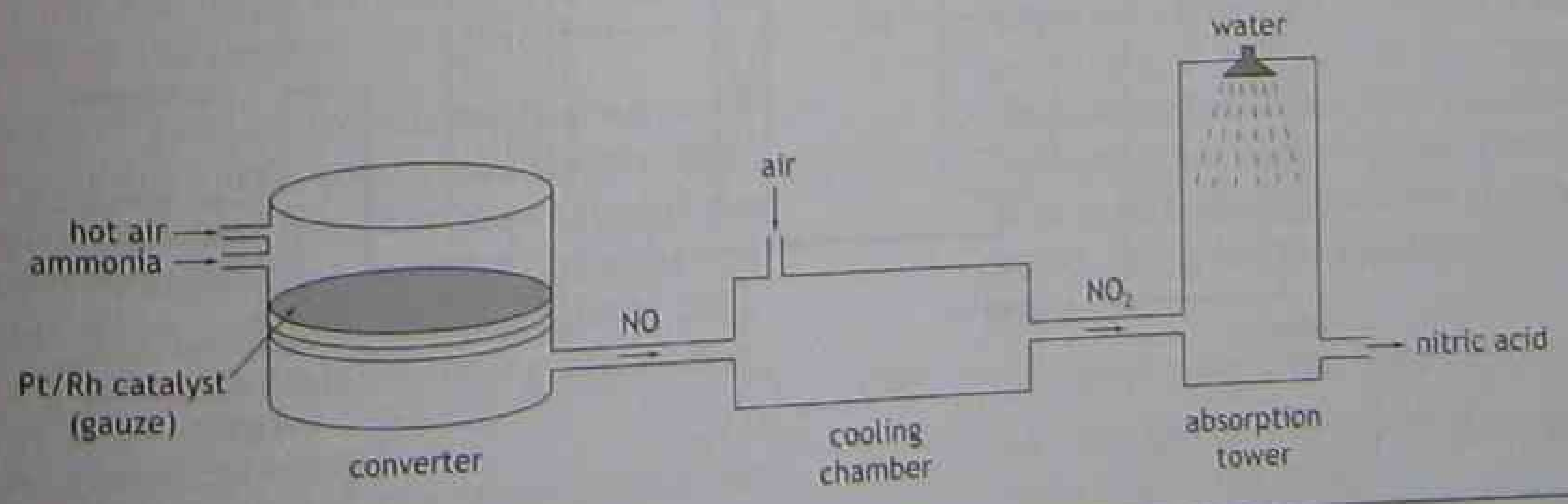


Figure 3.2 A flow diagram of the Ostwald process

3.4 Production of ammonia by the Haber process

Haber was a German chemist who investigated the reaction

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

Haber's research was of great interest to the German chemical industry. Germany was preparing for World War I and nitrogen compounds were needed for explosives. By 1913, Haber had produced ammonia in a large scale from atmospheric nitrogen.

Hydrogen must be of high purity and low cost. The catalyst used must not be poisoned. Hydrogen is now obtained by reforming light petroleum fractions or natural gas (methane) by adding steam.

$$CH_4(g) + H_2O(g) \xrightarrow[700°C]{\text{Ni catalyst}} CO(g) + 3H_2(g)$$

Only enough steam is added to react with about 45% of the methane as shown in the above equation. The rest of the methane is reacted with air over another nickel catalyst:

$$\underbrace{2CH_4(g) + O_2(g) + 4N_2(g)}_{\text{air}} \xrightarrow{\text{Ni catalyst}} 2CO(g) + 4H_2(g) + 4N_2(g)$$

This reaction removes all the O_2 from the air leaving N_2 and some H_2. All the CO in the mixture is oxidised to CO_2 by adding steam and using an iron oxide catalyst.

$$CO(g) + H_2O(g) \rightarrow H_2(g) + CO_2(g)$$

$CO_2(g)$ is removed using a suitable base and the N_2 and H_2, which are in the ratio of 1:3 after compression, enter the converter where they combine to form ammonia:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92 \text{ kJ mol}^{-1}$$

Since the reaction is exothermic and involves a decrease in the number of total gaseous molecules the position of equilibrium could be forced to the right by lowering the temperature and increasing the pressure (*Le Châtelier's Principle*).

A suitable catalyst is used so that it is possible to achieve acceptable reaction rates at temperatures which give acceptable equilibrium yields. The optimum operating conditions in terms of cost and yield in the reactors of modern ammonia plants are as follows:

(a) The N_2 and H_2 gases enter in a 1:3 ratio.

(b) Temperatures used range from 400 to 500°C.

(c) Pressures of 250 atmospheres are used, so the converter must have very thick walls to withstand such pressures.

(d) A porous iron catalyst made from iron oxide (Fe_3O_4) is used (better catalysts such as osmium are too costly) to reduce the activation energy needed to break N_2 and H_2 bonds.

The yield of ammonia is about 10–20%. During commercial production, the gas mixture does not reach equilibrium. The gas mixture leaving the reactor is cooled to liquefy and remove the ammonia formed. The remaining mixture of gases is recycled to improve the yield. Heat released by the initial reaction between nitrogen and hydrogen must be removed to keep the temperature within the desired limits. The 'waste heat' is used to heat the incoming gas mixture.

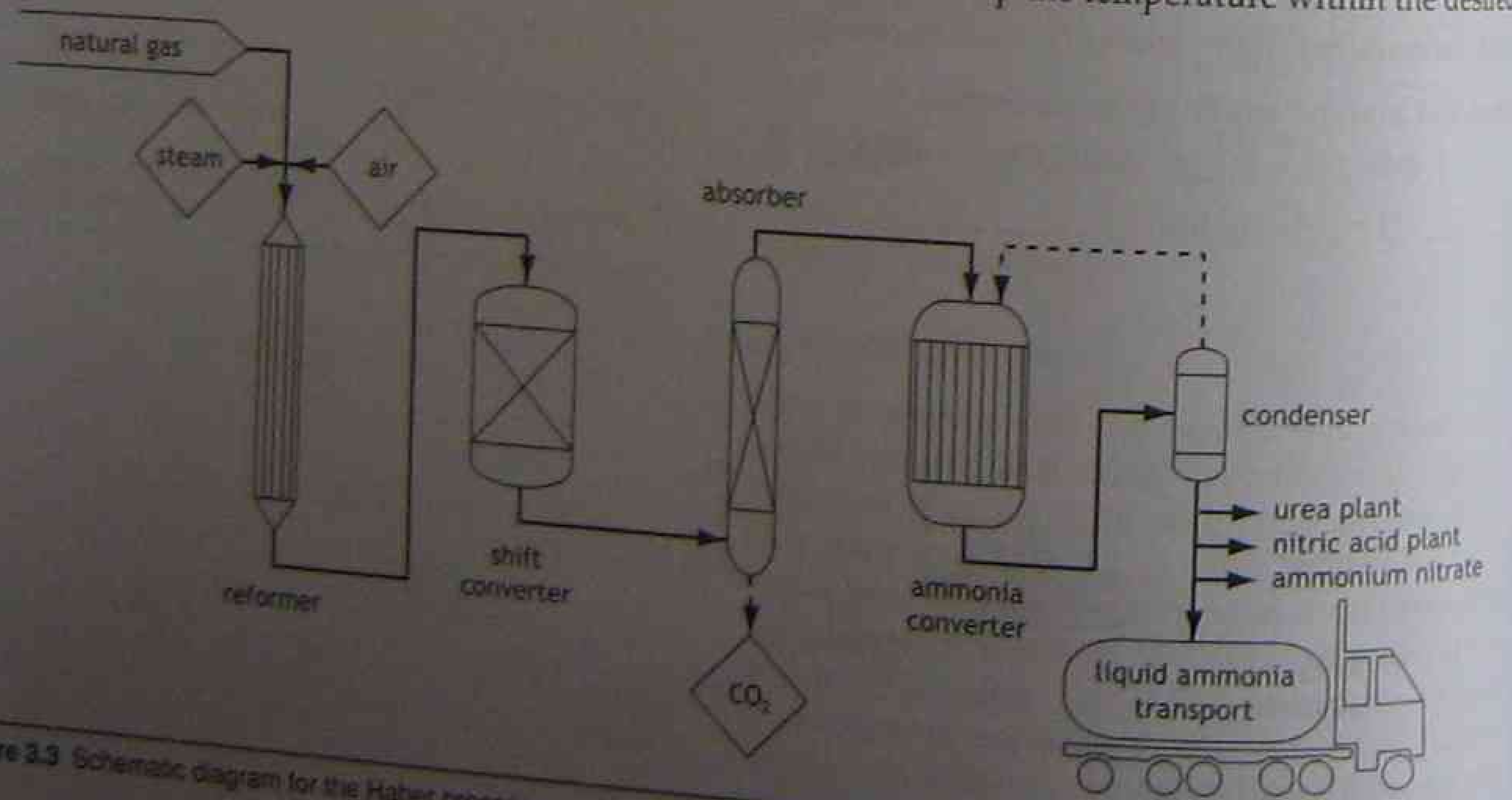


Figure 3.3 Schematic diagram for the Haber process

Note: A control system is vital for this process. Automatic controls are used to adjust, for example, the rate of feed of the incoming gases according to the pressure of the recycled gases.

Under normal atmospheric conditions, the reaction basically does not occur (K is very small). The reaction, in fact, needs a *catalyst* (an added substance which allows the reaction to occur). In the presence of a catalyst, it has been found that reaction is most efficient when subjected to high pressures — several hundred times atmospheric pressure — but that increasing the temperature in fact causes a decrease in ammonia production. Figure 3.4 shows the effect of temperature and pressure on the process.

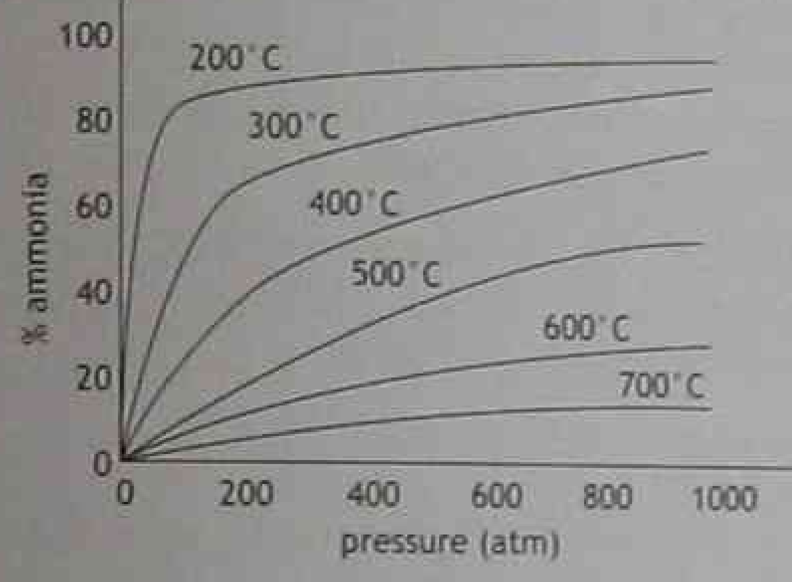


Figure 3.4 Effect of temperature and pressure on the Haber process

At 200°C, it is evident that an almost 100% conversion of reactants is obtained at pressures above 750 times atmospheric. In practice, most production systems use significantly lower pressures (around 200 atmospheres) because of the difficulties of containing large amounts of materials at the high pressures. This, of course, reduces the yield of ammonia. The temperature used is around 500°C, which also limits the percentage conversion, but speeds up the process.

According to Figure 3.4, the percentage of ammonia obtained under these conditions is only 20%. Although this seems low, it is the choice of the engineers who design the plant to maximise the rate of producing the ammonia and to minimise costs and safety concerns in the building and during operation of the plant.

Note 1: The Haber process is an industrial procedure which is not done under equilibrium conditions. Instead, moderately high temperatures and pressures are used and the liquefied ammonia is drawn off constantly. The high temperature is used because reactions (including exothermic reactions) will proceed more rapidly when molecules have more energy.

According to the equilibrium system (where ΔH = –92 kJ), high temperature would reduce the concentration of ammonia but the reaction would be extremely slow at room temperature.

Note 2: A catalyst is used in the Haber process to lower the activation energy so that the N_2 bonds and H_2 bonds may be broken more readily.

3.5 Tests to identify specific ions

The following tests can be carried out to identify the ions below:

Anions

CO_3^{2-}	Add a dilute inorganic acid, e.g. HCl. Bubble any gas evolved into a test-tube containing limewater. If a carbonate is present, the limewater will turn milky. $CO_3^{2-}(aq) + 2H^+(aq) \rightarrow CO_2(g) + H_2O(l)$ $CO_2(g) + Ca(OH)_2(aq) \rightarrow CaCO_3(s) + H_2O(l)$
SO_4^{2-}	Add $Ba(NO_3)_2$ solution. A white precipitate indicates the presence of a sulfate. $SO_4^{2-}(aq) + Ba^{2+}(aq) \rightarrow BaSO_4(s)$ **Note:** Ensure that a carbonate is absent by testing with dilute acid
Cl^-	Add a solution of $AgNO_3$. A white precipitate which turns purple on exposure to light indicates the presence of a chloride. $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$
PO_4^{3-}	Yellow precipitate is formed on warming with a solution of ammonium molybdate and nitric acid.

Cations

Ba^{2+}	Carry out a flame test. A Pt wire is mounted in a glass holder. It is dipped in concentrated HCl and then cleaned in the non-luminous Bunsen flame. The clean Pt wire is then dipped into the sample to be tested. Ba^{2+} gives an apple-green colour to the flame.
Ca^{2+}	Ca^{2+} gives a brick-red colour to the flame.
Cu^{2+}	Add NH_4OH and a deep blue complex ion forms if Cu^{2+} is present. $Cu^{2+}(aq) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+}(aq)$

Pb^{2+} 1. Add dilute HCl. A white precipitate of $PbCl_2$ forms which dissolves in hot water.
$Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s)$

2. Add KI and a yellow precipitate of PbI_2 forms.
$Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$

Fe^{2+} 1. Forms a white precipitate when NaOH is added. The precipitate rapidly turns brown.

2. Forms a deep blue precipitate with potassium ferricyanide.

Fe^{3+} 1. Forms a red-brown precipitate of $Fe(OH)_3$ when NaOH is added.

2. Forms a blood-red complex ion when potassium thiocyanate solution is added to the Fe^{3+} ion.
$Fe^{3+}(aq) + NCS^-(aq) \rightarrow [Fe(NCS)]^{2+}(aq)$

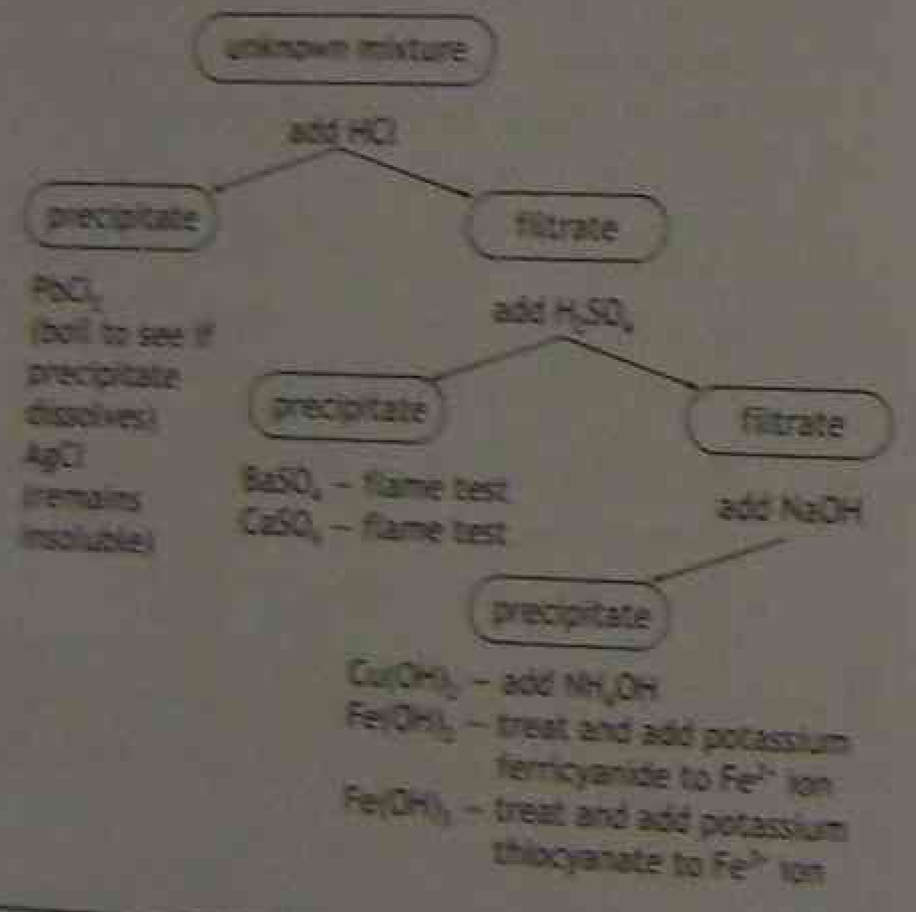


Figure 3.5 Scheme to deduce the above cations present in an unknown mixture of their solutions

Gravimetric analysis is used to determine the percentage by weight of an element or group in a compound or mixture.

Example experiment:

To find the sulfate content of a fertiliser. Ammonium sulfate is the main constituent in 'sulfate of ammonia' which is a common lawn fertiliser.

Method:

1. Accurately weigh a small sample (about 1.5 g) of the fertiliser into a clean, dry beaker.
2. Dissolve in 100 mL of hot, distilled water.
3. Add a slight excess of saturated barium chloride solution.
4. Heat with stirring to coagulate the white barium sulfate precipitate.
5. Filter quantitatively through a pre-weighed sintered glass crucible and wash with small amounts of hot water, using a wash bottle, to remove any soluble salts.
6. Dry crucible in an oven at 120°C. Cool in a desiccator and weigh. Difference in mass of crucible masses = mass of barium sulfate.

Calculation:

$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4(s)$ $[nBaSO_4 = nSO_4^{2-}]$

Step 1: Convert the mass of $BaSO_4$ to moles $[n(BaSO_4)]$.

Step 2: Convert the moles of sulfate $[n(SO_4^{2-})]$ to grams $(m = nM)$.

Step 3: Express this as a percentage of the weight of the fertiliser sample.

Note: A suitable filter paper may be used to replace the crucible.

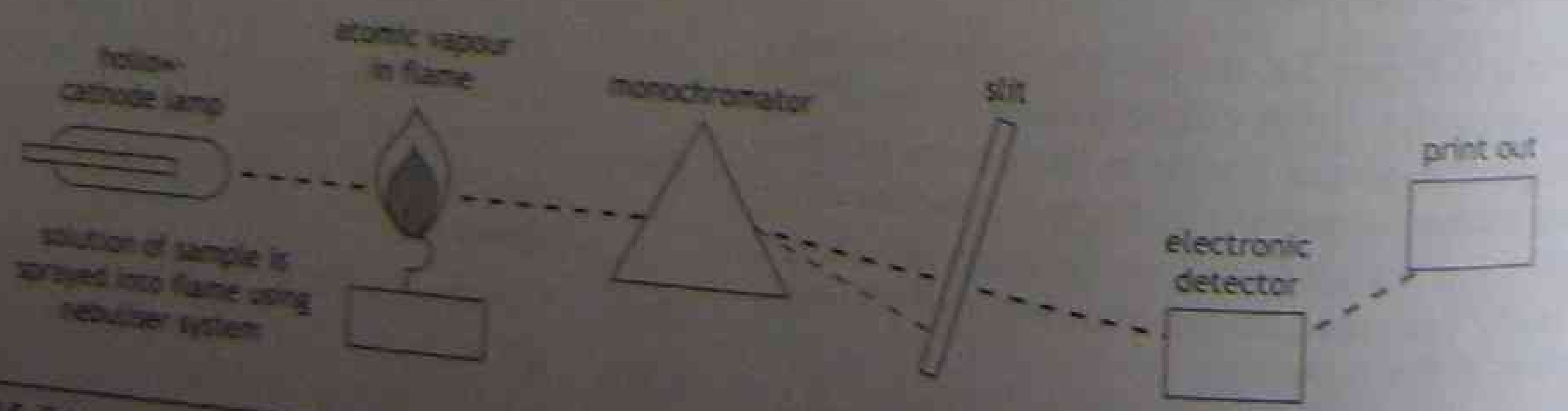


Figure 3.6 Schematic diagram of an atomic absorption spectrograph

3.6 The use of atomic absorption spectrograph to determine metal ion concentrations

The atomic absorption spectrograph (AAS) was invented by the Australian Alan Walsh in 1953. It is a special lamp (a hollow-cathode lamp) used to produce a sharp-line emission spectrum of the metal to be determined. The radiation from the lamp of a chosen wavelength passes through a flame (usually an air-acetylene flame) into which a solution of the metal of interest is sprayed using a nebuliser to obtain a fine mist.

Atoms of the element being analysed are converted to an atomic vapour and then absorb some of the radiation.

The light beam passes through a filter (monochromator) to separate light of the chosen wavelength from other light. The intensity of the light is measured by an electronic detector (photomultiplier tube).

The amount of light absorbed by the sample is proportional to the concentration of the metal in the solution being tested. Atoms of each metal absorb light at characteristic wavelengths in proportion to the amount present.

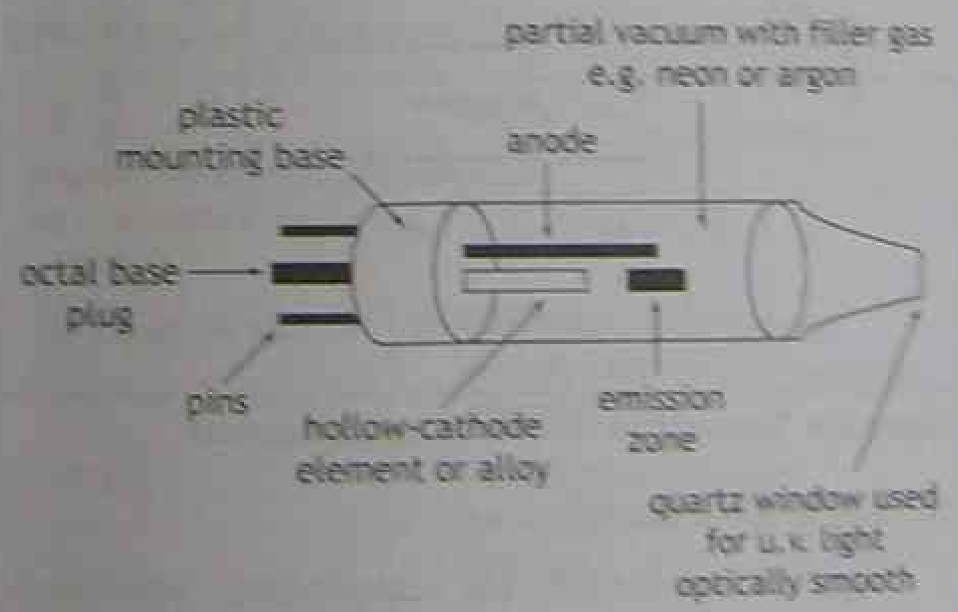


Figure 3.7 Hollow-cathode lamp

The determination of concentrations of metal ions in solutions

Principle

Flame atomic absorption spectroscopy (AAS) relies on the following:

(a) Heating a sample sufficiently to produce free atoms.

(b) Free atoms of an element being able to absorb energy only at certain discrete wavelengths. Such a wavelength is called a resonance wavelength and corresponds to the transfer of an electron between the ground state and a higher energy level in a specified atom.

(c) The energy absorbed being a function of the concentration of the absorbing atoms.

Techniques

- A solution of the metal is nebulised into a flame.
- The absorption of energy is measured at a specified wavelength.
- The absorption measurement is independent of any radiation emitted by the flame.
- In calibrating solutions, use Analar grade reagents (AR).
- Use high purity water.
- Make up
  - (i) a blank set solution,
  - (ii) a set of suitable standard solutions, and
  - (iii) duplicate sample solutions.
- Calibration graphs should be linear.

Use

The atomic absorption spectroscopy is one of the most widely used instrumental techniques and is capable of detecting 68 metals in the range of parts per million to pure metal. In the metals industry, volumetric and gravimetric analysis is outdated. The mining industry uses AAS for the analysis of geological samples, testing the purity of products such as copper, silver and gold and monitoring pollution levels in effluents. It is used for quality control of alloys and in the detection of dangerous metal particles in the air.

An example of the use of AAS analysis in determining the concentration of an M^{2+} ion in parts per million is given below. Parts per million are used for very small concentrations (1 part to 10^6 parts of solvent by mass).

Question

The level of iron in two brands of multivitamin tablets was determined by AAS. One tablet from each brand was crushed and separately dissolved in 1 L of pure water. Standard solutions of Fe^{2+} were made up using ARs; a 'blank' solution was also made up. Their absorbances were tested followed by those of samples of the multivitamin solutions.

The following data were recorded:

Solution concentration (ppm)	Absorption
0.00	0.010
1.00	0.080
2.00	0.150
3.00	0.220
4.00	0.290
Sample 1	0.190
Sample 2	0.250

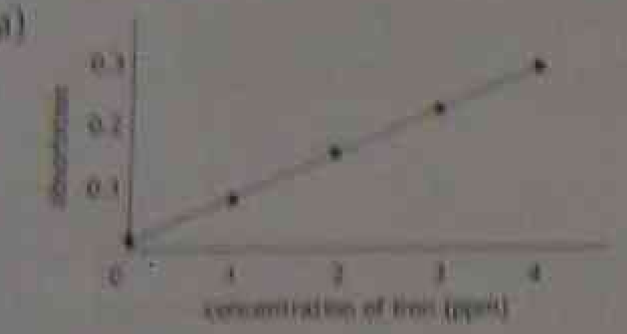
(a) Plot a graph of absorption against concentration of iron in ppm. State the concentration of iron (ppm) for each sample.

(b) Why did the standard containing no added iron give a small absorption reading?

(c) Most multivitamins contain other metal ions such as Cu^{2+}, Zn^{2+} and Ca^{2+} as well as Fe^{2+}. How can Fe^{2+} be selectively analysed?

Solution

(a)



Sample 1 — Iron concentration is 2.5 ppm
Sample 2 — Iron concentration is 3.8 ppm

(b) Very small amounts of iron could be present in the water used to make up the blank.

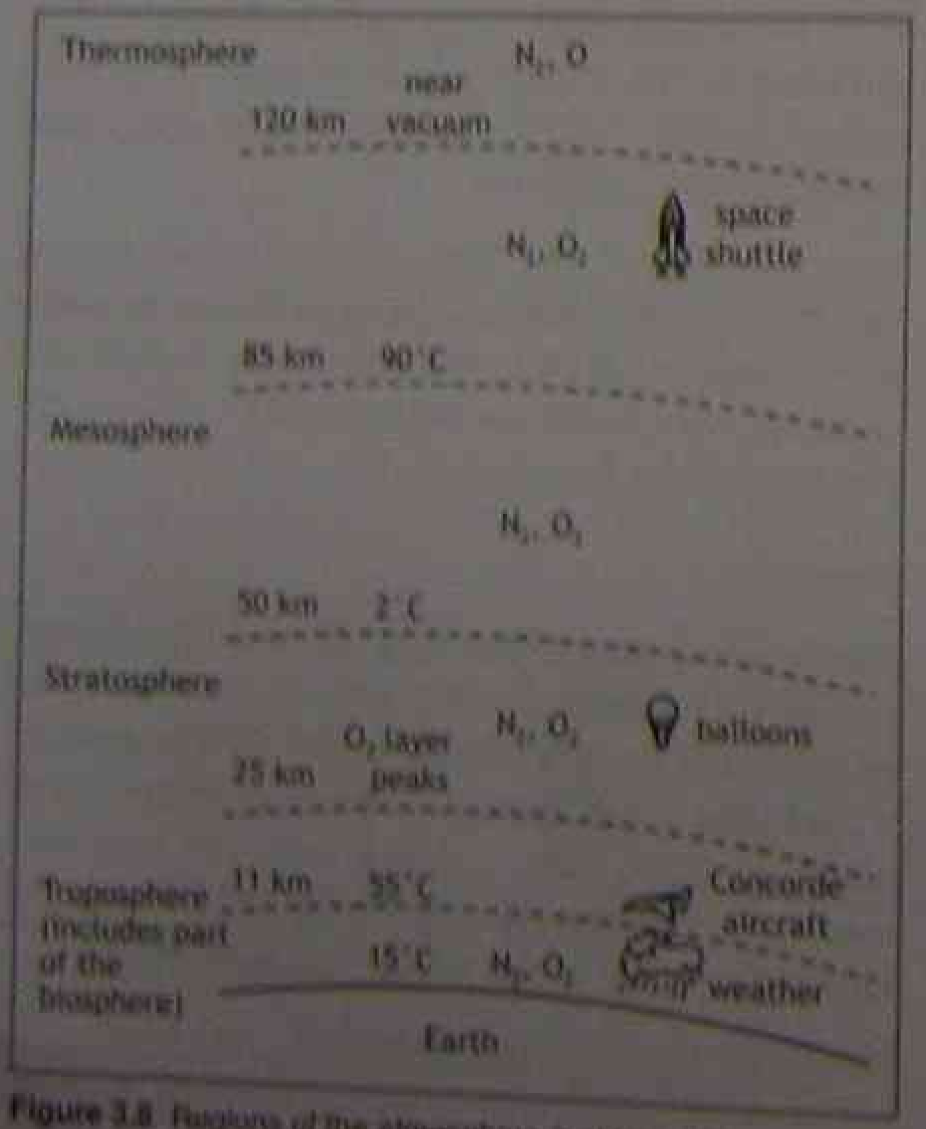


Figure 3.8 Regions of the atmosphere (not to scale)

(c) The hollow-cathode lamp is changed for each element, being specific for the element being analysed.

3.7 The main regions of the atmosphere

The layers of the atmosphere are defined by temperature changes. They are, however, distinct in other ways, e.g. the weather systems are confined to the troposphere because the warmer stratosphere acts as a lid. The stratosphere is the region of the atmosphere containing the ozone layer.

Atmospheric pollution problems include the following.

(a) Photochemical smog

Produced in the tropospheric ozone from burning of fossil fuels, e.g. nitric oxide (NO) from car exhausts. NO(*g*) interacts with sunlight to product NO_2 (nitrogen dioxide) which not only contributes to urban haze, but also produces oxygen atoms which combine with O_2 in the air to produce toxic ozone (O_3).

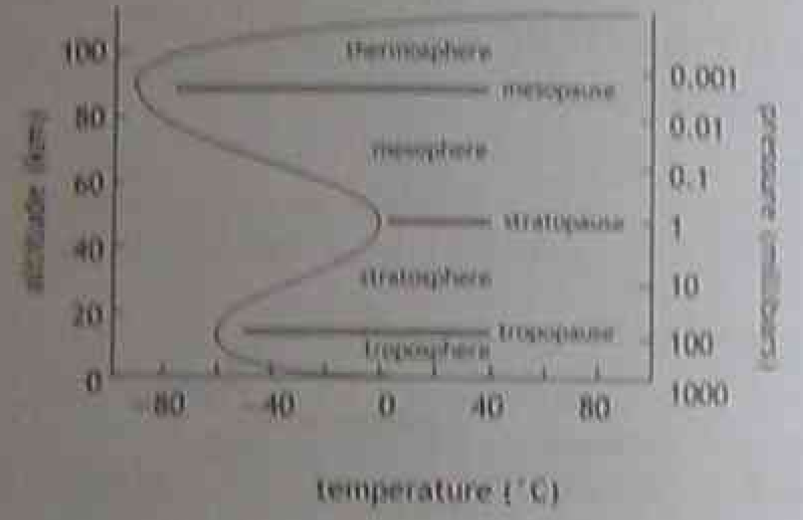


Figure 3.9 Temperature variation in the atmosphere

(b) The greenhouse effect

Light rays penetrate the atmospheric boundary and are absorbed by the plants, animals and soil. They are then re-radiated as longer-wave infrared heat rays from the Earth's surface. The atmospheric boundary reflects these rays back to earth. Greenhouse gases absorb some of these infrared rays.

Figure 3.10 The greenhouse effect

The enhanced greenhouse effect is brought about by human activity. The atmosphere's ability to absorb infrared radiation has increased. Greenhouse gases such as water vapour, carbon dioxide, methane, nitrogen oxides and chlorofluorocarbons (CFCs) all absorb some of the infrared radiation emitted by the Earth without absorbing energy from the sun's radiation. Some of them are natural components of the atmosphere, so Earth has always had a greenhouse effect which maintains the average temperature of the planet at about 16°C.

Table 3.2 Main gases in the enhanced greenhouse effect

Gas	% effect	Warming potential ranking
Carbopn dioxide	57	1
Methane	12	11 (11 times that of CO_2)
CFC-11, CFC-12	15 – 25	~5000
N_2O	6	270

3.8 Lower atmospheric pollutants

The most disturbing consequences of atmospheric modification are

- the enhanced greenhouse effect,
- the depletion of ozone in the stratosphere, and
- pollution in the troposphere due to acid rain and photochemical smog.

Table 3.3 Lower atmospheric pollutants and their sources

Gas	Source
Troposphere pollutants	
(a) Enhanced greenhouse gases:	
(i) increased CO_2	decomposition of organic matter, fossil fuel combustion, deforestation
(ii) CH_4	mainly from anaerobic decomposition of organic matter, ruminants, landfill, rice paddies
(iii) CFCs	manufactured chemicals used in aerosols, foams, refrigerants, air conditioners
(iv) oxides of nitrogen	motor car engines, combustion of organic matter
(v) ozone	mostly by diffusion from the stratosphere, photochemical smog
(b) Particulates (especially in cities)	increases are due to soot, smoke, oil and salt spray
(c) SO_2	volcanic gases, fossil fuels, industrial processes
Stratosphere pollutants	
CFCs	aerosols, foams, refrigerants, air conditioners
oxides of nitrogen	vehicle exhausts, burning of fossil fuels, volcanic gases

3.9 Role of ozone in the troposphere and stratosphere

Ozone

Ozone reacts readily with other gases in the atmosphere and so it remains in the lower atmosphere (troposphere) for a relatively short time. Ozone is a greenhouse gas formed throughout the atmosphere. In the troposphere it contributes to the greenhouse effect, coming from two sources:

(a) Mostly from the stratosphere. Ozone in the stratosphere is formed largely by the impact of light on oxygen molecules.

$$O_2(g) \rightarrow 2O(g)$$

$$O(g) + O_2(g) \rightarrow O_3(g)$$

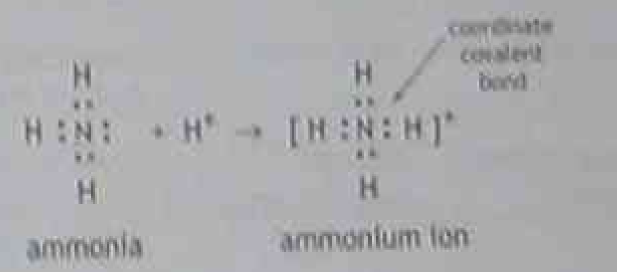
(b) Some ozone forms in the troposphere as a result of chemical reactions between a number of gases such as oxides of nitrogen and volatile hydrocarbons.

In the lower atmosphere, ozone is both a pollutant and an irritant. Ninety per cent of ozone is found in the stratosphere where it shields the planet from damaging solar ultraviolet radiation.

Structure of ozone

A covalent bond between two atoms consists of a pair of shared electrons. Each atom may contribute an electron to the pair. However, one atom may provide both electrons and is called a donor atom. The bond formed is called a coordinate covalent bond.

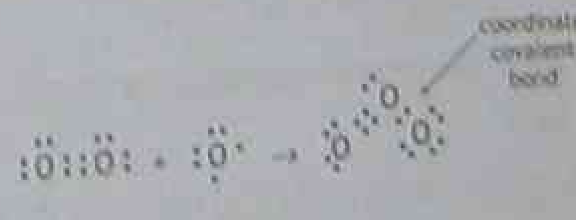
Example



$$NH_3 + H^+ \rightarrow [NH_4]^+$$

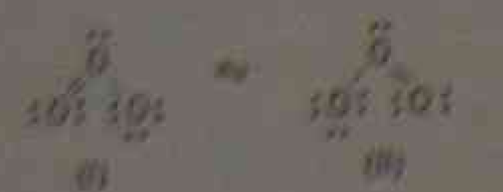
Electrons cannot be distinguished once bonds are formed.

Ozone and O_2 are allotropes of the element oxygen. *Allotropes* are different forms of the same element in the same state (both gases). Below is a theoretical example of the formation of a coordinate covalent bond:



O_2 + O → O_3 (ozone)

This Lewis formula representing ozone shows that one double and one single bond is present. From bond length measurements, however, both bonds are of equal length and are intermediate between a double and single bond. The ozone molecule can be represented by the following resonance forms.



If the structure of the ozone molecule can be represented by a structure intermediate between formulas I and II, then bond lengths and bond energies can be accounted for. The structures differ only in the position of the electrons.

Oxygen occurs as a diatomic molecule and the short bond distance and high bond energy suggest that O_2 has a double bond. The following Lewis structure is consistent with this:

But according to the Lewis structure, all valence electrons are paired. In fact, the O_2 molecule is paramagnetic and contain two unpaired electrons. This can only be resolved using the more complex molecular-orbital theory.

3.10 The structure and properties of O_2, O_3 and O

Table 3.4 Properties of O_2 and O_3

Property	O_2	O_3
Odour	odourless	slightly pungent
Presence in air	supports life	causes respiratory and eye problems
Reaction with elements	reactive, oxidising agent	more reactive at lower temperatures, strong oxidising agent

Ozone can be used to sterilise water supplies (more soluble in water than O_2).

Ozone is less stable than oxygen and more reactive. The bond dissociation energy of

$$O_3(g) \rightarrow O_2(g) + O(g)$$

is 107 kJ mol^{-1} whereas for $O_2(g)$ the bond energy is 495 kJ mol^{-1}.

The lower bond energy of $O_3(g)$ explains its greater reactivity.

Properties of $O_2(g)$

Oxygen is a covalent molecular gas at room temperature. Oxygen consists of small discrete molecules with low melting and boiling points. Sharing of electrons occurs.

Structure of the oxygen radical 

At high altitudes, oxygen molecules are decomposed to atoms by the high energy ultraviolet radiation of the sun. Some of the oxygen atoms formed react with oxygen molecules to form ozone O_3.

A possible reaction is $O_2 + O \rightarrow O_3$
(See equation on previous page.)

3.11 The origins of CFCs and halogens in the atmosphere

Chlorofluorocarbons are synthetic chlorine-containing compounds. They were originally chosen because of their inertness and because they were non-toxic and safe to use. Eventually they move up into the stratosphere where they can be broken down by ultraviolet light releasing free halogen atoms, e.g. chlorine.

Example

CFC-11 has the formula CCl_3F

$$CCl_3F(g) \xrightarrow{\text{UV radiation}} CCl_2F(g) + Cl(g)$$

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

$$ClO(g) + O(g) \rightarrow O_2(g) + Cl(g)$$

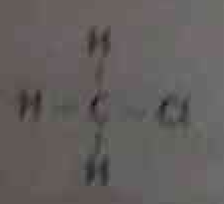
$$O_3(g) + O(g) \rightarrow 2O_2(g)$$

Since chlorine atoms are not permanently used up in the reaction, they can attack more ozone molecules. The O_3 molecule is not being replaced in the above cycle of reactions.

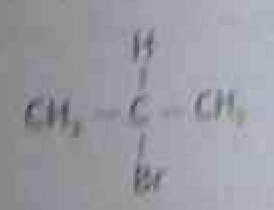
Increasingly HCFCs are replacing CFCs since they have much less ozone-destroying potential.

3.12 Naming straight chain haloalkanes

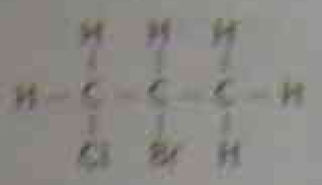
These derivates are formed when a hydrogen atom is replaced by a halogen atom (Br, Cl, F and I):



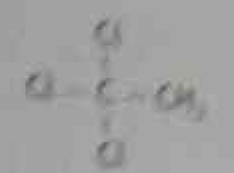
chloromethane



2-bromopropane



2-bromo-1-chloropropane



1,1,1-trichloroethane

Exercise 1

(a) Name each of the following haloalkanes:

- (i) $CH_3-CHBr-CHCl-CH_3$
- (ii) $CHBr_2CH_2Cl$
- (iii) $CH_2Cl-CH_2-CH_2-CH_2I$
- (iv) $CH_3-CHCl-CHI-CHBr-CH_3$

(b) Draw structural formulas for the following:

- (i) 2-bromopropane
- (ii) dibromodichloromethane
- (iii) 2,2-diiodopropane
- (iv) 1-bromo-2-iodopropane

3.13 Identifying and naming isomers of haloalkanes

Isomers are two or more different compounds having the same molecular formula.

Examples of isomers of haloalkanes

1-chlorobutane $ClCH_2-CH_2-CH_2-CH_3$

2-chlorobutane $CH_3-CH_2Cl-CH_2-CH_3$

1-chloro-2-methylpropane 

$ClCH_2-\underset{CH_3}{CH}-CH_3$

2-chloro-2-methylpropane 

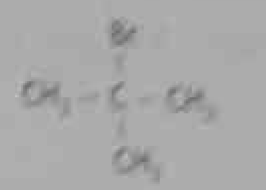
$CH_3-\overset{Cl}{\underset{CH_3}{C}}-CH_3$

Exercise 2

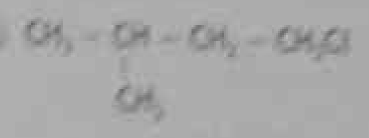
(a) Name each of the following branched chains haloalkanes:

(i) 

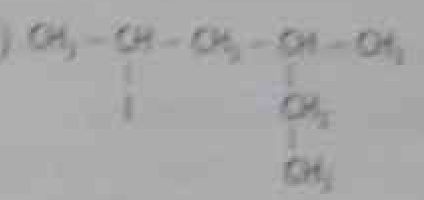
$CH_3-\underset{CH_3}{CH}-CH_2-Cl$

(ii) 

$CH_3-\overset{Br}{\underset{CH_3}{C}}-CH_3$

(iii) 

$CH_3-\underset{CH_3}{CH}-CH_2-CH_2Cl$

(iv) 

$CH_3-\underset{I}{CH}-CH_2-\underset{\underset{CH_3}{CH_2}}{CH}-CH_3$

(b) Draw structural formulas for the following:

- (i) 1,2-dichloro-2-methylbutane
- (ii) 2-bromo-2,3-dimethylpentane
- (iii) 2-chloro-3-methylpentane
- (iv) 1-fluoro-3-ethylhexane

Table 3.5 Main commercial CFCs of the 1980s

Coded compound	Formula	Name	Uses
CFC-11	CCl_3F	trichlorofluoromethane	refrigeration, aerosols, foams
CFC-12	CCl_2F_2	dichlorofluoromethane	refrigeration, aerosols, air conditioning, foams
CFC-13	CCl_2FCClF_2	1,1,2-trichloro-1,2,2-trifluoroethane	electronics, dry cleaning, fire extinguishers
CFC-14	$CClF_2CClF_2$	1,2-dichloro-1,1,2,2-tetrafluoroethane	aerosols

Table 3.6 Substitutes used for CFCs to reduce ozone depletion

Coded compound	Formula	Name	Uses
HCFC-22	$CHClF_2$	chlorodifluoromethane	air conditioning, refrigeration, foams
HCFC-142b	CH_3CClF_2	1-chloro-1,1-difluoroethane	aerosols
HFC-152a	CH_3CHF_2	1,1-difluoroethane	aerosols, refrigerant

3.14 Rules for naming haloalkanes

Haloalkanes

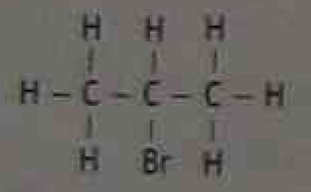
1. Bromo-, chloro-, fluoro-, and iodo- are used as prefixes to the hydrocarbon name.
2. The position of the halogen (halo) atom is denoted by a number if more than one of a particular type of halo atom is present, di-, tri-, tetra- are used and a location number is given for each such atom.
3. If more than one type of halo atom is present, they are listed alphabetically with any di-, tri-, tetra- being ignored in deciding this order.
4. Halo atoms are given before alkyl side chains.

Answers

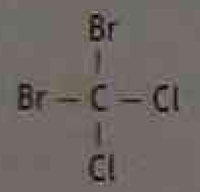
Exercise 1

(a) (i) 2-bromo-3-chlorobutane
(ii) 1,1-dibromo-2-chloroethane
(iii) 1-chloro-4-iodobutane
(iv) 2-bromo-4-chloro-3-iodopentane

(b) (i)



(ii)



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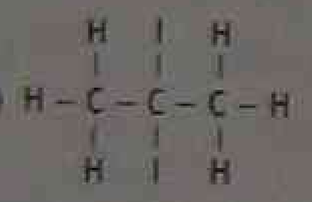
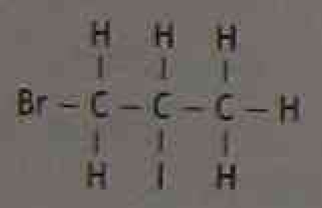


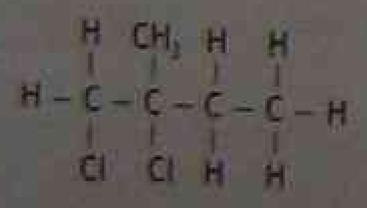
(iv)



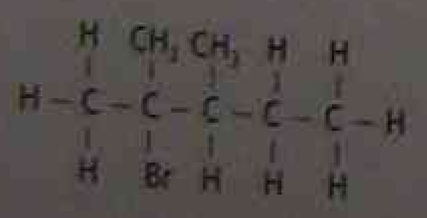
Exercise 2

(a) (i) 1-chloro-2-methylpropane.
(ii) 2-bromo-2-methylpropane.
(iii) 1-chloro-3-methylbutane.
(iv) 2-iodo-4-methylhexane.

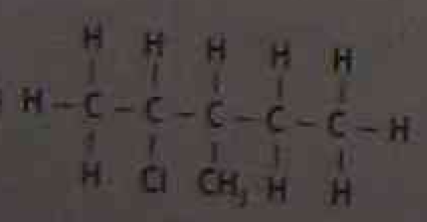
(b) (i)



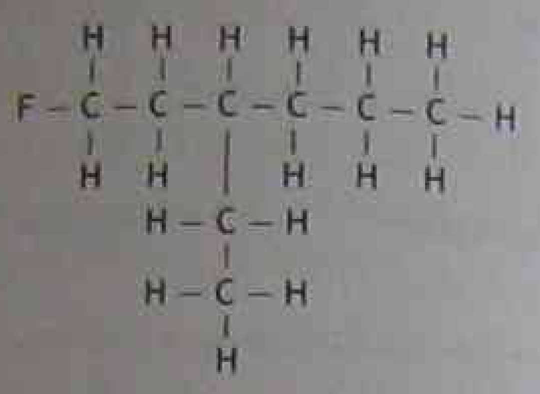
(ii)



(iii)



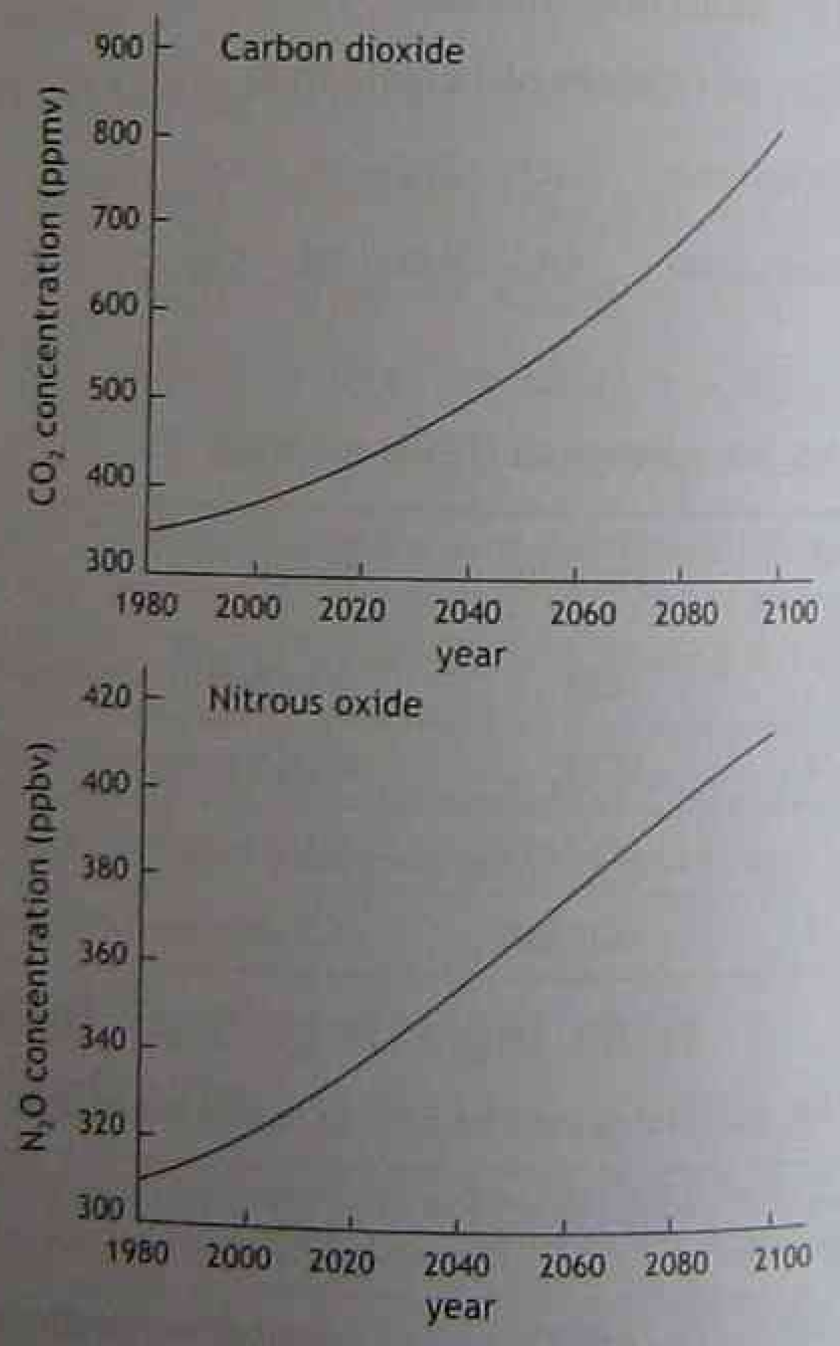
(iv)



3.15 The enhanced greenhouse effect

The following graphs are a result of the following assumptions put forward by the Intergovernmental Panel on Climate Change (IPCC):

- Global population reaches 9.5 billion by 2050.
- Economic growth in OECD countries is 2–3% per year, and 3–6% in Eastern European and developing countries.
- Energy supply is coal-intensive.
- Carbon dioxide controls are modest.
- Deforestation continues until the tropical forests are depleted.
- The Montreal Protocol governing the release of CFCs is implemented, but with partial compliance only.



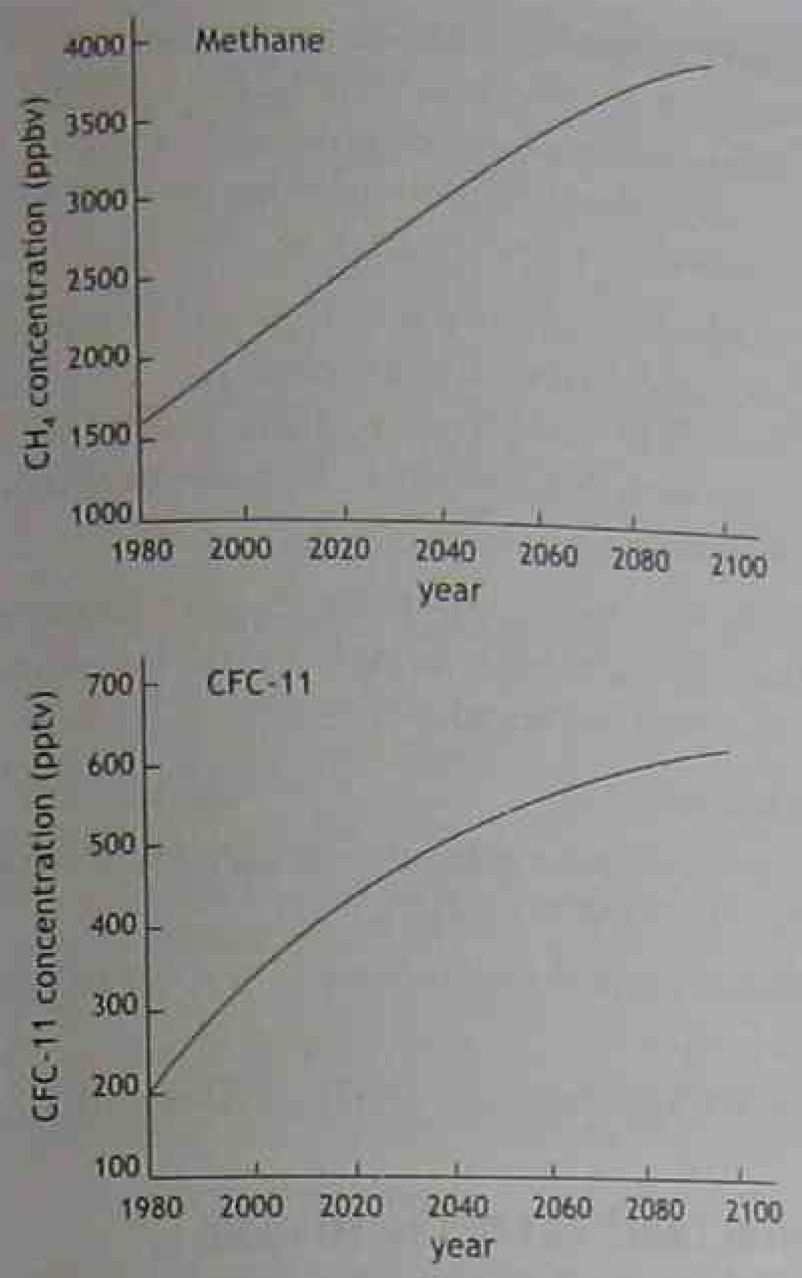


Figure 3.11 Atmospheric concentrations of greenhouse gases

Predictions of future global changes in climate

These predictions include

- a rise in sea level (20–50 cm);
- tropical cyclones may become more intense;
- temperature rises (1– 4°C) may occur; and
- there may be major shifts in the Earth's climatic zones.

To limit the impact of the enhanced greenhouse effect

- alternatives to fossil fuels should be developed;
- energy conservation should be encouraged;
- tree plantings should be promoted; and
- the use of CFCs must be phased out.

3.16 Depletion of the ozone layer

Changes caused by human activity are not confined to the troposphere but extend into the stratosphere. Ultraviolet radiation in the stratosphere releases the chlorine in manufactured CFCs with the consequence that ozone is destroyed. The ozone layer absorbs high energy ultraviolet radiation which could be damaging to life if it reaches the Earth's surface. Ozone in the stratosphere is constantly being formed and decomposed by natural effects. The ozone formed strongly absorbs ultraviolet radiation (230–290 nm band) and undergoes photochemical decomposition to form O_2 and oxygen atoms. The ozone then reforms releasing heat energy:

$$O_3(g) \rightarrow O_2(g) + O(g)$$

When supersonic aircraft destined to fly at very high altitudes were on the drawing board, warning was given that the jet engines could produce nitrogen oxide (NO) which could act as a catalyst in the decomposition of ozone (O_3).

In the engines

$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$

In the stratosphere

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$
$$NO_2(g) + O(g) \rightarrow NO(g) + O_2(g)$$

The net effect is

$$O_3(g) + O(g) \rightarrow 2O_2(g)$$

The high flying aircraft fleets were never developed as a result of commercial decisions. The Concorde (a prototype) is still flying. As explained earlier, the CFCs have seriously depleted the ozone layer by releasing free chlorine atoms (one chlorine atom could remove almost 100 000 ozone molecules). Halons, which are similar to CFCs, where chloride atoms are replaced with bromine atoms and which were used in fire extinguishers, have an even greater damaging effect on the ozone layer, e.g. $CBrF_3$ and CBr_2F_2.

Ozone loss is greatest over Antarctica, the decline being most significant at the beginning of spring. In 1982, specially equipped aircraft flew at a height of 18.5 km across the boundary of ozone destruction and found ClO (free radicals) at least 100 times the normal level. The chlorine atoms were from CFCs. Ozone loss is worst in the World's coldest region because of polar stratospheric clouds (PSCs) which form when temperatures fall below –80°C. In 1986, it was suggested that these clouds are necessary, for the chemical reactions to occur late in the Antarctic winter. Once spring appears and light shines on the PSCs, rapid destruction of ozone occurs.

With a continuing rise in temperature, the PSCs are reduced and the ozone destruction levels off. The ozone depleted air eventually disperses to areas farther from the South Pole. The greater the loss of stratospheric ozone, the more UV-B reaches ground level. Assuming that global CFC release is soon halted (in line with the revised Montreal Protocol of 1990) the area of the ozone 'hole' is likely to increase since Antarctic stratosphere ozone levels will take several decades to recover. Peak ozone depletion levels are expected in 2002.

Ozone concentrations are measured in Dobson units. One unit represents one molecule of ozone to every billion molecules of air. The 'hole' in the ozone layer is a region where the concentration of ozone has been reduced.

3.17 Water analysis

- Before you start designing and planning your sampling program, look at your local catchment area and determine the factors which may be polluting the waterway.
- When collecting samples, for safety reasons
  (i) work in pairs,
  (ii) always wear gloves and safety glasses, and
  (iii) place all rubbish in a plastic bag for removal from the site.
- Take water samples as far away from the bank and as close to midstream as possible.

Experiment 3.1

Aim:

To investigate the dissolved oxygen content of a water sample.

Materials:

10 mL of alkaline iodide solution (3.3 g NaOH, 2.0 g KI in 10 mL of distilled water).

10 mL of manganese chloride solution (4 g of $MnCl_2$ in 10 mL of distilled water)

5 mL of conc. HCl.

Starch solution — 0.0125 **M** sodium thiosulfate solution $Na_2S_2O_3.5H_2O$ (1 mL of this solution is equivalent to 0.1 mg of oxygen).

Method:

1. Collect the two water samples under water. Put one aside away from the light.
2. To the other, add 2 mL of $MnCl_2$ solution and 2 mL of alkaline iodide solution using pipettes with tips placed at the bottom of each sample bottle. Replace stopper and shake.
3. Add 2 mL of HCl and stopper. Shake to dissolve the brown precipitate. This leaves a solution of iodine in an excess of potassium iodide. The iodine formed is directly proportional to the dissolved oxygen.
4. Pipette 50.0 mL of this solution into a conical flask and titrate with the 0.0125 **M** sodium thiosulfate using starch as the indicator. The endpoint is reached when the blue-black colour disappears.

Note: To determine the BOD, repeat the above titration after the other sample bottle has spent 5 days in a dark cupboard.

Calculations:

If DO on day 1 = 8 mg L^{-1} and DO on day 5 = 5 mg L^{-1}, then BOD level = 3 mg L^{-1}.

Unpolluted natural waters have a BOD of below 5 mg L^{-1}.

Treated sewage may have levels of 20–30 mg L^{-1}.

Chemical reactions in the Winkler determination of dissolved oxygen

1. $O_2(\text{dissolved}) + 4Mn^{2+} + 8OH^- \rightarrow 2Mn_2O_3(s) + 4H_2O$
2. $Mn_2O_3(s) + 6H^+ \rightarrow 2Mn^{3+} + 3H_2O$
3. $2Mn^{3+} + 2I^- \rightarrow 2Mn^{2+} + I_2$
4. $I_2 + \underset{\text{thiosulfate}}{2S_2O_3^{2-}} \rightarrow 2I^- + \underset{\text{tetrathionate}}{S_4O_6^{2-}}$

Thus 1 mole is $S_2O_3^{2-}$ is equivalent to 0.5 mole of I_2 which is equivalent to 0.25 mole (8.00 g) of O_2.

Significance

The concentration of dissolved oxygen (DO) in water is an important parameter in the assessment of water quality. The survival of plants and animals in any body of water depends on the ability of the water to maintain a minimal concentration of dissolved oxygen. Oxygen in the water is replenished by absorbency from the atmosphere and from photosynthesis. The primary causes of oxygen depletion are the presence of biodegradable wastes and the excessive growth of plant life. This latter effect, called eutrophication, follows a build-up in the levels of plant nutrients such as ammonium nitrate or phosphates. In a river or lake with a low DO concentration (less than 10–20% saturation), only anaerobic bacteria survive. The metabolic products include NH_3 and H_2S.

Table 3.7 Tests for some metals found in water (all metals except Group I must be absent)

Ion	Reagent (or test)	Positive result (colour)
Al^{3+}	aluminon	pink-red
Mg^{2+}	magneson I	light blue
Na^+	(flame test)	yellow
K^+	(flame test)	lilac (through cobalt glass)
Ca^{2+}	(flame test)	brick-red
NH_4 and NH_3	Nessler's reagent	yellow-brown

Table 3.8 Tests for some ions

Anion	Reagent	Positive result
PO_4^{3-}	acidify with HNO_3 then add excess ammonium molybdate solution	a yellow crystalline precipitate of ammonium phosphomolybdate
Cl^-	silver nitrate solution	white turbidity which darkens on exposure to light
S^{2-}	lead acetate solution or paper	a black deposit of PbS is formed
SO_4^{2-}	boil with HCl (to expel CO_2) and add barium chloride solution	a white precipitate of $BaSO_4$ forms

Heavy metal pollution of water

Detection

This can be carried out by precipitation with the sulfide ion. For qualitative testing to be carried out, the water sample must be concentrated by boiling (500 mL to 50 mL).

Trace amounts of Zn, Cu and Mn (0.05 mg L^{-1}) are usually present in natural waters. Zinc and copper may be present at higher levels in irrigation water, due to extensive use of galvanised iron, copper and brass in plumbing fixtures and for water storage. For irrigation, acceptable levels are 0.2 mg L^{-1} for Cu and 2.0 mg L^{-1} for Zn and Mn. Concentrations are measured by AAS using direct aspiration.

Table 3.9 Spot testing

Ion	Reagent	Positive result (colour)
Fe^{3+}	ammonium thiocyanate	blood-red
Cu^{2+}	* dithizone in 1,1,1-trichloroethane	yellow-brown
Pb^{2+}	* dithizone in 1,1,1-trichloroethane	brick-red
Zn^{2+}	* dithizone in 1,1,1-trichloroethane	pink

* Paper chromatography can be used. Ions are in 2 **M** HCl. Solvent is acetone, HCl and H_2O in ratio of 8:1:1. Dithizone solution is sprayed onto the paper after the movement of the solvent front to identify the cations.

3.18 Factors affecting concentrations of ions in natural water systems

Rivers

- Groundwater which has increased concentrations of Ca^{2+} and Mg^{2+} is a result of water passing through limestone areas, e.g. area around the Jenolan Caves in New South Wales.
- Increased salinity in river systems where, due to the clearing of native forest, the recharge rates for groundwater have increased and, with rising groundwater, dissolved salts are brought to the surface, e.g. the Murray-Darling catchment. Sodium concentrations in the Murray River near Adelaide are as high as 60 mg L^{-1}.
- An increase in the use of fertilisers containing phosphates and nitrates raises the amount of

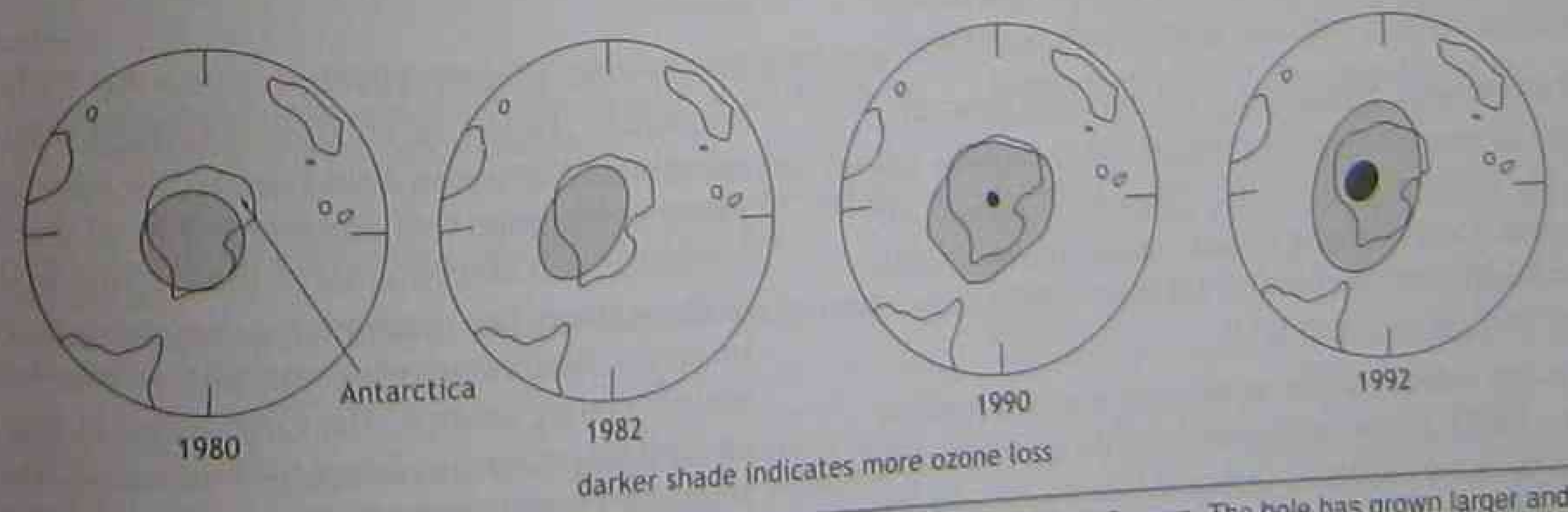


Figure 3.12 Antarctic zone. The development of the Antarctic ozone hole over a period of 12 years. The hole has grown larger and ozone loss become more severe in the centre.

nitrogen and phosphorus in water run-off. At the same time, there is a reduction of the flow of water in inland rivers due to the removal of water for irrigation, industry and domestic supply. Nitrogen and phosphorus are also carried into rivers from sewage treatment plants, irrigation drains and extensive animal industries. As a result, algal blooms can form. Levels at Swan Hill in Victoria can reach 0.8 mg/L of nitrogen and 1.0 mg/L of phosphorus.

Oceans

The disposal of sewage and other aqueous effluents from large coastal cities in a way that does not compromise the use of the coastal environment is an ongoing problem. To define the dispersion and subsequent ecological impact of the released waste waters, radiotracers are used to monitor sewage releases to the ocean. Marine pollution is worst near the shore.

Sewage can over-fertilise areas of the sea, especially in late summer when, due to high light intensity, eutrophication can occur. The death and decay of such plankton blooms can prove fatal to fish. Another pollutant in ocean waters which can affect shellfish, e.g. oysters, is lead. Ninety-eight per cent of lead in ocean waters is estimated to come from the atmosphere, that is, from motor car emissions.

3.19 Treatment of waste water

Until 1991, millions of tonnes of raw sewage were dumped close to Sydney's popular beaches. Ocean outfalls were opened in 1991 to pump sewage through pipelines 4 kilometres out to sea and release it 80 m under the surface. At the Malabar waste treatment plant near Sydney, radiotracers are used near the deep ocean outfall to validate the plant's computer models. The two radioisotopes used are gamma-emitting gold-198 to provide accurate information about the dispersing plume, and tritium which is used for accurate dilution measurements.

Modern sewage treatment is a four-stage process:

- *Preliminary treatment by screening* to remove the larger floating and coarser suspended solids. Air is bubbled through the mixture to cause turbulence and to remove odours. Total solids in raw sewage is about 0.1%.
- *Primary sedimentation* where settling tanks allow about 60% of the suspended solids to settle out. The primary sludge is pumped into heated sludge digesters. At Malabar, the clarified liquid is treated with chlorine and released into the sea.
- During *secondary treatment*, bacteria already present act on the effluent from the primary treatment process which has been pumped into aeration tanks where air is bubbled through the mixture. This is called the 'activated sludge' method, which can remove up to 90% of the suspended solids.
- The final stage is *chlorination* which removes most of the remaining bacteria. The resulting effluent is released into rivers, lakes or the Pacific Ocean, or is used for irrigation.

Note: Chemically, the objective of the 'activated sludge' method is the complete conversion of the wastes to inorganic materials. This is dependent on

(i) the ability of micro-organisms to form aggregates (flocs) which absorb colloidal materials and allow oxidation and settling, and

(ii) the chemical hydrolysis and oxidation of the soluble carbohydrates and proteins to form, for example, CO_2, H_2O, NH_3, NH_4^+, as well as nitrate, sulfate and phosphate ions.

In this process, active micro-organisms are continually recycled.

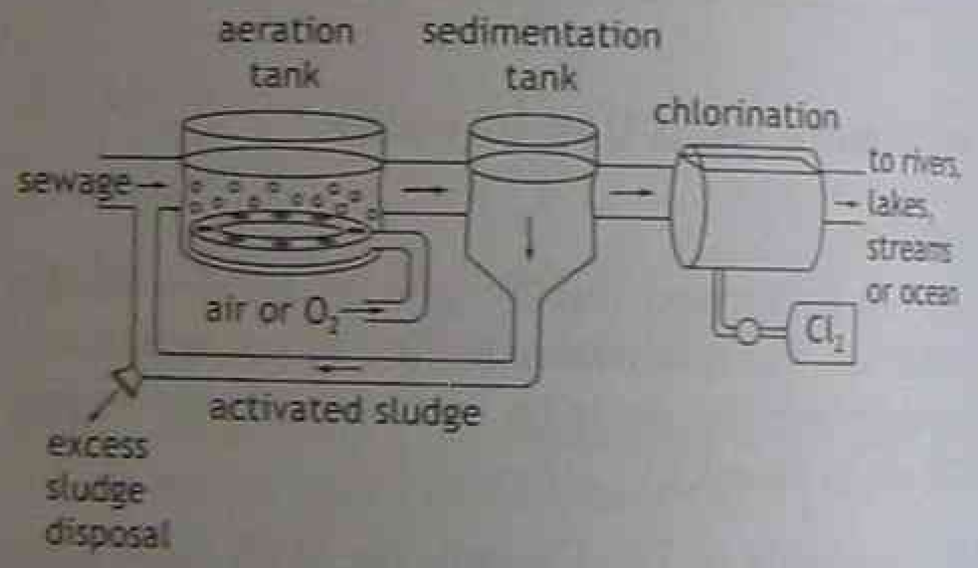


Figure 3.13 Secondary sewage treatment by the 'activated sludge' method

Other methods for secondary treatment include the following:

- *The Sirofloc process* developed by the CSIRO. Magnetite (Fe_3O_4) in an unmagnetised state is stirred into the water. Acid is added to adjust the pH of the solution to a range of 5–7.5, so that the magnetite will absorb most of the organic matter in the sewage. The magnetite is then passed close to large permanent magnets and forms large rapidly setting clumps. The clear water is run off and the magnetite can be reactivated using NaOH solution. This process needs only 10% of the land area and is much faster than other techniques.
- *Trickle filter method.* Effluent from primary treatment flows over a bed of rocks on the surface of which aerobic bacteria grow. These bacteria break down the organic matter in the sewage. Gaps in the rocks allow circulation of the air which the bacteria require to function.
- *Lagooning.* Most of Melbourne's sewage is treated at Werribee Farm by this method. Raw sewage is treated by lagooning and by soil and grass filtration. Lagooning is a less popular method because of the large amounts of land required.

Table 3.10 Water analysis – some tests

Test	Reason
Temperature Use an alcohol thermometer in a hard plastic cover.	Temperature influences the amount of dissolved oxygen hence the survival of aquatic organisms.
pH Use a pH meter in a hard plastic cover, pH paper or Universal Indicator solution.	pH is a measure of acidity or alkalinity of the water. pH of rain water = 5.5–6. pH will rise during photosynthesis (CO_2 drops). Acidic water (pH < 5) is most damaging to eggs and larvae of aquatic organisms.
Turbidity Use a Sechi disc ◐ (you can make one from a tin lid and string), or use a 500 mL measuring cylinder standing on paper marked with a cross.	Turbidity is a measure of water clarity. Suspended solids can stop light reaching submerged plants and also raise water temperature.
Total dissolved solids Use an appropriate TDS meter. Freshwater meters (0–1990 ppm). Dual range brackish water meters (0–19 900 ppm). Saltwater meters – higher range to above 35 000 ppm.	This is a conductivity test of available ions in the water. Most important ions include Ca^{2+}, Na^+, K^+, Fe^{2+}, Fe^{3+} and HCO_3^- as well as ions containing phosphorus, sulfur and nitrogen.
Dissolved oxygen (DO) 1. Use the Winkler titration method (see Experiment 3.1). 2. Use a colorimetric method ('Smart' colorimeter for field work). Sample must be collected under water to ensure that there are no trapped air bubbles. Collect two samples, one for a DO and one for a BOD determination.	The dissolved oxygen test measures the current oxygen status of a stream or river. DO levels vary with temperature. DO levels are highest in the afternoon (due to photosynthesis) and lowest just before dawn.
Biochemical oxygen demand (BOD) The sample is kept in a dark cupboard at collection temperature for 5 days, then the dissolved oxygen is determined.	The BOD measures the rate of consumption of oxygen by organisms in the water over a 5-day period.
Salinity in water A determination of the chloride content using $AgNO_3$ soln. (2.73 g/100 mL) and K_2CrO_4 as the indicator. The end point of the titration is given by the reddening of the AgCl precipitate. The volume of the $AgNO_3$ used = chloride content in g L^{-1}.	Many species can only survive in a very narrow range of salt concentrations since salts control osmotic pressure.
Hardness Calcium ions are usually determined by complexometric titration using EDTA (ethylenediaminetetraacetic acid) at a pH of 12–13. At this pH, Mg^{2+} ions are precipitated and not complexed with EDTA. Magnesium ions also contribute to total hardness of water. They can be titrated by EDTA at a pH = 10. The titration measures both Ca^{2+} and Mg^{2+} so a correction must be supplied using the result of the first Ca^{2+} determination. Potentiometric techniques using ion selective electrodes can be used. Soluble Ca^{2+} and Mg^{2+} can be measured by AAS.	Ca^{2+} is a major contributor to the hardness of water. Temporary hardness is due to $Ca(HCO_3)_2$ which, on boiling, deposits $CaCO_3$ as a scale. Industries involving low pressure boilers use water softened by an ion exchange process. Mg^{2+} levels are often high in irrigation water and can cause scouring in stock. Soil structure can also be affected. Ca^{2+} and Mg^{2+}, when combined with Cl^- and/or SO_4^{2-} ions, cause permanent hardness which is not removed by boiling.
Gravimetric method This is sometimes used to detect and/or determine the amount of $CaCO_3$ precipitated from a measured volume of hard water by the addition of a standard Na_2CO_3 solution (usually about 0.02 M). Flame testing can also be used to detect Ca^{2+} ions (brick-red colour in a non-luminous Bunsen flame).	

3.20 Treatment of drinking water

In Australian cities, water is treated before being supplied to consumer. The following steps are involved:

- *Flocculation* is the addition of electrolytes to force colloidal particles to aggregate and form filterable precipitates. The electrolytes neutralise the surface charge on the colloidal particles and allow flocculation to occur. The higher the charge on the electrolyte ions, the more efficient the electrolyte is as a floccing agent. Aluminium ions (Al^{3+}) are effective at floccing negatively charged colloids, e.g. clay colloids. Aluminium ions are used in preference to iron (III) ions as the iron ions impart a metallic taste to the water. Calcium hydroxide is added to adjust the pH of the water.

- *Settling*. In Sydney, under the present system, primary settling tanks are located with filtration systems, e.g. at Woronora dam, Prospect reservoir, Pott's Hill and Pipe Head. The 'floc' is allowed to settle in the tanks until a sludge forms. The clear water is then moved to the filtration stage and the sludge is removed from the bottom of the settling tank.
- *Filtration*. Water from the settling tank is filtered through a bed of sand over gravel to remove other suspended solids, including mineral particles.
- *Chemical additives* to water include the following:
  - (i) Gaseous chlorine which is used after filtration to destroy bacteria.

    $Cl_2(g) + H_2O(l) \rightarrow HOCl(aq) + H^+(aq) + Cl^-(aq)$

    It is the hypochlorite ion (OCl^-) that removes biological contaminants, such as bacteria, so that the water becomes fit for human consumption.
  - (ii) Many water supplies also have fluoride ions added to them in the final stages. Certain levels of fluoride will reduce dental decay in children by being incorporated into tooth enamel (and also into bones). Excess fluoride can cause mottling in teeth. Fluoride is added as sodium fluoride (NaF), sodium silicofluoride (Na_2SiF_6) or calcium fluoride (CaF_2).

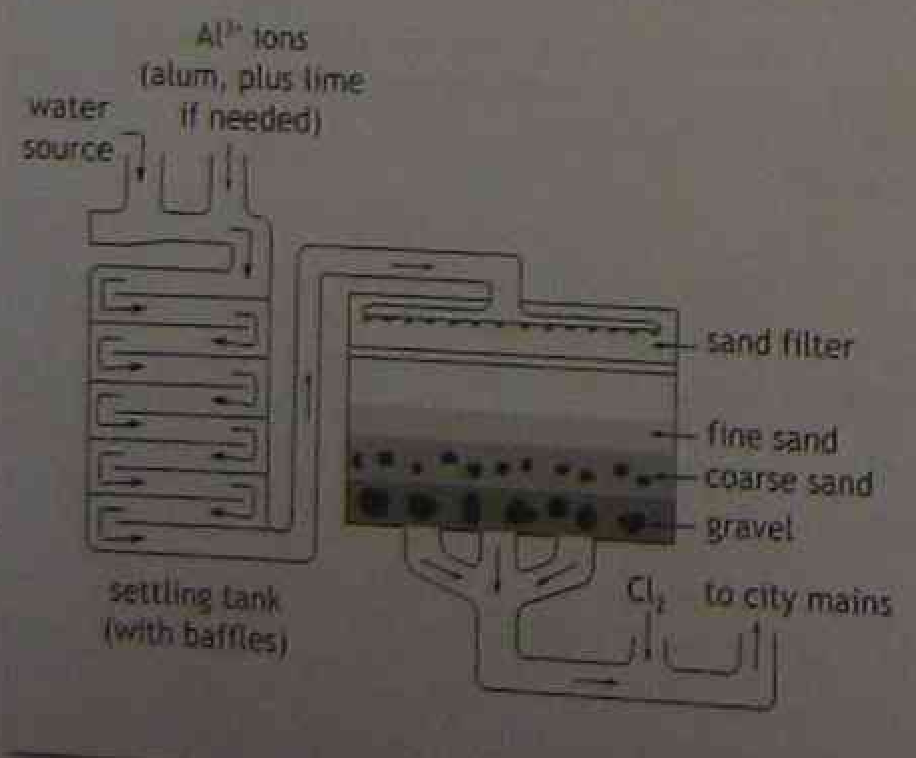


Figure 3.14 Treatment of city water supplies

3.21 Desalination of water

Desalination can be carried out by several techniques:

- *Multistage flash distillation* from seawater is used in countries where the energy costs are relatively low, e.g. Saudi Arabia.
- The Commonwealth Scientific & Industrial Research Organisation (CSIRO) has developed a *Sirotherm process* where the ion exchange resin removes Na^+ and Cl^- ions from the water with a high saline level, replacing them with H_3O^+ and OH^- ions. Beads of this ion exchange resin can reduce salt levels from 3000 ppm to acceptable levels of 500 ppm for human consumption. The resin is regenerated by flushing it with hot water.
- The *reverse osmosis process* required the use of a semi-permeable membrane which allows the passage of water molecules but not dissolved solids. The salinity can be lowered from 35 000 to 500 ppm. In an industrial plant, pressure is used to reverse the natural direction of the flow of water into salt water by osmosis. Membranes are of pliable cellulose triacetate or polyamides. This process is used in many household types of water purifiers where tap water produces sufficient pressure. Many Sydney people now use microscopic membrane filters after the protracted cryptosporidium and giardia crisis several years ago. One type of filter with fine pores is used. Water first passes through a pre-filter, then through a pliable cellulose triacetate membrane using a reverse osmosis system, and lastly, through a post-filter containing carbon to remove any odours.

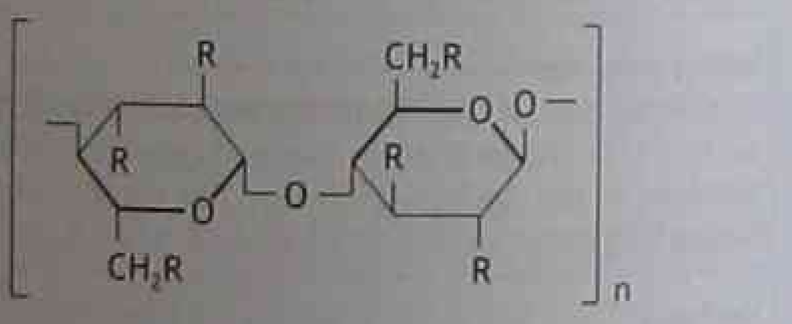


Figure 3.15 Cellulose triacetate

Another type of filter uses a polyamide type of membrane.

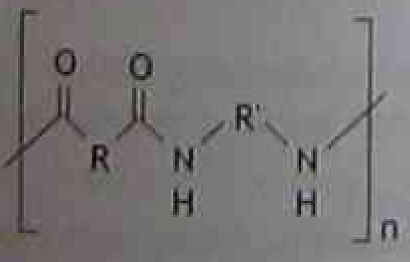


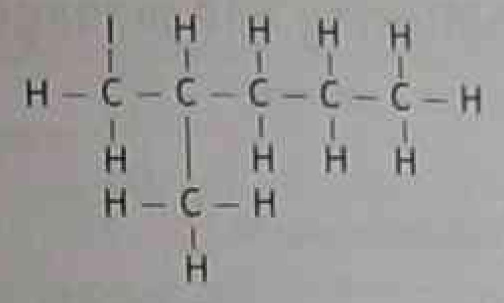
Figure 3.16 Amide link (R and R' are alkyl groups)

Test on Chapter 3 – Chemical monitoring and management

Part A

Questions 1 – 5 are worth 1 mark each

1. The IUPAC systematic name for the compound with the following structure is



(A) 5-iodo-4-methylpentane
(B) 1-iodo-2-methylpentane
(C) 2-methyl-iodopentane
(D) 1-methyl-2-iodopentane

2. Which of the following pairs of substances are isomers?
(A) 2-methylpropane and 2-methylbutane
(B) 3-iodobutane and 3-chlorobutane
(C) 2-methylpropane and butane
(D) 1,2-dichlorobutane and 1-chlorobutane

3. In 1913, Haber developed an industrial process which enabled Germany to manufacture nitrates for explosives in World War I.
The process involved the manufacture of ammonia:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92 \text{ kJ}$$

Which of the following changes is most likely to increase the yield of NH_3?
(A) Increasing the temperature.
(B) Decreasing the pressure.
(C) Increasing the amount of $N_2(g)$.
(D) Decreasing the amount of $N_2(g)$.

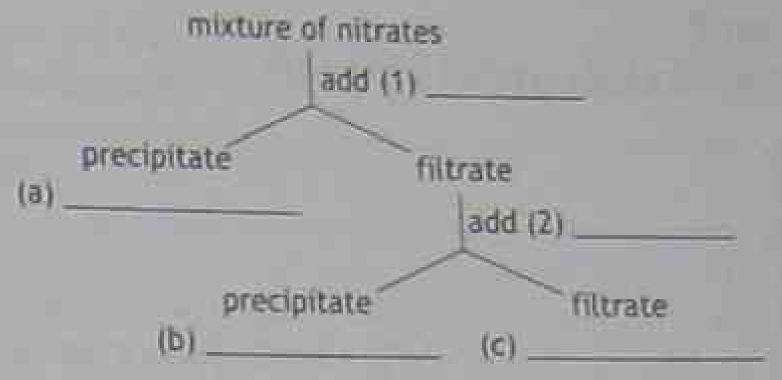
4. Trichloromethane is produced as a by-product of the chlorination of tap water. The formula of trichloromethane is
(A) CH_3Cl
(B) CH_2Cl_2
(C) CCl_4
(D) $CHCl_3$

5. Eutrophication of our waterways results in a deterioration of water quality.
Results of tests on water samples would be expected to show for total phosphorus and total nitrogen contents
(A) low phosphorus and high nitrogen content
(B) high phosphorus and high nitrogen content
(C) high phosphorus and low nitrogen content
(D) low phosphorus and low nitrogen content

Part B

Extended answer questions

6. [9 marks]
You are given a solution containing nitrates of the metals barium, lead and copper. Complete the schematic diagram shown below to separate and then identify each cation.



Name and give definitive tests and equations to identify (a), (b) and (c). Name reagents (1) and (2).

7. [10 marks]
Ozone (O_3) is produced in the stratosphere by the following reactions:
(a) O_2 molecules form O atoms by UV radiation

$$O_2(g) \rightarrow O(g) + O(g)$$

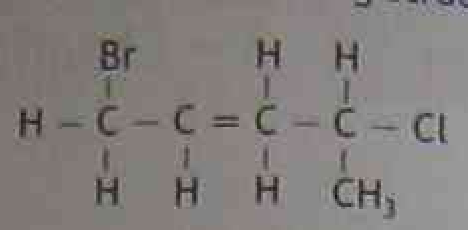
(b) O_2 reacts with O atoms

$$O_2(g) + O(g) \rightarrow O_3(g)$$

The production of ozone is disrupted by the presence of chlorofluorocarbons such as CF_2Cl_2.
(i) Explain using relevant chemical equations how CF_2Cl_2 could disrupt the formation of ozone.
(ii) O_2 and O_3 are allotropes. Explain.
(iii) Draw Lewis formula to show the structure of O_2 and O_3.
(iv) Explain the importance of the ozone layer to life on earth.

8. [10 marks]
Many country people in Australia use bore water which is a 'hard' water.
(a) Name two metal ions which are found in hard water.
(b) What happens when, in the case of temporary hardness, the water is boiled? Write an equation for the reaction and use it to explain why temporary hardness causes undesirable effects on steam irons, kettles and motor vehicle radiators.
(c) What is a simple way of detecting whether water is hard?
(d) In large cities, water from catchment areas is treated before it reaches consumers. One of the early stages of this water treatment involves flocculation. What is this and why is it carried out?

9. [4 marks]
(a) Draw the structural formula for 1,2- dibromobutane.
(b) Draw the structural formula for one of the branched chain isomers of 1,2 dibromobutane.
(c) State the empirical formula for 1,2-dibromobutane.


$\mathrm{H-\underset{H}{\overset{Br}{C}}-\underset{H}{C}=\underset{H}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}-Cl}$

Answers to test on Chapter 3 – Chemical monitoring and management

Part A
Multiple choice worth 1 mark each

1. B
2. C
3. C
4. D
5. D

Part B
Extended Answers

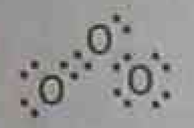
6. [9 marks]
Reagent 1 is dilute hydrochloric acid.
Reagent 2 is dilute sulfuric acid.
(a) Lead chloride. A white precipitate of lead chloride is formed which is soluble in hot water.
$Pb(NO_3)_2(aq) + 2\ HCl\ (aq) \rightarrow PbCl_2\ (s) + 2\ HNO_3(aq)$
(b) Barium sulfate. A white precipitate of barium sulfate is formed.
$Ba(NO_3)_2(aq) + H_2SO_4(aq) \rightarrow BaSO_4(g) + 2HNO_3(aq)$
(c) Copper nitrate. Various options, e.g. add NaOH and obtain a pale blue precipitate of copper hydroxide.
$Cu(NO_3)_2(aq) + NaOH(aq)$
$\rightarrow Cu(OH)_2(s) + 2NaNO_3(aq)$

7. [10 marks]
(i) $CF_2Cl_2(g) \xrightarrow{\text{UV radiation}} CF_2Cl(g) + Cl(g)$
$Cl(g) + O_3(g) \rightarrow ClO(g) + O_2(g)$
$ClO(g) + O(g) \rightarrow O_2(g) + Cl(g)$
the net result is

$$O_3(g) + O(g) \rightarrow 2O_2(g)$$

Since chlorine atoms are not permanently used up in the reaction, they can attack more ozone molecules. The O_3 molecule is not being replaced in the above cycle of reactions.
(ii) Allotropes are different forms of the same element, which have distinctly different physical properties, e.g. colour, density, hardness.
(iii) $:\ddot{O}::\ddot{O}:$

O_2

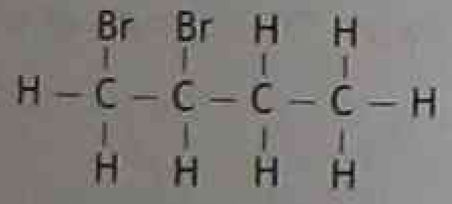


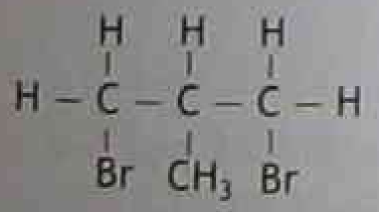
O_3 (ozone)

(iv) Ozone in the stratosphere shields the planet from damaging solar UV-B radiation. Changes in DNA molecules including their ability to code for proteins could result without the UV screening of the ozone layer.

8. [10 marks]
(a) Calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions.
(b) Calcium hydrogen carbonate forms a precipitate of calcium carbonate which forms a 'scale' in appliances.
$Ca(HCO_3)_2(aq) \xrightarrow{\text{heat}} CaCO_3(s) + CO_2(g) + H_2O(l)$
(c) Wash your hands with soap. The 2+ ions in hard water react with soap (sodium stearate) to form a curd (calcium stearate).
(d) Flocculation is the process by which small suspended particles join to form larger particles which then sink and settle. The agent used is alum (aluminium sulfate). Aluminium hydroxide is a gelatinous precipitate called the 'floc' which traps suspended solids from the water.

9. [4 marks]

(a)

$\mathrm{H-\underset{H}{\overset{Br}{C}}-\underset{H}{\overset{Br}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H}$

(b) Example:

$\mathrm{H-\underset{Br}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}-\underset{Br}{\overset{H}{C}}-H}$

1,3-dibromo-2-methylpropane

(c) C_2H_4Br
(d) 1-bromo-4-chloropent-2-ene

Total marks = 33 × 3 + 1 = 100%

Glossary

Acid	Proton donor.
Acid rain	Rain with a low pH due to dissolved gases such as SO_2 and NO_2.
Addition polymerisation	Produces a polymer from unsaturated monomers by an addition reaction.
Aerobic	Involves cellular respiration using molecular oxygen.
Algal bloom	Excessive growth of algae in waterways.
Alkanes	Saturated hydrocarbons (C_nH_{2n+2}).
Alkenes	Unsaturated hydrocarbons (C_2H_{2n}) containing a double bond (–C=C–).
Alkanols	Contain an –OH functional group ($C_nH_{2n+1}OH$).
Alkanoic acids	Contain a –COOH functional group ($C_nH_{2n}O_2$).
Alkyl groups	Alkane chains minus a hydrogen atom. The -ane of the parent hydrocarbon is dropped and the -yl is added.
Allotropy	Different structural forms of an element in the same state.
Alpha particle (α)	A helium nucleus ^4_2He.
Anaerobic	Involves cellular respiration in which molecular oxygen is not used.
Amphiprotic ions and molecules	May act as Brønsted-Lowry acids or bases depending on the reaction, e.g. HCO_3^-, NH_3.
Anion	An ion with a negative charge.
Anode	The electrode where oxidation occurs.
Atmosphere	The blanket of gases surrounding the Earth.
Atomic absorption spectrum	Dark absorption lines resulting from the absorption of particular wavelengths of light by the atoms.
Base	Proton acceptor.
Beta particle (β)	High speed electron.
Biodegradable	Able to be broken down by living organisms such as bacteria.
Biomass	Animal or plant matter used as fuel.
Biopolymers	Naturally occurring polymers, e.g. cellulose and starch. They are biodegradable and are renewable resources.
BOD	Biological oxygen demand which is a measure of oxidisable organic matter in water.

Brønsted-Lowry theory	An acid/base theory which states that an acid acts as a proton donor and a base as a proton receptor in all solvents.
Buffer solutions	Solutions resisting change in pH when acids or bases are added to them. They often contain a weak acid and its salt or a weak base and its salt.
Carbohydrates	Compounds composed of carbon hydrogen and oxygen $[C_n(H_2O)_n]$. Most are sugars or starches.
Catalyst	A substance that increases the rate of a chemical reaction.
Cathode	The electrode where reduction occurs.
Cation	An ion with a positive charge.
Cellulose	A complex carbohydrate made up of long unbranched chains of glucose units. It is a polysaccharide.
Chlorofluorocarbons (CFCs)	Organic compounds made up of atoms of carbon, fluorine and chlorine, e.g. CCl_2F_2 or CFC-12.
Condensation polymerisation	Produces a polymer from monomers with two or more functional groups. A small molecule, e.g. H_2O, is split off.
Coordinate covalent bond	One of the combining atoms supplies both electrons to the covalent bond.
Covalent bond	A bond between two atoms where the electrons are shared.
Cracking	The decomposition of petroleum hydrocarbons into fractions of lower molecular mass by heat. Catalytic cracking involves the use of a catalyst but thermal cracking does not.
Dehydrating agent	1. Removes water from a substance. 2. Removes hydrogen and oxygen atoms from a substance in a 2:1 mole ratio.
Desalination	The process of removal of salts from seawater to make it drinkable.
Deoxyribonucleic acid (DNA)	Main type of nucleic acid which is a component of all living cells.
Diffusion	The movement of one substance through another.
Dissolved oxygen (DO)	A measure of water quality.
Distillation	The separation by the use of a still of 1. a liquid from a solid, and 2. two liquids with different boiling points by vaporising followed by condensation.
Effluent	Waste water.
Electrochemical cell	The cell is made up of two half-cells.
End point	The point in a titration where the indicator undergoes a sharp colour change. A correctly chosen indicator has its end point at the equivalence point.
Endothermic reaction	Heat is taken in by the system (ΔH is +ve).
Enhanced greenhouse effect	An increase in the natural process where greenhouse gases are being released into the atmosphere at a far greater rate.

Equilibrium	Occurs in a closed system when forward reaction rate equals the reverse reaction rate.
Ester	An organic compound with a functional group –COOR, where R is an alkyl group.
Esterification	The formation of an ester by the reaction of an alkanol and an alkanoic acid.
Eutrophication	An increase of nutrients in a body of water that often leads to 'algal bloom' which results eventually in lowering of the DO and death of aquatic organisms.
Exothermic reaction	Heat is given out from the system (ΔH is –ve).
Flocculation	The coagulation and precipitation of colloidal particles.
Fossil fuels	Carbon or hydrocarbon fuels, derived from the remains of once-living organisms and found underground, that are burned to release energy, e.g. coal, oil and natural gas.
Functional group	The atom or group of atoms in an organic molecule which gives the compound its characteristic chemical properties.
Geiger counter	An instrument to measure radiation.
Glucose	A monosaccharide (a 6-carbon sugar) $C_6H_{12}O_6$.
Haber process	A process using $N_2(g)$ and $H_2(g)$ to manufacture ammonia $NH_3(g)$.
Half-life	The time it takes for half the atoms in a radioactive material to break down to a non-radioactive element.
Haloalkanes	Derivatives of alkanes in which a hydrogen atom is replaced by a halogen atom (Br, Cl, F, I).
Hard water	Groundwater containing cations Ca^{2+}, Mg^{2+} and anions HCO_3^-, Cl^- and SO_4^{2-}.
Heat of neutralisation	Heat evolved when the equivalence point is reached in a neutralisation reaction.
Hydrochlorofluoro-carbons (HCFCs)	Compounds like CFCs but with extra hydrogen atoms and a lower ozone destruction potential.
Hydrogen bonding	Occurs when a hydrogen atom is covalently bonded to strongly electronegative atoms such as oxygen, nitrogen or fluorine.
Indicators	Brønsted-Lowry acids or bases where the acid colour is different from the basic colour. $K_{in} = \frac{[H^+][I^-]}{[H_{in}]}$
Ionic bond	A bond formed when electrons are completely transferred from one atom to another. The bond is an electrostatic attraction between anion and cation.
Ionisation constant	$K_a = \frac{[H^+][A^-]}{[HA]}$ (for monoprotic weak acids).
Isomers	These have the same molecular formula but different structural formula.
Isotopes	Atoms with the same atomic number but different mass numbers.
Le Châtelier's Principle	States that if the conditions of a system at equilibrium are changed, the system wil adjust to try to oppose that change.
Ozone (O_3)	A gaseous allotrope of O_2.

Ozone layer	The layer of ozone in the stratosphere which absorbs damaging ultraviolet rays.
Oxidation	Loss of electrons from a substance.
PAN	Peroxyacetyl nitrate.
Passivating metals	Reactive metals that form an inactive coating as a result of reaction with substances such as water or oxygen. Aluminium has an inherent oxide film which is inert, tenacious and reforms immediately if cleaned with steel wool.
Photochemical smog	A haze produced by the action between air pollutants from cars and industry resulting in O_3 and PAN formation. Temperature inversion and sunlight are needed to produce the 'brown haze'.
Polar molecules	Molecules where the charge is unevenly distributed so that dipoles (with opposite charges) occur, for example, H_2O.
Qualitative analysis	Used to identify constituents of a substance.
Quantitative analysis	Used to determine the composition of a mixture or compound.
Radioactivity	The spontaneous decay of an unstable atomic nucleus, giving rise to the emission of radiation.
Radioisotopes	Isotopes with unstable nuclei that emit radioactive particles and sometimes also gamma radiation.
Reduction	Gain of electrons by a substance.
Reverse osmosis	Depends on the use of a semi-permeable membrane which will allow the passage of water molecules but not dissolved solids.
Stratosphere	Is the layer of atmosphere above 11 km and extending upwards to about 50 km. The ozone layer is concentrated at 30 km.
Transuranic elements	Artificially formed. They start at element 93 (Neptunium) and go on to element 107.
Troposphere	The layer of the atmosphere extending to 11 km.
UV-B	Ultraviolet radiation in this band (290–320 nm) is not completely absorbed by the ozone layer, so it passes through the stratosphere into the troposphere.
Yellowcake	A mixture of uranium oxides represented by the formula U_3O_8.
Zeolites	A naturally occurring group of substances containing a mixture of oxides of aluminium and silicon. They are used as catalysts in the catalytic cracking of alkanes.

4 option one

Industrial Chemistry

Contents

4.1 Timber – a world natural resource

Biomes

Timber is a natural resource that is not a fossil fuel. Major biomes (large ecosystems occurring in major land regions) include deciduous forest, tropical rainforest and coniferous forest. Each biome is unique because of its location, climate and soil conditions. Animals and plants in each region adapt accordingly.

Removal of forests

Tropical rainforest has the greatest variety of plants and animals. These are threatened by activities such as the Japanese wood-chipping industry in the forests of Papua New Guinea, Thailand and Malaysia. The wood chips from these forests are used to make cardboard packaging. Tropical forests in Queensland are also being felled to make more land available for agriculture.

Australia exports paper pulp to Japan. Bleached paper mills have operated in Tasmania for over 50 years. Chlorine is traditionally used to bleach timber pulp to produce white paper products. This produces organochlorides and dioxins as by-products of the high-temperature bleaching process.

The immediate economic gain from destroying forests is greater than if they were used in a sustainable way. In India, mainly as a result of population explosion, the entire subcontinent is being deforested to produce more land for crops. Forests are being felled faster than they can regenerate so the Earth's biodiversity is threatened.

Dangers of land clearing include:

- *Reduction in genetic variability.* As humanity destroys biodiversity in yet another forest to develop high-yield agriculture, this reduces the pool of genetic variability. Genetic engineers cannot create brand new genes but only transfer genes of known functions from one organism to another.
- *Salinity.* Salinity is a problem on land which is cleared of trees, farmed and irrigated. While native vegetation used water through evapotranspiration, the water table remained at a safe depth, preventing salt rising to the surface. In cleared areas, saline seepage occurs when the ground surface falls below the natural water table. (Salt bush and salt-resistant red gum eucalypts can be planted to reduce salinity.)
- *Unbalanced water cycle.* Irrigation results in the natural water cycle being unbalanced, and the water tables rise. Salts accumulate in the root zones of crop plants (e.g. deciduous orchard trees, cotton and fodder crops) which results in crop losses.
- *Loss of useful plant products.* Many effective medicines were originally evolved as plant defences, e.g. quinine (used for treating malaria and muscle cramps) and aspirin (currently being trialled in a combination pill to prevent strokes and heart attacks). Eucalyptus and tea-tree oil can be extracted from Australian trees and used as antiseptics or diluted in vaporisers as inhalants.

Reversing the trend of deforestation

There are many strategies that can be used to reverse the present trend of deforestation:

- Replant forests to help remove carbon dioxide from the atmosphere and slow global warming. This will reduce desertification and slow soil erosion due to agriculture.
- Give up, where possible, the use of tropical hardwood.
- Carefully monitor the logging of old-growth (natural) forests.
- Decrease the flood of paper from computer printers and copying.
- Eliminate oversized newspapers.
- Reduce unnecessary cardboard and paper packaging.
- Recycle paper products.
- Support National Tree Day and join groups involved in local tree-planting.
- Be aware that population explosion is an important environmental problem and is a main factor in rainforest destruction.
- Join community efforts to stop environmental degradation. Remember that community effort stopped the damming of the Franklin River in Tasmania. This saved endangered species and even promoted tourism in the area.

Controlled use of timber

Where possible, the use of plantation pine forests which are relatively fast-growing, should be used in the building industry. Treated pine timber, however, contains arsenic and cannot be used in children's playgrounds.

Replacement materials for timber

- Metal or concrete for posts and poles (e.g. power and lighting posts)
- Sheet metal or galvanised steel mesh for fences instead of wood palings
- Fibreglass or metal for boats
- Anodised aluminium for window frames, doors and balconies
- Cement and tiles instead of wooden floors
- Metal and glass roofing materials for patios and verandahs
- Plastic, glass or metal furniture
- Brick for exterior walls in buildings
- Aluminium or fabric for blinds or curtains instead of wooden slat blinds
- Gyprock for wall panels.

Recycling

Recycling is essential in a world which has a 'population explosion'. Metals such as aluminium cans, low carbon steel (e.g. in car bodies and cans) and copper can be recycled (see *Excel Preliminary Chemistry*, Section 2.12). Paper, glass and some plastics can be recycled by many local councils, who provide separate bins for their collection. Reclaimed timber can also be recycled.

Briquettes are produced from waste paper, wood residues (e.g. sawdust) and bagasse (a residue of sugar refining which would otherwise be a waste product). These can be used as an alternative fuel source in heating, steam and power.

Wood as a fuel

Wood is still a major fuel source in underdeveloped countries. In some developing countries (e.g. Eritrea), the use of regulated slow wood-burning stoves has reduced pollutants and the use of fuel resources.

Wood is mainly composed of cellulose $(C_6H_{10}O_5)_n$ and burns exothermally to produce carbon dioxide and water. It can be converted into energy which can be more efficiently used. Two main thermochemical processes are:

(a) *Pyrolysis.* Pyrolysis of wood (and other biomass) results in its breakdown in the absence of oxygen at a temperature above 250°C. The process produces char or charcoal, a liquid bio-oil and a mixture of gases. Fast pyrolysis is used to maximise the gas and liquid products. Present interest lies in the liquid output due to its high-energy density.

(b) *Gasification.* This is a form of pyrolysis and involves the complete thermal breakdown of biomass (any type of wood, bamboo, grasses, etc). The gas produced can be used for heat or power generation.

Step 1. Manufacture of synthetic gas.
Biomass + $O_2 \rightarrow CO + H_2$
Step 2. Water shift to adjust CO/H_2 ratio.
$CO + H_2O \rightarrow CO_2 + H_2$
Step 3. Synthesis with catalyst to produce methane.
$CO + 2H_2 \rightarrow CH_4$ or
$CO + H_2 \rightarrow$ diesel or gasoline

Developments in gasification of biochemical processes include biomass + metabolic action of microbial organisms to produce gaseous and liquid fuels (e.g. ethanol and methanol).

Alternative ways of producing energy

Research is being carried out into ways to grow crops to obtain 'stored solar energy' in plants ('energy farming'). Plants absorb solar radiation with wavelengths of 400–700 nm only. This is about half the solar energy reaching the earth's surface. Of the radiation absorbed by plants, only about a third is used for photosynthesis. Scientists are investigating ways of improving the efficiency of photosynthesis so that more plant matter grows for a given quantity of absorbed solar energy.

Starches and sugars in rice, wheat and sugar cane can be converted by fermentation to ethanol. Cellulose in waste products can be converted to methane by bacterial action in the absence of air (anaerobic fermentation).

A good fuel must be:

- available in large quantities
- able to be easily collected and used
- easily stored
- environmentally and socially acceptable.

4.2 Reversible reactions

Equilibrium occurs when the forward reaction rate equals the reverse reaction rate. Concentrations of all species are then constant.

- Reversibility is shown by the double arrow.
- Reaction rate can be shown graphically.

- Dynamic equilibrium occurs in a closed system.
- Steady state conditions occur in open systems and are not reversible.

Phase changes

Phase changes are explained by the kinetic theory. Surface molecules in a liquid may have enough kinetic energy to escape as vapour, causing vapour pressure. At the same temperature, liquid with the strongest attractive force between molecules will have the lowest vapour pressure (See Table 4.1).

Phase changes involving equilibrium

Example 1

Consider the equilibrium between liquid water and gaseous water:

Table 4.1 Changes of state (phase changes – physical changes)

Change	Name	Energy change
Solid to liquid	melting, fusion	endothermic (heat needed)
Liquid to solid	freezing	exothermic (heat given out)
Liquid to gas	vaporisation,boiling	endothermic
Gas to liquid	condensation	exothermic
Solid to gas	sublimation	endothermic
Gas to solid		exothermic

$$H_2O(l) \rightleftharpoons H_2O(g)$$

For a system containing a gas to reach equilibrium it must be in a closed system.

The forward reaction is evaporation

$$H_2O(l) \rightarrow H_2O(g)$$

The backward reaction is condensation

$$H_2O(l) \leftarrow H_2O(g)$$

In a closed container $\boxed{\begin{array}{c} H_2O(g) \\ \uparrow\downarrow \\ H_2O(l) \end{array}}$

When equilibrium is reached, the number of molecules in each phase is constant. This equilibrium is a dynamic system.

If the container was left open, the rate of evaporation would be greater than the rate of condensation so there would not be an equilibrium system (see Figure 4.1).

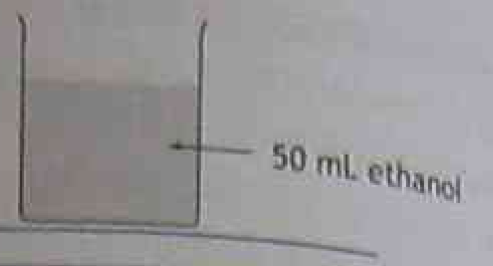


Figure 4.1 Open system. Ethanol evaporates.

Example 2

A simple laboratory experiment to show liquid-gas phase change can be set up as in Figure 4.2.

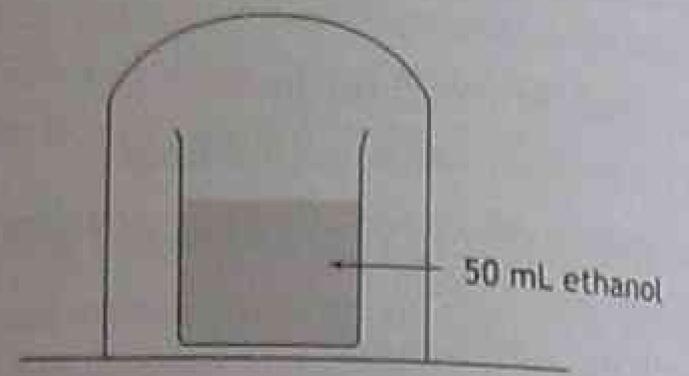


Figure 4.2 Closed system. Liquid-vapour equilibrium.

Example 3

A closed system is needed for equilibrium to occur between $I_2(s) \rightleftharpoons I_2(g)$.

Take a large evaporating dish and place a few dark grey shiny iodine crystals in it. Leave it in the fume cupboard overnight. Also, place some iodine crystals in a clear screw-top glass jar and put the sealed jar in the fume cupboard overnight. Observe what happens.

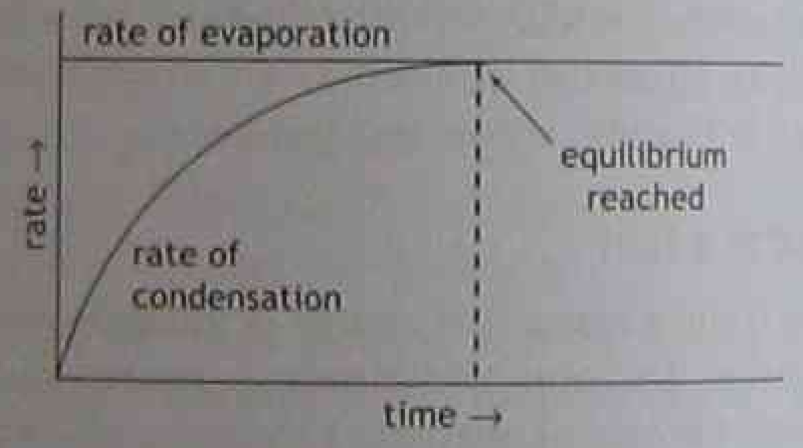


Figure 4.3 Reaching liquid-vapour equilibrium in a closed system

Table 4.2 Vapour pressure of some liquid (kPa)

Temp (°C)	Water	Ethanol	Carbon tetrachloride	Benzene
10	1.23	3.15	7.46	6.00
20	2.33	5.85	12.13	9.86
30	4.24	10.50	19.06	15.73

Homogenous equilibrium reactions

Some examples are given below.

1. $2\,NO_2(g) \rightleftharpoons N_2O_4(g)$

   Here all species are in the gaseous state.

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

Here all species are in the liquid state.

Homogenous reactions have their products and reactants in the same phase (state).

The rate of such homogeneous reactions depends on three factors:

(a) The concentration of the reactants. If the reactants are gases, then the pressure will be used.

(b) The temperature at which the reaction takes place.

(c) The presence of a catalyst. A catalyst can be used to increase the rate of a reaction but does not undergo any permanent change during that reaction. It provides a pathway of lower activation energy.

3. The first scientific study of an equilibrium system was a homogeneous reaction carried out in 1893 by the German chemist Max Bodenstein. He studied the formation and decomposition of hydrogen iodide in steel containers at 445°C (see Figure 4.4).

Reaction 1

	H_2	I_2	HI
Initial amounts moles	1	1	0
Gases reacted until the system contained moles	0.2	0.2	1.6

Reaction 2 (reverse of Reaction 1)

	HI	H_2	I_2
Initial amounts moles	2	0	0
Gases reacted until the system contained moles	1.6	0.2	0.2

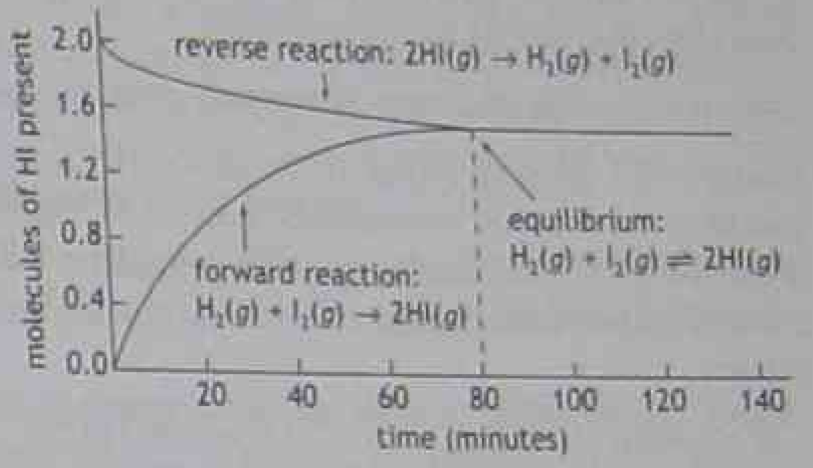


Figure 4.4 Bodenstein's equilibrium experiment

Bodenstein's experiment showed the reversibility of the chemical reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$.

Table 4.3 Some effects of change to the equilibrium system

Change	Effect of change on equilibrium position
For concentrations:	
Concentration of products increased by adding product	backward reaction is favoured so more reactants will be formed
Concentration of reactants increased by adding reactant	forward reaction is favoured so more products are formed
SUMMARY Let [R] be concentration of reactants and [P] be concentration of products; then	
Increase in [R]	increase in [P]
Increase in [P]	increase in [R]
For gases:	
Increase in pressure	equilibrium will favour the direction which results in a decrease in the number of molecules of gas produced
Increase in volume	equilibrium will favour the direction which results in an increase in the number of molecules of gas produced
Temperature:	
Increase in temperature	shifts to absorption of heat (endothermic reaction favoured)
Decrease in temperature	shifts to release of heat (exothermic reaction favoured)

It also showed that the equilibrium position was independent of the starting point of the reaction.

Heterogeneous equilibrium reactions

Heterogeneous reactions are systems involving more than one state of matter.

Example

Calcium carbonate on heating in a closed system.

Some suggested student activities

In a reversible reaction it is possible to shift the position of the equilibrium by changing the concentration of one of the reactants.

Example 1— The chromate-dichromate reaction

Using a 0.1 M potassium dichromate ($K_2Cr_2O_7$) solution which is coloured orange, add 0.1 M NaOH dropwise until a colour change takes place, then add 0.1 M HCl until the solution reverts to its original colour.

$$\underset{\text{chromate ion}}{2CrO_4^{2-}(aq)} + 2H^+(aq) \rightarrow \underset{\text{dichromate ion}}{Cr_2O_7(aq)} + H_2O(l)$$

Example 2

Some homogeneous equilibria involving transition metal ions include an investigation into what happens when concentration of reactants in the equilibrium reaction is changed.

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

- The $FeSCN^{2+}(aq)$ ions are deep blood red. Their concentration in solution can be estimated by the intensity of colour. The complex must not be too dark so that changes can be noticed.
- The $Fe^{3+}(aq)$ ions will appear almost colourless since their concentration will be less than 0.05 M.
- The $SCN^-(aq)$ ions are colourless.

The effects on the equilibrium can be investigated by adding to separate portions of the equilibrium solution

(i) $Fe^{3+}(aq)$ ions,
(ii) $SCN^-(aq)$ ions

To detect whether the forward or reverse reaction is exothermic, place a sample of the complex

(i) in ice, and then
(ii) in hot water,

and note any lightening or darkening in colour.

Example 3

A pink colour is due to the $Co(H_2O)_6^{2+}(aq)$ ions for cobalt.

A blue colour is due to the $CoCl_4^{2-}$ ion.

$$Co(H_2O)_6^{2+}(aq) + 4Cl^- \rightleftharpoons CoCl_4^{2-}(aq) + 6H_2O$$

To separate samples of a $CoCl_2$ solution,

(i) add ethanol [which removes water molecules from the $Co(H_2O)_6^{2+}(aq)$ complex] and note any colour change; and
(ii) heat a solution of $CoCl_2$ and note any colour change.

4.3 The effect of a change in conditions on equilibrium reactions

Equilibrium systems are sensitive to changes in conditions. When a system in chemical equilibrium is changed in some way, a chemical reaction will occur in order to regain the state of equilibrium.

Two factors that can alter an equilibrium are

(a) a change in concentration of a reactant or product; and
(b) a change in temperature.

Effect of a change in concentration on equilibrium

> **Le Châtelier's Principle**
> If any chemical system at equilibrium is subjected to a change in concentration or temperature, the system will react in the direction that will minimise the effect of that change.

Le Châtelier's Principle allows qualitative predictions to be made regarding the effect of changes on the equilibrium system.

Effect of heat on solubility

If the heat of solution is exothermic, then the solid will be less soluble on heating. If the heat of solution is endothermic, then the solid will be more soluble on heating.

Effect of pressure on the solubility of gases

Increase of pressure results in an increase of solubility of the gas in the liquid.

Example 1 — concentration

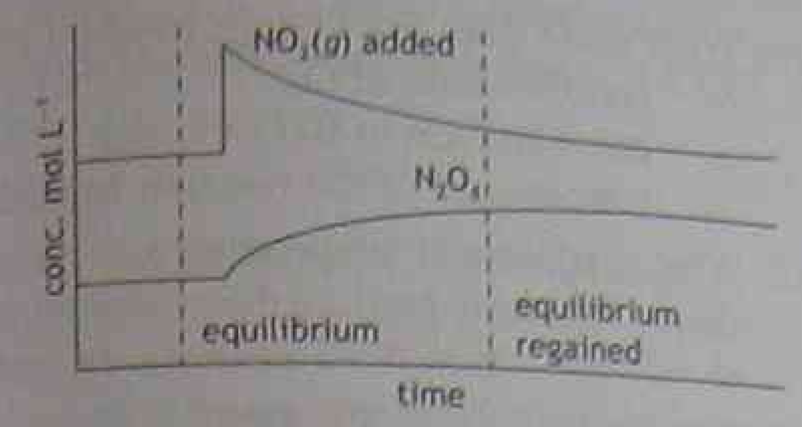


Figure 4.5 Equilibrium in the system NO_2/N_2O_4

Example 2 — temperature

Reversible reaction:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Consider the forward reaction:

$$H_2(g) + I_2(g) \rightarrow 2HI(g) \qquad \Delta H = 47.7\ kJ$$

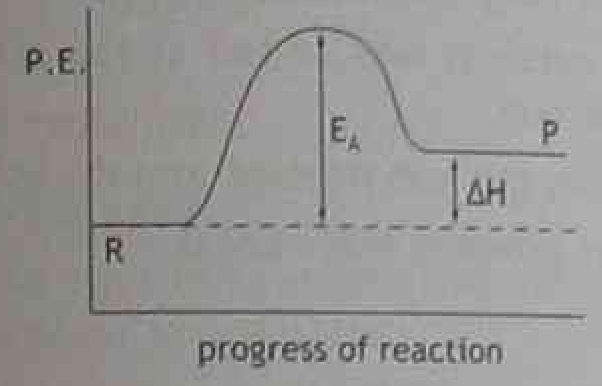


Figure 4.6 Energy change in forward reaction

Since ΔH is positive, this is an endothermic reaction.

Consider the backward reaction:

$$2HI(g) \rightarrow H_2(g) + I_2(g) \qquad \Delta H = -47.7\ kJ$$

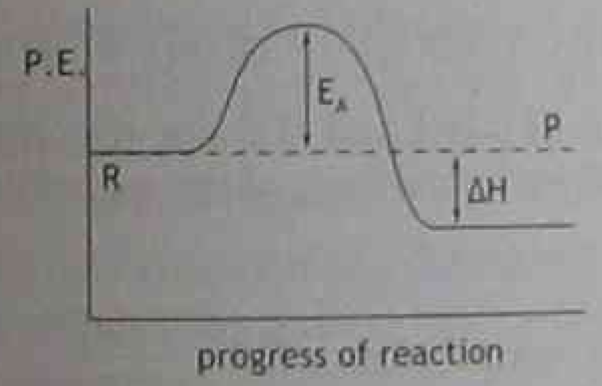


Figure 4.7 Energy change in backward reaction.

Since ΔH is negative, this is an exothermic reaction.

Key:			
	R	—	reactants
	P	—	products
	E_A	—	activation energy*
	ΔH	—	change in heat content

*(E_A) – activation energy is the energy that colliding particles need to form an activated complex.

(a) A product is removed

In the reaction $2NO_2(g) \rightleftharpoons N_2O_4(g)$, if the product $N_2O_4(g)$ was steadily removed as it formed, then more $NO_2(g)$ would react to form more product, so the equilibrium would shift to the right.

(b) A reactant is added

In the above reaction, adding $NO_2(g)$ would again shift the equilibrium to the right as more $NO_2(g)$ would react.

(c) A product is added

In the above reaction, adding $N_2O_4(g)$ would shift the equilibrium to the left as the system tries to minimise the change.

(d) A reactant is removed

In the above reaction, removing $NO_2(g)$ would result in a shift to the left as more reactant is produced.

(e) A change in the total pressure of the reacting mixture

This applies only to gaseous reactions. An increase in pressure (or decrease in volume) would cause an increase in concentration and a decrease in pressure (an increase in volume) would cause a decrease in concentration. This only affects the equilibrium if the number of molecules is different on one side of the equation from the other:

(i) $\underset{\text{2 molecules}}{2NO_2(g)} \rightleftharpoons \underset{\text{1 molecule}}{N_2O_4(g)}$

Increase in pressure will result in the equilibrium favouring the direction of the reaction where fewer molecules of gas are produced.

(ii) $\underset{\text{2 molecules}}{H_2(g) + I_2(g)} \rightleftharpoons \underset{\text{2 molecules}}{2HI(g)}$

Reaction not affected.

(f) The addition of a reagent which reacts with a reactant or product

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

In the above reaction, if a dilute acid was added, the H^+ ions would combine with the OH^- ions to form water, so the equilibrium would shift to the right.

4.4 Catalysts and equilibrium

Catalysts are used to speed up reactions, especially in industry. Catalysts cannot change the position of the equilibrium in a reaction. Catalysts reduce the activation energy by providing an alternative reaction (pathway mechanism) for the reaction. Catalysts do not change the concentration of substances at equilibrium.

Biological catalysts, for example, are called enzymes.

glucose $\rightleftharpoons$ ethanol + carbon dioxide

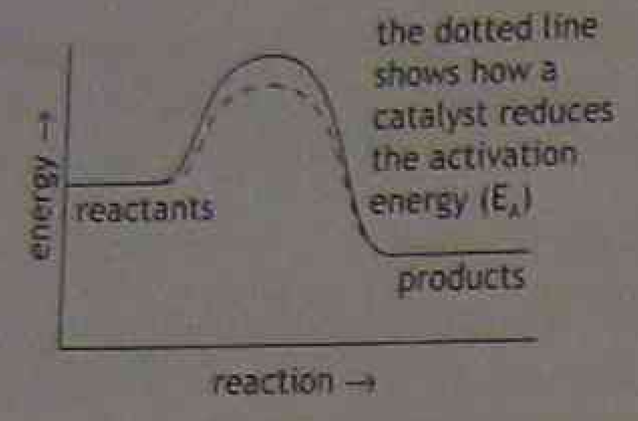


Figure 4.8 Effect of catalyst on the activation energy of reaction

Exercise 4.1

Problems on equilibrium

1. Complete the following table:

(a) Equilibrium reaction

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

ΔH for forward reaction is 47.7 kJ

Change made	Direction and explanation of any equilibrium shift
(i) $[I_2]$ ↑	
(ii) $[H_2]$ ↓	
(iii) pressure ↑	
(iv) volume ↑	
(v) temperature ↑	

(b) Equilibrium reaction

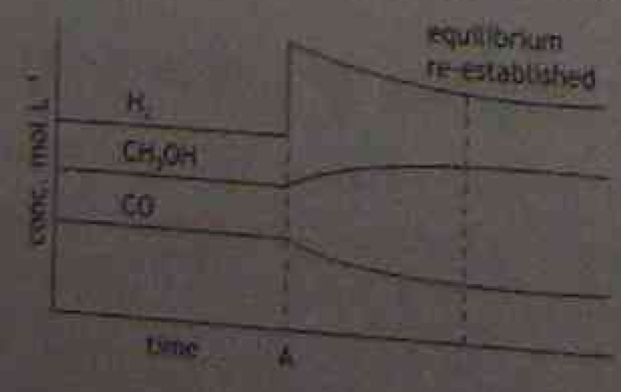
$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$

ΔH for forward reaction is 41 kJ

Change made	Direction and explanation of any equilibrium shift
(i) $[CO]$ ↑	
(ii) $[H_2]$ ↑	
(iii) pressure ↑	
(iv) temperature ↓	

2. Consider the following equation and graph

$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -52\ kJ$



(a) What is added to the reaction vessel at time A?

(b) What effect does this change have on the
   (i) concentration of CO;
   (ii) concentration of CH_3OH; and
   (iii) temperature of the reaction vessel?

(c) What conditions of temperature and pressure should be used to produce the maximum yield of methanol from fixed amounts of carbon monoxide and hydrogen gases?

(d) Industrially, this reaction requires a catalyst. What is the role of a catalyst?

3. For the reaction

$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g) + 185\ kJ$

How would the equilibrium change if the following changes were made?

(a) The temperature was decreased.

(b) The $[Cl_2]$ was increased.

(c) A catalyst was added at the start of the reaction.

(d) Neon gas was injected into the system.

(e) The pressure was halved.

4.5 The equilibrium constant K

The Law of Mass Action expresses the relative concentrations of reactants and products at equilibrium in terms of a single number called the equilibrium constant K. In general, for a homogenous reaction

$$aA(aq) + bB(aq) \rightleftharpoons cC(aq) + dD(aq)$$

where [A], [B], [C] and [D] are the equilibrium concentrations (molarities) of the quantities A, B, C and D.

At constant temperature, $K = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$.

Equilibrium constants are found experimentally

Equilibrium constants are given as numbers only.

Example 1

The gas phosgene is extremely poisonous and decomposes into the gases carbon monoxide and chlorine at 900°C.

$$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$$

In a series of experiments, different amounts of $COCl_2$ were placed in closed containers at 900°C and the reactions left until equilibrium was established. The value of K at equilibrium was the same, although the initial concentrations of $COCl_2$ were different.

Example 2

$$CH_3OH(aq) + CH_3COOH(aq)$$
$$\rightleftharpoons CH_3COOCH_3(aq) + H_2O(l)$$

At a given temperature, K is the same for a specific reaction.

Example 3

From the Bodenstein equilibrium experiment, using the data from Figure 4.4 and assuming that a one litre container was used, for the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

$$K = \frac{[HI]^2}{[H_2][I_2]} = \frac{[1.6]^2}{[0.2][0.2]} = 64$$

Points to remember

(a) Involving gases:
   (i) The equilibrium must be established at constant temperature.
   (ii) The reaction must occur in a closed container or a closed system where no reactant or product gases are lost before equilibrium is established.

(b) When solid reactions or products are present at equilibrium:
   (i) The position of equilibrium and the value of the equilibrium constant at a given temperature are independent of the amounts of the solids present.
   (ii) The concentration of solids in mol L^{-1} cannot be changed by adding more solid.

   Example

   $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

   Since $[CaCO_3(s)]$ and $[CaO(s)]$ will both remain constant:

   $$K = [CO_2(g)]$$

(c) Equilibrium reactions involving a solvent:

   If a solvent takes part in a reaction, its concentration is said to remain constant.

   Example

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

   $$K = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

(d) Many industrial processes involve equilibrium reactions.

Calculations involving K values

Consider the reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

The expression

$$\frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$$

is called the concentration quotient (Q).

- Q is only equal to K at equilibrium.
- Q < K, reaction will go from L → R to reach equilibrium.
- Q > K, the reverse will happen.

(a) Calculations where all the molar concentrations of reactants and products are known

Example 1

In the reaction

$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$

at 900°C at equilibrium, the $[COCl_2]$ is 3.0×10^{-6} M whereas that of [CO] and $[Cl_2]$ is 4.97×10^{-4} M. Find K at 900°C.

Step 1: Write the expression for K

$$K = \frac{[CO][Cl_2]}{[COCl_2]}$$

Step 2: Substitute the values given

$$K = \frac{(4.97 \times 10^{-4})^2}{3.0 \times 10^{-6}} = 0.082$$

(b) Calculations where the initial concentrations of the reagents and the equilibrium concentration of one component are known

Example 2

A mixture of 5.0 mol of H_2 and 10.0 mol of I_2 is placed in a 5 L container at 450°C and allowed to reach equilibrium. At equilibrium, the [HI] is 1.87 M. Calculate K for the reaction

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Step 1: Use the equation to establish mole ratios.

$1\ mol\ H_2 + 1\ mol\ I_2 \rightleftharpoons 2\ mol\ HI$

Step 2: Make sure all initial concentrations are expressed as mol L^{-1}.

The volume of the container was 5 L so each of the initial amounts must be divided by 5.

Step 3: Write out the initial concentration

	$[H_2]$	$[I_2]$	$[HI]$
Init. conc.	1.0 M	2.0 M	0

Step 4: Find the amounts of each reactant used.

(i) H_2 used $[HI(aq)] \times$ mol ratio H_2/HI
$= 1.87 \times 0.5 = 0.935$ M

(ii) I_2 used $= 1.87 \times 0.5 = 0.935$ M

Step 5: Find the amount of each reactant present at equilibrium.

(i) H_2 initial conc. – amount used
$1 - 0.935 = 0.065$ M

(ii) I_2 $2 - 0.935 = 1.065$ M

Step 6: Write out final concentration at equilibrium and substitute the values in the equilibrium expression to find K.

	$[H_2]$	$[I_2]$	$[HI]$
Final conc.	0.065	1.065	1.87

$$K = \frac{[HI]^2}{[H_2][I_2]}$$

$$= \frac{(1.87)^2}{(0.065)(1.065)} = 50.51$$

(c) Calculations where the initial concentration of the reactant is known, and the amount of it which has dissociated when equilibrium is established is stated

Example 3

The equilibrium reaction

$2NOCl(g) \rightleftharpoons 2\,NO(g) + Cl_2(g)$

was carried out in a 2 L vessel at 460°C with 4.0 moles of NOCl present. At equilibrium the NOCl(*g*) was 33% dissociated. Calculate the equilibrium constant.

Step 1: Use the equation to establish mole ratios.

2 mol NOCl $\rightleftharpoons$ 2 mol NO + 1 mol Cl_2

Step 2: Write out initial concentration in mol L^{-1}.

	$[NOCl]$	$[NO]$	$[Cl_2]$
Init. conc.	2.0 M	0	0

Step 3: Find the moles of NOCl dissociating in the 2.0 M NOCl.

$2 \times 33 \div 100 = 0.66$ mole

Step 4: Find the number of moles remaining in the 2.0 M NOCl.

This will be $2 - 0.66 = 1.34$ mole

Step 5: Use Step 1 to find mole ratios and hence final concentration.

Final conc. at equilibrium

$[NOCl] = 1.34$ M

$[NO] = 0.66$ M

$[Cl_2] = 0.33$ M

Step 6: Substitute the values in the equilibrium expression to find K.

$$K = \frac{[NO]^2[Cl_2]}{[NOCl]^2}$$

$$= \frac{(0.66)^2(0.33)}{(1.34)^2} = 8.0 \times 10^{-2}$$

Table 4.4 A comparison of equilibrium constants

Equation	Temp. (°C)	Eq. expr.	K value
(a) $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$	350	$\frac{[NO_2]^2}{[NO]^2[O_2]}$	2×10[illegible]
(b) $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$	450	$\frac{[CO][Cl_2]}{[COCl_2]}$	0.017
(c) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$	25	$\frac{[NO]^2}{[N_2][O_2]}$	4×10[illegible]

Summary:

Large K [see (a) above]: [P] > [R]

Small K [see (c) above]: [P] < [R]

where [P] is product and [R] is reactant.

Temperature is the only factor that changes the value of the equilibrium constant (K).

4.6 Changes of K with temperature

If K increases with temperature, the forward reaction is endothermic (ΔH +ve).

If K decreases with temperature, the forward reaction is exothermic (ΔH –ve).

Table 4.5 The effect of temperature on K

Reaction	Temp. (°C)	Eq. expr.	K value
$N_2O_4(g) \rightleftharpoons 2NO_2(g)$	0	$\frac{[NO_2]^2}{[N_2O_4]}$	2.55×10[illegible]
ΔH for forward reaction = +57 kJ	100		0.22

Practical work

The effect of temperature on the equilibrium

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

By observing the colour of a sealed container: nitrogen tetroxide (N_2O_4) is an almost colourless gas whereas nitrogen dioxide is a strongly coloured red-brown gas.

- A large K shows that the concentration of products is greater than the concentration of reactants [P] > [R]. A large K shows that the equilibrium favours the products. A small K shows that the equilibrium favours the reactants.
- K remains constant at constant temperature in spite of changes in concentration of reactants or products.
- K changes with temperature changes. For an exothermic reaction, K will decrease with an increase in temperature. In some industrial processes, although the reaction is exothermic, the temperature may be raised to enable the equilibrium to be reached sooner.

Exercise 4.2

Problems involving K

1. (a) In the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, carried out at 27°C, the equilibrium concentrations were $[H_2] = 0.8$ M; $[I_2] = 0.9$ M; $[HI] = 0.6$ M. Write the expression for the equilibrium constant and find the value for K.

   (b) If K for the above reaction was 50 at a temperature of 450°C, would you expect the forward reaction to be exothermic or endothermic? Explain your answer.

2. (a) An equilibrium mixture contains 1.00 mole of $Br_2(g)$, 0.125 mole of HBr and 0.0500 mole of $H_2(g)$ contained in a 5.00 litre flask.
   $Br_2(g) + H_2(g) \rightleftharpoons 2HBr(g)$
   $\Delta H = -165$ kJ mol^{-1}
   Find the equilibrium constant for this reaction.

   (b) If the pressure on the reacting vessel were doubled, how would the reaction be affected?

3. (a) Write the equilibrium expression for the reaction
   $I_2(g) + Cl_2(g) \rightleftharpoons 2ICl(g)$

   (b) 0.5 mole of $I_2(g)$ and 0.5 mole of $Cl_2(g)$ were mixed in a 1 L flask at a certain temperature. When equilibrium was reached, 0.4 mole of ICl(*g*) was present. Find K.

   (c) If ΔH = 35.0 kJ for the forward reaction, would you expect K to increase or decrease when the equilibrium temperature is doubled?

   (d) Would an increase of pressure affect the equilibrium? Explain your answer.

   (e) Use Le Chatelier's Principle to explain how the equilibrium would shift if the $[Cl_2]$ was halved.

4. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ $\Delta H = -93$ kJ

   (a) Explain how the equilibrium would alter in each case to
      (i) increased temperature,
      (ii) a higher concentration of $Cl_2(g)$,
      (iii) a higher concentration of $PCl_5(g)$, and
      (iv) the presence of a catalyst added at the start of the reaction.

   (b) A quantity of $PCl_5(g)$ was heated in a 12 L vessel at 250°C. At equilibrium, the vessel contained 0.21 mole of $PCl_5(g)$ and 0.32 mole of each of the gaseous products. Find K at 250°C.

5. Consider the equilibrium

   $3I_2(g) + 6F_2(g) \rightleftharpoons 2IF_5(g) + I_4F_2(g)$

   At a certain temperature 3.0 moles of F_2 and 2.0 moles of I_2 are introduced into a 10.0 L container. At equilibrium, the $[I_4F_2]$ is 0.02 M. Calculate the K for the reaction.

4.7 Uses of sulfuric acid in industry

Sulfuric acid is one of the most important industrial chemicals with many practical applications:

- Sulfuric acid is important for the fertiliser industry because it is needed to make ammonium sulfate and phosphoric acid.
- Sulfuric acid is used to remove oxides from iron

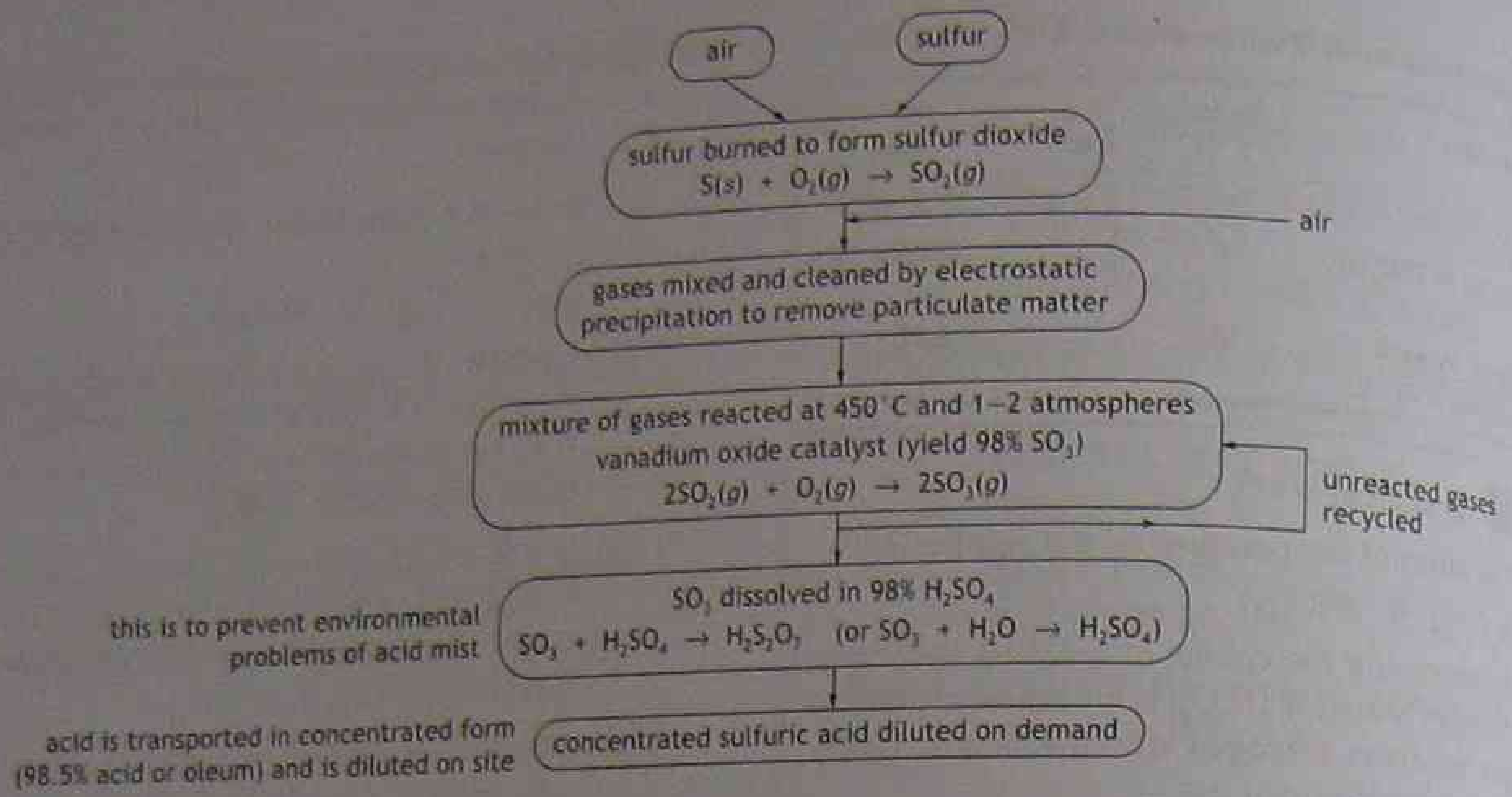


Figure 4.10 Flow chart for the contact process for making sulfuric acid

and steel before galvanising or electroplating.

- As a dehydrating agent, sulfuric acid plays an essential role in the manufacture of such explosives as nitroglycerine. The nitration process liberates water which is removed by the sulfuric acid to allow the reaction to go to completion.
- Sulfuric acid has a variety of uses in the paint, petroleum, soaps, detergents and dyestuffs industries.
- It is the electrolyte used in the lead-acid accumulators.

4.8 The Frasch process

Sulfur occurs in the elemental state in large underground deposits in the USA (particularly in Texas and Louisiana). Between the surface and the sulfur deposit there is usually a layer of quicksand which prevents ordinary mining methods from being used. The Frasch extraction process depends on the low melting point (less than 120°C) and low density (about 2 g cm^{-3}) of sulfur.

This method uses a concentric system of pipes. Superheated water (170°C under pressure) is pumped into the sulfur deposit where it melts the sulfur. Compressed air then forces the molten sulfur up a concentric pipe. The sulfur may then be shipped as a liquid in ocean-going tankers or allowed to solidify in large wooden moulds and then be broken up into pieces for shipment. This method easily removes sulfur from beds that lie under water or quicksand. Offshore mining is impractical as it could result in unsightly platforms. If discharged directly into the surrounding water, the hot water could result in water pollution. Sulfur fumes could also prove unpleasant.

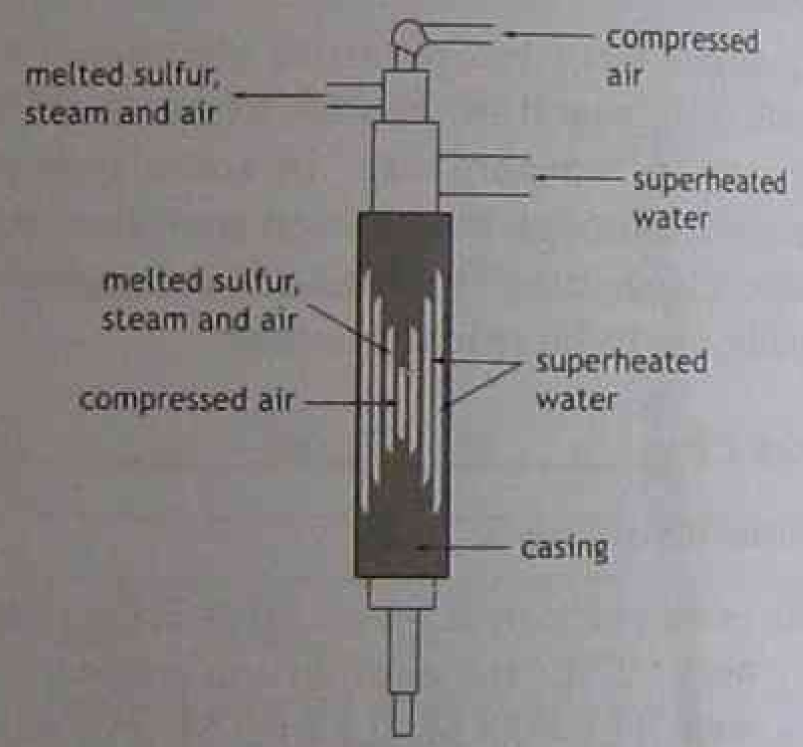


Figure 4.9 The system of concentric pipes used in the Frasch process of extracting sulfur

4.9 Contact process for the manufacture of concentrated sulfuric acid

Sulfuric acid is made by the contact process. The reversible reaction in which sulfur dioxide and oxygen form sulfur trioxide is essential. Conditions needed to give the optimum chemical position result in a 98% yield of $SO_3(g)$.

Although the oxidation of $SO_2(g)$ is an exothermic reaction, the temperature of 450°C is high enough to cause the reaction to proceed at a practical rate. According to Le Chatelier's Principle, an increase in pressure for the reaction $2SO_2 + O_2 \rightarrow 2SO_3$ will cause an equilibrium shift in the direction which will decrease the total number of molecules that is more $SO_3(g)$ will form under conditions of increased pressure.

4.10 Reactions of sulfuric acid

(a) As an oxidising agent

Hot concentrated sulfuric acid is a vigorous oxidising agent. The sulfur is reduced from the +6 oxidation state to the +4 or –2 state. The reduction depends on the concentration of the acid and on the reducing agent used.

Example

$$Cu(s) + 2H_2SO_4(g) \rightarrow Cu^{2+}(aq) + SO_2(g) + SO_4^{2-}(aq) + 2H_2O(l)$$

(b) As a dehydrating agent

The strong attraction by sulfuric acid for water makes it a very good dehydrating agent. Gases which do not react with it can be bubbled through the concentrated acid to dry them. Sulfuric acid is such an active dehydrating agent that it will remove hydrogen and oxygen in the proportion found in water from some substances.

Example

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + 11H_2SO_4 \rightarrow 12C + 11H_2SO_4.H_2O$$

4.11 The dilution of concentrated sulfuric acid

Concentrated sulfuric acid is a dense oily liquid and contains 95% to 98% (by mass) of sulfuric acid with the balance being water. When concentrated sulfuric acid is added to water, a large amount of heat is released as the hydrates $H_2SO_4xH_2O$ are formed. These are *strongly* exothermic reactions so safety precautions *must* be taken in diluting concentrated sulfuric acid.

- Add the sulfuric acid *slowly* to the water with stirring. (*Never* add the water to the acid since this will cause a violent reaction which produces steam and splatters the acid.)
- Carry out the dilution in a fume cupboard.
- Wear protective clothing, covered shoes and safety glasses.
- Allow the diluted solution to cool before transferring it into reagent bottles. Normal dilute sulfuric acid (around 3 M) is made by adding one volume of concentrated acid (around 18 M) to five volumes of distilled water.

4.12 Differences between energy requirements in galvanic cells and electrolysis

The industrial production of sodium hydroxide requires the use of electrical energy. Spontaneous reactions are used to make galvanic cells which are electrochemical devices which generate electricity. Electrical energy may be used to produce non-spontaneous oxidation-reductions. Instead of generating electricity by chemical change, electricity is being used to produce chemical change. This process is called *electrolysis*. Electrolysis takes place on the surface of the electrodes and is really the reverse operation of a galvanic cell where the applied voltage is greater than the voltage that the cell can produce. The cost of electricity is an important factor in locating possible sites for an industrial chlor-alkali plant.

4.13 The chlor-alkali industry

This is a major branch of the chemical industry that has been built up around a single electrolysis reaction using concentrated brine (salt water). Three different types of electrolytic cell have been used for the procedure — the Castner-Kellner mercury cell, the Nelson diaphragm cell and the membrane cell. The success of these methods depends on preventing the chlorine produced from coming into contact and reacting with either the sodium hydroxide or hydrogen.

(a) The mercury process

In the Castner-Kellner cell, titanium (coated with a rare earth metal) is used as the anode and mercury flowing along the bottom of the cell is the cathode.

Anode (oxidation) $2Cl^- \rightarrow Cl_2 + 2e^-$

Cathode (reduction) $Na^+(aq) + e^- \rightarrow Na(s)$

The sodium dissolves in the liquid cathode and the sodium amalgam (Na/Hg) is removed continuously.

The amalgam is prevented from reacting with the sodium chloride solution by the cell voltage. It is pumped into a separate vessel where it reacts with water forming NaOH and H_2. The mercury is then returned to the electrolytic cell.

$$2Na/Hg + 2H_2O \rightarrow 2Na^+ + 2OH^- + H_2 + 2Hg$$

The environmental problem in this case is the danger of loss of mercury into natural waters and its concentration reaching dangerous levels in edible marine life.

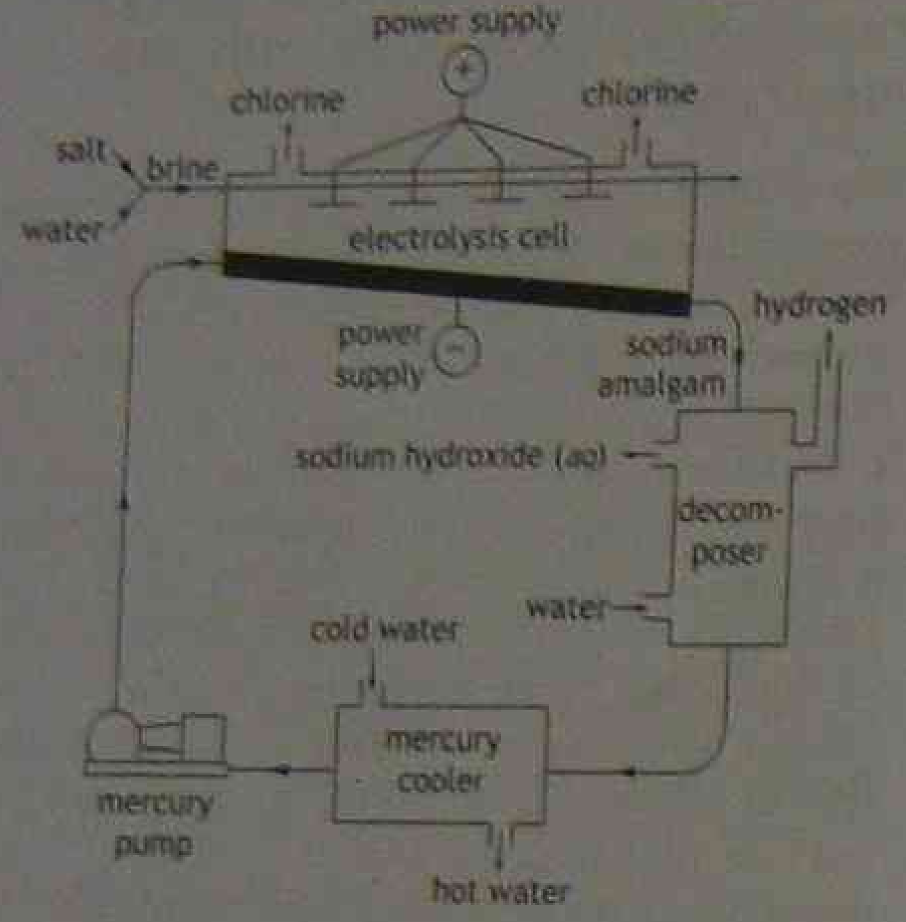


Figure 4.11 Schematic diagram of the Castner-Kellner cell used in Australia to produce chlorine and sodium hydroxide from brine using the mercury process.

(b) The diaphragm process

The Nelson diaphragm cells provide an alternative. Here the products of electrolysis are kept apart by an asbestos diaphragm which is used to prevent contact between the chlorine produced at the anode and the H_2 and NaOH solution produced at the cathode. Because of the inherent danger to workers using asbestos, it must be carefully monitored to limit the risk of contracting mesothelioma through exposure to airborne asbestos fibres. The asbestos diaphragm provides a lining for the steel-mesh cathode. When electrolyte solution soaks through the asbestos to the cathode, electrolysis takes place. At the cathode, hydrogen is preferentially discharged before sodium.

Cathode $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

Because of the high concentration of chloride ions in solution, chlorine is discharged before oxygen from the oxidation of water.

Anode $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

Sodium ions are attracted to the cathode and, with the hydroxide ions produced in the cathode reaction, are washed to the bottom of the cell. Steam is passed over the cathode screen to form a hot water solution at the bottom of the cell. Solid NaOH can be crystallised out.

Overall cell $2Na^+(aq) + 2Cl^-(aq) + 2H_2O(l)$
$\rightarrow 2Na^+(aq) + 2OH^-(aq) + H_2(g) + Cl_2(g)$

where Na^+ are spectator ions.

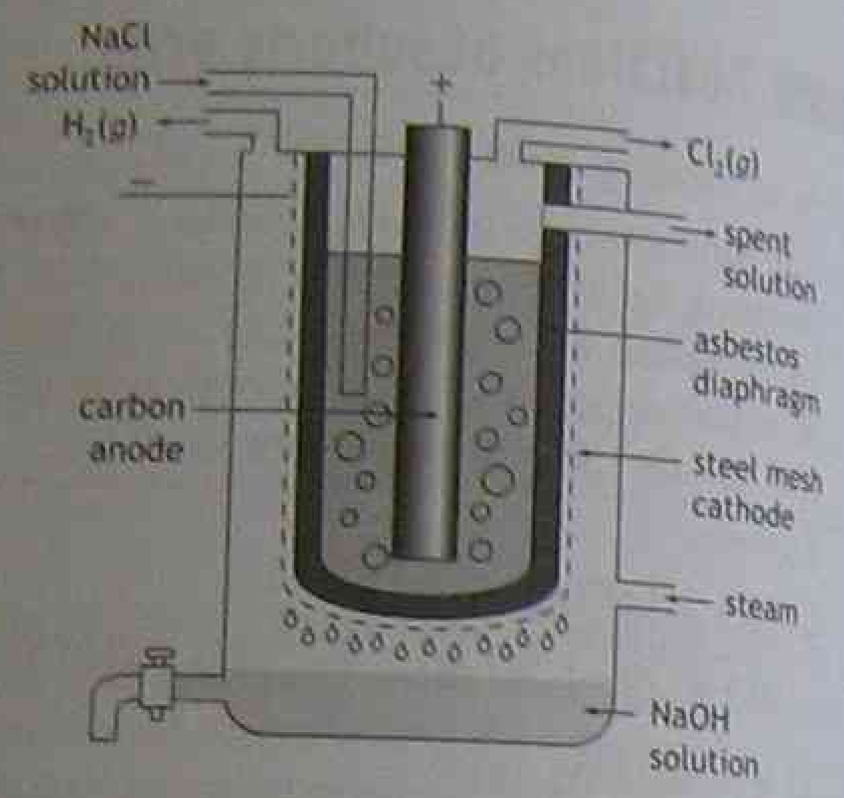


Figure 4.12 The Nelson cell used in the electrolysis of aqueous sodium chloride

(c) The membrane process

The membrane process has a titanium anode and a nickel cathode. Titanium is chosen as the anode as it is not attacked by chlorine. The anode and cathode compartments are separated by an ion exchange membrane. This is a selective membrane which allows Na^+ ions and water to flow freely through to the cathode but blocks the other products. The Na^+ ions and OH^- ions collect in the cathode compartment. The sodium hydroxide solution is then removed and purified.

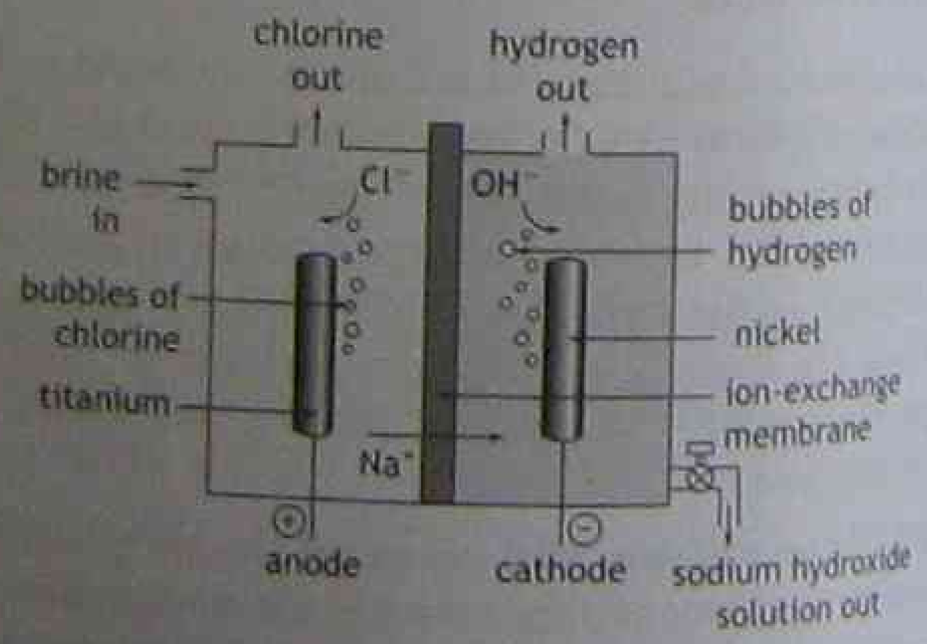


Figure 4.13 The membrane cell for the electrolysis of concentrated brine

Note: Each of the three systems is currently in use but the membrane cell system is likely to replace the others.

Table 4.6 Uses of chlor-alkali

Chlorine	Sodium hydroxide	Hydrogen
a poisonous yellow-green gas	alkaline and corrosive	flammable gas
used for: • PVC (plastic) • CCl_4 (dry-cleaning solvent) • HCl (gas and acid) • bleaches, weed killers • paints and dyes • killing bacteria in water supplies and pools	used for: • soaps • detergents • textiles • paper	used for: • margarine • nylon • HCl (gas and acid)

4.14 Electrolysis of molten sodium chloride

Sodium metal and chlorine gas are produced industrially using the Downs cell. In the molten state, ions move through the melt. Sodium metal is discharged at the circular iron cathode:

$$Na^+(l) + e^- \rightarrow Na(l)$$

Chlorine is evolved at the carbon anode.

$$2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$$

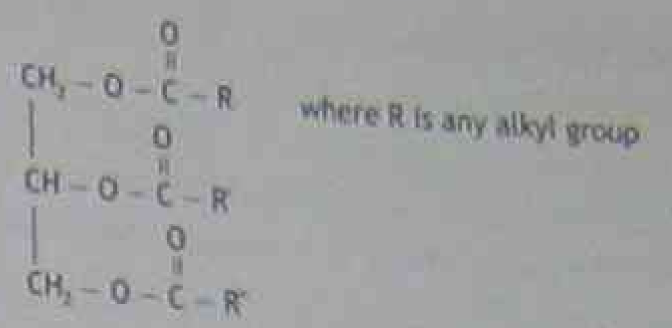
Overall reaction:

$$2Na^+(l) + 2Cl^-(l) \rightarrow 2Na(l) + Cl_2(g)$$

4.15 Saponification

Saponification is a process used in soap making which has one of the World's oldest organic chemical reactions. Ancient Egyptians made a crude soap from animal fat and wood ash. Saponification is the hydrolysis in a basic solution of fats and oils to produce glycerol and salts of fatty acids.

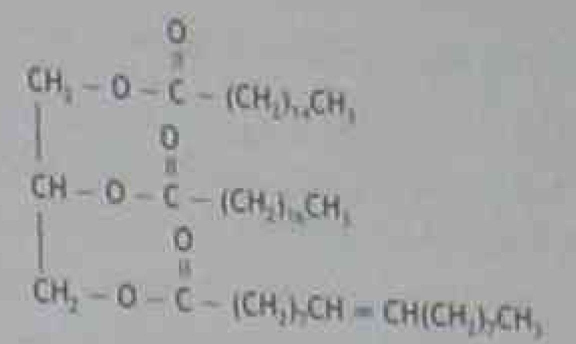
- Solid animal fats and animal and vegetable oils are natural esters. They are generally formed from 1,2,3-propanetriol (c.n. glycerol) and saturated and unsaturated fatty acids.
- The esters formed from glycerol and fatty acids are called triglycerides.
- Structure of triglycerides



$$\begin{array}{l} CH_2-O-\overset{O}{\overset{\|}{C}}-R \\ | \\ CH-O-\overset{O}{\overset{\|}{C}}-R' \\ | \\ CH_2-O-\overset{O}{\overset{\|}{C}}-R'' \end{array}$$

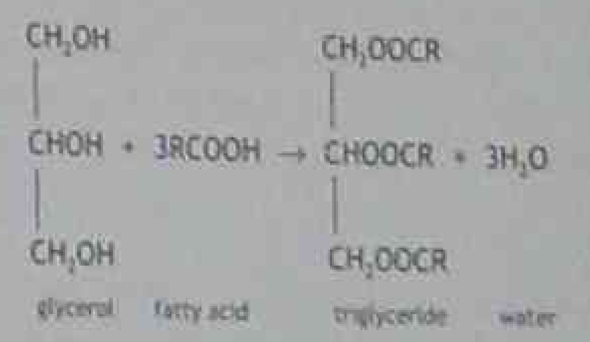
where R is any alkyl group

Example



$$\begin{array}{l} CH_2-O-\overset{O}{\overset{\|}{C}}-(CH_2)_{14}CH_3 \\ | \\ CH-O-\overset{O}{\overset{\|}{C}}-(CH_2)_{16}CH_3 \\ | \\ CH_2-O-\overset{O}{\overset{\|}{C}}-(CH_2)_7CH=CH(CH_2)_7CH_3 \end{array}$$

- Fats usually contain several acids with 14 to 18 carbons (an even number of carbon atoms is always present).



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3RCOOH \rightarrow \begin{array}{l} CH_2OOCR \\ | \\ CHOOCR \\ | \\ CH_2OOCR \end{array} + 3H_2O$$

- Fats contain mainly saturated fatty acids, e.g. beef tallow contains 30% palmitic acid, 24% stearic acid and 40% of unsaturated oleic acid. Oils, especially those derived from vegetables, contain a greater proportion of unsaturated fatty acids, e.g. peanut oil contains 10% palmitic acid, 3% stearic acid, 48% of unsaturated oleic acid and 34% of unsaturated linoleic acid.
- Fatty acids are long chain aliphatic carboxylic acids which are found in natural esters in fats and oils. They can have saturated or unsaturated carbon chains. The carbon chains of unsaturated fatty acids must contain at least one C=C double bond.

Activity 1.1

Making soap

Aim

To make soap from olive oil.

Procedure

1. Pour about 30 mL of 6 **M** NaOH solution into a 250 mL beaker. (**Care** — concentrated NaOH is used)

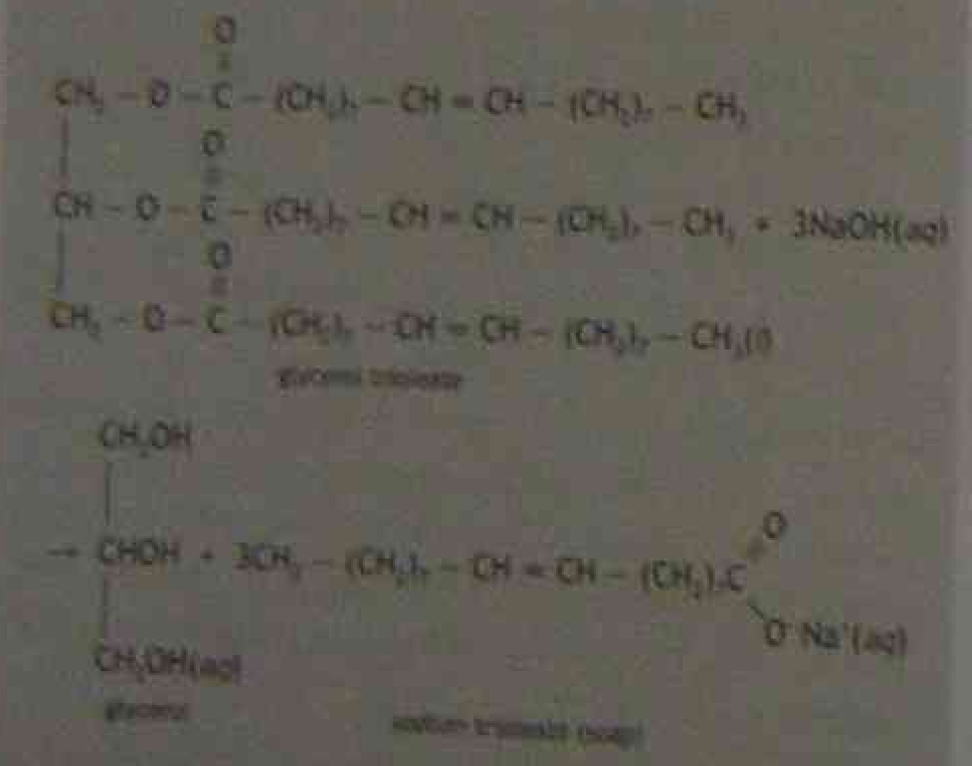
2. Add about 10 mL of olive oil to the solution in the beaker.
3. Put a few boiling chips in the beaker (to stop bumping) and gently heat the mixture on an electric hot plate or a Bunsen burner.
4. While stirring, allow the mixture to boil slowly until the olive oil is no longer visible (10–15 min).

   Note: Safety glasses must be worn at all times

5. Allow the mixture to cool for a few minutes before adding 40 mL of a saturated solution of sodium chloride ('salting out' occurs).
6. Boil the mixture for a further 2–3 min, then cool it in a water bath.
7. Filter the mixture through cotton wool. Wash the residue with water to remove excess NaOH and NaCl.
8. Use a spatula to remove a portion of the collected soap into a large test tube where further tests may be carried out if required.

Result

Olive oil on analysis contains almost 80% of oleic acid. Glycerol trioleate is the chief constituent of olive oil.



Questions

1. Why is olive oil insoluble in water but glycerol and sodium trioleate are soluble?
2. How does the process of 'salting out' increase the yield of soap?

Exercise 4.3

Given the formula for (i) stearic acid — $C_{17}H_{35}COOH$ and (ii) palmitic acid — $C_{15}H_{31}COOH$ write balanced equations for

(a) the reaction between glycerol and the fatty acid and

(b) the reactions between the fat formed in (a) with potassium hydroxide.

4.16 Industrial soap making

Soaps are usually made by a two-step process which consists of an initial neutralisation of fatty acids by soda ash (Na_2CO_3) and then a final saponification of unreacted fatty acids by caustic soda (NaOH). Today, tallow (rendered oil from animal fats) and coconut oil (from copra) are the basis of modern soaps. Oils are treated with bleaching earth and carbon at high temperatures before filtering.

Soda ash is the preferred neutralising agent because of its price and its lower metallic impurities. These impurities could affect the perfume and colour stability of the soap. Fatty acids and soda ash are heated and, since there is an incomplete conversion, small amounts of caustic soda are added. The soap that comes off this final caustic soda neutralisation is called neat soap and consists of about 65% soap and 35% water with minor levels of impurities. The soap is then sent to a vacuum drier.

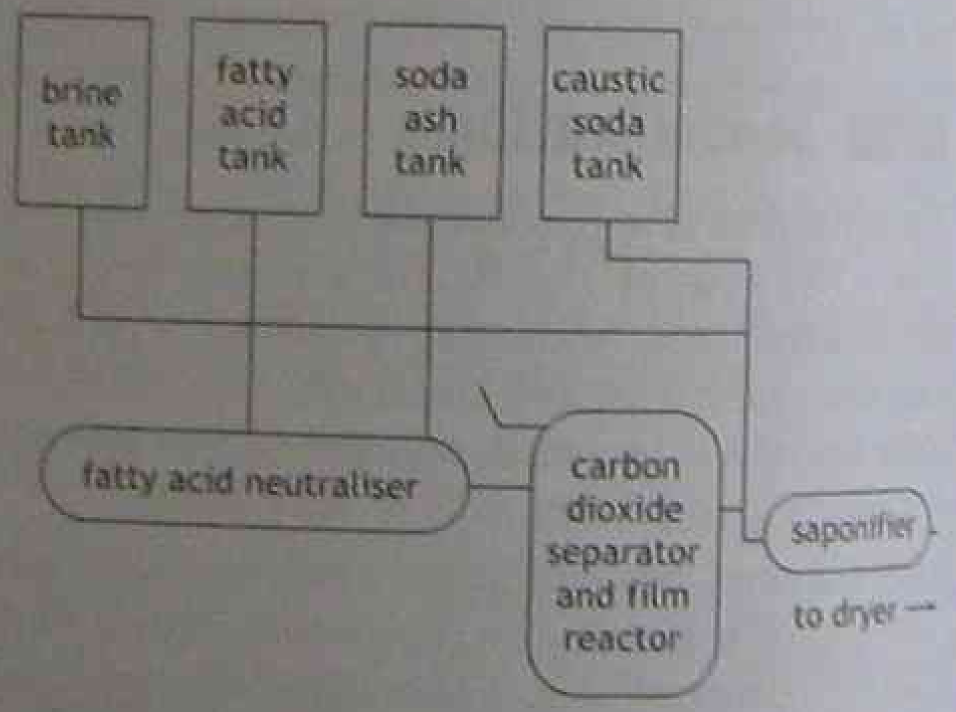


Figure 4.14 Soap can be produced by a continuous fatty acid neutralisation process

In some processes, these fats and oils are pumped with caustic soda into huge kettles. The mixture is heated by steam pipes. More caustic soda is added gradually until the contents of the kettle are homogeneous. The caustic soda is added with salt and water to separate the by-product such as glycerine (glycerol) and to allow the oils to saponify. Samples from each stage are taken for laboratory testing. When the proper stage of boiling is reached, the steam is shut off and salt is added to the kettle, the contents of which are then allowed to settle. During the settling, soap rises to the top, leaving below a briny liquid made up of salt, spent lye and glycerine. The lye is drawn off from the bottom of the kettle to the glycerine evaporating and distilling section. The soap is boiled up again and then pumped into insulated storage tanks. The hot soap is released from the storage tanks and flows by gravity down to the chilling roll where it is solidified. It is then cut into shavings that are fed into a drier to reduce the water content from 30% to 13%.

After drying, the soap chips are weighed out into a amalgamator (a mixer with strong blades) where perfume and colour are added. The mixture then falls by gravity into a plodder (which looks like a giant mincer) where the soap is mixed thoroughly before being forced out (like spaghetti) onto the rolling mills. The ribbons of soap are fed into a big vacuum plodder which compresses it into a long bar. This bar is cut by a rotary cutter into short cakes of soap.

4.17 The cleaning action of soap

The cleaning action of soaps can be explained in terms of the solubility of polar and non-polar substances in water.

- A soap is an active surface agent (surfactant) which is a 'wetting' agent that lowers surface tension in the water.
- When soaps dissolve in water, ions are produced in solution.

$$\underset{\text{soap}}{RCOO^-Na^+} \xrightarrow{H_2O} \underset{\text{surfactant ion}}{RCOO^-(aq)} + \underset{\text{sodium ion}}{Na^+(aq)}$$

- The nature of the surfactant ion consists of a long non-polar hydrocarbon end with the COO^- ion being the charged end of the ion.
- Water is a polar substance and can form hydrogen bonds with the charged end of the surfactant.

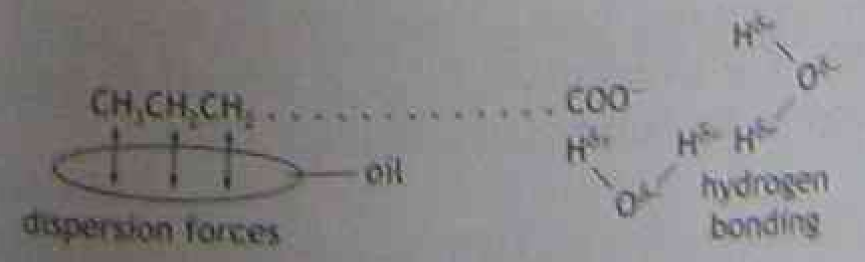


Figure 4.15 Bonding in soap

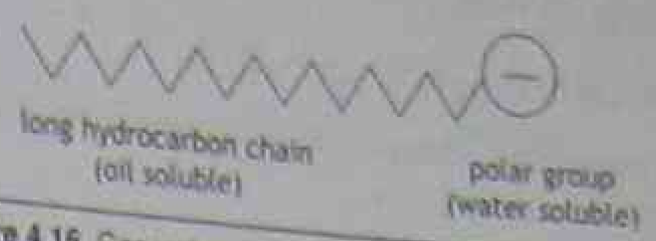


Figure 4.16 General structure for soaps (anionic)

- The charged end is called the hydrophilic (water-loving) end; the hydrophobic (water-hating) end is non-polar and will not dissolve in water but will mix with non-polar dirt, grease or oil. The main action of the surfactant is to stimulate emulsification.

The substrate has a solid surface (dirt held there by oil or grease). The 'tails' or hydrophobic ends of the soap molecules enter the soiled layer since they are non-polar (i.e. similar to the oil). They surround the soiled layer with a water-soluble sheath. When agitated, the soiled area is broken up into small particles which 'float' off and remain emulsified and dispersed in the washing water.

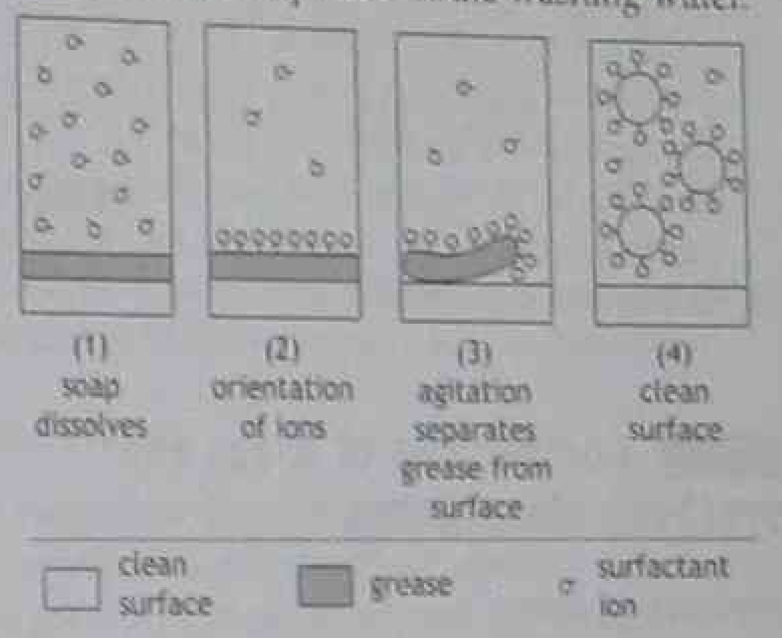


Figure 4.17 The cleaning action of soap

4.18 Synthetic detergents

(a) *Anionic detergents*, where the surfactant has a negatively charged head.

Example

Alkylbenzenesulfonates which can be represented as 

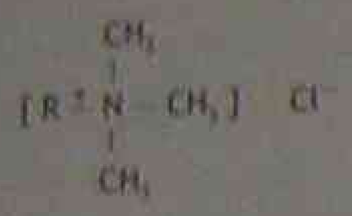
In general 

Anionic detergents are high sudsing and are used mainly in laundry and dishwashing detergents, e.g. Omo, Rinso, Morning Fresh.

(b) *Cationic detergents*, where the surfactant has a positive head.

In general

Quaternary ammonium compounds are typical cationic detergents.



$$[\mathrm{R} \overset{+}{-} \overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{N}}} - \mathrm{CH_3}]\quad \mathrm{Cl^-}$$

Because of their positive charge, cationic surfactants are useful as fabric softeners. Most fabrics accumulate negative charges on their surfaces. Repulsion between charges can cause resistance to folding and fabrics may feel hard as a result. Detergent cations in a rinse can neutralise these charges so that fabric feels softer, e.g. Comfort.

(c) *Non-ionic detergents* do not ionise in water and have no electrical charge. They have polar uncharged groups in their molecules and are resistant to water hardness. They are usually polyethoxymethoxylates. Many have ether linkages in the hydrocarbon chain, e.g. ($-CH_2-O-CH_2-$). They are low sudsing and are commonly used in automatic dishwashing detergents, e.g. Finish.

4.19 Comparison of soaps and synthetic detergents

Hardness of water

Soap has problems in 'hard' water. Hard water contains calcium and magnesium ions in solution, usually as hydrogen carbonates. When sodium stearate is added to the water, calcium stearate and magnesium stearate are precipitated, forming an insoluble scum. Synthetic detergents such as sodium alkylbenzenesulfonates do not form a scum with hard water. They have a similar long hydrocarbon chain to soap molecules but the ionic group at the hydrophilic head has been changed. The calcium and magnesium salts of these molecules are water soluble.

Are they biodegradable?

Modern soaps are biodegradable, but early detergents were not and caused pollution problems in rivers and streams. The problem with synthetic detergents has been largely overcome by replacing detergents with branched chain hydrocarbon tails with straight chain hydrocarbons.

Cost

Soaps which are manufactured from a renewable source are cheaper than synthetic detergents made from petrochemicals.

General efficiency

(a) Soaps are not as soluble as synthetic detergents.

(b) Soaps, unlike synthetic detergents, deteriorate.

(c) Soaps are harder to rinse from fabrics.

(d) Soaps, unlike synthetic detergents, clog sewerage reticulation systems owing to their 'gelling' properties.

4.20 The Solvay process

Raw materials

The Solvay process has been used since the 1860s to produce sodium carbonate (Na_2CO_3). Sodium carbonate is an important industrial chemical used in the manufacture of glass, soaps, detergents, paper and dyes. It is manufactured in a continuous process that uses carbon dioxide (produced by heating calcium carbonate as limestone) and ammonia dissolved in brine (concentrated sodium chloride solution) as its starting materials.

Process chemistry

The chemistry involved in the sequence of steps used in the Solvay process is as follows:

Brine purification

The brine enters the scrubber where it absorbs ammonia generated in the ammonia still. The scrubber consists of a number of vertical compartments. The brine forms a layer on the surface of each and runs down vertical tubes from one compartment to the next. Ammonia passes up the centre of the column and is caused by 'hoods' to bubble through the brine on each floor. The ammonia from the still always contains some carbon dioxide, so that salts of calcium, magnesium and iron, present as impurities in the brine, are deposited as carbonates during the saturation stage. The carbonates form a sludge which is allowed to settle. The ammoniated brine is run off through a cooler to the Solvay (carbonating) tower.

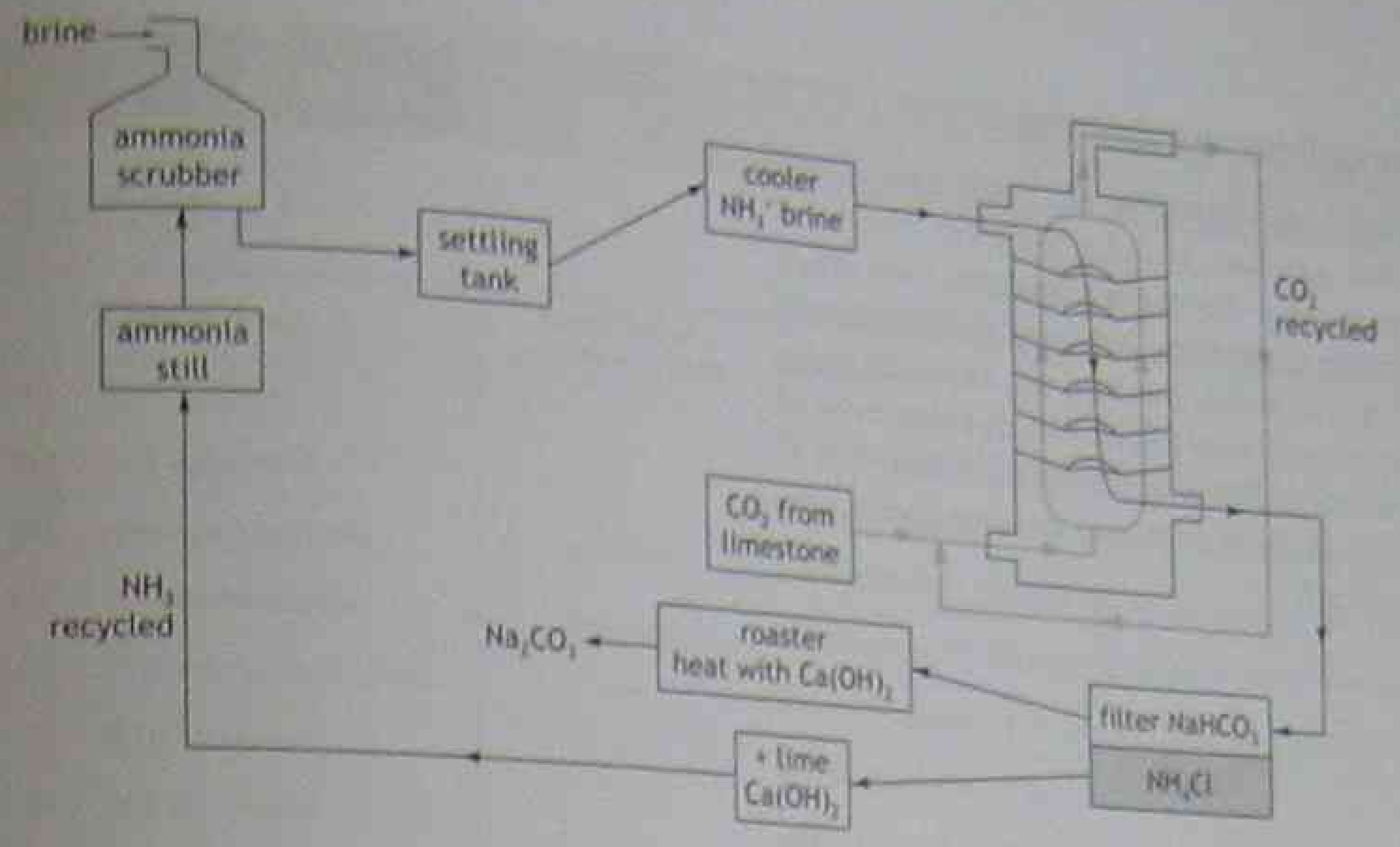


Figure 4.18 A flow chart of the Solvay process

Hydrogen carbonate formation in the tower

Carbon dioxide is bubbled through brine saturated with ammonia.

$$CO_2(g) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H^+(aq)$$

This equilibrium is displaced to the right by the ammonia which combines with H^+ ions to form NH_4^+ ions. The HCO_3^- ions then unite with the Na^+ ions in the brine to form a suspension of sodium hydrogen carbonate. This is due to the common ion effect of the Na^+ ions so that the $NaHCO_3$, though soluble in water, is nearly insoluble in brine.

$$NaHCO_3^-(aq) \rightleftharpoons Na^+(aq) + HCO_3^-(aq)$$

$$\xleftarrow{(Na^+ \text{ in excess})}$$

Equation 1

$$NH_3(aq) + CO_2(aq) + NaCl(aq) + H_2O(l) \\ \rightarrow NaHCO_3(s) + NH_4Cl(aq)$$

Sodium carbonate formation

The suspension of sodium hydrogen carbonate is removed from the tower and changed into sodium carbonate by heating.

Equation 2

$$2NaHCO_3(s) \xrightarrow{heat} Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

Ammonia recovery

Ammonia is recovered by heating the ammonium chloride with calcium hydroxide.

Equation 3

$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3(g) + 2H_2O + CaCl_2$$

4.21 Environment and safety issues associated with the Solvay process

When installing plant and equipment for the Solvay process, the following environmental and safety requirements need to be put in place.

Air pollution

Continuous monitoring should be carried out since the escape of ammonia gas could be hazardous.

Water pollution

In many cases, factories are located adjacent or close to large bodies of water. Cooling water used during the process must not be returned to adjacent rivers or lakes until it has passed through a cooling pond system.

Ammonia residues or ammonium chloride run off as filtrate after separation from sodium hydrogen carbonate crystals must not be discharged directly into water bodies. Strict control of effluents is essential and such factors as dissolved oxygen, turbidity and pH should be regularly monitored.

Personal safety

All staff should undergo routine safety educational programs which should be regularly updated.

Location

Plant can only be located in an industrial area.

Environmental impact and monitoring

With regard to new projects, environmental impact assessment studies should look for the least environmentally damaging options and reach agreement on acceptable levels of environmental change. Areas of public concern, e.g. ammonia leaks, should be clearly identified. The development of environmental monitoring strategies is essential to warn of any problems that my develop during the life of the plant.

Answers

Answers for Exercise 4.1

1.

		Change made	Direction of equilibrium shift	Explanation
(a)	(i)	$[I_2]$ increased	→	by Le Chatelier's Principle will try to reduce $[I_2]$
	(ii)	$[H_2]$ decreased	←	by Le Chatelier's Principle will try to increase $[H_2]$
	(iii)	pressure increased	no effect	same number of moles of gas on each side of the equation
	(iv)	volume increased	no effect	same number of moles of gas on each side of the equation
	(v)	temperature increased	→	will try to absorb heat, forward reaction is endothermic
(b)	(i)	[CO] increased	←	will try to reduce [CO]
	(ii)	$[H_2]$ increased	→	will try to reduce $[H_2]$
	(iii)	pressure increased	no effect	same number of moles of gas on each side of the equation
	(iv)	temperature decreased	←	will try to produce heat

2. (a) $H_2(g)$
   (b) (i) decreased; (ii) increased; (iii) increased (if insulated).
   (c) Low temperature — as heat is released by the forward reaction which is exothermic.
   High pressure — as concentration is higher and there are more moles of reactant than product.
   (d) A catalyst increases the rate of the forward and reverse reactions equally. A catalyst lessens the time taken for the reaction to reach equilibrium. The equilibrium position is not changed.

3. (a) to the right (forward reaction exothermic)
   (b) to the right
   (c) no change (only a change in rate at which equilibrium is reached)
   (d) no change
   (e) no change (2 moles → 2 moles)

4. According to Le Chatelier's Principle:
   (a) Increased temperature in endothermic reaction means a shift to the right.
   (b) Increased $[Cl_2]$ means a shift to the left.
   (c) Increased $[PCl_5]$ means a shift to the right.
   (d) A catalyst affects both the forward and backward rate of a reaction so it has no effect on the equilibrium position. It does cause the reaction to come to equilibrium at a more rapid rate.
   (e) $$K = \frac{[PCl_3](g)[Cl_2](g)}{[PCl_5](g)} = \frac{\left[\frac{0.32}{12}\right]\left[\frac{0.32}{12}\right]}{\left[\frac{0.21}{12}\right]} = 0.041$$
   Must divide each number of moles by 12 to find molar conc.

5. 0.30 mol $F_2(g)$ and 0.20 mol of $I_2(g)$ are present in 1 L.

	$3I_2$	$6F_2$	$2IF_5$	I_4F_2
Initial concentration in mol L^{-1}:	0.20	0.30	0	0
Amount reacted:	0.20 − (3 × 0.020)	0.30 − 0.120		
At equilibrium:	0.140	0.180	0.040 (2 × 0.020)	0.020

$$K = \frac{[I_4F_3][IF_5]^2}{[I_2]^3[F_2]^6} = \frac{[0.020][0.040]^2}{[0.140]^3[0.180]^6} = 342.87 = 3.43 \times 10^2$$

Answers for Exercise 4.2

1. (a) $$K = \frac{[HI]^2}{[H_2][I_2]} = \frac{[0.6]^2}{[0.8][0.9]} = 0.5$$
   (b) endothermic

2. (a) $$K = \frac{[HBr]^2}{[H_2][Br_2]} = \frac{\left[\frac{0.125}{5}\right]^2}{\left[\frac{0.05}{5}\right]\left[\frac{1.00}{5}\right]} = 0.313$$
   (b) No change: 2 moles of reaction, 2 moles of products.

3. (a) $$K = \frac{[ICl]^2}{[I_2][Cl_2]}$$ (b) $$\frac{[0.4]^2}{[0.3][0.3]} = 1.8$$
   (c) increase (d) no
   (e) back reaction favoured

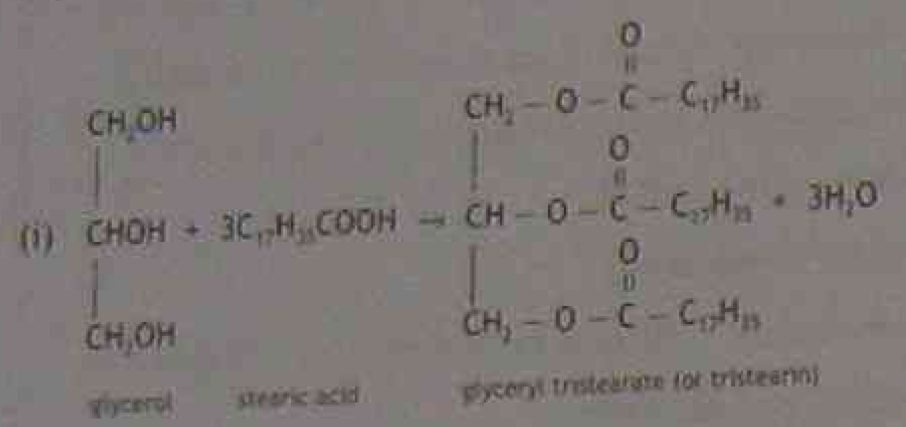
Answers for Activity 4.1

1. Olive oil is non-polar but glycerol and sodium trioleate are polar.
2. The solubility of many organic compounds, e.g. sodium trioleate, in water is considerably reduced by dissolved salts such as sodium chloride. This is an example of the common ion effect.

Answers for Exercise 4.3

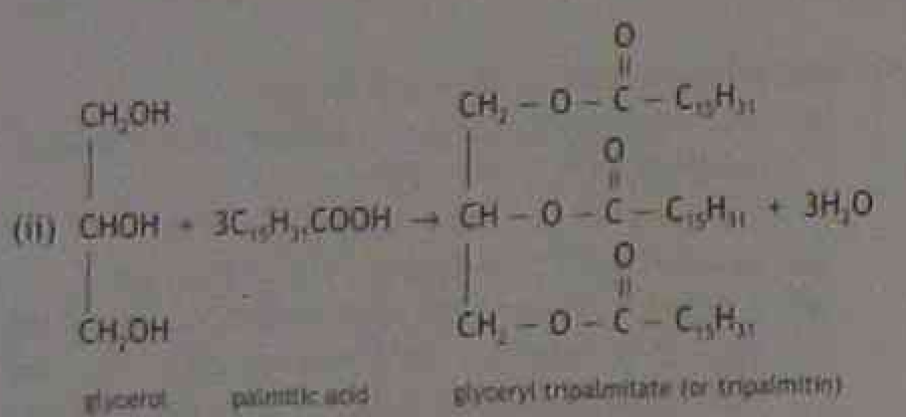
(a)

(i)



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3C_{17}H_{35}COOH \rightarrow \begin{array}{l} CH_2-O-\overset{O}{\overset{\|}{C}}-C_{17}H_{35} \\ | \\ CH-O-\overset{O}{\overset{\|}{C}}-C_{17}H_{35} \\ | \\ CH_2-O-\overset{O}{\overset{\|}{C}}-C_{17}H_{35} \end{array} + 3H_2O$$

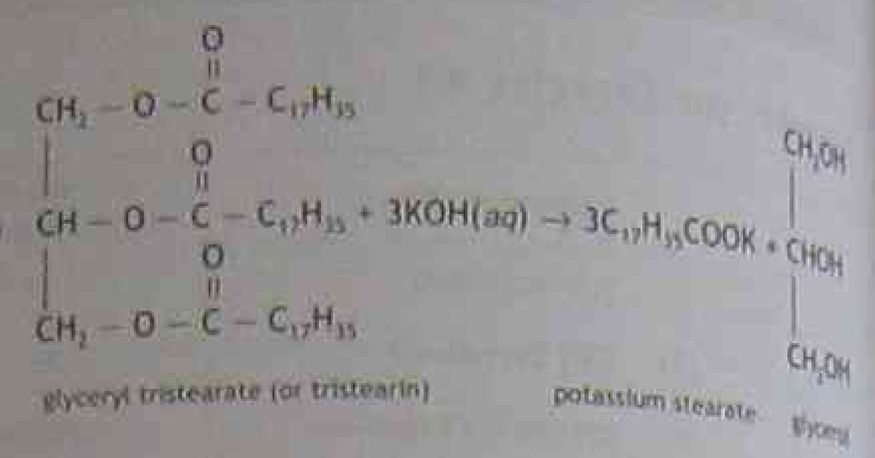
(ii)



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3C_{15}H_{31}COOH \rightarrow \begin{array}{l} CH_2-O-\overset{O}{\overset{\|}{C}}-C_{15}H_{31} \\ | \\ CH-O-\overset{O}{\overset{\|}{C}}-C_{15}H_{31} \\ | \\ CH_2-O-\overset{O}{\overset{\|}{C}}-C_{15}H_{31} \end{array} + 3H_2O$$

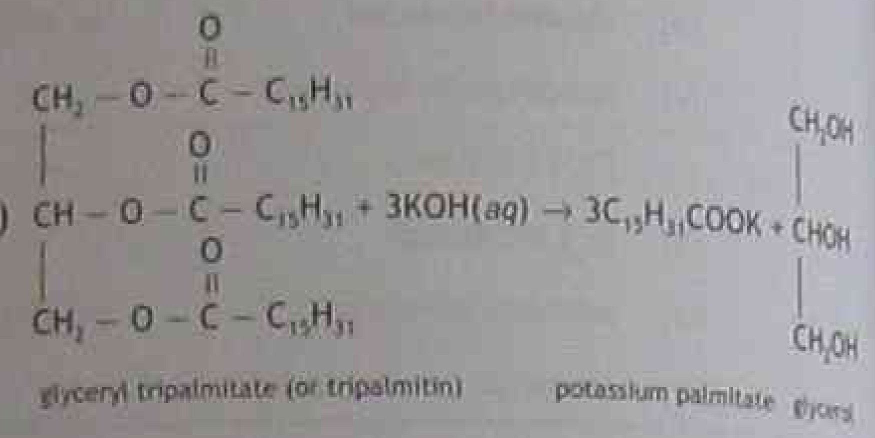
(b)

(i)



$$\begin{array}{l} CH_2-O-\overset{O}{\overset{\|}{C}}-C_{17}H_{35} \\ | \\ CH-O-\overset{O}{\overset{\|}{C}}-C_{17}H_{35} \\ | \\ CH_2-O-\overset{O}{\overset{\|}{C}}-C_{17}H_{35} \end{array} + 3KOH(aq) \rightarrow 3C_{17}H_{35}COOK + \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

(ii)



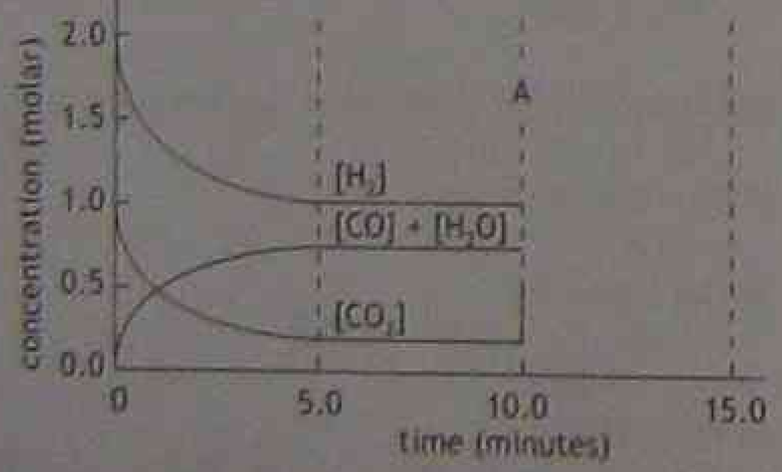
$$\begin{array}{l} CH_2-O-\overset{O}{\overset{\|}{C}}-C_{15}H_{31} \\ | \\ CH-O-\overset{O}{\overset{\|}{C}}-C_{15}H_{31} \\ | \\ CH_2-O-\overset{O}{\overset{\|}{C}}-C_{15}H_{31} \end{array} + 3KOH(aq) \rightarrow 3C_{15}H_{31}COOK + \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Test on Chapter 4 – (option 1) Industrial chemistry

1. [5 marks]

Consider the following equilibrium and graph:

$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$ $\Delta H = 40\ kJ\ mol^{-1}$



(a) What is added to the reaction vessel at time A?

(b) What effect does this change have on
- (i) the concentration of carbon monoxide,
- (ii) the concentration of carbon dioxide, and
- (iii) the temperature of the reaction vessel?

Indicate qualitatively these changes on the axes provided (equilibrium will be reached before 15 minutes have elapsed).

(c) What effect, if any, would occur if the total pressure of the system were increased?

(d) What effect would an increase (at time = 15 minutes) in temperature have on this equilibrium? Illustrate your answer by qualitatively plotting these changes on the axes supplied (temperature is to increase at time = 15 minutes).

(e) How would the graph shown be different if the reaction was repeated in the presence of a catalyst? Illustrate your answer by plotting (on the axes supplied) the changes in concentrations of reactants and products for the first ten minutes of the catalysed reaction.

2. [4 marks]

(a) Sulfur occurs in the elemental state in large deposits in the USA. Ordinary mining methods cannot be used because of quicksand or water which cover the deposits. The Frasch process is used successfully for the extracting of sulfur. On what two physical properties of sulfur does the Frasch process depend?

(b) Sulfuric acid is made by the contact process. The main reaction is the reversible reaction in which sulfur dioxide and oxygen form sulfur trioxide.
- (i) Write a balanced equation for the reaction.
- (ii) Name the catalyst used.

(c) Dilute sulfuric acid consists of one part by volume of concentrated sulfuric acid to six parts of volume of water. Briefly explain how you would dilute concentrated sulfuric acid to produce one litre of dilute sulfuric acid. State ALL the safety procedures you would use.

3. [7 marks]

(a) Briefly distinguish between the two current electrolysis methods used to extract sodium hydroxide from brine solution and state which process you would prefer to be used, giving environmental reasons for your choice.

(b)
- (i) Name the important chemical manufactured by the Solvay process.
- (ii) Name the starting materials.
- (iii) State two manufactured substances for which the chemical produced by the Solvay process is an essential constituent.

4. [4 marks]

Ammonia is produced commercially from hydrogen and nitrogen by the Haber process. All substances are gases.

(a) Write a balanced equation for the reaction.

(b) Apply the Law of Chemical Equilibrium to obtain the equilibrium constant (K_c) for the reaction.

(c) What would be the effect on the equilibrium of each of the following changes (which reaction would be favoured)?
- (i) Increasing the hydrogen concentration.
- (ii) Decreasing the ammonia concentration.
- (iii) Increasing the temperature ($\Delta H = -92 kJ\ mol^{-1}$)
- (iv) Increasing the pressure.

Briefly explain your answer in each case.

(d) Why is the Haber process carried out at 450°C when the forward reaction is exothermic?

5. [6 marks]

Stearic acid, $C_{17}H_{35}COOH$ is a fatty acid which is used to make the fat, tristearin (triglyceryl stearate).

(a) Write the formula for the fat.

(b) Name
- (i) the type of reaction, and
- (ii) the two products, and write a formula for each when tristearin is reacted with hot sodium hydroxide solution in the laboratory.
- (iii) Why is saturated sodium chloride solution added after the tristearin is no longer visible?

(c) State why fat is insoluble in water whereas both the products of its reaction with hot concentrated sodium hydroxide are water soluble.

(d) Briefly distinguish between anionic, cationic and non-ionic synthetic detergents and give an example of a use for each type.

Answers to Test on Chapter 4 – (option 1) Industrial chemistry

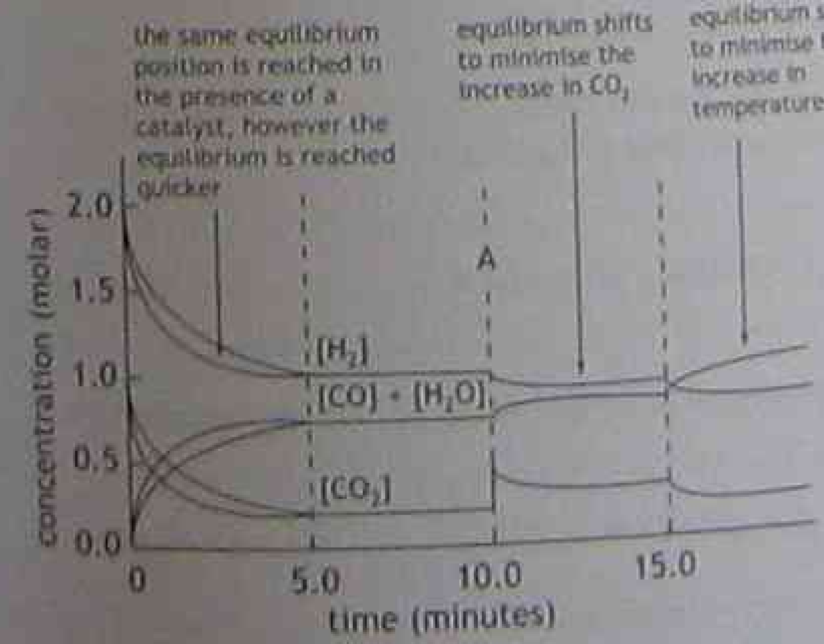
1. [5 marks]

(a) At A, the $[CO_2]$ was increased. Carbon dioxide gas was added.

(b)
- (i) [CO] increases,
- (ii) $[CO_2](g)$ decreases, and
- (iii) The temperature of the system decreases as the forward (endothermic) reaction is favoured.

(c) An increase in pressure has no effect on this reaction as there is no change in the number of moles of gas during the course of this reaction.

(d) If the temperature is increased, then the forward reaction will be favoured. Therefore, the concentrations of products will increase.



(e) The presence of a catalyst increases the rate of reaction, thus the equilibrium will be reached sooner. However, the catalyst does not affect the equilibrium position, thus the same equilibrium concentrations will be reached.

2. [4 marks]

(a) The low melting point (below 120°C) of sulfur and its low density (about 2 g cm^{-3}).

(b)
- (i) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$
- (ii) Vanadium oxide.

(c)
- (i) The concentrated acid is added slowly to the water with continuous stirring. Dilute sulfuric acid consists of one part of concentrated acid to six parts of water. To make up one litre of dilute H_2SO_4, about 167 mL of concentrated acid should be added to about 833 mL of distilled water.
- (ii) The dilution should be carried out in a fume cupboard.
- (iii) Protective clothing, covered shoes and safety glasses should be worn.
- (iv) Allow the diluted sulfuric acid to cool before transferring it to reagent bottles.

3. [6 marks]

(a) (i) The mercury cathode cell – Sodium (Na) is produced and dissolved in the flowing mercury (Hg) cathode. Sodium hydroxide is produced by treating the Na/Hg amalgam with water.

(ii) The diaphragm cell — The products of electrolysis are kept apart by an asbestos diaphragm.

(iii) The membrane cell — This cell has a titanium anode (not attacked by chlorine) and a nickel cathode. The anode and cathode are separated by an ion-exchange membrane. This membrane is selective allowing only Na^+ and water to flow through it. Na^+ ions flow to the cathode where OH^- ions also collect. The membrane cell is the most modern process and does not pose environmental risks, such as mercury leaking from the mercury cathode cell or the risk to plant operators in using asbestos materials.

(b) (i) Sodium carbonate.

(ii) Ammonia dissolved in brine (strong NaCl); carbon dioxide (produced by heating limestone).

(iii) Manufacture of glass, soaps, detergents, paper and dyes.

4. [4 marks]

(a) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \quad \Delta H = -92 \text{ kJ mol}^{-1}$

(b) $K = \frac{[NH_3]^2}{[N_2][H_2]^3}$

(c) (i) According to Le Chatelier's Principle, the reaction would move to the right to minimise the effect of increasing $[H_2]$.

(ii) Decreasing the $[NH_3]$ would drive the reaction to the right to increase the $[NH_3]$.

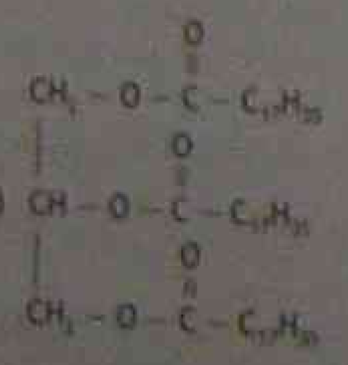
(iii) Increasing the temperature in an exothermic reaction would drive the reaction to the left, favouring an endothermic reaction.

(iv) Increasing the pressure would drive the reaction to the right (four moles of reagent and only two moles of product).

(d) In some industrial processes, e.g. the Haber process, although the reaction is exothermic, the temperature is raised to 450°C to enable the equilibrium to be reached sooner by raising the kinetic energy of the molecules.

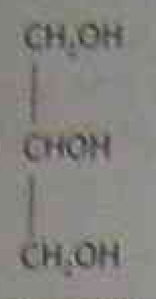
5. [6 marks]

(a)



(b) (i) Saponification

(ii)



and $C_{17}H_{35}COONa$

glycerol sodium stearate

(iii) The solubility of many organic compounds in water, e.g. sodium stearate is considerably reduced by dissolved salts such as sodium chloride. This is an example of the common ion effect.

(c) Fat is non-polar substance while both glycerol and sodium stearate are polar. Water is a polar substance and 'like dissolves like'.

(d) (i) Anionic detergents, where the surfactants has a negatively charged head.

Example:

Alkylbenzenesulfonates represented as

In general

Anionic detergents are high sudsing and are used mainly in laundry and dishwashing detergents, e.g. Omo, Rinso, Morning Fresh.

(ii) Cationic detergents where the surfactant has a positive head.

Quaternary ammonium compounds are typical cationic detergents. They are generally used in fabric softeners, e.g. Comfort.

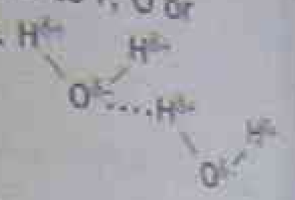
(iii) Non-ionic detergents do not ionise in water and have no electrical charge. They are resistant to water hardness, and have polar uncharged groups.

Non-ionics detergents are usually polyethoxymethoxylates They are low sudsing and are commonly used in automatic dishwashing detergents, e.g. Finish.

Total 25 marks

Glossary

Activation energy	The smallest amount of energy needed to cause a reaction to occur (E_a).
Alkyl group	An alkane minus a hydrogen atom.
Biodegradable	A substance that is easily broken down by bacteria so that waterways are not polluted.
Catalyst	Any substance that makes possible or alters the rate of a chemical reaction but remains unchanged at the end of the reaction.
Common ion effect	The effect of an ion common to an equilibrium which shifts that equilibrium. The addition of a common ion always decreases solubility.
Contact process	Used in the manufacture of sulfuric acid. The main reaction is the reversible one in which sulfur dioxide and oxygen form sulfur trioxide.
Dehydrating agent	A substance, e.g. concentrated H_2SO_4, which will remove water from other substances.
Detergent	A substance added to water to improve its cleaning ability, e.g. soaps and synthetic detergents.
Dispersion forces	The forces of attraction between atoms or molecules arising from temporary dipoles.
Electrolysis	The decomposition of a substance, in either solution or the molten state, by the application of an electric current.
Equilibrium constant	At equilibrium: [A] = concentration of A; [B] = concentration of B; [C] = concentration of C; [D] = concentration of D. At a particular temperature: if $aA + bB \rightleftharpoons cC + dD$, then $K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$.
Fatty acids	Long chain aliphatic carboxylic acids. They can have saturated or unsaturated carbon chains.
Frasch process	A system of concentric pipes which is used to mine elemental sulfur where quicksand and/or water cover the deposit to be mined.
Glycerol	A trihydric alkanol 1,2,3 propanetriol.
Heterogeneous	Systems involving more than one state of matter.
Homogeneous	Systems involving only one state of matter, e.g. all gases.

Hydrogen bonds	These bonds occur in polar interactions where a hydrogen atom bound to F, O or N can be attached to another one of these atoms in another molecule. 
Hydrophobic	Repelling the solvent water.
Hydrophilic	Attracting the solvent water.
Le Châtelier's Principle	If conditions in a system at equilibrium are changed, the system will adjust to try to minimise change.
Polar molecules	Molecules having an uneven distribution of charge, e.g. $H^{\delta+} - Cl^{\delta-}$.
Reaction quotient (Q)	[A] = conc. of A; [B] = conc. of B; [C] = conc. of C; [D] = conc. of D. The reactant quotient can be determined for equilibrium and non-equilibrium systems. It is defined as $Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ for the reaction $aA(aq) + bB(aq) \rightarrow cC(aq) + dD(aq)$. Only at equilibrium does Q = K.
Saponification	The basic reaction in soap manufacture that occurs between a fat or oil and an alkali resulting in the formation of soap and glycerol $C_3H_5(O_2CR)_3 + 3\,NaOH \rightarrow 2RCO_2Na + C_3H_5(OH)_3$ where R is the carbon chain containing 8 to 18 carbon atoms.
Soap	The oldest surfactant (surface active agent). The surfactant is an anion (negatively charged species COO^-) and the charge is concentrated in the hydrophilic head.
Solvay process	A continuous process that uses carbon dioxide and ammonia dissolved in brine (concentrated NaCl) as the starting materials. The product formed is sodium carbonate (Na_2CO_3).
Synthetic surfactants	(a) Anionic detergents, where the surfactant has a negatively charged head, e.g. alkyl benzene sulfonates. (b) Cationic detergents, where the head carries a positive charge, e.g. quaternary ammonia compounds. (c) Non-ionic detergents, do not have a specific charge, e.g. alcohol ethoxylates.
Triglycerides	Esters formed from glycerol and fatty acids.

5 option two

Shipwrecks, Corrosion and Conservation

The ocean can be regarded as a massive solution of different electrolytes. The impact of such an environment can be investigated and analysed from observations on the reduction of corrosion for present-day ships and the effects of corrosion on earlier iron ships determined by salvage efforts.

Contents

5.1 The origins of minerals in oceans

Its chemical composition shows that the ocean is a massive solution of different electrolytes and contains 97% of all available water. When a litre of seawater is evaporated to dryness, about 35–40 grams of salts are recovered. They include about 78% of NaCl, 16% of magnesium chloride and sulfate and 6% of potassium salts.

Minerals in oceans originated from the following routes:

- *Leaching by rainwater from terrestrial environments.* River water contains many dissolved substances from the chemical breakdown of continental rock. Examples are calcium hydrogen carbonates, magnesium sulfates, iron and aluminium compounds and salts of sodium and potassium (mainly chlorides). If evaporation exceeds precipitation (rainfall) and drainage into the ocean, then the concentration of salts (salinity) increases.
- *Hydrothermal vents (hot springs) that spout smoke and water at temperatures up to 400°C.* These vents yield sulfides of copper, zinc and iron that come from the magma. As new crust forms at ocean ridges, it develops cracks into which seawater enters, dissolving minerals. One such site is off the coast of Papua New Guinea.

5.2 Reactions involving ions – electron transfer

Definition of an electrolyte

An electrolyte, as defined by Michael Faraday, is a substance which either in the fused (molten) state or in solution conducts an electric current and is decomposed by it:

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

The formation of NaCl(s) involves transfer of an electron from the sodium atom to the chlorine atom.

Later, Arrhenius proposed his theory of electrolytic dissociation which stated that some molecules when dissolved in water break up into ions of opposite charge (see Figure 5.1).

Example

When sodium chloride crystals dissolve in water, since water is a polar molecule the sodium ion in the lattice would be surrounded by the negative ends of the water molecules and the chloride ion by the positive ends. As the outer ions in the lattice are moved apart, more water molecules enter the lattice.

The strength of an electrolyte is determined by the concentration of its ions in solution. Substances that are very soluble in water form solutions with high concentrations and are called *strong electrolytes*. If the ionic concentration is low, the substances are called *weak electrolytes*.

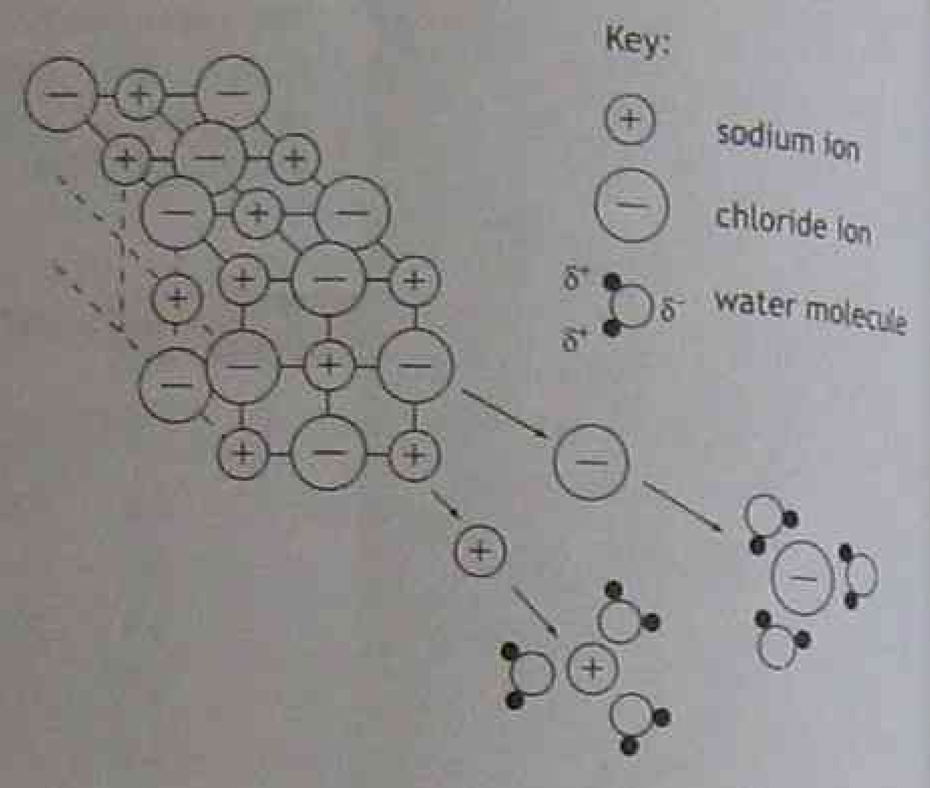


Figure 5.1 Water breaking down a NaCl crystal

Practical work (Demonstration)

Aim:

To show the electrical conductivity of a fused salt — sodium chloride. (To be carried out in a fume cupboard.)

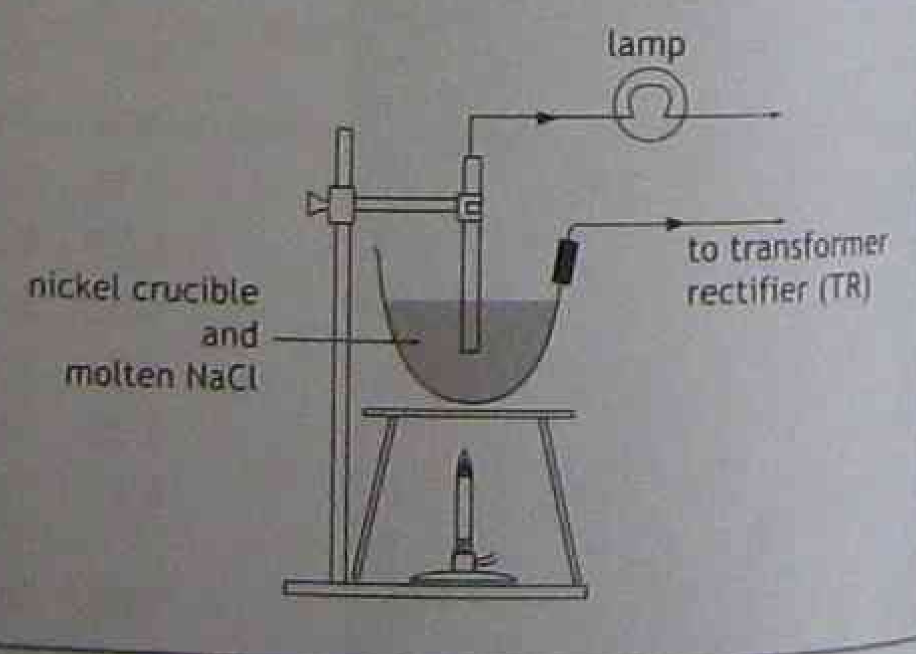


Figure 5.2 Conductivity of fused NaCl.

Note: During fusion or dissolution, the NaCl(s) spontaneously forms Na^{+} and Cl^{-} ions.

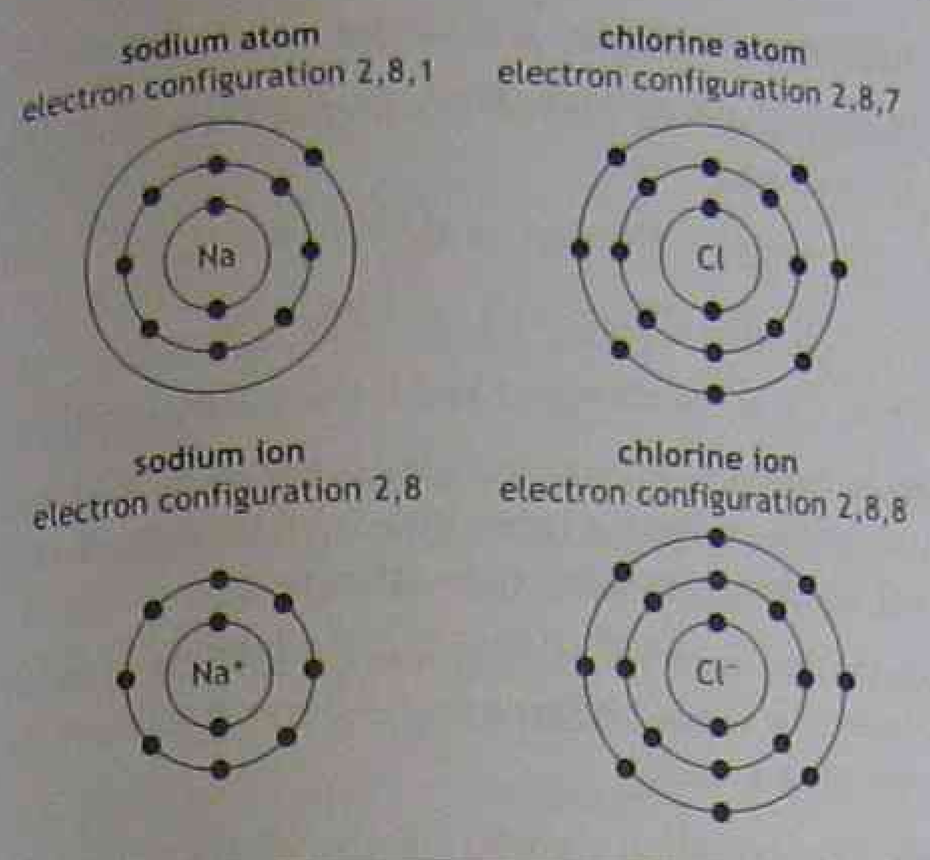


Figure 5.3 Spontaneous formation of Na^{+} and Cl^{-} ions

Typical electron transfer reactions

The reactions that produce ionic compounds from elements are oxidation-reduction reactions (see Chapter 1 — Section 1.12). Examples of these reactions are

(a) metals with non-metals, e.g. magnesium with chlorine;

(b) metals with dilute replacement acids, e.g. magnesium with dilute hydrochloric acid; and

(c) metals with metal ions, e.g. iron in a copper (II) sulfate solution.

Exercise 5.1

For examples (a), (b) and (c), indicate

(i) which species is oxidised;
(ii) which species is reduced;
(iii) the oxidant (oxidising agent which is itself reduced);
(iv) the reductant (reducing agent which is itself oxidised);
(v) the reduced species (product);
(vi) the oxidised species (product); and
(vii) the half-equations for each reaction.

5.3 Concept of redox

The redox reaction has the following characteristics:

- Oxidation and reduction involves a transfer of electrons between species.
- Oxidation is the loss of electrons from a substance.
- Reduction is the gain of electrons by a substance.
- An oxidising agent or oxidant is an electron acceptor.
- A reducing agent or reductant is an electron donor.
- Oxidation number of an element in a molecule is the charge that atom would have if it were completely ionic.

Table 5.1 Redox reaction

Process	No. of electrons	Oxidation number
Oxidation	decreases	increases
Reduction	increases	decreases
Oxidant	increases	decreases
Reductant	decreases	increases

The higher the metal in the activity series, the more powerful a reductant it is. Hydrogen is included in the activity series. Metals above it in the series will reduce the H^{+} ion of replacement acids (for example, HCl) so H_2 is evolved. Metals below hydrogen (such as Cu) do not react.

Any metal in the series will displace any metal below it from a solution of its salt. For example,

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

Ionic equations must be balanced atomically and electrically.

Active metal + replacement acid → metal salt + hydrogen

Half-equations:

(i) $Mg \rightarrow Mg^{2+} + 2e^{-}$ (oxidised)

(ii) $2H^{+} + 2e^{-} \rightarrow H_2$ (reduced)

Add (i) and (ii):

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

Reactions of metals with oxidising acids

(a) *Dilute nitric acid.* In dilute nitric acid, the presence of NO_3^{-} ions with H^{+} ions makes it a strong oxidising agent. Metals, even those below hydrogen in the activity series, are oxidised and nitric oxide and water are formed.

Example — copper + dilute nitric acid

Half-equations:

(i) $Cu \rightarrow Cu^{2+} + 2e^{-}$ (oxidation)

(ii) $NO_3^{-} + 4H^{+} + 3e^{-} \rightarrow NO + 2H_2O$ (reduction)

Multiply (i) by 3:

(iii) $3Cu \rightarrow 3Cu^{2+} + 6e^{-}$

Multiply (ii) by 2:

(iv) $2NO_3^- + 8H^+ + 6e^- \rightarrow 2NO + 4H_2O$

Add (iii) and (iv):

$$3Cu(s) + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3Cu^{2+}(aq) + 2NO(g) + 4H_2O(l)$$

Note: Nitric oxide (NO) is a colourless gas which reacts rapidly with air to form nitrogen dioxide (NO_2) which is a red-brown gas.

$$2NO + O_2 \rightarrow 2NO_2$$

(b) *Concentrated nitric acid.* The products formed in the reaction of concentrated nitric acid on metals are usually nitrogen dioxide and water. Rate of reaction is a key factor in determining what products are formed.

Example — copper + concentrated nitric acid

Half-equations:

(i) $Cu \rightarrow Cu^{2+} + 2e^-$ (oxidation)

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

Multiply (ii) by 2:

(iii) $2NO_3^- + 4H^+ + 2e^- \rightarrow 2NO_2 + 2H_2O$

Add (i) and (iii):

$$Cu(s) + 2NO_3^-(aq) + 4H^+(aq) \rightarrow Cu^{2+}(aq) + 2NO_2(g) + 2H_2O(l)$$

(c) *Concentrated sulfuric acid.* When hot, concentrated H_2SO_4 acts on metals, the main gas formed is sulfur dioxide (SO_2). When writing equations, we ignore any H_2S or S which may form.

Example — copper + concentrated sulfuric acid

Half-equations:

(i) $Cu \rightarrow Cu^{2+} + 2e^-$ (oxidation)

(ii) $SO_4^{2-} + 4H^+ + 2e^- \rightarrow SO_2 + 2H_2O$ (reduction)

Add (i) and (ii):

$$Cu(s) + SO_4^{2-}(aq) + 4H^+(aq) \rightarrow Cu^{2+}(aq) + SO_2(g) + 2H_2O(l)$$

Displacement of a metal from its salt solution by another metal

These can predicted by the activity series.

Half-equations:

(i) $Mg \rightarrow Mg^{2+} + 2e^-$ (oxidised)

(ii) $2Ag^+ + 2e^- \rightarrow 2Ag$ (reduced)

Add (i) and (ii):

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

Reactions of halogens with halides

Halogens can be ranked in order of their strength as oxidants.

$$Cl_2(g) + 2Br^-(aq) \rightarrow Br_2(l) + 2Cl^-(aq)$$

$$Br_2(l) + 2I^-(aq) \rightarrow I_2(g) + 2Br^-(aq)$$

Thus, Cl_2 is the strongest and I_2 the weakest oxidant.

Note: In reactions where metal atoms show different oxidation states, e.g. transition metals (iron +2 and +3), oxidation numbers are often used.

Oxidation number is very useful in dealing with elements whose compounds show a variety of oxidation states.

The *oxidation number* is the charge, real or imaginary, that an atom would have if it existed as an ion in a compound.

Iron is a typical transition metal, showing more than one oxidation state. Another example is titanium which has oxidation states of +2, +3 and +4.

Other metals, which are not transition metals, may exist in more than one oxidation state, for example tin (+2 and +4).

Rules for assigning oxidation numbers (O.N.)

1. In uncombined elements, each atom has an oxidation number of zero, for example Na, Cl_2 have an oxidation number of zero.
2. The oxidation number of a monatomic ion is equal to the charge on that ion, for example Na^+ (O.N. = +1), Fe^{3+} (O.N. = +3), S^{2-} (O.N. = −2).
3. Oxygen has an oxidation number of −2 in compounds. [Peroxides and superoxides are the exceptions, for example H_2O_2 (O.N. = −1) and KO_2 (containing O_2^- ion).]
4. Hydrogen has an oxidation number of +1 in compounds. [Ionic hydrides are the exception where the O.N. = −1, for example NaH (O.N. = −1).]
5. The sum of the oxidation numbers of all atoms:
   (a) in a neutral molecule is zero;
   (b) in a polyatomic ion, is equal to the charge on the ion.

Example 1

In the compound $FeCl_3$, the O.N. for iron is +3. In the compound $FeCl_2$, the O.N. for iron is +2.

Example 2

Find the O.N. for manganese in the following compounds:

(a) $MnCl_2$ [+2]

(b) $MnCl_3$ [+3]

(c) $KMnO_4$ [1 + Mn + (−8)] = [+7]

Example 3

Write half-equations for the reaction which takes place when iron (II) nitrate has bromine added to it. Write the balanced equation for the reaction and state the oxidant and the reductant.

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

(ii) $Br_2 + 2e^- \rightarrow 2Br^-$ (reduction)

Multiply (i) by 2:

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

Add (ii) and (iii):

$$2Fe^{2+}(aq) + Br_2(l) \rightarrow 2Fe^{3+}(aq) + 2Br^-(aq)$$

Br_2 is the oxidant; Fe^{2+} is the reductant.

5.4 Historical development in electron transfer reactions

- In 1791, Luigi Galvani passed a discharge from a Leyden jar through the leg of a frog and noticed twitching. He called this effect 'animal electricity'; the effect was later was called 'galvanism'.
- In 1800, Alessandro Volta made a 'voltaic pile' from a stack of silver/zinc discs separated by felt pads soaked in brine (salt solution). When the bottom zinc disc was joined to the upper silver disc, the current would flow. This was the prototype of electrical batteries.
- In that same year, William Nicholson and Anthony Carlisle, inspired by Volta's work, produced the prototype of a voltameter which could split water into its elements.
- In 1807, Sir Humphry Davy isolated the elements magnesium, calcium, strontium and barium, again by electrolysis of their molten compounds.
- In March 1813, Michael Faraday was formally appointed as Davy's laboratory assistant at the Royal Institution in London.
- In 1833 in London, Faraday published his studies on electrolysis. He had carefully measured the amount of electricity involved during electrolysis and related it to the amount of substances produced.

Extension: *Faraday's Laws of Electrolysis* are as follows:

1. The amount of any substance deposited, dissolved or evolved at an electrode during electrolysis is directly proportional to the amount of electricity passed through the electrolyte.
2. The amount in moles of different substances deposited, evolved or dissolved at an electrode by the passage of the same amount of electricity are inversely proportional to the charges on their ions.

   The Faraday experiments were the original bases for the notion that electricity consisted of individual charges called electrons, but it was not until 1897 that this was verified. Faraday also introduced some of the terminology we still use today, e.g. electrolysis, electrolyte, anode and cathode, anion and cation.

Activity 5.1

The corrosion of iron

Part A

Inquiry

To determine what substances cause iron to corrode.

Materials

4 × iron nails

2 × large dry stoppered test tubes

2 × large dry test tubes

test-tube rack

anhydrous calcium chloride

olive oil or paraffin oil, distilled water, dilute NaCl solution

emery paper

Procedure

1. Clean the four nails with emery paper (or steel wool) to remove any coating present.
2. Label test tubes 1–4 and place a cleaned nail in each.
3. In test tube 1, place a few pieces of anhydrous calcium chloride to absorb any water vapour present. Stopper immediately.
4. Boil some distilled water to drive out any

dissolved oxygen. Cover the nail in test tube 2 completely with the boiled water. Pour a thin layer of oil on top of the water and stopper the test tube.

5. Pour distilled water into test tube 3 to cover half the nail only. Leave the test tube open to the air.
6. Pour a dilute solution of sodium chloride into test tube 4 to cover half the nail. Leave the test tube open to the air.
7. Leave the test tubes for at least one day. Re-examine them.

Results

1. Note which test tube contained the nail that rusted the most.
2. Note which nails did not rust.

Questions

1. The average motor vehicle muffler is replaced every 3–4 years. Why do mufflers corrode so rapidly?
2. Why do motor vehicles in Manly rust more rapidly than in Dubbo?
3. Why do motor vehicle radiators often become blocked?
4. What substances must be present for iron to corrode?

Part B

Inquiry

To investigate how rusting occurs.

Materials

3 Petri dishes

3 iron nails

1 piece of copper wire (free from lacquer)

1 strip of zinc

Prepared agar ferroxyl gel

The gel is prepared by boiling on a water bath 1.5–2 g of agar gel in 100 mL of water. To this mixture add 15 mL of a 1% solution of potassium ferricyanide and 2 mL of phenolphthalein solution. To hasten the results, 1 mL of a saturated solution of sodium chloride is also added. Add dropwise enough 2 M KOH to turn the gel pink, then just decolourise using a few drops of 0.5 M HCl.

Procedure

1. Clean the nails with emery paper.
2. Wind copper wire tightly around the centre part of one nail.
3. Wind a narrow strip of zinc tightly around the centre part of the other nail.
4. Place all three nails in three separate Petri dishes and just cover them with prepared agar gel.
5. Re-examine in 24 hours and draw neat diagrams of the Petri dishes and their contents. Show on your diagrams the sites of anodic and cathodic reactions as seen from the colours in the gel. Explain any differences that you observe in the three diagrams.
6. Lift out the nails and examine them and the gel for rust.

Results

Diagram 1: Petri dish + gel + iron nail

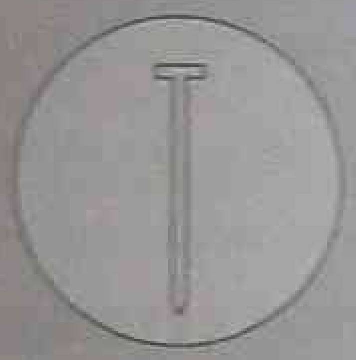


Diagram 2: Petri dish + gel + iron nail + copper wire

Diagram 3: Petri dish + gel + iron nail + zinc strip

Questions

1. Write
   (a) anode, and
   (b) cathode reactions for each Petri dish.
2. From your results, state the colours of the complex ions formed. For iron, $Fe[Fe(CN)_6]^-$ ion is formed and for zinc, $Zn[Fe(CN)_6]^-$ ion is formed.
3. If OH^- ions are present in an area of the gel, what colour would the gel be?
4. In two of the reactions, cathode protection occurs.
   (a) State what you mean by the term 'cathode protection'.
   (b) In which case is iron protected?
   (c) In which case is the other metal protected?
5. When you lifted the nails from the Petri dish, where was the rust? What does this imply about corrosion of iron?

5.5 Difference in the corrosion rate of metals

Corrosion is the oxidation of metals by certain substances (mostly water and oxygen) in the environment. A metal corrodes when it gives up its electrons and loses strength and elasticity. Corrosion is an electrochemical process similar to that of an electrolytic cell (except for wrecks at great depths, e.g. the *Titanic*, where anaerobic bacteria are responsible for rusting). The two half-reactions of the electrochemical cell use the corroding metal as both the electrodes and the electronic conductor of the external circuit. The ionic conductor is usually a film of aqueous solution (seawater in the case of shipwrecks) on the surface of the metal (see Figure 5.4).

Note the following:

- Not all metals corrode spontaneously. Metals such as gold, platinum and palladium are resistant to corrosion and can be found uncombined in nature.
- Aluminium is a reactive metal that, from its position in the table of redox reactions, should be easily corroded, yet it is not. The reason is that aluminium is extremely reactive to oxygen, forming aluminium oxide which is so tightly held on the surface of the metal that it forms a protective layer which prevents further corrosion.

$$4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$$

If aluminium is anodised, a thick layer of oxide is produced which makes it even more corrosion-resistant. (In the process of anodising, aluminium is made the anode of an electrolytic cell. A copper cathode is used in an electrolyte of 2 M H_2SO_4.)

- Aluminium is an example of a passivating metal, that is a reactive metal which forms an inactive coating as a result of reaction with substances such as water or oxygen. Aluminium has an inherent oxide film which is inert, tenacious and reforms immediately if cleaned with steel wool. In metallurgical laboratories, aluminium samples are dissolved by adding hydrogen peroxide (H_2O_2) to hydrochloric acid.
- Other passivating metals include chromium, which forms a protective oxide layer in air and can be used as an electroplated deposit to protect and decorate. It is also used in alloys.
- A polished steel surface can be made 'passive' by concentrated nitric acid (HNO_3). The acid produces a dark blue, reasonably adherent protective layer of oxide (Fe_3O_4).
- Stainless steels are composed mostly of iron alloyed with chromium (about 18%) and nickel (about 8%). They resist corrosion due to the formation of an adherent film of oxide owing to the presence of passivating metals.
- Carbon steel corrodes, as does iron , by the slow formation of a brown non-adherent coating called rust. This coating forms in the presence of oxygen and moisture and contains iron (III) oxide, hydroxide and carbonate. The iron (III) oxide dehydrates to rust ($Fe_2O_3.H_2O$). Rust spots indicate the points where pure iron has been oxidised. These rust spots form the location of the anode half-cell of an electrochemical cell.

5.6 The rusting of iron

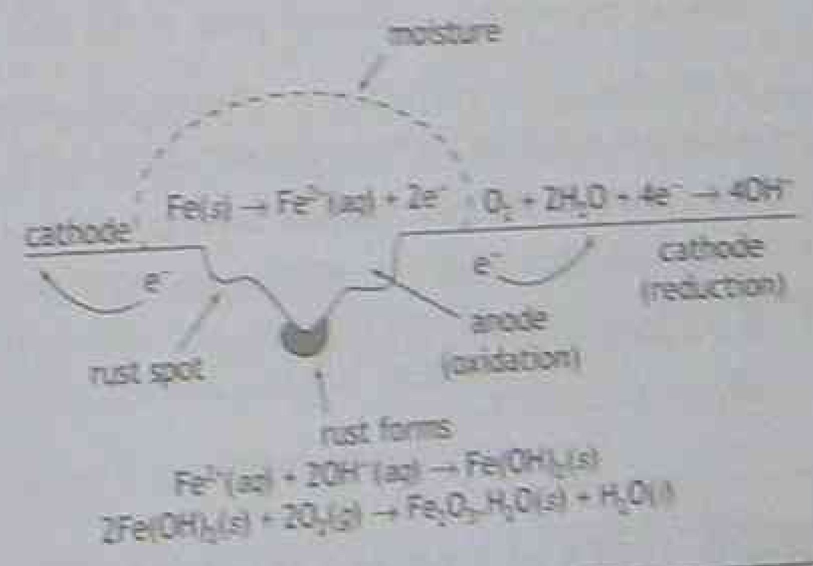


Figure 5.4 Mechanism of electrochemical corrosion

In the moist region, OH^- ions will move towards the anode and Fe^{2+} ions will move towards the cathode. These ions are traced towards the anode in Activity 5.1, Part B. The blue colour in the gel indicates the presence of Fe^{2+} ions:

$$\underset{\text{ferricyanide ion}}{Fe^{2+} + Fe(CN)_6^{3-}} \rightarrow \underset{\text{Prussian blue}}{Fe[Fe(CN)_6]^-}$$

The zinc complex ion, $Zn[Fe(CN)_6]^-$ is colourless.

The presence of OH^- ions in the gel is shown by the pink colour of the phenolphthalein. When, after a few days, the iron nail is removed from the gel, there is no rust on the nail nor on the gel. In diagrams 1 and 2, there is no rust on the nail but there is rust on the gel. This shows that the rust does not form directly on the metal surface.

The rusting of iron will be hastened by the following conditions:

1. The presence of oxygen is large concentrations at the surface of iron which will accelerate the corrosion of another area with less oxygen if there is electrical contact between them. This helps to explain why corrosion pits in iron can be very deep. Since the bottom of the pit has less oxygen than the top, it will act as an anode and corrosion in the pit will be accelerated.
2. Pure iron is more resistant to corrosion than impure iron (wrought iron is more resistant than cast iron). Electrochemical cells can occur if, for example, copper is present. Copper can serve as a cathode half-cell since its atoms are less readily oxidised than iron atoms. The electrons travel through the iron and the ions through a moisture film to complete the circuit.
3. Iron corrodes more readily where ions in the metal lattice have been distorted by stress. This can be readily seen by examining the areas around the nail in Activity 5.1, Part B. The blue colour due to the Fe^{2+} ions is concentrated around the worked head and point of the nail.

   Note: For iron and for any other metal, any region of electrochemical corrosion must have
   (a) an anode where oxidation occurs;
   (b) a cathode where reduction occurs;
   (c) a metal path for electrons; and
   (d) an electrolyte.

5.7 Types of iron and steel ships

The main metals used in ships are iron and steel. Examples of their historical use are listed below.

- In the early 1860s, British tea clippers introduced the composite hull in which iron frames were added to a wooden ship, e.g. *Cutty Sark* (1869).
- In the remaining years of the 19th century, fully rigged ships, mostly 4-masted barques, were built first of iron and then of steel, to succeed the wooden clippers.
- In 1905, the steel barque *Pamir* was one of the last sailing ships built. By then remnants of sail were being ousted by steam. With the advent of steam tugs for berthing, ships were able to be built much larger.
- In 1906, the *Dreadnought* class battleships were able to be built as a result of progress in the quality of steel, the invention of the steam turbine engine and improvements in weaponry.
- In 1912, the *Titanic* was launched with a displacement of 46 328 tons making her the largest liner in the world at that time. She had 25 boilers and her reciprocating engines were fitted with four funnels. There were two masts with a lookout cage on the foremast.
- The first ocean-going diesel-driven ship, the *Selandra*, was also launched in 1912.
- Large modern ships now use diesel or steam turbine-driven engines and a few are powered by nuclear reactors.
- The world's first nuclear-powered, steam turbine-driven surface ship, the icebreaker *Lenin*, was built in 1959.

5.8 Composition of cast and wrought iron and some steel alloys

- The refining process of iron is

$$\begin{tikzcd}\text{pig iron} \arrow[r] & \text{cast iron} \arrow[r] \arrow[d] & \text{steel (alloy)} \\ & \text{wrought iron} & \end{tikzcd}$$

- All steel contains some carbon, e.g.
  <0.25% C in mild steel
  0.25–0.6% C in medium steel
  0.6–1.4% C in high steel
- With a higher carbon content, the metal lattice becomes harder, stronger and less ductile.
- The two main stages in the production of steel from cast iron are
  (i) the removal of impurities from the iron; and
  (ii) the addition of elements to form alloys.
- An alloy is a material that contains more than one element and has the characteristic properties of metals. The alloying of metals is one of the main ways of modifying the properties of pure metallic elements.
- Cast iron contains about 2.4% C and 1.1% Si. It is used for marine equipment such as anchors, chains and capstans (which are used to haul up an anchor).
- Wrought iron is made by melting cast iron and oxidising silicon and manganese and other impurities to form a slag. Wrought iron contains 0.04% C and 0.10–0.15% Si.
- Wrought iron is superior to low carbon steel owing to the following properties:
  (i) Its ability to withstand the stress of shock (impact) and vibration.
  (ii) Its corrosion resistance. The *James Craig*, moored at Darling Harbour in Sydney, would have been impossible to salvage if it had been made of steel instead of riveted wrought iron plates.
  (iii) Its ability to hold protective coatings, e.g. zinc. The lower the carbon and silicon content, the more tightly a zinc galvanised coating will adhere to it.
- Wrought iron is used for plates (where a high resistance to corrosion is needed) and chains (where weldability and impact strength are needed).
- Pure iron is malleable but steel, because of the presence of carbon and other elements, is less malleable.
- Changes with temperature in the crystal structure of iron show that it is body-centred cubic at moderate temperatures but changes to face-centred at high temperatures.

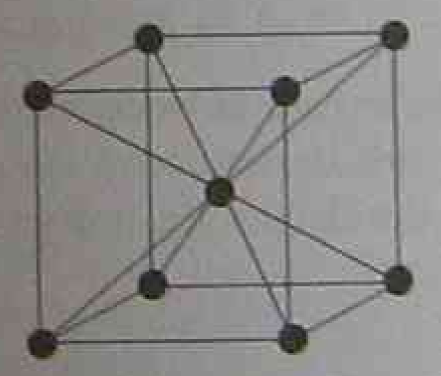


Figure 5.5 Body-centred cubic

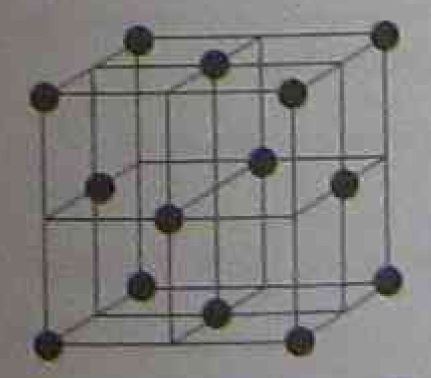


Figure 5.6 Face-centred cubic

- Carbon atoms are small enough to fit in the tetrahedral holes in the face-centred structure, but are too large to fit into the much smaller holes of the body-centred structures. The carbon therefore dissolves in iron at high temperatures but precipitates as FeC (cementite) at low temperatures. This compound is hard and brittle and stops the planes of atoms from slipping over each other in the crystal under stress, as they do in pure iron. This hardens the steel.
- Steels are iron alloys containing carbon and often such other elements as nickel, chromium, molybdenum, tungsten and vanadium. The metals nickel, chromium and manganese are found in solid solution with the iron, where they provide added strength to the alloy. Vanadium and molybdenum are found in the cementite phase.

5.9 Classification of alloys

Alloys can be classified as solution alloys, substitutional alloys and intermetallic compounds.

The solution alloys are homogenous mixtures with the components dispersed randomly and uniformly. Atoms of the solute can take positions normally occupied by the solvent, forming a substitutional alloy, or they can occupy interstitial spaces, forming an interstitial alloy.

Figure 5.7 Types of alloys

In *interstitial alloys*, the interstitial atoms bond with neighbouring atoms. The presence of these extra bonds causes the metal lattice to become harder, stronger and less ductile. Iron containing less than 3% carbon, is much harder than pure iron and has other desirable physical properties such as a much higher tensile strength.

Table 5.2 Examples of different carbon steels

Type	Use	Special properties
Carbon steels mild steel (0.15–0.25%); most commonly used steel	car bodies, ships, bridges, buildings	cheap, ductile, easily welded
Medium steel (0.25–0.6%)	girders and rails	tougher than mild steels
High carbon steel (up to 1.5%)	scissors, axes, knives	the addition of more carbon increases hardness but lowers ductility

In *heterogeneous alloys*, the components are not dispersed uniformly, e.g. in a form of steel called pearlite, there is a mixture of iron and FeC called cementite. These mixtures do not generally have characteristic melting points but in some cases, e.g. solders, there are definite melting points.

Intermetallic alloys are homogeneous and have specific properties and composition, e.g. the compound $CuAl_2$ called duralumin. The intermetallic compound, cementite, is distributed through some steels.

5.10 Electrochemical galvanic cells

Redox reactions may be spontaneous and are called electrochemical reactions. These reactions can generate electric current. In 1835, John Daniell investigated the reason for Volta's cells rapidly losing their potential to supply electrons. He then constructed his Daniell cell (see Figure 5.8) which gave a constant potential. This cell produces electricity as a result of a chemical oxidation-reduction reaction and is called a galvanic cell (after Luigi Galvani).

Examples of a simple galvanic cell

The Daniell cell is divided into two half-cells:

(a) The electron donor half-cell where loss of electrons (oxidation) occurs, which is called the anode.

Anode half-cell reaction:

$$Zn \rightarrow Zn^{2+} + 2e^-$$

(b) The electron acceptor half-cell where electrons are gained (reduction) which is called the cathode.

Cathode half-cell reaction:

$$Cu^{2+} + 2e^- \rightarrow Cu$$

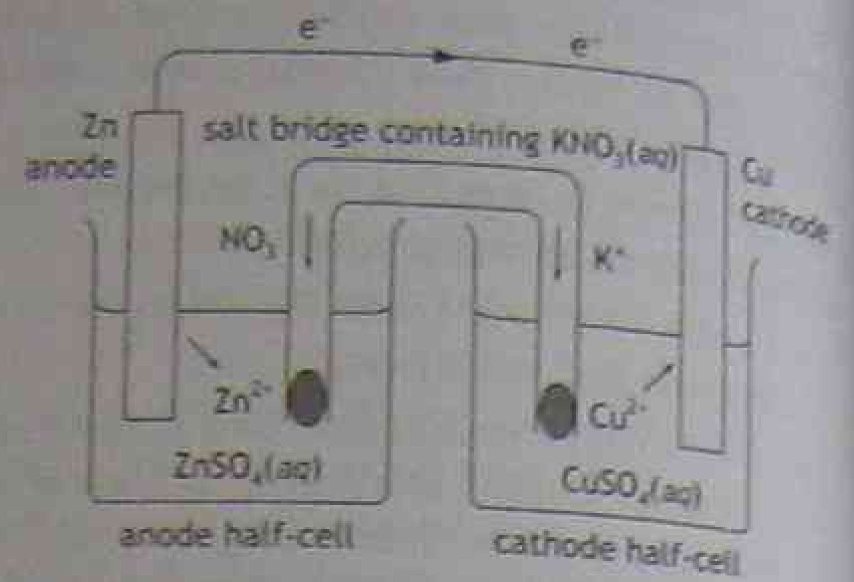


Figure 5.8 The Daniell cell

The half-cells are connected by an external wire. The external circuit enables the electrons to move from the anode to the cathode.

A salt bridge, usually filled with KNO_3, between the two half-cells, completes the circuit and enables ions to move. The salt bridge may be an inverted U-tube of KNO_3, containing an aqueous solution with cotton wool plugs at the ends or strips of filter paper soaked in the salt. The movement of ions through the salt bridge balances the charges due to the electron flow in the external circuit.

The overall cell reaction is obtain by adding the anode and cathode half-cell reactions. The electrons must be balanced.

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

The potential difference or electromotive force (emf) of a galvanic cell depends on the nature of the electrodes and the electrolyte. It does not depend on the size of the cell.

Table 5.3 Examples of special steel alloys

Type	Use	Special properties
Cobalt steel 73.5% Fe, 17% Co, 2.5% Cr, 8% W+C	magnets, jet engines	improves magnetic properties
Chrome-vanadium steel 98% Fe, 1% Cr, 0.2% V+C	tools, grinders	hard wearing and shock resistant
Stainless steel 74% Fe, 18% Cr, 8% Ni+C	sinks, cisterns, cutlery	corrosion resistant, chemically unreactive, hard and strong
High-speed steel 75% Fe, 18% W, 6% Cr+C	drills, cutting tools	hard at high temperatures
Alnico 61% Fe, 12% Al, 22% Ni, 5% Co+C	permanent magnets	very high magnetic permeability

Table 5.4 Some standard potentials at 298 K (25°C)

Increasing strength as oxidants

Increasing strength as reductants

Oxidant		Reductant	E°
$K^+ + e^-$	⇋	$K(s)$	−2.92 V
$Ba^{2+} + 2e^-$	⇋	$Ba(s)$	−2.90 V
$Ca^{2+} + 2e^-$	⇋	$Ca(s)$	−2.87 V
$Na^+ + e^-$	⇋	$Na(s)$	−2.71 V
$Mg^{2+} + 2e^-$	⇋	$Mg(s)$	−2.36 V
$Al^{3+} + 3e^-$	⇋	$Al(s)$	−1.66 V
$Mn^{2+} + 2e^-$	⇋	$Mn(s)$	−1.18 V
$H_2O + e^-$	⇋	$\frac{1}{2}H_2(g) + OH^-$	−0.83 V
$Zn^{2+} + 2e^-$	⇋	$Zn(s)$	−0.76 V
$S(s) + 2e^-$	⇋	S^{2-}	−0.48 V
$Fe^{2+} + 2e^-$	⇋	$Fe(s)$	−0.41 V
$Ni^{2+} + 2e^-$	⇋	$Ni(s)$	−0.23 V
$Sn^{2+} + 2e^-$	⇋	$Sn(s)$	−0.14 V
$Pb^{2+} + 2e^-$	⇋	$Pb(s)$	−0.13 V
$CO_2(g) + 4H^+ + 4e^-$	⇋	$HCHO + H_2O$	−0.07 V
$CO_2(g) + 4H^+ + 4e^-$	⇋	$\frac{1}{6}C_6H_{12}O_6$(glucose) $+ H_2O$	−0.01 V
$H^+ + e^-$	⇋	$\frac{1}{2}H_2(g)$	0.00 V
$CO_2(g) + 6H^+ + 6e^-$	⇋	$CH_3OH + H_2O$	0.03 V
$Sn^{4+} + 2e^-$	⇋	Sn^{2+}	0.15 V
$CO_2(g) + 8H^+ + 8e^-$	⇋	$CH_4(g) + 2H_2O$	0.17 V
$HCHO + 2H^+ + 2e^-$	⇋	CH_3OH	0.24 V
$Cu^{2+} + 2e^-$	⇋	$Cu(s)$	0.35 V
$O_2(g) + 2H_2O + 4e^-$	⇋	$4OH^-$	0.40 V
$HCHO + 4H^+ + 4e^-$	⇋	$CH_4(g) + H_2O$	0.41 V
$NiO_2(s) + 2H_2O + 2e^-$	⇋	$Ni(OH)_2(s) + 2OH^-$	0.49 V
$Cu^+ + e^-$	⇋	$Cu(s)$	0.52 V
$I_2(s) + 2e^-$	⇋	$2I^-$	0.54 V
$I_2(aq) + 2e^-$	⇋	$2I^-$	0.62 V
$Fe^{3+} + e^-$	⇋	Fe^{2+}	0.77 V
$Ag^+ + e^-$	⇋	$Ag(s)$	0.80 V
$Br_2(l) + 2e^-$	⇋	$2Br^-$	1.07 V
$Br_2(aq) + 2e^-$	⇋	$2Br^-$	1.09 V
$O_2(g) + 4H^+ + 4e^-$	⇋	$2H_2O$	1.23 V
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	⇋	$2Cr^{3+} + 7H_2O$	1.33 V
$Cl_2(g) + 2e^-$	⇋	$2Cl^-$	1.36 V
$Cl_2(aq) + 2e^-$	⇋	$2Cl^-$	1.40 V
$MnO_4^- + 8H^+ + 5e^-$	⇋	$Mn^{2+} + 4H_2O$	1.51 V
$F_2(g) + 2e^-$	⇋	$2F^-$	2.87 V

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(a) The electron donor half-cell where loss of electrons (oxidation) occurs, which is called the anode.

Anode half-cell reaction:

$$Zn \rightarrow Zn^{2+} + 2e^-$$

(b) The electron acceptor half-cell where electrons are gained (reduction) which is called the cathode.

Cathode half-cell reaction:

$$Cu^{2+} + 2e^- \rightarrow Cu$$

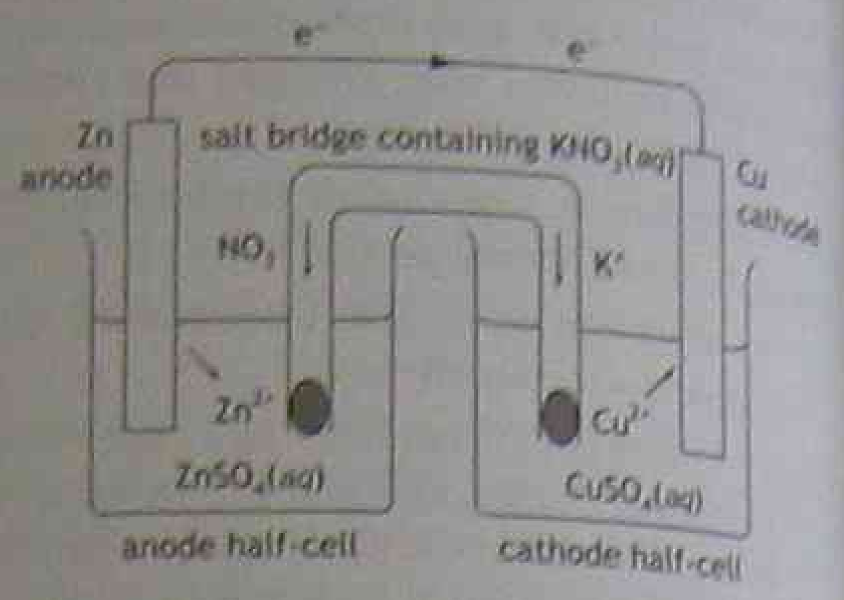


Figure 5.8 The Daniell cell

The half-cells are connected by an external wire. The external circuit enables the electrons to move from the anode to the cathode.

A salt bridge, usually filled with KNO_3, between the two half-cells, completes the circuit and enables ions to move. The salt bridge may be an inverted U-tube of KNO_3, containing an aqueous solution with cotton wool plugs at the ends or strips of filter paper soaked in the salt. The movement of ions through the salt bridge balances the charges due to the electron flow in the external circuit.

The overall cell reaction is obtain by adding the anode and cathode half-cell reactions. The electrons must be balanced.

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

The potential difference or electromotive force (emf) of a galvanic cell depends on the nature of the electrodes and the electrolyte. It does not depend on the size of the cell.

Table 5.3 Examples of special steel alloys

Type	Use	Special properties
Cobalt steel 73.5% Fe, 17% Co, 2.5% Cr, 8% W+C	magnets, jet engines	improves magnetic properties
Chrome-vanadium steel 98% Fe, 1% Cr, 0.2% V+C	tools, grinders	hard wearing and shock resistant
Stainless steel 74% Fe, 18% Cr, 8% Ni+C	sinks, cisterns, cutlery	corrosion resistant, chemically unreactive, hard and strong
High-speed steel 75% Fe, 18% W, 6% Cr+C	drills, cutting tools	hard at high temperatures
Alnico 61% Fe, 12% Al, 22% Ni, 5% Co+C	permanent magnets	very high magnetic permeability

Table 5.4 Some standard potentials at 298 K (25°C)

Increasing strength as oxidants

Oxidant		Reductant	E°
$K^+ + e^-$	⇌	$K(s)$	−2.92 V
$Ba^{2+} + 2e^-$	⇌	$Ba(s)$	−2.90 V
$Ca^{2+} + 2e^-$	⇌	$Ca(s)$	−2.87 V
$Na^+ + e^-$	⇌	$Na(s)$	−2.71 V
$Mg^{2+} + 2e^-$	⇌	$Mg(s)$	−2.36 V
$Al^{3+} + 3e^-$	⇌	$Al(s)$	−1.66 V
$Mn^{2+} + 2e^-$	⇌	$Mn(s)$	−1.18 V
$H_2O + e^-$	⇌	$\frac{1}{2}H_2(g) + OH^-$	−0.83 V
$Zn^{2+} + 2e^-$	⇌	$Zn(s)$	−0.76 V
$S(s) + 2e^-$	⇌	S^{2-}	−0.48 V
$Fe^{2+} + 2e^-$	⇌	$Fe(s)$	−0.41 V
$Ni^{2+} + 2e^-$	⇌	$Ni(s)$	−0.23 V
$Sn^{2+} + 2e^-$	⇌	$Sn(s)$	−0.14 V
$Pb^{2+} + 2e^-$	⇌	$Pb(s)$	−0.13 V
$CO_2(g) + 4H^+ + 4e^-$	⇌	$HCHO + H_2O$	−0.07 V
$CO_2(g) + 4H^+ + 4e^-$	⇌	$\frac{1}{6}C_6H_{12}O_6$(glucose) $+ H_2O$	−0.01 V
$H^+ + e^-$	⇌	$\frac{1}{2}H_2(g)$	0.00 V
$CO_2(g) + 6H^+ + 6e^-$	⇌	$CH_3OH + H_2O$	0.03 V
$Sn^{4+} + 2e^-$	⇌	Sn^{2+}	0.15 V
$CO_2(g) + 8H^+ + 8e^-$	⇌	$CH_4(g) + 2H_2O$	0.17 V
$HCHO + 2H^+ + 2e^-$	⇌	CH_3OH	0.24 V
$Cu^{2+} + 2e^-$	⇌	$Cu(s)$	0.35 V
$O_2(g) + 2H_2O + 4e^-$	⇌	$4OH^-$	0.40 V
$HCHO + 4H^+ + 4e^-$	⇌	$CH_4(g) + H_2O$	0.41 V
$NiO_2(s) + 2H_2O + 2e^-$	⇌	$Ni(OH)_2(s) + 2OH^-$	0.49 V
$Cu^+ + e^-$	⇌	$Cu(s)$	0.52 V
$I_2(s) + 2e^-$	⇌	$2I^-$	0.54 V
$I_2(aq) + 2e^-$	⇌	$2I^-$	0.62 V
$Fe^{3+} + e^-$	⇌	Fe^{2+}	0.77 V
$Ag^+ + e^-$	⇌	$Ag(s)$	0.80 V
$Br_2(l) + 2e^-$	⇌	$2Br^-$	1.07 V
$Br_2(aq) + 2e^-$	⇌	$2Br^-$	1.09 V
$O_2(g) + 4H^+ + 4e^-$	⇌	$2H_2O$	1.23 V
$Cr_2O_7^{2-} + 14H^+ + 6e^-$	⇌	$2Cr^{3+} + 7H_2O$	1.33 V
$Cl_2(g) + 2e^-$	⇌	$2Cl^-$	1.36 V
$Cl_2(aq) + 2e^-$	⇌	$2Cl^-$	1.40 V
$MnO_4^- + 8H^+ + 5e^-$	⇌	$Mn^{2+} + 4H_2O$	1.51 V
$F_2(g) + 2e^-$	⇌	$2F^-$	2.87 V

Increasing strength as reductants

Practical work

Construct a Daniell cell.

For the cell to operate as a galvanic cell, there must be

(a) two half-cell reactions (one oxidising and one reducing);

(b) an ion path; and

(c) an electron path.

Note: The emf generated depends on the nature of the half-cell reactions, the concentration of the electrolytes and the temperature.

When a galvanic cell is producing electricity the following events occur:

- The anode electrode releases electrons which flow through the metallic conducting wire to the cathode electrode which absorbs electrons.
- Ions migrate through the solutions and the connecting salt bridge to keep electron neutrality.
- Negative ions move towards the anode and positive ions move towards the cathode.

A comparison of the oxidising strengths of metals using cell voltages

Instead of drawing diagrams to represent cells, it is simpler to represent them symbolically.

The Daniell cell, in Figure 5.8, can be represented as

$$Zn/Zn^{2+} \,//\, Cu^{2+}/Cu.$$

By convention, the anode is written at the left with a single line between the two species present showing a phase change (in this case Zn and Zn^{2+}). The double line in the middle shows that a salt bridge is present, providing an ion path. The cathode is written at the right and again there is a single line between the species present (in this case Cu^{2+} ions and Cu).

Example

Given the following information:

(a) Cu/Cu^{2+} // Ag^+/Ag, cell voltage = 0.45 V

(b) Zn/Zn^{2+} // Cu^{2+}/Cu,cell voltage = 1.11 V

(c) Mg/Mg^{2+} // Cu^{2+}/Cu, cell voltage = 2.71 V

write the four metals in order of their strength as reductant. All ions are at the same concentrations.

Calculation

For cell (a): at the anode

$$Cu \rightarrow Cu^{2} + 2e^-$$

so copper will be a stronger reductant than silver.

For cell (b): at the anode

$$Zn \rightarrow Zn^{2+} + 2e^-$$

so zinc will be a stronger reductant than copper.

For cell (c): at the anode

$$Mg \rightarrow Mg^{2+} + 2e^-$$

so magnesium will also be a stronger reductant than copper.

However, the cell voltage of cell (c) is much higher than that of cell (b), so magnesium will be a stronger reductant than zinc.

The order from weakest to strongest reductants is silver, copper, zinc, magnesium.

The use of the electrochemical series to predict either the order of reductant strength of metals or the direction of reactions is subject to some restrictions.

1. The order of half-cells close together in the activity series can be changed with concentration change. The ease with which a metal ion can be reduced depends on concentration.
2. The series only applies to reactions in aqueous solution.
3. The emf of a galvanic cell is temperature-dependent.
4. The emf of a galvanic cell depends in some cases on pH.

Note:

- The further apart the half-equations are on the table, the larger is the emf of the cell.
- As the cell operates and reactants are used up, the emf will decrease.

Calculation of cell emf

Reactions take place in a galvanic cell at the anode and cathode. For a Zn/Zn^{2+} // Ag^+/Ag cell (see Figure 5.9) at 298 K and with all ionic species at 1 M the required standard potentials (see Table 5.4) can be extracted.

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

This difference is the cell potential.

$$E^\circ_{cell} = 0.80\text{ V} - (-0.76\text{ V}) = 1.56\text{ V}$$

From the table:

$E^\circ_{cathode}$ $\quad Ag^+ + e^- \rightleftharpoons Ag \quad$ 0.80 V

E°_{anode} $\quad Zn^{2+} + 2e^- \rightleftharpoons Zn \quad$ –0.76 V

Balancing the half-cell equations for electrons and reversing the anode reaction and adding gives the cell reaction

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

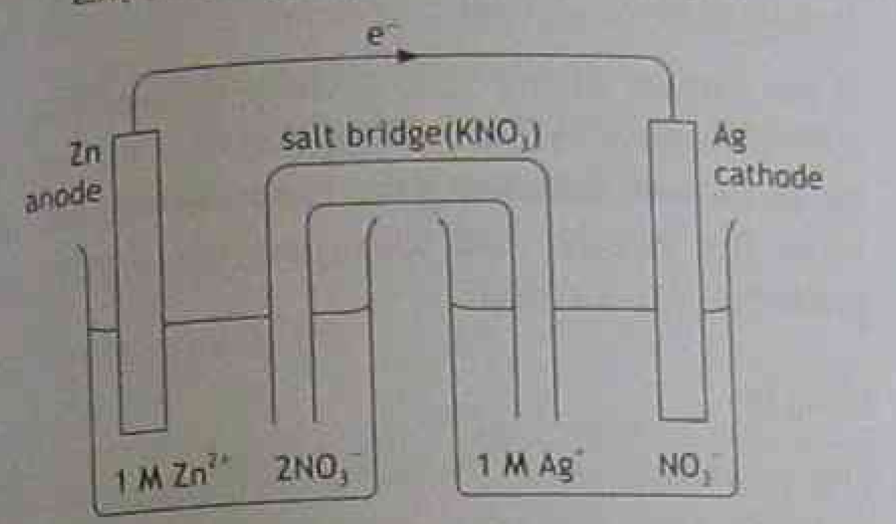


Figure 5.9 $Zn/Zn^{2+}//Ag^+/Ag$ cell

Exercise 5.2

1. (a) Draw a cell represented by

   $$Cu/Cu^{2+}//Ag^+/Ag.$$

   Label the anode, the cathode and the direction of electron flow in the connecting wire.

   (b) Write

   (i) the anode reaction;

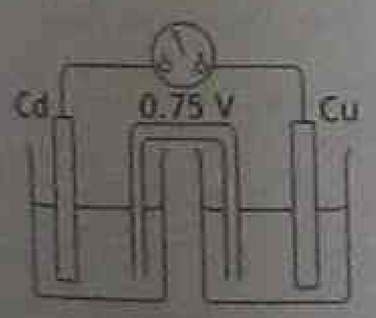
   (ii) the cathode reaction; and hence

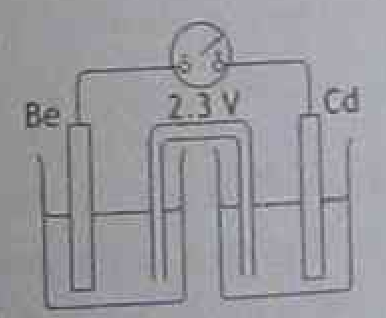
   (iii) the cell reaction.

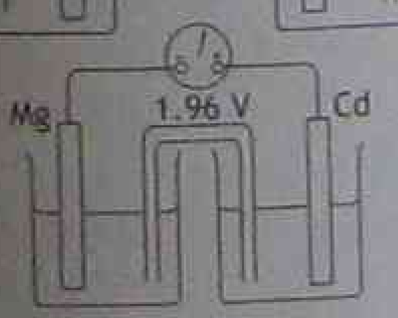
   (c) Calculate the E° value for the cell.

2. Three electrochemical galvanic cells are shown below with the emf given for each cell. All ions are at the same concentration.

   Give the metals in order of their strength as reducing agents (most powerful → least powerful reductants).







5.11 Electrolytic cells

It is possible for non-spontaneous oxidation-reduction reactions to occur. In Figure 5.10, electricity is used to decompose water into hydrogen and oxygen.

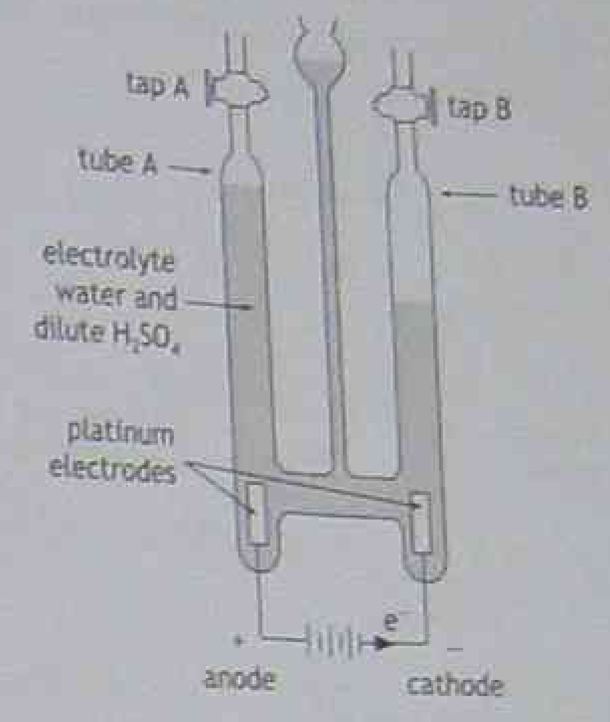


Figure 5.10 The voltameter

Such processes, which are supplied by an external source of electricity, are called electrolysis reactions and are carried out in electrolytic cells. Electrolysis takes place on the surface of the electrodes. An electrolytic cell is really the reverse operation of a galvanic cell where the applied voltage is greater than the voltage that the cell can produce.

Practical work

Use a voltameter to decompose water.

Note: The addition of small quantities of electrolytes, e.g. dilute H_2SO_4 to pure water increases the electrical conductivity.

Cathode reaction

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad E^\circ = -0.83\text{ V}$$

Anode reaction

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad E^\circ = +1.23\text{ V}$$

Overall reaction

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$$

Examples of electrolytic cells

The simplest example of electrolysis involves fused (molten) salts such as sodium and potassium chlorides.

Example 1

In the electrolysis of fused sodium chloride the products will be sodium and chlorine.

Cathode: $Na^+ + e^- \rightarrow Na$

Anode: $2Cl^- \rightarrow Cl_2 + 2e^-$

Electrolysis is more complex when aqueous salts are used as the electrolyte.

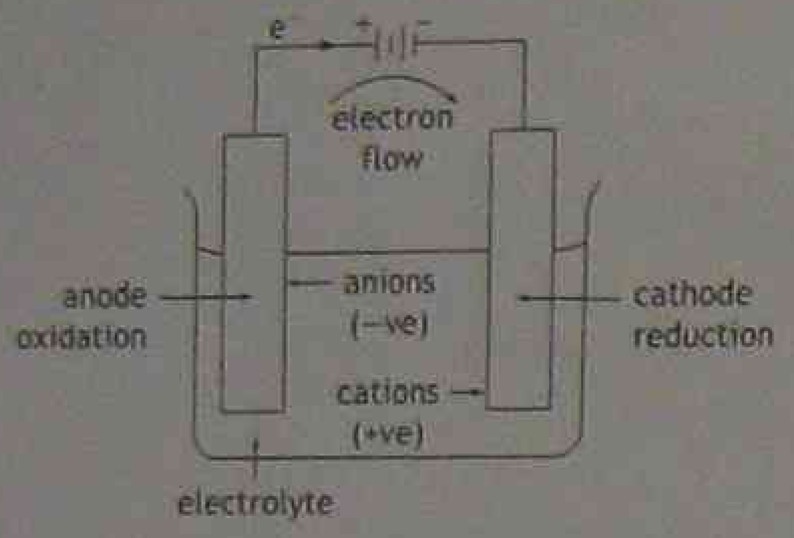


Figure 5.11 A typical electrolytic cell

Example 2

In the electrolysis of aqueous sodium chloride, the positive ions present will be Na^+ and H^+, while the negative ions are OH^- and Cl^-.

In aqueous solutions, water will be reduced before alkali metals. Using the standard potential from Table 5.4, we can predict that electrolysis of the dilute NaCl will produce H_2 at the cathode and O_2 at the anode.

Cathode: $2H^+ + 2e^- \rightarrow H_2$ (a)

Anode: $4OH^- \rightarrow 2H_2O + O_2 + 4e^-$ (b)

Overall reaction: $[2 \times (a) + (b)]$

Collect like terms

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$$

This reaction depends on the applied voltage and, with an increase, hydrogen, oxygen and chlorine may be formed.

Electroplating

This process uses electrolytic cells.

- The plating material is used as the anode.
- The electrolyte must contain the ion of the plating material.
- The object to be plated is used as the cathode.
- The plating material is oxidised by a direct current (DC) source which is applied to the cell.

Plating iron and steel

Using zinc

Production of galvanised iron for roofing involves dipping the iron sheets in molten zinc. Zinc reacts with oxygen, carbon dioxide and water to form basic zinc carbonate. This protective coating is firmly attached to the zinc and provides a long-lasting defence against corrosion.

If the surface of the zinc is deeply scratched, an electrochemical cell involving Zn, O_2, H_2O and Fe can be formed. Zinc being the more active metal will form the anode and can provide 'galvanic' protection for the iron.

Using tin

This process is used to plate steel cans by forming an oxide layer. If the tin layer is scratched the iron will be the anode, so the can will rapidly corrode.

Using chromium

Chromium, like zinc and tin, is a passive metal and forms a protective layer in air.

5.12 Differences between electrolytic and galvanic cells

Differences

Table 5.5 Comparison of electrolytic and galvanic cells

Electrolytic cells	Galvanic cells
A non-spontaneous reaction. Reactions are forced by an applied emf which must be greater than that which the cell can produce.	A spontaneous reaction. The emf of the cell must be positive for a reaction to occur.
Converts voltage to a chemical reaction.	Converts a chemical reaction to a voltage.
Electrodes are usually immersed in a common electrolyte.	Two half-cells are used with separate electrolytes.

Similarities

1. The electrolyte is the substance that conducts electricity within the cell. Electrical charge is carried by anions to the anode and by cations to the cathode.
2. The electrode at which oxidation occurs is called the anode.
3. The electrode at which reduction occurs is called the cathode.
4. In the external circuit, electrons travel through the wire from the anode to the cathode.
5. Electrons always flow towards the positive electrode in both cells.

The products of electrolysis depend on the following:

(a) The E° value of the half-reaction.

(b) The type of electrodes used (inert or reactive).

(c) The concentration of the reactants.

(d) The current density.

(e) The temperature.

Activity 5.2

A simple electroplating experiment

Introduction

By carrying out the procedure for the electroplating experiment given below, it is possible to obtain a value for the Faraday constant which is the quantity of electricity carried by one mole of electrons.

Procedure

Step 1. Thoroughly rinse two pieces of copper with distilled water and dry them with a paper towel. Without handling their surfaces, mark one piece '+' and the other '–'.

Step 2. Weigh each piece and record its mass.

Step 3. Pour about 100 mL of 0.5 M copper sulfate solution into a small beaker.

Step 4. Carefully place the two pieces of copper in the beaker with their tops bent over the edge.

Step 5. Set up the circuit as shown in Figure 5.12 and ensure that the two electrodes are connected correctly.

Step 6. Set the current selector to 500 mA, switch on and allow the current to flow for exactly one hour. Ensure that the reading on the ammeter does not vary during this period.

Step 7. Rinse the two electrodes by gently dipping each into a beaker of cold water and then in a beaker of acetone. (**Care: flammable substance.**) Allow them to dry for a few minutes by evaporation.

Step 8. When dry, weigh each electrode and record its mass.

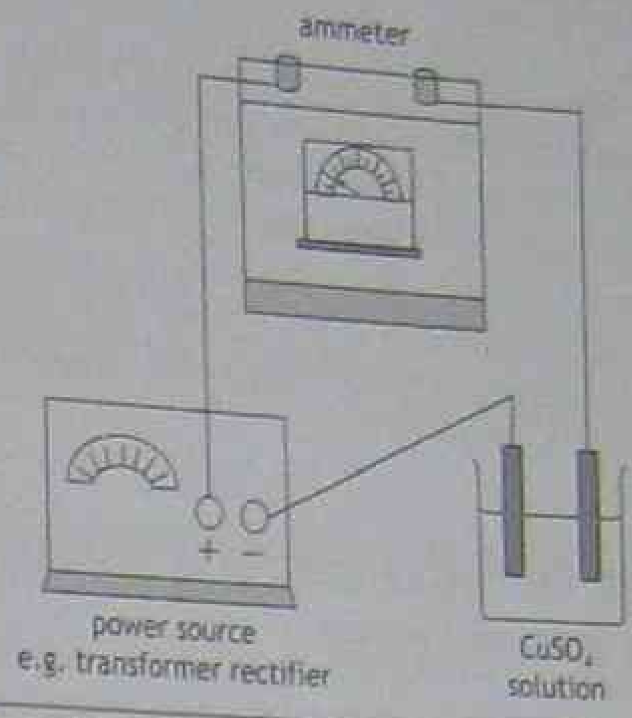


Figure 5.12 Circuit diagram

Results

Mass of negative electrode

start = 5.21 g end = 5.80 g

Mass of positive electrode

start = 5.69 g end = 5.10 g

Current in circuit (ammeter reading) = 500 mA

Time taken for electrolysis = 1 hour

Calculations

1. Using your results, evaluate the following:
   (a) Av. mass of copper electrolysed = 0.59 g
   (b) Moles of copper electrolysed = $\frac{0.59}{63.55}$ mol
2. The charge on copper ion is 2^+. Calculate the number of moles of electrons which must have travelled through the circuit to electrolyse the copper = 0.018568 mole
3. Calculate the number of coulombs of charge which is transferred during the electrolysis:
   No. of coulombs = A × s = 1800 C
4. Use the above calculated values to evaluate the following:
   (a) The charge carried by one mole of electrons = 96 941 C
   (b) The charge carried by one electron = 1.61×10^{-19} C

Discussion

The negative electrode increased its mass due to copper atoms being plated onto it.

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

The positive electrode decreased its mass by the same amount:

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

Note: One coulomb (C) is the charge involved when one ampere of current flows for one second. The Faraday constant is the quantity of electricity carried by one mole of electrons and is 96 500 C mol^{-1}. It follows that by dividing the Faraday constant by Avogadro's constant (6.02×10^{23} mol^{-1}), the charge on an electron (1.602×10^{-19} C) can be found.

5.13 Corrosion control in iron and steel marine vessels

Nearly all metals react with their environment with corrosion products being formed.

- Atmospheric corrosion

  Protection against atmospheric corrosion is important during the construction of a ship. Serious rusting may occur if the humidity is above 70%. The rate of rusting is determined mainly by air pollution and/or sea spray.

- Corrosion due to immersion

  When a ship is in service, a steel hull can provide ideal conditions for the formation of electrochemical corrosion cells.

- Corrosion in the absence of other metals

  Iron will rust without contact with other metals. The surface oxide layer formed by direct oxidation with moist air will have imperfections, e.g. fine cracks, so that when an electrolyte film covers the surface, anodic areas develop at these points. This occurs since iron atoms migrate more readily through the oxide layer to become oxidised.

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

  Oxygen is reduced to hydroxide ions at cathodic sites by electrons migrating from anodic areas.

  $$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$

  $Fe(OH)_2$ forms and further oxidises to rust.

  Overall equation

  $$4Fe(s) + 3O_2(g) + 2H_2O \rightarrow 4FeO(OH)(s)$$

  When iron undergoes oxidation, the parts of the iron surface which are most exposed to oxygen will become cathodic and then be protected from corrosion, whereas areas of limited oxygen contact will be anodic and corrode.

  The mechanism of corrosion is referred as the 'differential aeration principle'. This explains why riveted steel plates will corrode in crevices between plates and not on the surface.

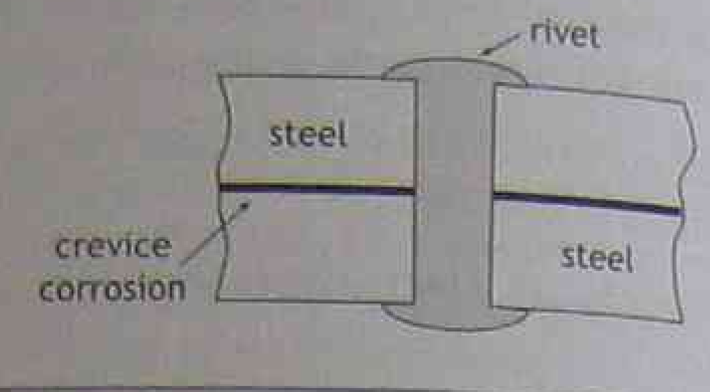


Figure 5.13 Crevice corrosion between riveted plates.

Rusting as an electrochemical process

In an electrochemical cell, e.g. the Daniell cell (see Section 5.10), the more active metal, zinc, is oxidised. Electrons are generated and the zinc anode corrodes away.

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$$

At the copper cathode, electrons are accepted by copper ions from the electrolyte to deposit copper metal.

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

If the copper (II) electrolyte is replaced by aerated sodium chloride solution, the anode reaction will be the same but the cathode reaction will be

$$O_2(aq) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$

so that at the cathode, oxygen is reduced and hydroxide ions are formed.

In similar cells, the more reactive metal is 'anodic' whereas the less reactive metal is 'cathodic' (see Table 5.4 and Section 5.10).

If iron and copper electrodes are placed in an aerated NaCl solution, as shown in Figure 5.14, the more reactive iron corrodes to iron (II) ions.

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

At the copper cathode, oxygen is reduced to hydroxide ions.

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$

Both ionic products will drive towards the opposite electrode, the Fe^{2+} towards the cathode and the OH^- towards the anode. In between, they form a precipitate of green iron (II) hydroxide. The iron (II) hydroxide will slowly oxidise further to brown iron (III) hydroxide by reaction with more dissolved oxygen in solution.

$$4Fe(OH)_2(s) + 2H_2O(l) + O_2(g) \rightarrow 4Fe(OH)_3(s)$$

The iron (III) hydroxide may partially dehydrate to form rust. The most likely formula for rust is $Fe_2O_3.H_2O$.

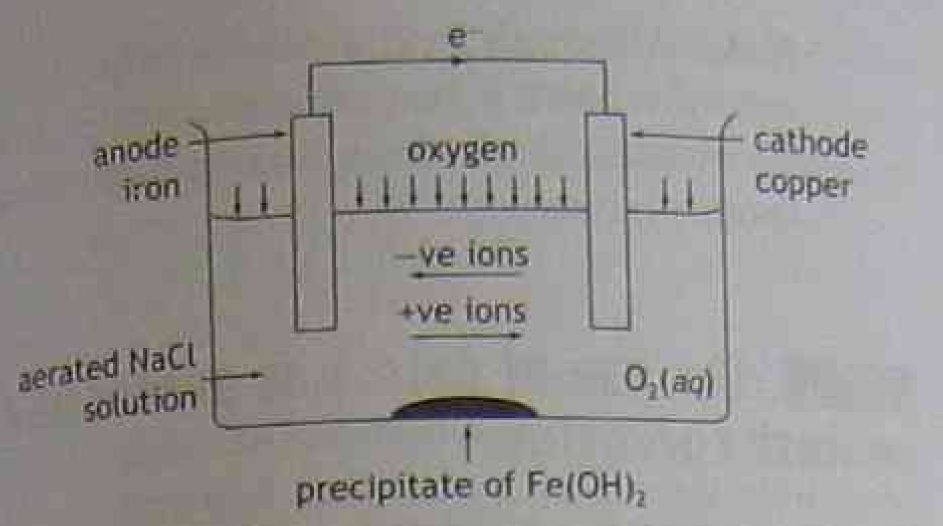


Figure 5.14 Galvanic cell

Exercise 5.3

For each of the reactions given below, where solutions are 1 M and temperature is 25°C, calculate the standard emf, using Table 5.4, then decide in which direction the reaction goes (as written left to right → or reversed right to left ←). In each case, state which metal will corrode.

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

(b) $Zn(s) + Ni^{2+}(aq) \leftrightarrow Zn^{2+}(aq) + Ni(s)$

(c) $Fe^{2+}(aq) + Cu(s) \leftrightarrow Fe(s) + Cu^{2+}(aq)$

(d) $Mg^{2+}(aq) + Fe(s) \leftrightarrow Fe^{2+}(aq) + Mg(s)$

(e) $Sn(s) + 2Ag^+(aq) \leftrightarrow Sn^{2+}(aq) + 2Ag(s)$

Table 5.5 is a typical galvanic series in seawater. The positions of the metals in the table apply only under seawater conditions. Some metals (and alloys) are said to be passive when the surface is exposed to an electrolyte solution but shows no sign of corrosion. Passivation results from the formation of an oxidation barrier on the metal surface, usually in the form of an oxide film.

Examples of common problems in ships hulls include

(i) a mild steel hull with a phosphor bronze or nickel alloy propeller, and

(ii) aluminium superstructures attached to a mild steel hull.

Table 5.5 Galvanic series of metals and alloys in seawater

Noble (cathodic or protected) end	Gold
	Silver
	Stainless steels, passive
	Nickel, passive
	Phosphor bronze
	Copper
	Naval brass (60% Cu 40% Zn)
	Tin
	Lead
	Iron, steel
	Aluminium alloys
	Aluminium
Ignoble (anodic or corroding) end	Zinc
	Magnesium

5.14 Predictions of metal corrosion

Predictions of which metal will corrode when two metals form an electrochemical cell relating to E° values can be made by using the table of standard potentials (see Table 5.4).

5.15 Use of electrolysis to protect metals against corrosion

Metals

Metals such as iron can be protected from corrosion in a number of ways:

(a) Reduce the rate at which the corrosion reactions occur by using *protective coatings* such as paintings or tar, to help keep out oxygen, water and electrolyte salts, e.g. sea salts. Electrolyte salts can speed up corrosion by reducing the electrolyte resistance in the corrosion cell. Protective coatings are only effective in preventing corrosion when they adhere firmly to the metal surface being protected.

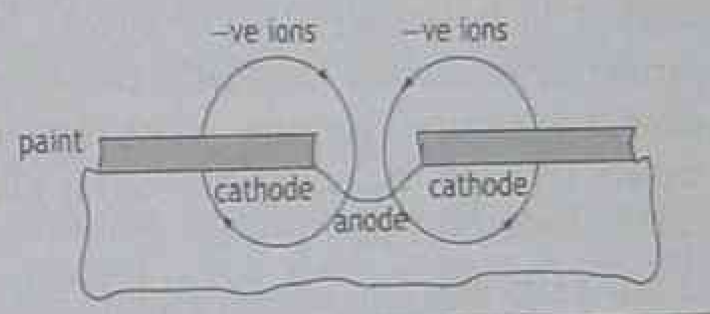


Figure 5.15 Corrosion cell set up by breaks in the paint film on plate surface

The destructive corrosion occurs beneath the paint film at the edges of the crack due to 'differential aeration'.

(b) Reduce the electromotive force of the corrosion cell or transfer the electrons by conduction to a location where corrosion can occur without causing damage to the structure being protected.

5.16 The use of cathodic protection

Only where metals are immersed in an electrolyte can the possibility of corrosion be prevented by cathodic protection. The metal to be protected is made the cathode of the corrosion cell so that it will not lose electrons and dissolve.

Two main types of cathodic protection are presently in use.

- Sacrificial anode systems

In the case of ships, sacrificial anodes are metals or alloys which are attached to the hull. They have a more anodic potential than steel when immersed in seawater. For many years, zinc plates fitted between bronze propellers and the hull, were replaced once they had corroded. Modern anodes are based on alloys of zinc, aluminium or magnesium, which have been shown to be the most suitable. High purity zinc anodes are also used.

Zinc anodes provide electrons for

$$H_2O/O_2 \rightarrow OH^-(aq)$$

as a means of preventing corrosion (but not to reduce Fe^{2+}). Sacrificial anodes may be fitted within the hull, e.g. in ballast tanks. Zinc anodes may also be used in pipelines carrying oil or natural gas. Magnesium anodes are used in largely non-aqueous environments, e.g. petrol storage tanks.

- Impressed current systems

These systems are used for the protection of the immersed external hulls only (see Figure 5.16). In Western Australia this system is being applied to the preservation of wrecks from further deterioration. Originally, consumable anodes were used but now relatively noble metals are used, including lead/silver alloys and platinised titanium anodes.

1. The reference cell (silver/silver chloride) is mounted externally to detect voltage differences between itself and the hull.
2. The amplifier controller measures the difference between current control.
3. The reactor rectifier controls the current from the ship's electrical system to the external anodes (charged +ve).
4. Anodes are usually of non-consumable, relatively noble metals.

Note: Although initial cost is high, these systems have a longer life, reduce hull maintenance and weigh less than sacrificial anode systems.

5.17 The use of paints as protection against corrosion

Paints are often the main and sometimes the only form of readily available protection. Paint consists of pigment dispersed in a liquid called the 'vehicle'. *Corrosion-inhibiting paints* for application to steel have the following vehicle types:

(a) Bitumen or pitch, either dissolved in solvent naphtha or heat-blended.

(b) Oils, consisting mainly of vegetable drying oils, e.g. linseed oil and tung oil. Drying oils are highly unsaturated and polymerise to resin under the influence of oxygen from the air.

(c) Alkyl resins which have improved drying time and film-forming properties. They are cross-linked polymers of maleic anhydride.

(d) Chemical-resistant paints.

(i) *Epoxy resins*. These contain more than one epoxide group:

Chemicals produced from petroleum and natural gas are a source of epoxy resins. These paints often consist of a 'two pack' formulation, a solution of epoxy resin with a solution of a cold curing agent such as an amine or polyamide resin. They are mixed before application.

(ii) *Coal tar/epoxy resin*. This type combines the chemical resistance of epoxy resin with the impermeability of coal tar.

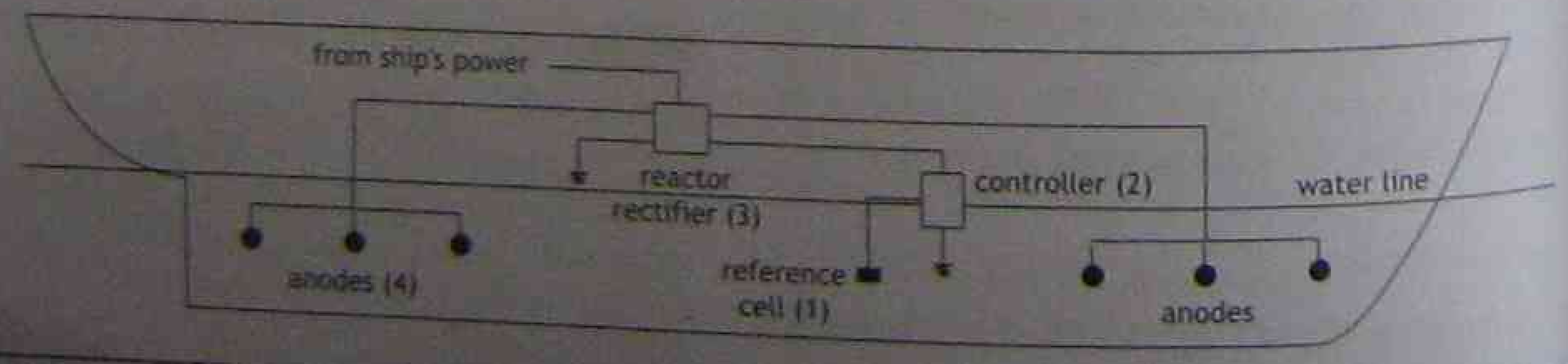


Figure 5.18 Impressed current cathode protection system

(iii) *Polyurethane resins*. A reaction between isocyanates and hydroxyl containing compounds produces the 'urethane' linkage:

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

These paints are tough, hard, glossy, abrasion resistant and chemical and weather resistant. Polyurethanes are not used under water on steel ships but only on superstructures.

(iv) *Vinyl resins*. These are obtained by the polymerisation of organic compounds containing the vinyl group $H_2C{=}CH-$. As vinyl resin paints have poor adhesion to bare steel surfaces, they are generally applied over a pre-treatment powder. Vinyl paints are among the most effective for the underwater protection of steel and are used widely in shipbuilding.

(v) *Zinc-rich paints*. These contain metallic zinc as a pigment in sufficient quantity to ensure electrical conductivity through the dry paint film to the steel. They are said to be capable of protecting the steel cathodically. Protection could be due mainly to the corrosion resistance of zinc. The pigment content should be greater than 90%, the vehicle usually being an epoxy resin.

(e) Anti-fouling paints. These consist of pigments which give body and colour to the paint together with materials that are poisonous to marine vegetable and animal growth. To prolong the life of the paint, the poisonous compounds must dissolve slowly in seawater, e.g. copper-based paints. The *James Craig* is a three-masted iron barque, built in 1874 and abandoned at Recherche Bay in Tasmania in the early 1930s. The restoration process now being carried out at Wharf 7, Darling Harbour in Sydney has used the following modern paints:

(i) An underwater anticorrosive paint, Inertuf HS Vinyl, which has vinyl tar as the vehicle.

(ii) An anti-fouling maintenance and repair paint, Red Interviron, which contains copper oxide.

(iii) A topsides and internal bulwarks paint, which includes Interzinc 72 containing pure zinc powder (>90% Zn). Polyurethane resins have also been used on the superstructure.

(iv) The final coat, as on Sydney's Harbour Bridge, contains micaceous iron oxide.

5.18 The solubility of selected gases and salts in aqueous solutions

Solubility in aqueous solution with changes in pressure and temperatures

(a) *Pressure*. The mass of a gas dissolved by a given mass of solvent at a particular temperature is proportional to the pressure of the gas above the solution. As the gas pressure above the liquid increases (at constant temperature) the solubility of the gas increases.

(b) *Temperature*. Gases vary in their solubility in water. The solubility increases as the temperature is lowered (at constant pressure).

Solubility of water-soluble salts with changes in pressure and temperature

(a) *Pressure*. In liquids, pressure has a minimal effect on solubility.

(b) *Temperature*. Most salts (except sodium chloride) increase in solubility with temperature.

Composition of the atmosphere

The following table gives the composition in dry air of selected gases. Water vapour in air varies between 1.2% and 3.3% by volume.

Table 5.6 Composition of selected gases in dry air

Gas	% composition (by volume)
N_2	78
O_2	21
Ar	0.9
CO_2 and other gases	0.04

Composition of the oceans

This is thought to be constant with time. The dissolved gases, oxygen, carbon dioxide and nitrogen are as important to life in the ocean as they are in the atmosphere. These gases have different solubility values in water at different temperatures. The volume of gas dissolved by a unit volume of water at 101.3 kPa pressure (1 atmosphere) is called the absorption coefficient of the gas.

Table 5.7 Absorption coefficients of selected gases in water

Gas	Absorption coefficient		
	0 °C	20 °C	40 °C
N_2	0.24	0.016	0.012
O_2	0.49	0.31	0.23
CO_2	1.71	0.88	0.53

Carbon dioxide in seawater

(106 parts per million: concentration is 2.3 mmol L^{-1})

The carbon dioxide present in the atmosphere is in equilibrium with the carbon dioxide dissolved in the ocean. The solubility of CO_2 in seawater is much higher than in pure water. Under the same pressure of gas over solution, in each case CO_2 is 15 times more soluble than oxygen and 30 times more soluble than nitrogen. The ocean contains more CO_2 than air. Most of the CO_2 dissolved in the ocean is in the form of HCO_3^- and CO_3^{2-}.

Photosynthesis in the sea

The simplest members of the food chain are the phytoplankton that convert CO_2, water and other nutrients into plant organic matter. Photosynthesis occurs in the light zone near the surface to a depth of about 200 m. In this zone, the oxygen concentration is high because it is released during photosynthesis. At lower depths, the oxygen level drops sharply because the oxygen is used up in oxidising dead plant and animal matter.

Note: Earlier predictions of slow corrosion at great depths have been shown to be incorrect in more recent investigations of the causes of corrosion in the *Titanic*.

5.19 Specific shipwrecks and their salvage

Many shipwrecks have occurred in Australia's early and more recent history. Some of these are marked in Figure 5.17.

In 1602, the Dutch United East India Company was formed to trade in the riches of the Spice Islands of the Indian Archipelago. Well-known shipwrecks of that period include the following:

(i) The 59-metre flagship *Batavia*, which in 1629 struck a coral reef and sank off the west coast of Australia. A horrible tale followed of mutiny, murder and rape amongst the survivors. A replica of the armed merchant vessel was put on exhibition at Darling Harbour, Sydney, in the year 2000.

(ii) The Dutch East Indiaman *Gilt Dragon* which foundered on a reef north of Perth on her way to Batavia (the Company's main East Indies base). She was reputed to be carrying eight chests of silver. A large amount of cargo from the wreck was salvaged in 1963.

- The immigrant ship *Dunbar* sank off the Sydney Heads in 1857, with only one survivor. Her cargo consisted of gold sovereigns and silver coins minted for the developing colony of New South Wales.
- The barque *James Craig* was built in 1874 with a riveted hull of wrought iron. It was found as a result spectrographic analysis to have a carbon content of 0.01%; other impurities were also very low. The vessel was raised from the mud of Recherche Bay in Tasmania and restored first in Rozelle Bay and later at Darling Harbour. If the hull had been made of steel it would have corroded too badly to have been salvaged. All iron found on wrecks prior to 1900 can be classified as either wrought or cast iron depending on carbon content and corrosion behaviour.
- The *Titanic*, on its maiden voyage in 1912, struck an iceberg off the coast of Newfoundland and sank in about 3800 m of water. The 46 000 tonne vessel broke in two as it sank and the bow and stern now lie separated by more than a kilometre. Of the 2227 passengers and crew, 1523 people froze and drowned. The RMS Titanic Inc. is now the company with sole ownership rights for salvaged material. Andrew Rogers from Harbord, New South Wales dived in the MIR2 submersible to a depth of 3895 m where the lights from the submersible illuminated the stern of the *Titanic*. He spent five and a half hours on the ocean floor; at one stage, the giant propeller snagged the MIR. The ascent took a further three hours. Andrew has made available photos from his collection to show the effects of corrosion on the detritus of the disaster.

Recreational diving around wrecks in becoming an increasingly popular sport.

- The *SS President Coolidge* was sunk by a mine during the Second World War off Espirito Santo, Vanuatu. There was only one casualty.
- In June 1940, the RMS *Niagara* hit a German mine and sank off the coast of New Zealand in deep and treacherous waters. The ship had been attempting to deliver eight tonnes of gold to

Figure 5.17 Historical shipwrecks

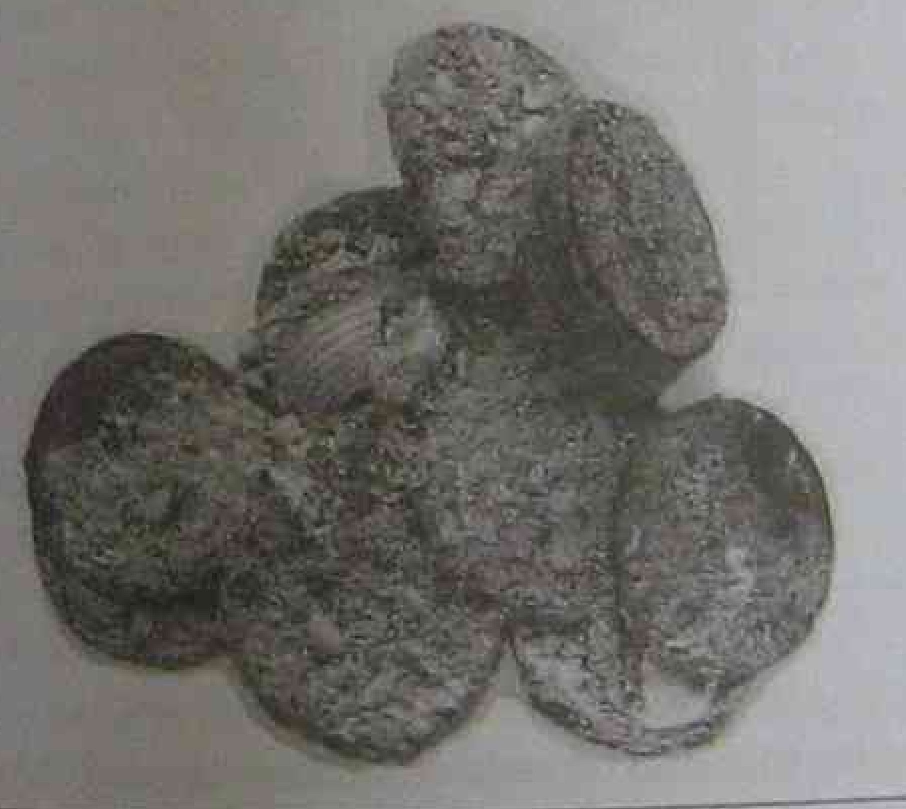


Figure 5.18 Concretions around silver coins from a Spanish shipwreck

Figure 5.19 Spanish 'pieces of eight'

America to purchase arms. Salvage attempts were essential and the Australians, Captain Williams and his diver Johnstone, invented a 'bell' to work at up to 600 feet under water, having located the wreck using a derelict coast boat, the *Claymore*, with a crew of sixteen. After 11 months at great risk to themselves, they retrieved all but 35 of the original 590 gold bars. Gold, being a noble metal, was not affected by the seawater and, thanks to the efforts of these Australian heroes, was put to good use in the war effort.

- During the Falklands War, several British destroyers and frigates were damaged or lost as a result of fires caused by Exocet missiles. These ships were built with an aluminium alloy which contained as much as 5% magnesium and 1.6% silicon. The resulting Mg_2Si formation resulted in the alloy having a high resistance to corrosion. In addition, the alloy offered a weight-saving of up to 60% over mild steel and was non-magnetic. Exocet missiles would cause very little damage to steel ships but the aluminium alloy vessels were extremely vulnerable to fire damage (owing to the presence of 5% Mg in the aluminium alloy) which caused heavy losses.

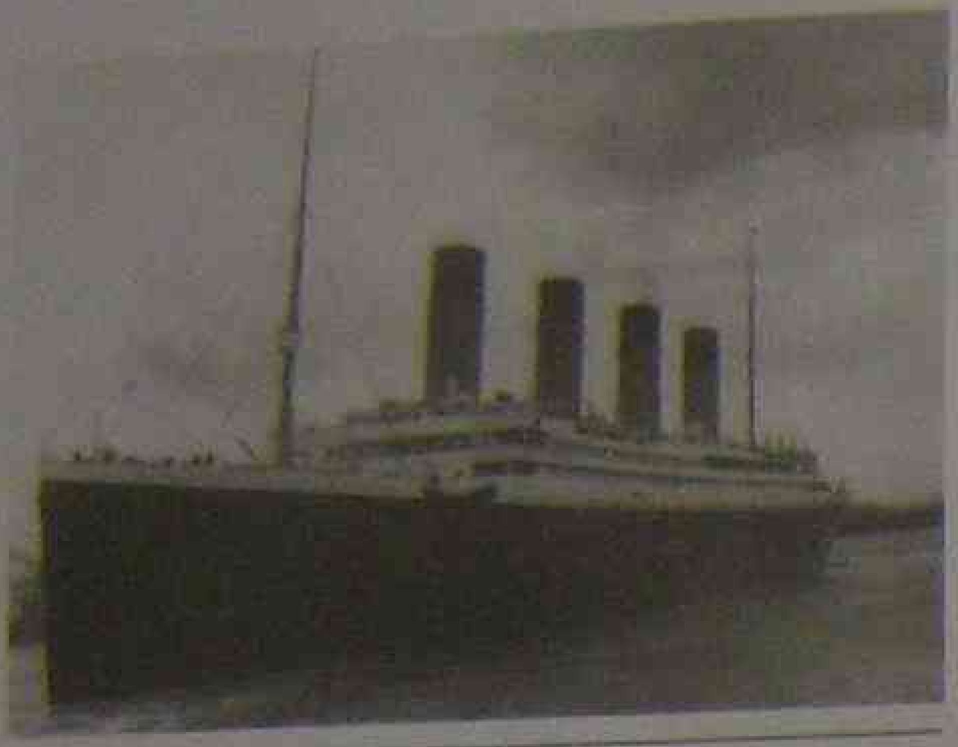


Figure 5.20 The *R.M.S. Titanic*

Figure 5.21 Bow of the *Titanic*, which is rapidly corroding and showing rusticles

5.20 Conservation of shipwrecks

- The larger scale and composite nature of shipwrecks causes complications in conservation.
- Conservation is aimed at stabilising materials and preventing further deterioration rather than cleaning and restoring materials to their original appearance.
- Many alternative conservation treatments are used, so the conservator must assess the composition and condition of each individual object before selecting the most appropriate treatment.
- With waterlogged wood the main treatments are as follows:
  - (i) *Desalination* which involves the removal of soluble salts such as chlorides and sulfates.
  - (ii) *Impregnation* with a solid material to replace the water and support the degraded cellular structure.
  - (iii) Very slow *controlled dryness* or, for preference, freeze-drying.
  - (iv) Maintaining of stable environment.
- Marine archaeological conservation is a relatively new field of scientific research and application. When metal objects are recovered from a shipwreck they generally have a thick layer of concretion on them. The metals are generally corroded or eroded to some degree and contain quantities of salts, especially chlorides, in the attached corrosion products. Once the artefacts are excavated, they can deteriorate very rapidly and must be carefully washed and stored in tanks of water on the salvage vessel while awaiting transfer to shore. Once the bulk of the concretion is removed and the artefacts are separated into the material types, the chemical treatment commences. Methods used depend on the metal being treated.
- One or more of the following methods may be used to achieve the long-term stabilisation of metals:
  - (i) It is necessary to remove salts, especially chlorides. This can rarely be done simply by washing artefact with water, because the ions are tied up in corrosion products or reactions, and many metals are unstable in water.
  - (ii) Electrochemical and/or electrolytic treatments are commonly used. The most effective stabilisation treatments for metals involve some type of reduction process which will facilitate the release of chloride ions.
  - (iii) Chemical corrosion inhibitors are also widely used during treatments, and protective surface coatings may be needed after treatment.
  - (iv) Objects must be carefully handled using gloves.
  - (v) It is critical to maintain metals in a stable environment after treatment.

5.21 Shipwrecks at great depth – the Titanic

When a ship sinks, the rate of decay and corrosion may depend on the final depth of the wreck. Sufficient light for plant growth does not penetrate below 200 m. Below this level the fall of dead organisms and other wastes from above supplies energy and nutrients for deep-dwelling animals and micro-organisms. Scattered across the ocean floor are thermal vents where hot, sulfur-rich water spouts up from the Earth's crust. Simple inorganic compounds from these vents provide a source of energy for some bacteria called chemotrophs.

Apart from these special areas, the temperature at the bottom of the abyssal plain stays constant at about 4°C whether the ocean is at the poles or the equator. It is dark, the pressure is intense and oxygen is scarce. Anaerobic conditions exist in the bottom mud. These are all factors which would be expected to slow down the rate of deterioration in the case of the *Titanic*, which sank to a depth of 3800 m.

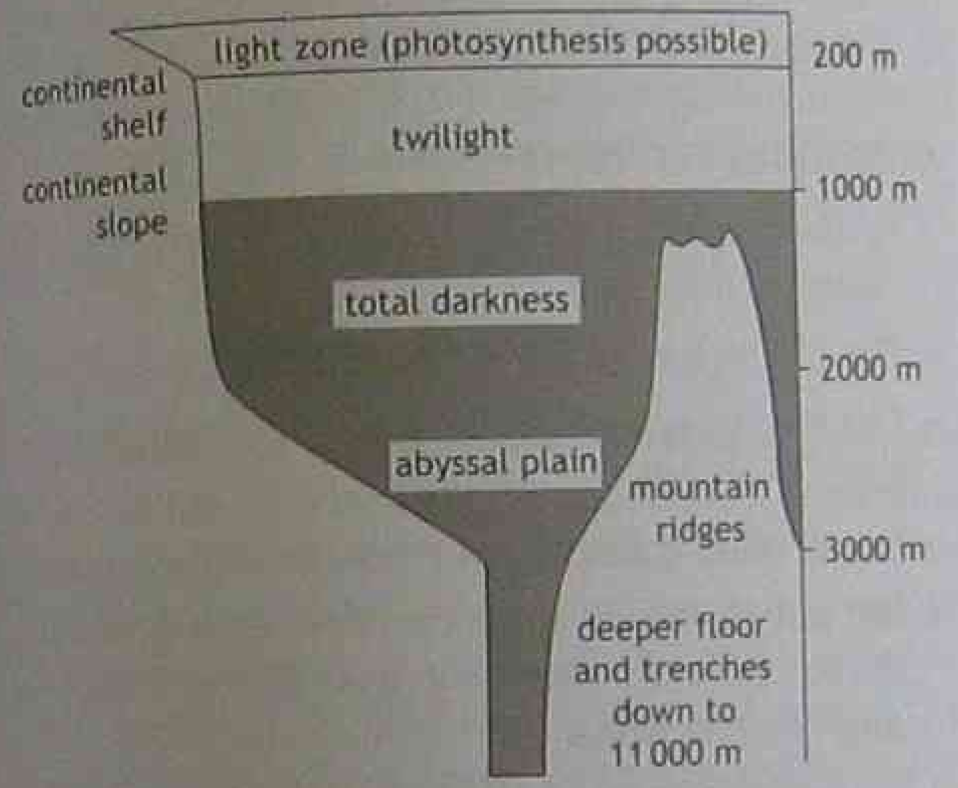


Figure 5.22 Zones of the ocean

One small piece of the hull, distant from the main wreck, brought to the surface by one of the MIRs showed very little corrosion and had its original paint, possibly due to the absence of bacterial action. The edges of the piece were jagged and gave signs of brittleness. Physical testing established that the *Titanic*'s hull was brittle and that when it met the iceberg, the plates did not bend in, they fractured. A high sulfur content results in brittleness but here the steel was embrittled, not as a result of nearly a century of exposure on the ocean floor, but because of sulfide occlusions in the original steel.

Because the *Titanic* lies so far below the surface of the Atlantic Ocean, the following factors are reasons for its present condition:

- Complete absence of light.
- Very little oxygen (0.2 parts per million).
- Water which is near freezing should have slowed the rate of deterioration considerably. However, the action of marine organisms has caused a great deal of damage.
- Shipworms have burrowed through wooden structures and weakened them.
- Seafloor bacteria have produced black sulfides that have stained artefacts badly.
- Anaerobic bacteria live in the mud and are sulfate-reducing. Seawater contains 840 mg L^{-1} of sulfates so
  - (i) $\underset{\text{sulfate ions}}{SO_4^{2-}(aq)} \xrightarrow[\text{in mud}]{\text{anaerobic bacteria}} \underset{\text{sulfide ions}}{S^{2-}(aq)}$
  - (ii) $Fe(s) + \text{acidic environment} \rightarrow Fe^{2+}(aq)$
  - (iii) $Fe^{2+}(aq) + S^{2-}(aq) \rightarrow \underset{\text{iron (II) sulfide}}{FeS(s)}$
- Although some metals have escaped bacterial action, they have become corroded by electrochemical action involving seawater as the electrolyte. Bronze objects appear to be in good condition, but others, e.g. iron objects, are badly corroded.
- A large differential voltage exists between anaerobic and aerobic conditions so that corrosion caused by anaerobic bacteria is trapped close to the metal.
- All mitochondria need iron, so there are also aerobic bacteria living in the rust. There is only 0.2 parts per million of oxygen present at these depths. In such cases, the corrosion products are not trapped but run off to form rust.
- 'Rust flows' (found mostly on the deck) and 'rust flakes' (similar in composition to rusticles containing goethite and lepidocrite) are other unusual forms of corrosion. It is thought that both bacterial colonisation and iron have produced these minerals.
- After 88 years of submersion, the *Titanic* shows bioconcretious rusticles, involving many communities of bacteria and fungi. From its discovery in 1985 until further expeditions in 1996 and 1998, the rusticles — which vary in colour, texture, size and form — are growing larger and denser as the ship continues to disintegrate. Rusticles which have been recovered and analysed by electron diffraction X-ray tehniques have shown iron to be the dominant atom present.

- Rusticles are the most obvious corrosion products on the *Titanic*. They resemble stalactites in shape and are often longer than 30 cm. Rusticles have a smooth red outer surface of ironoxyhydroxide. When broken open, a bright orange core of needle-shaped crystals called goethite [$\alpha FeO(OH)$] is seen. A key factor in determining how long the *Titanic* will remain intact is the rate at which these biologically driven rusticles will grow and extract iron from the steel plating of the ship.
- In shallow water, shell growth, e.g. limpets and barnacles, would occur but under the conditions of cold and high pressure, calcium carbonate ($CaCO_3$) cannot precipitate and there are no shells growing over the wreck, so corrosion can occur on base metal. There are no bones present in the wreck of the *Titanic* since calcium ions are readily produced.
- Biological activity in seawater is therefore a significant feature in the rate of corrosion of the *Titanic*.

5.22 The nature and chemical treatment of marine iron artefacts

Marine iron artefacts

(a) Marine *cast iron* artefacts typically consist of an uncorroded metal core surrounded by graphitised corrosion products. These products contain H_2O, $FeO(OH)$, iron chlorides, SiO_2, Fe_3C and graphite. If the marine cast iron is allowed to dry out in the air, the iron chloride components decompose to form Fe_2O_3, HCl and $FeO(OH)$. This mixture of compounds provides ideal corrosion conditions so in the presence of atmospheric oxygen, very rapid corrosion occurs. As the corrosion reaction proceeds, heat is generated and the rate of reaction increases. The overall degradation process is increased by the presence of *chloride ions*.

$$Fe^{3+}(aq) + 6Cl^-(aq) \rightarrow FeCl_6^{3-}(aq)$$

If the object is kept wet, the entry of atmospheric oxygen is minimised and the cathodic reaction of oxygen is reduced. Immersion in NaOH solution is more effective since it neutralises any HCl formed and acts as an anode inhibitor by forming a passivating film on the metallic iron particles.

(b) Marine *wrought iron* artefacts have a much lower carbon content than cast iron and, with no graphite network to hold the corrosion products together, they are not as susceptible to post-excavation corrosion as cast iron.

Chemical treatments for marine iron artefacts

(a) Washing methods. Extraction of chloride ions into the wash water usually using a 0.5 M NaOH solution. The OH^- ion diffuses into the corrosion product, reacts with chlorine-containing compounds to produce free Cl^- ions. The Cl^- ions then diffuse into the wash solution. When the Cl^- levels in the wash solution are less than 50 ppm, the washing is completed.

$$Fe(OH)Cl(s) + OH^-(aq) \rightarrow Fe(OH)_2(s) + Cl^-(aq)$$

(b) The most effective means of increasing Cl diffusion within the corrosion products is to *increase their porosity*. This can be done by converting the iron compounds to a denser state, e.g. to $Fe_3O_4[Fe(FeO_2)_2]$.

Conditions for electrolysis

- Tanks used cannot be made of plastic (NaOH causes brittleness).
- The electrolyte is 0.5–1.0 M NaOH.
- The stainless steel (inert) anode is made positive (O_2 is evolved).
- The artefact (cathode) is made negative.
- The power source must be capable of producing 150 A at 6 V for wrought iron (lower voltage is used for cast iron).
- For wrought iron, an applied voltage of 5 V results in vigorous H_2 evolution at the metal surface (cathode). This loosens concretions and chloride ions are also drawn into the electrolyte.
- During electrolysis (over several weeks), the chloride rate of release should be carefully monitored and the electrolyte changed when necessary.

Alkaline-sulfite reduction

This washing method increases the rate of chloride release from the artefact and, like electrolysis, weakens the bond between concretions and corrosion products. It is more suited to small artefacts. The solution used is 0.5 M Na_2SO_3 and 0.5 M NaOH. The artefact is immersed in the solution in a suitable container which is sealed at about 70°C for several weeks. The objects are then removed and treated by the simple washing method described above.

Heat treatment methods

Two types of heat treatment are used to volatilise the chlorides:

(i) Heating the object in air at high temperatures (400–500°C) to remove chlorides.

(ii) Heating in a reducing atmosphere to remove chlorides by volatisation and also to convert some of the products to metallic iron so that the mechanical strength of the artefact is improved. FeOCl is converted to $FeCl_2$ between 100°C and 300°C; $FeCl_3$ is also converted to $FeCl_2$. At temperatures above 350°C, direct reduction of both $FeCl_2$ and iron oxides by hydrogen occurs. This results in the formation of metallic iron and the evolution of $HCl(g)$ and $H_2O(g)$.

$$FeCl_2(s) + H_2(g) \rightarrow Fe(s) + 2HCl(g)$$
$$Fe_3O_4(s) + 4H_2(g) \rightarrow 3Fe(s) + 4H_2O(g)$$

Note: Artefacts with cutting edges, such as knives and swords, should not be conserved by heat treatment, since information about their metallurgical structure, such as types of smelting and forging procedures would be lost.

Surface applications

For marine cast- or wrought-iron artefacts, surface applications leading to some passivity of iron using phosphoric acid or tannic acid may be used. 'Ferronite' is a water-based chemical with an active ingredient, tannin. It produces a stable surface of iron tannate/haematite (Fe_2O_3) and magnetite (Fe_3O_4) onto which such conventional coating systems as clear varnishes can be applied.

5.23 The nature and chemical treatment of marine copper and copper alloys

The nature of marine copper and its alloys

In shipwreck materials this group consists of copper, brass, gunmetal and bronze.

(a) Because of their high copper content, all of these alloys are treated in a similar manner.

(b) In general, they have little or no marine growth on their surfaces when found (unlike iron) since they are poisonous to marine growth.

(c) Corrosion products on copper-based artefacts recovered from the sea always contain large amounts of chloride, usually in the form of copper (I) chloride (CuCl) and copper (II) hydroxychloride [$Cu_2(OH)_3Cl$].

Table 5.8 Composition and use of copper and some of its alloys

Substance	Composition	Where used
Pure copper	copper	nails, sheeting
Phosphor bronze (corrosion resistant)	copper/tin, 90/10 with about 0.6% phosphorus	propellers
Gunmetal	copper, tin, lead and zinc, 85/5/5/5	cannon, fittings and bells
Brass (marine)	copper/zinc, 60/40	sheathing and rudder fittings

Chemical treatments for marine copper artefacts

(a) *Chemical stripping*. An effective stripping agent for copper-based alloys is a solution of citric acid (5–10% by mass) and thiourea (1–2% by mass) added to tap water. The initial pH of the solution (pH~2) rises to a pH of 3–4 owing to neutralisation of some of the citric acid due to the carbonate ions (CO_3^{2-}).

(b) *Chloride removal*. Crevices in the artefact will contain chlorides and residual citric acid which must be removed by prolonged soaking in Na_2CO_3 solution (4%). In this washing, CuCl and $Cu_2(OH)_3Cl$ hydrolyses with the release of Cl^- ions.

(c) *Electrolysis*. Applied voltage is determined and an electrolyte of 5% by mass of Na_2CO_3 is used. Electrolysis is carried out until the Cl^- ions release from the artefact ceases. During electrolysis, some of the copper-bearing corrosion products, e.g. CuO, $Cu(OH)_3Cl$ and CuCl, are reduced to the denser copper and free Cl^- ions are formed which diffuse out into the bulk electrolytic solution. After electrolysis, the artefact is soaked in a $Na_2CO_3/NaHCO_3$ solution to ensure that all traces of Cl^- are removed. The artefact is then rinsed with deionised water and dried.

5.24 The nature of silver artefacts and their chemical treatment (extension work)

Silver artefacts

Silver artefacts from shipwrecks contain a corrosion product layer of AgCl and Ag_2S.

(a) The outer surface of the corrosion product layer often corresponds to the original artefact layer and many inscription details may be preserved in it. If this corrosion product layer is lost, so too will be many details on the artefact surface.

(b) Most silver artefacts recovered are coins.

(c) 'Silver' coins may contain different amounts of silver, e.g. coins from Dutch East Indiaman wrecks of the 17–19th centuries have been found to contain from 90% down to 60% Ag with the balance being Cu.

Chemical treatments for marine artefacts

(a) Removal of silver concretion. Silver artefacts are immersed in 1 M HCl which dissolves $CaCO_3$ and removes copper corrosion products. Ag_2S will not dissolve.

(b) All methods for converting silver corrosion products to metallic silver use reduction reactions for the silver compounds. The reducing electrons are supplied by either of the following processes.

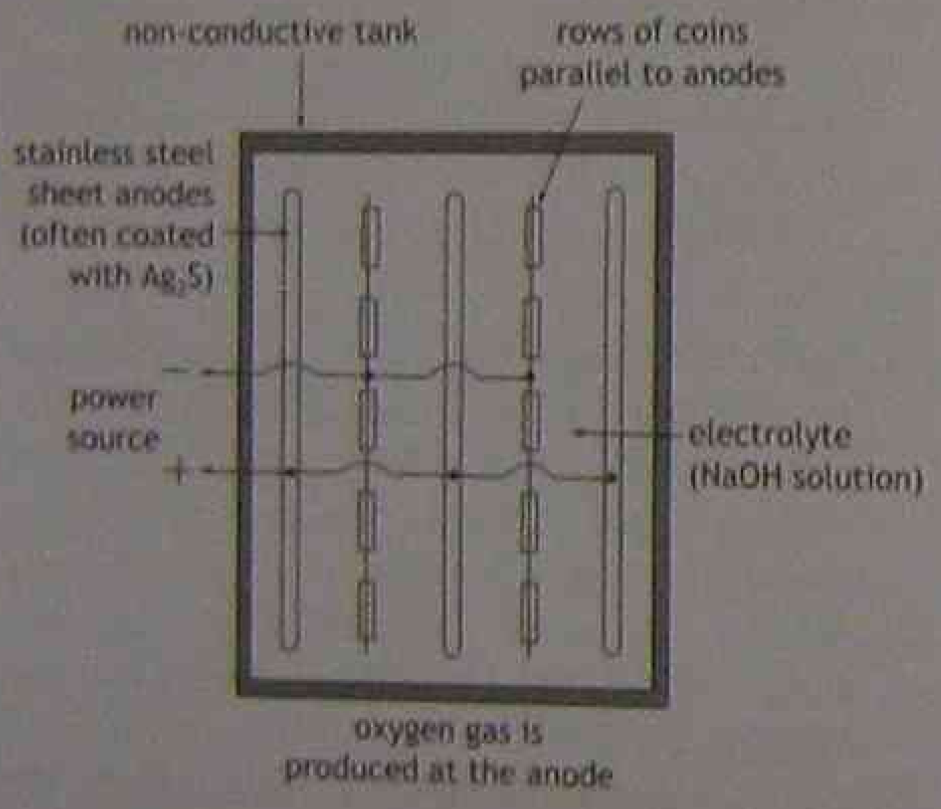


Figure 5.23 Schematic diagram of mass electrolysis treatment for silver coins

(i) *Electrolysis* (using an impressed voltage)
- The electrolyte is NaOH (2–10% by mass).
- The anode is generally stainless steel.
- The cathode is the artefact which has the uncorroded core.
- The power supply is 3–12 V.
- After electrolysis, the artefacts are washed with deionised water until pH = 7.

Anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e$
Cathode: $Ag^+(aq) + e^- \rightarrow Ag(s)$

(ii) *Galvanic reduction*. This is carried out by wrapping the artefact with aluminium foil and covering with a 30% weight/volume formic acid solution. It is chemically inefficient since most of the electrons from the aluminium are used in reducing H^+ to H_2 so relatively few reduce Ag^+ to Ag. After reduction, silver coins are dried and then coated with a clear protective lacquer.

Analysis of solutions and artefacts for chloride content

This is the most frequently used analysis in marine archaeological conservation. One method commonly used is the *Mohr titration method*. To the previously treated known volume of chloride-bearing solution, a few crystals of K_2CrO_4 are added. The solution is then titrated with 0.1 M $AgNO_3$ until the first permanent red-brown colour appears (silver chromate Ag_2CrO_4).

Other methods include potentiometric titration and conductometric analysis.

5.25 The nature and chemical treatment of lead artefacts

Lead corrosion

The corrosion of metals is an electrochemical process with the anodic reaction metal dissolution and the cathodic reaction oxygen reduction.

e.g. $Pb \rightarrow Pb^{2+} + 2e^-$
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Corrosion products should be identified by rapid qualitative analysis to prevent inappropriate conservation treatment. Corrosion products found on lead are Pb^{2+} compounds, the nature of which will depend on the environment.

At a pH > 7, $PbCO_3$ would be expected and a partly passivating film reduces the rate of corrosion. Lead corrodes rapidly in soft acidic waters where pH < 7.

Lead from marine sites may have a greater variety of corrosion products where sulfide and chloride concentrations are approximately the same as those found in sea water.

Treatment

The treatment of lead artefacts usually involves the reduction or removal of corrosion products. Conservation of a lead artefact (e.g. a seal attached to a document) can be carried out by immersing it in a 5% solution of EDTA. Surface and some compact corrosion is removed. Reduction involves the use of strongly alkaline solutions and is accomplished by either an electric current or metals such as zinc. In both cases, the metal is cathodically protected from corrosion during treatment. All artefacts must be thoroughly washed after chemical cleaning.

If electrolysis is used:
- The elecrolyte is NaOH (5% by mass).
- The anode is stainless steel.
- The cathode is the artefact with an uncorroded core.
- The power supply is about 5 V.

  After electrolysis the artefact is washed with distilled water until pH = 7.
- Anode: $2H_2O(l) \rightarrow O_2(g) + 4H^-(aq) + 4e^-$

  Cathode: $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$

5.26 Chemical treatment and restoration of ceramics and organic material

Usually after the removal of concretions, any stains are treated followed by washing and finally repair and restoration. Cleaning is carried out by electrophoresis during which the artefact is placed between two electrodes carrying a high electric potential. Particles of salts, corrosion products and dirt move in the electric field and migrate to one or other of the poles. Letters, bank notes and leather can be cleaned in this way. Metallic stains, e.g. rust, are removed as complex metal ions. Artefacts are stored away from sunlight in conditions of controlled temperature and humidity.

Conservation of waterlogged wood

Principles

1. Dimensions of treated objects should closely approach those of the waterlogged condition (i.e. avoid shrinkage).
2. Conservation should give durability to the materials that make up the objects.
3. Reversibility should be possible (e.g. if retreatment is needed).
4. The best treatment is that which modifies the wood to the least extent.

Some techniques used for wood treatment

(a) *Impregnation* which is aimed at filling up the spaces, e.g. lumina and cell wall capillaries within the wood, with a chemically inert material that provides structural support. Impregnation functions by replacing waterlogging water so that the capillary tension effects of drying (leading to collapse) are prevented. Drying stresses and distortion of the wood cells are thus also prevented. The impregnation agent should solidify in the lumina before drying commences.

(b) *Cell wall bulking* may be used to strengthen the cell walls where filling the microspores essentially eliminates the normal absorption and desorption by the cell wall. Polyethylene glycol (PEG) of a low molecular mass is effective in controlling shrinkage. The formula for PEG is
$H\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O(CH_2\text{-}CH_2\text{-}O)_nCH_2\text{-}CH_2\text{-}O\text{-}H$

(c) *Replacement of water with a non-aqueous solvent*, e.g. acetone. Such organic solvents have the following properties:

(i) Much lower surface tensions than water, so capillary tension forces will be reduced.

(ii) Without hydrogen bonding, the cell walls will be less plasticised giving more protection against cell collapse.

(iii) Such lower viscosity solvents have enhanced diffusion and permeation rates.

(iv) Freeze-drying where water is removed to eliminate forces of capillary tension and preserve structure. Prior treatment with PEG solutions is needed.

(v) Slow drying, where some of the water in the wood has been replaced by a water-soluble resin, may reduce drying stresses due to shrinkage.

Answers

Answers for Exercise 5.1

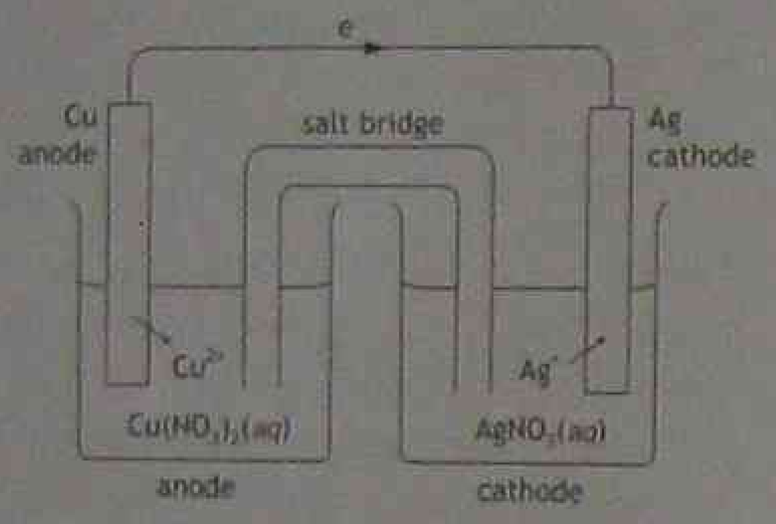
Example (a) (i) Mg (ii) Cl_2
(iii) Cl_2 (iv) Mg
(v) Cl^- (vi) Mg^{2+}
(vii) $Mg \rightarrow Mg^{2+} + 2e^-$; $Cl_2 + 2e^- \rightarrow 2Cl^-$

Example (b) (i) Mg (ii) H^+
(iii) H^+ (iv) Mg
(v) H_2 (vi) Mg^{2+}
(vii) $Mg \rightarrow Mg^{2+} + 2e^-$; $2H^+ + 2e^- \rightarrow H_2$
(Cl^- ions are spectator ions)

Example (c) (i) Fe (ii) Cu^{2+}
(iii) Cu^{2+} (iv) Fe
(v) Cu (vi) Fe^{2+}
(vii) $Fe \rightarrow Fe^{2+} + 2e^-$; $Cu^{2+} + 2e^- \rightarrow Cu$

Answers for Exercise 5.2

1. (a)



(b) (i) Anode reaction: $Cu \rightarrow Cu^{2+} + 2e^-$
(ii) Cathode reaction: $Ag^+ + e^- \rightarrow Ag$
2 × (ii): $2Ag^+ + 2e^- \rightarrow 2Ag$
(iii) Cell reaction:
$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{cathode} - E^\circ_{anode} \\ &= 0.80\ V - 0.35\ V \\ &= 0.45\ V \end{aligned}$$

2. Order of increasing strength as reductants: beryllium (Be), magnesium (Mg), cadmium (Cd) and copper (Cu).

Answers for Exercise 5.3

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

(a) → [0.80 − 0.35] V = 0.45 V; Cu
(b) → [0.23 − (−0.76)] V = 0.53 V; Zn
(c) ← [0.35 − (−0.41)] V = 0.76 V; Fe
(d) ← [0.41 − (−2.36)] V = 1.95 V; Mg
(e) → [0.80 − (−0.14)] V = 0.94 V; Sn

Answers to Activity 5.1

Part A

1. Because of the presence of water in the muffler which has condensed during the combustion of petrol.
2. The presence of salt water as sea spray increases the corrosion of motor vehicles in Manly.
3. As a result of rusting, the iron oxides cause blockage.
4. For rusting to occur, moisture and oxygen must be present.

Part B

1. Diagram 1
(a) Anode: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$ (found at areas of stress, e.g. at head and point of nail)
(b) Cathode: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$
Diagram 2
(a) Anode: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$
(b) Cathode: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$
Diagram 3
(a) Anode: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
(b) Cathode: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

2. (i) The $Fe[Fe(CN)_6]^-$ ion is Prussian blue.
(ii) The $Zn[Fe(CN)_6]^-$ ion is colourless.

3. Pink, which is the colour of phenolphthalein in alkaline solutions.

4. (a) In cathodic protection, the metal to be protected is made the cathode half-cell so that it will not lose electrons and dissolve.
(b) In diagram 3, where the zinc strip is the more active metal and acts as the anode.
(c) In diagram 2, where iron is a more active metal than copper. The cathode being copper is protected.

5. When the iron nail is removed from the gel, the surface of the nail is not coated with rust but there is rust on the gel. This shows that the rust does not appear to form directly on the metal surface.

Test on Chapter 5 – (option 2) Shipwrecks, Corrosion and Conservation

1. [8 marks]
Numerically, the most common silver artefacts recovered from shipwrecks are 'silver' coins. In Dutch East Indiaman wrecks of the 17–19th centuries recovered by the Western Australian Museum, 'silver' coins have been found ranging from 95% Ag down to 60% Ag, the other major element being copper.
(a) What would you expect the chemical coating on the retrieved 'silver' coins to be if they were found buried in mud? Give a reason for your answer.
(b) Methods of converting silver corrosion products to metallic silver all employ reducing reactions for the silver compounds. Electrolysis is the most usual method used. Draw a labelled diagram to illustrate this procedure using as electrodes a silver coin coated with silver sulfide and a stainless steel electrode. A dilute solution of sodium hydroxide was used as the electrolyte. Oxygen gas was produced at one electrode:
(i) Draw a labelled diagram for the electrolysis process.
(ii) Write the half-equations (including states) for the reactions at (a) the anode and (b) the cathode.
(iii) State the direction of the electron flow in the external circuit of the cell.
(c) Another method, galvanic reduction, is also used. Here the coin is wrapped in aluminium foil and covered with a formic acid solution.
Data:
$AgS_2(s) + 2e^- \rightarrow 2Ag(s) + S^{2-}(aq)$ E° = 0.71 V
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$ E° = −1.66 V
Use the given data to explain the coin cleaning process.

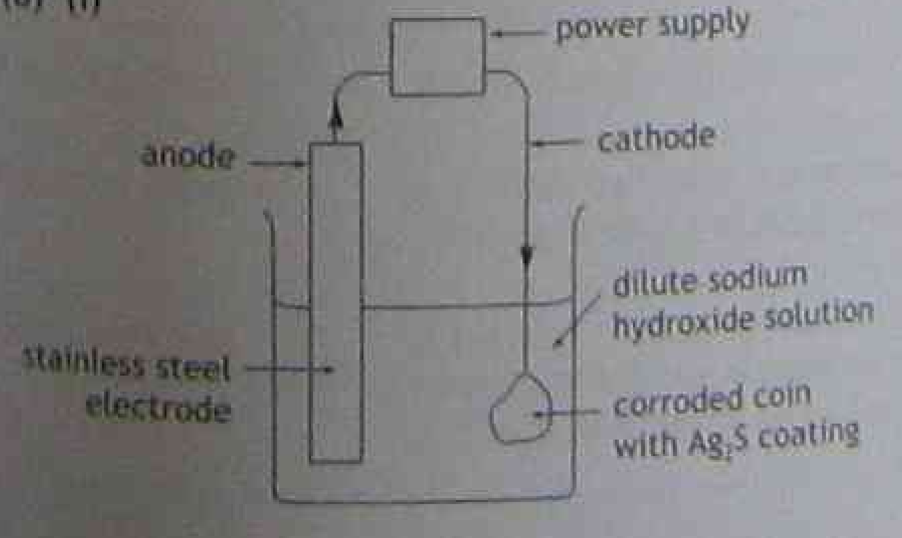
2. [9 marks]
(a) What element apart from iron is present in ALL steels.
(b) Stainless steel and alnico are two different alloys of steel. What do you understand by the term alloy?
(c) Complete the following table:

Alloy	Major metal additives	Properties of alloy	One use
Stainless steel	1. 2.		
Alnico	1. 2. 3.		

3. [8 marks]
Explain the following observations. Use the electrochemical data given in Table 5.4 and write any relevant equations in your answer.
(a) The iron hulls of ships are protected by fitting large blocks of pure zinc to them.
(b) Painted iron resists corrosion until the paint layer is deeply scratched.
(c) Impressed current systems with permanent anodes have been successful in corrosion prevention in the hulls of steel ships. State two reasons why they are more successful than sacrificial anode systems.
(d) Corrosion of the *Titanic* in deep cold water with low oxygen concentration has proceeded much faster than expected. Give a reason for this.

Answers for Test on Chapter 5 – Shipwrecks, Corrosion and Conservation

1. [8 marks]
(a) The chemical coating on the 'silver' coins would be silver sulfide (Ag_2S). The mud would contain anaerobic bacteria which would cause the corrosion.
(b) (i)



(ii) anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
cathode: $Ag_2S(s) + 2e^- \rightarrow 2Ag(s) + S^{2-}(aq)$
(iii) The direction of electron flow through the external circuit is from the stainless steel electrode to the coin.
(c) Here an electrochemical cell is formed with aluminium as the anode and the silver core as the cathode.
$2Al(s) + 3Ag_2S(s) \rightarrow 6Ag(s) + 2Al^{3+}(aq) + 3S^{2-}(aq)$
Since the reaction has a positive E° voltage, the reaction should occur. Silver is not lost from the coin.

$$\begin{aligned} E^\circ_{cell} &= E^\circ_{cathode} - E^\circ_{anode} \\ &= 0.71 - (-1.66)\ V \\ &= 2.37\ V \end{aligned}$$

2. [9 marks]
   (a) Carbon.
   (b) An alloy is any material made of a blend of a metal with another substance(s) to give it special qualities, such as resistance to corrosion or greater hardness.
   (c) (% composition of metals in alloys not required.)

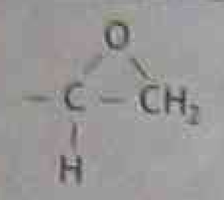
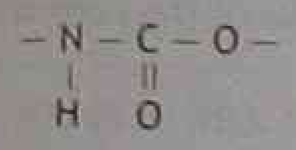
Alloy	Major metal additives	Properties of alloy	One use
Stainless steel	chromium (18%) nickel (8%)	hard, corrosion resistant, strong	sinks
Alnico	aluminium (12%) nickel (22%) cobalt (5%)	rigid structure, high magnetic permeability	permanent magnets

3. [8 marks]
   (a) This is an example of the use of zinc as a sacrificial anode.
   Anode reaction:
   $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$
   Cathode reaction:
   $O_2(aq) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$
   Zn(s) is a better electron donor than Fe(s) and so preferentially provides the electrons for the cathode reaction.
   (b) A layer of paint inhibits the passage of oxygen and water from diffusing to the iron surface so that corrosion will not occur.
   Cathode reaction:
   $2H_2O(l) + O_2(g) + 4e^- \rightarrow 4OH^-(aq)$
   Anode reaction:
   $2Fe(s) \rightarrow 2Fe^{2+}(aq) + 4e^-$
   Overall reaction:
   $$2Fe(s) + 2H_2O(l) + O_2(g) \rightarrow 2Fe^{2+}(aq) + 4OH^-(aq)$$
   $$\begin{aligned} E^\circ_{cell} &= E^\circ_{cathode} - E^\circ_{anode} \\ &= 0.40 - (-0.41)\ V \\ &= 0.81\ V \end{aligned}$$
   For corrosion to occur, iron, water and oxygen must be in electrical and physical contact. This happens when the paint layer is broken.
   (c) Although initial costs are higher, these systems have longer life, reduce hull maintenance and weigh less than sacrificial anode systems.
   (d) The most obvious corrosion products on the *Titanic* are rusticles. These form in the presence of sulfate-reducing bacteria which grow rapidly in anaerobic conditions. These bacteria have wastes that produce acidic environments around the wreck of the *Titanic* causing accelerated corrosion in non-passivating metals such as iron.

Total 25 marks

Glossary

Alkyl resins	Cross-linked polymers forming a rigid lattice structure. They are used as a 'vehicle' in paints.
Alloy	A material that contains more than one element and has the characteristic properties of metals such as lustre and electrical conductivity. Examples are brass, bronze and steel.
Alnico	A special steel (12% Al, 22% Ni and 5% Co) used as a permanent magnet.
Anaerobic process	A process which lacks free oxygen.
Anode	The electrode where oxidation occurs.
Artefact	A product of human art and workmanship often from early civilisations or shipwrecks.
Cathode	The electrode where reduction occurs.
Cathodic protection	When two metals are immersed in an electrolyte the metal to be protected is made the cathode of the corrosion cell so that it will not lose electrons and dissolve.
Concretion	A solid mass of foreign material attached to an artefact.
Corrosion	The oxidation of metals by water and oxygen in the environment. It is an electrochemical process.
Desalination	The removal of soluble salts, e.g. chloride.
Drying oils	Highly unsaturated oils which polymerise to resins using oxygen in the air, e.g. linseed oil. These resins in oil paints bind the pigment to the surface.
E° values	See standard electrode potential series (see Table 5.4).
Electrochemical cell	Electrons transferred in a redox reaction pass through an external circuit.
Electrode	A conductor used to permit the flow of electrons in an electrochemical cell and to act as the site of oxidation (anode) or reduction (cathode).
Electrolysis	The chemical change resulting from the application of a potential difference across an electrolyte.
Electrolyte	A substance which in the liquid (molten) state or aqueous solution will conduct an electric current and undergo decomposition.
Electrolytic cell	A cell in which electrolysis occurs.
Electron transfer	A process by which one or more electrons are transferred from one atom to another to form positively and negatively charged ions and ionic bonds.
Electroplating	A method of plating one metal with another by electrolysis. A solution containing a salt of the plating metal must be present. The object to be plated is the cathode. The anode is the plating metal or an inert electrode.

Epoxy resins	Resins which contain more than one epoxide group.  $-\underset{\underset{\displaystyle H}{\vert}}{C}\overset{O}{-}CH_2$
Galvanic cell	A system using spontaneous chemical change to produce electricity, e.g. the Daniell cell.
Impressed current system	A voltage difference is maintained between the hull and fitted anodes of a ship which will prevent corrosion.
Leaching from soil	The extraction of soluble material, e.g. Al^{3+} ions from the soil by water (solvent).
Naphtha	The name used in the oil industry for the light oil fraction produced in the fractional distillation of crude oil, e.g. solvent naphtha.
Oxidant	A substance which causes electron loss in another substance.
Oxidation	The process by which a species loses electrons.
Passivating metal	A reactive metal which forms an inactive coating as a result of reactions with substances such as water or oxygen, e.g. aluminium, chromium, tin and zinc. Aluminium has an inherent oxide film which is inert, tenacious and reforms immediately if removed by abrasive action.
Polyurethane resins	These resins have a 'urethane' linkage.  $-\underset{\underset{\displaystyle H}{\vert}}{N}-\underset{\underset{\displaystyle O}{\Vert}}{C}-O-$
Reductant	A substance which causes electron gain by another substance.
Reduction	The process by which a species gains electrons.
Rusting of iron	The slow formation of a red-brown non-adherent coating called rust ($Fe_2O_3.H_2O$). It forms on iron surfaces in the presence of O_2 and H_2O and is an example of electrochemical corrosion.
Sacrificial anode	A method of cathodic protection. The more active metal is used as the anode. It will dissolve preferentially before the less active metal, e.g. a block of Mg (anode) is attached to the ship's hull (cathode of Fe) to prevent corrosion of the hull.
Stainless steel	An alloy of steel which is corrosion-resistant. It usually contains about 18% Cr and 8% Ni.
Standard potential (E°)	The electric potential developed at an electrode when an oxidant and its conjugate reductant are present in their standard states. [All ions at 1 M concentration and gases at standard laboratory conditions (SLC) which is 25° C (298 K) and 100 kPa.]
Steel	An alloy of iron and contains some carbon. Many alloys of steel are made by adding metals.

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6 option three

The Biochemistry of Movement

An increased understanding of the nature of the biochemical reactions involved in muscular contraction leads to a better selection of foods in an athlete's diet, thus using natural methods to enhance performance.

Contents

6.1 Cellular metabolism and biochemical energy

(a) The metabolism of a living organism is a combination of all the chemical reactions that take place in the body.

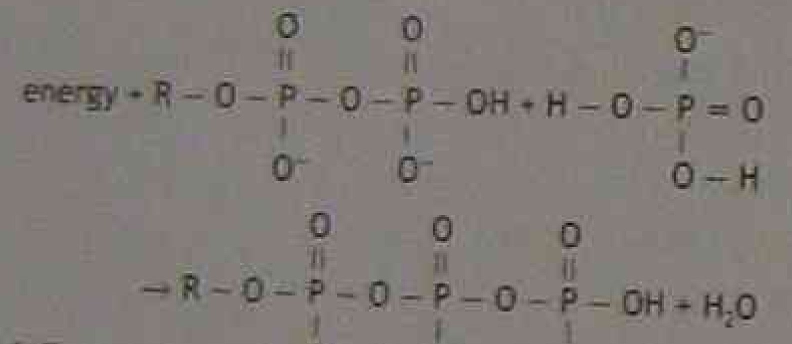
(b) Food provides the chemical compounds that are involved in metabolic reactions.

(c) Carbohydrates and lipids are the main sources of energy in humans.

(d) An initial enzyme-catalysed hydrolysis of carbohydrates to glucose must occur before energy production can start in the cell.

(e) When glucose ($C_6H_{12}O_6$) is oxidised in the body, a substantial amount of energy (2800 kJ mol^{-1}) is released. There must be some means of regulating this energy.

(f) In plant and animal cells, adenosine triphosphate (ATP) is the source of energy for reactions in the cell. It is a compound containing a nitrogen base (adenine) and a sugar (ribose) connected to three phosphate groups.



$$\text{energy} + R-O-\overset{\overset{O}{\|}}{\underset{\underset{O^-}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O^-}{|}}{P}}-OH + H-O-\overset{\overset{O^-}{|}}{\underset{\underset{O-H}{|}}{P}}=O$$

$$\rightarrow R-O-\overset{\overset{O}{\|}}{\underset{\underset{O^-}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O^-}{|}}{P}}-O-\overset{\overset{O}{\|}}{\underset{\underset{O^-}{|}}{P}}-OH + H_2O$$

When energy is needed, ATP reacts with water to give ADP and energy.

$$ATP + H_2O \rightarrow ADP + H_2PO_4^- + \text{energy}$$

(g) When the P–O–P bond at the end phosphate group of ATP is broken by hydrolysis with water, ADP is formed and 33 kJ mol^{-1} of energy is released. This energy is used to perform mechanical contraction of the muscles, synthesise reactions, maintain body temperature and transport metabolites from metabolic reactions.

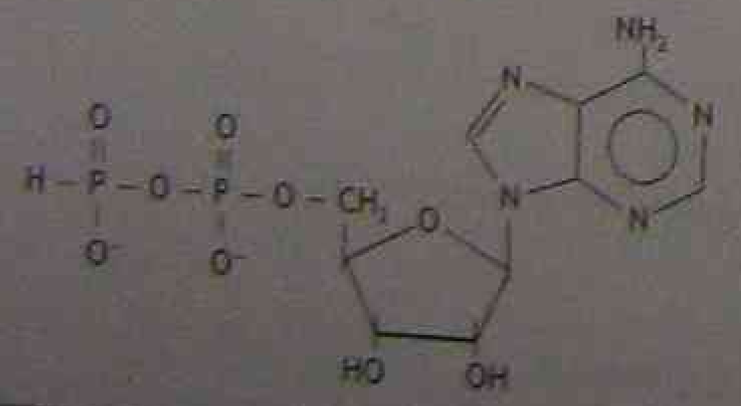


Figure 6.1 Adenosine diphosphate, ADP

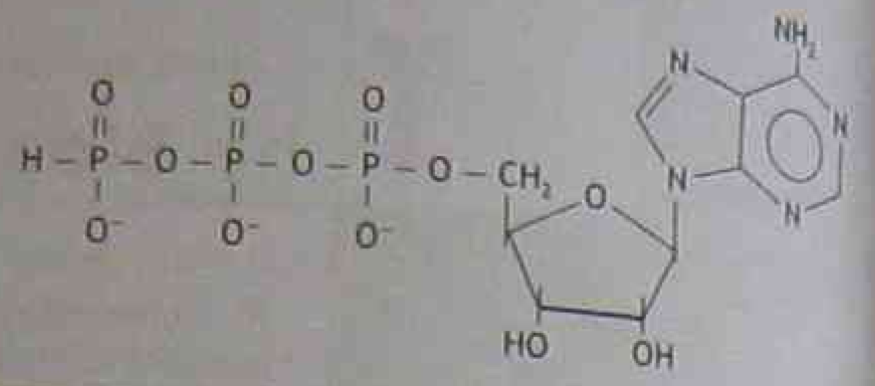


Figure 6.2 Adenosine triphosphate, ATP

(h) ATP is formed in an enzyme-controlled endergonic (endothermic) reaction:

$$ADP + P_i + \text{energy absorbed} \rightarrow ATP$$

Energy is released in an enzyme-controlled exergonic (exothermic) reaction:

$$ATP + H_2O \rightarrow ADP + P_i + \text{energy released}$$

ATP is the 'universal currency' in biological systems.

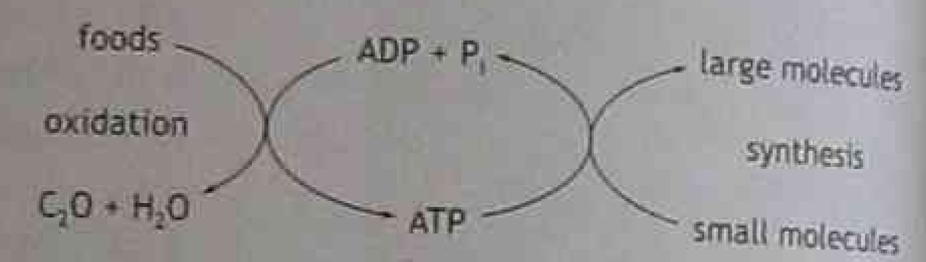


Figure 6.3 Reactions involving energy. Synthesis is an endergonic (energy-consuming) process; oxidation is an exergonic (energy-releasing) process

6.2 Enzymes

- Enzymes are physiologically active proteins which have specific functions. Often enzymes work in conjunction with each other, e.g. in glycolysis.
- Enzymes are protein bio-catalysts. A catalyst increases the rate of a chemical reaction but undergoes no permanent change.
- Enzymes provide a pathway of lower activation energy.
- Enzymes are much more efficient than non-biological catalysts. The 'turn-over' number of enzyme-catalysed events is in the rate of 10^3 to 10^7 s^{-1} at a particular active site.
- Protein molecules of enzymes are very large (molecular masses in the order of 100 000). The substance upon which the enzyme acts (the substrate) is made up of small molecules. There are only a few places on the surface of the enzyme molecule where a reaction can occur. These are called 'active sites'.

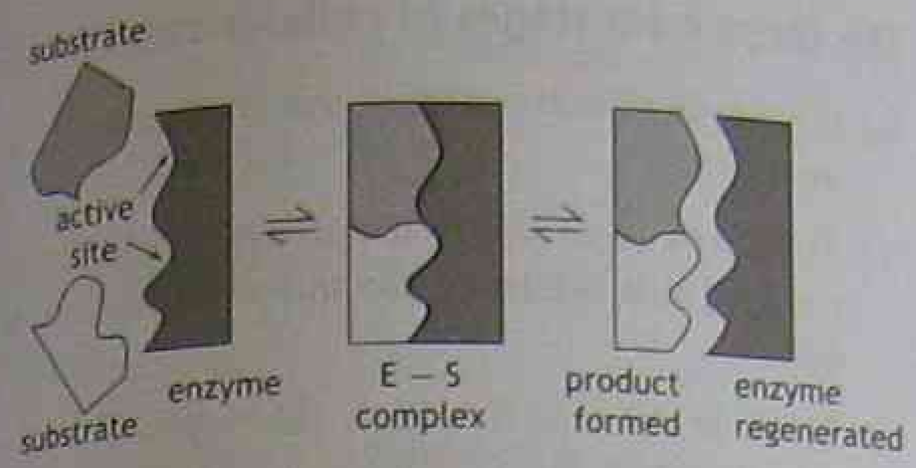


Figure 6.4 Action of enzyme by lock-and-key theory. The reaction may go in either direction.

6.3 Naming of enzymes

The name of the enzyme usually indicates the substrate with which it is reacted and ends in the suffix -ase.

Some catalysing enzymes

- *Hydrolases*

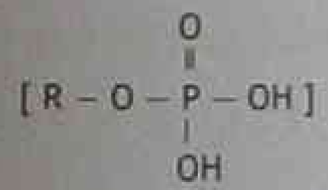
  Enzymes that catalyse hydrolysis reactions.
- *Sucrase*

  Hydrolysis of sucrose to glucose and fructose.
- *Amylase*

  Hydrolysis of starch, e.g. salivary amylase results in the hydrolysis of starch to maltose.
- *Lipases*

  Hydrolysis of fats to fatty acids and glycerol.
- *Phosphatases*

  Hydrolysis of phosphate esters to phosphoric acid and alcohol.



$$[\,R-O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-OH\,]$$

This is a key reaction in energy storage and transfer, especially in glucose metabolism.

6.4 pH and temperature effects on enzymes

The action of enzymes is influenced by pH and by temperature.

Temperature

Experimental studies have shown that the activity of a particular enzyme maximises at around the normal temperature of the organism in which it is found, e.g. 37°C in humans.

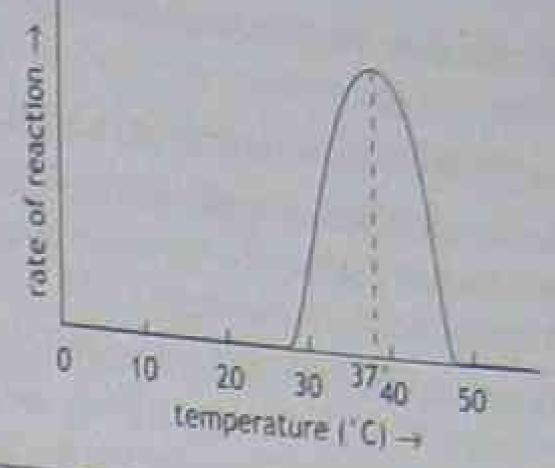


Figure 6.5 Change in temperature for an enzyme found in the small intestine of humans

High temperatures will destroy enzyme activity in humans.

Experiment

An experiment to investigate the effect of heat on enzymes could be carried out using chopped calf's liver which contains the enzyme catalase. This changes hydrogen peroxide to water and oxygen.

$$H_2O_2(g) \rightarrow \text{catalase } H_2O(l) + {}^1/2O_2(g)$$

The reaction rate can be monitored by determining the time taken for the sample in the test tube to stop evolving oxygen when placed in a water bath at a temperature of 25°C. The experiment can be repeated using other sets of test tubes to cover the range of 25–45°C. The same amount of chopped liver should be used in each case.

Note: Unfortunately an experiment using salivary amylase on starch is no longer permitted.

Method

1. Chop up some fresh calves' liver which will contain the enzyme catalase.
2. Set up five water baths at temperatures of 25°C, 30°C . . . 45°C.
3. Place 10mL of H_2O_2 (3 volumes) in 10 test tubes and place pairs of these in each of the five water baths.
4. Add the same mass of chopped liver to each test tube and measure the maximum height reached by the bubbling (or time the rate of O_2 evolution) so that the optimum activity can be found.
5. Another tube containing no liver is used as the control.

pH

Enzymes often show a sharp change in activity with change to the pH of the solution. This suggests that acid-based reactions are important in the catalysed reaction.

Experiment to show the effects of pH on reactions

(i) Dipping a cut piece of apple in lemon juice to stop it from turning brown. The low pH inhibits the enzyme causing browning.

(ii) In making junket, even if the temperature is at the optimum 37°C the junket will not set if the pH is raised above 7. The range for the rennin enzyme is pH 2–7 (acidic).

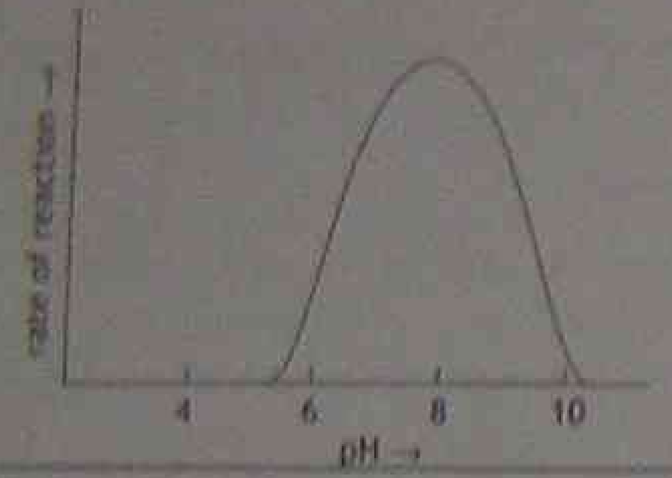


Figure 6.6 The effect of pH on a reaction

6.5 The cell as a chemical factory

The living cell can be looked on as a highly organised chemical factory using glucose (and decomposition products from fats and proteins) as its fuel source. The cell needs one mechanism for capturing and storing energy from its fuel and another for supplying this energy when and where it is needed. The molecule pairs ATP and ADP carry out this requirement. When the supply of ATP runs low, the cell produces more by oxidising glucose. More than 90% of the ATP is made in the mitochondria of the cell. Cells with high-energy requirements contain more mitochondria (about 5000 times more) than those with low-energy requirements. The mitochondria are sometimes called the 'powerhouses' of the cell and are the site of the aerobic stages of cellular respiration.

Figure 6.7 A mitochondrion. **Note:** Both inner and outer membranes contain enzymes used in the production of ATP

The three main stages of cellular respiration

(a) Glycolysis which occurs in the cytoplasm and is anaerobic.

(b) The Krebs cycle (*or* the tricarboxylic acid (TCA) cycle) which occurs in the mitochondria and is aerobic.

(c) Electron transport which takes place in the mitochondria and is aerobic.

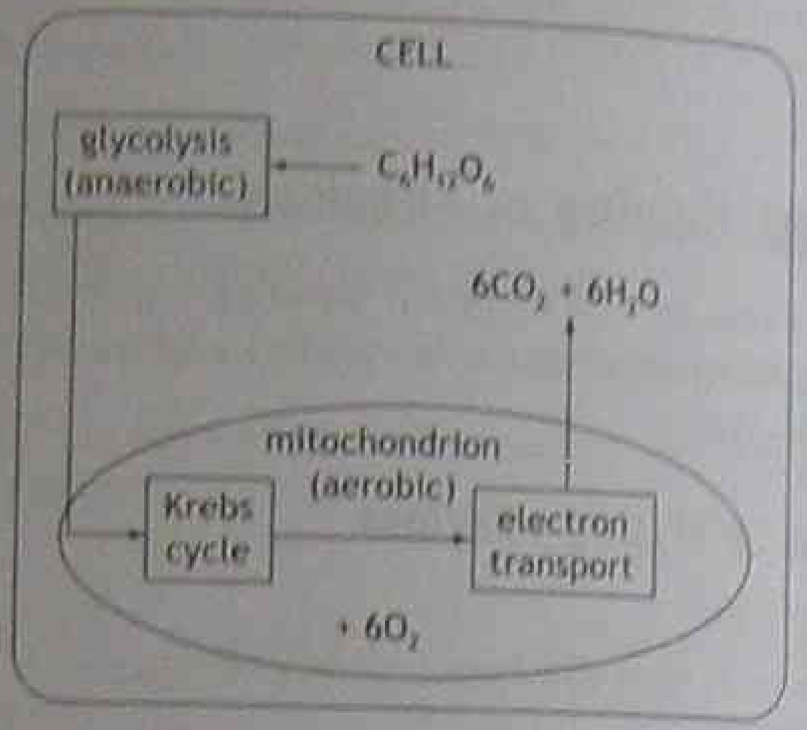


Figure 6.8 A brief summary of the breakdown of glucose to CO_2 and H_2O in a muscle cell

6.6 Aerobic and anaerobic respiration

Living cells can obtain energy from glucose in two different ways, both of which depend on certain conditions.

Reaction sequence I

$$\begin{array}{l}\text{glucose } (C_6H_{12}O_6)\\ \downarrow\\ \text{pyruvate}\\ \downarrow\\ \text{carbon dioxide + water } (6CO_2 + 6H_2O)\end{array}$$

This sequence is called *aerobic respiration* because oxygen is needed and it occurs in mitochondria cells. One molecule of glucose can produce 36 molecules of ATP (see Figure 6.9).

Reaction sequence II

$$\begin{array}{l}\text{glucose } (C_6H_{12}O_6)\\ \downarrow\\ \text{pyruvate}\\ \downarrow\\ \text{lactic acid } (CH_3\text{–CHOH–COOH})\end{array}$$

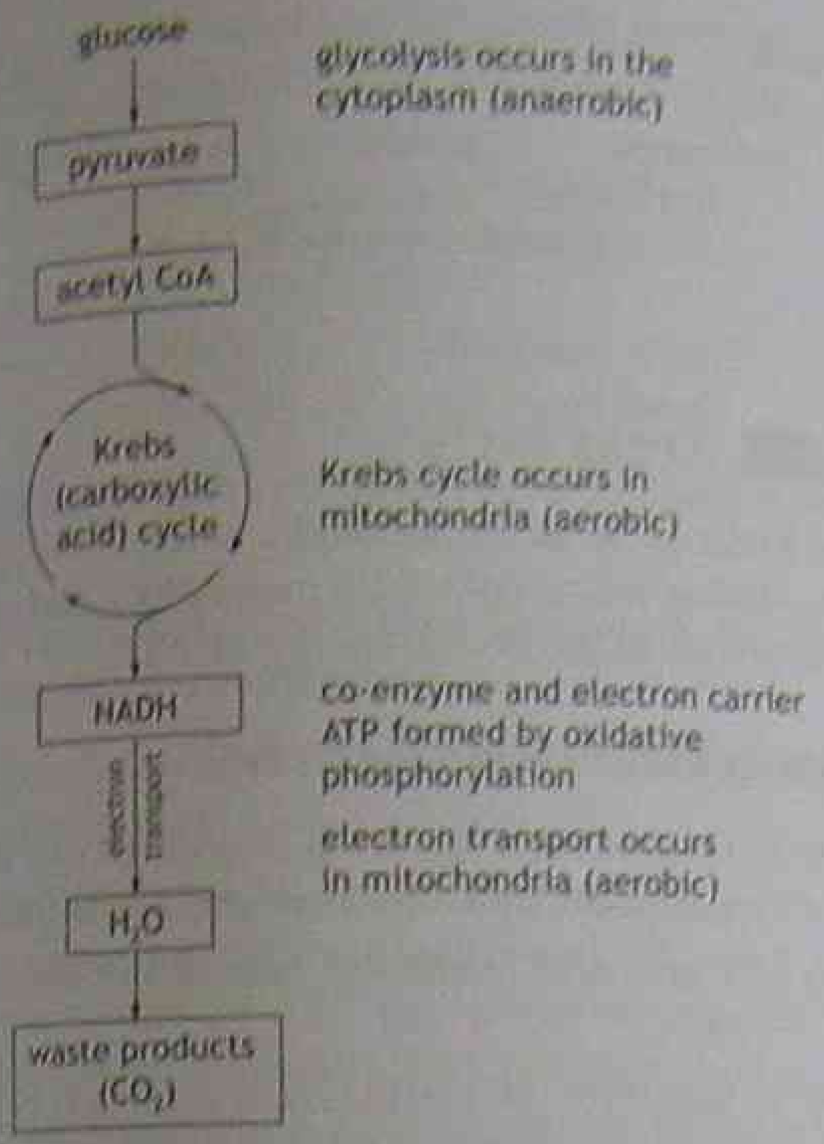


Figure 6.9 Respiration

This sequence is called *anaerobic respiration* because no oxygen is needed. One molecule of glucose produces two molecules of ATP. Despite its low yield of ATP, the process can be advantageous to muscle cells, for example, because it is a fast reaction.

Sequence II results in

- the breakdown of glucose in the absence of oxygen;
- one molecule of glucose forming two molecules of pyruvate with the release of energy;
- an overall yield of 2 ATP molecules per molecule of glucose; and
- a further breakdown of pyruvate resulting in lactic acid formation in animals and the production of ethanol and carbon dioxide in plants.

The build-up of lactic acid in muscle cells of humans can occur during such activities as long-distance running. This can result in lactic acidosis which can cause muscle pain and collapse.

6.7 Aspects of glycolysis

The anaerobic breakdown of glucose using a fermentation pathway is called *glycolysis*. The enzymes work in conjunction with one another as in a production line. The initial compound reacts with the first enzyme to form a product which in turn reacts with the next enzyme until the end product is reached. This series of steps is called a *biosynthetic pathway* and occurs in the process of glycolysis. This was the first complete biological pathway to be worked out.

The glycolysis reaction

1. glucose + ATP → glucose-6-phosphate + ADP + energy
2. glucose-6-phosphate $\xrightarrow{\text{enzyme}}$ fructose-6-phosphate
3. fructose-6-phosphate + ATP → diphosphorylated fructose + energy
4. diphosphorylated fructose $\xrightarrow{\text{enzyme}}$ 2 phosphoglyceraldehyde (PGAL)
5. In this reaction, nicotinamide adenine dinucleotide (NAD^+) acts as an oxidising agent. It works in conjunction with other enzymes and is called an enzyme co-factor.

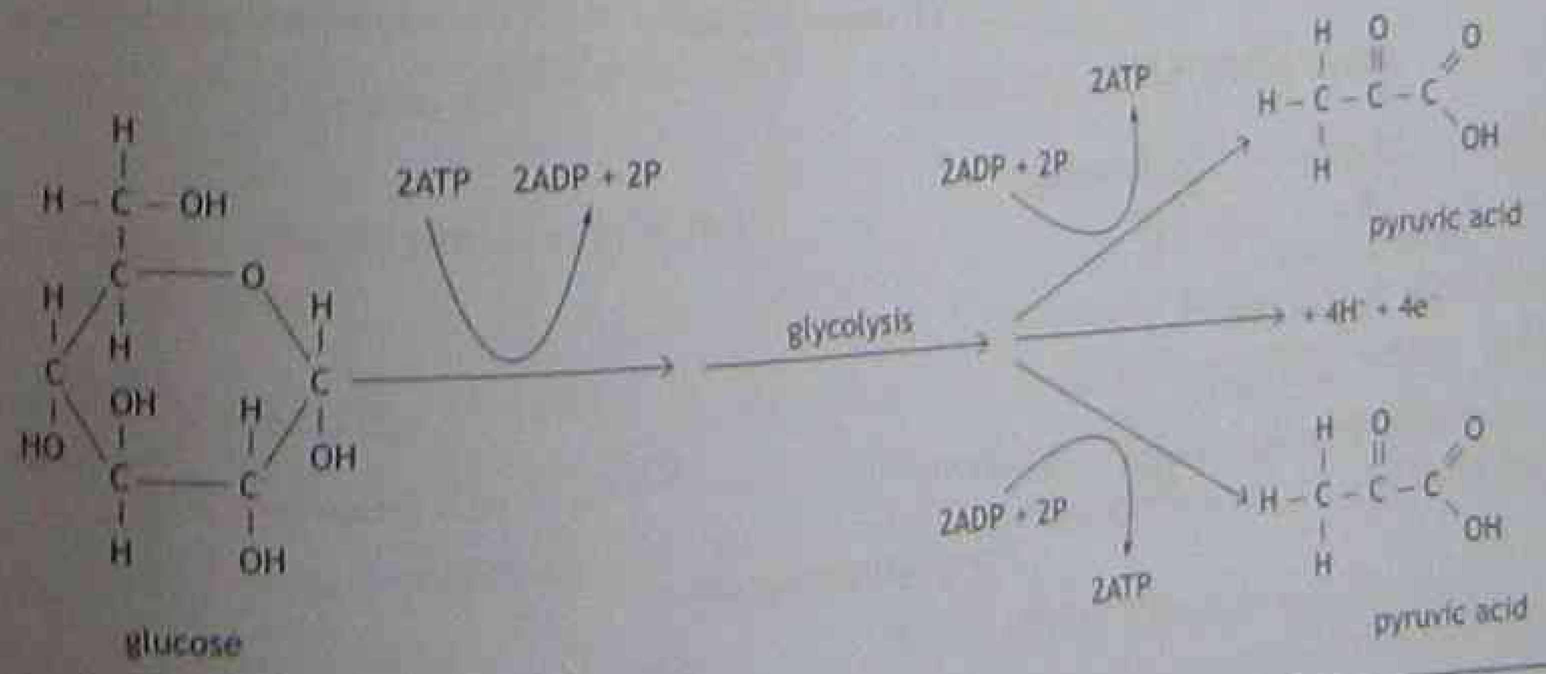


Figure 6.10 The mechanism of glycolysis

6. 2PGAL + 2 phosphate + $2NAD^+$ →
diphosphoglyceraldehyde + 2NADH

7. diphosphoglyceraldehyde + 2ADP →
2ATP + $2H_2O$ + pyruvate formation

Compounds such as glycogen undergo glycolysis once they have been converted to glucose 6-phosphate.

Note: During cellular respiration, energised electrons from glucose are used to restore ATP. The energised electrons are picked up by two molecules of the electron carrier NAD^+.

$$NAD^+ + 2e^- + H^+ + \text{energy} \rightleftharpoons NADH$$

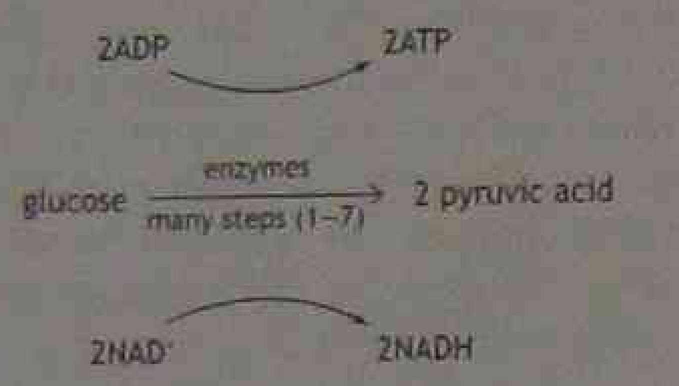
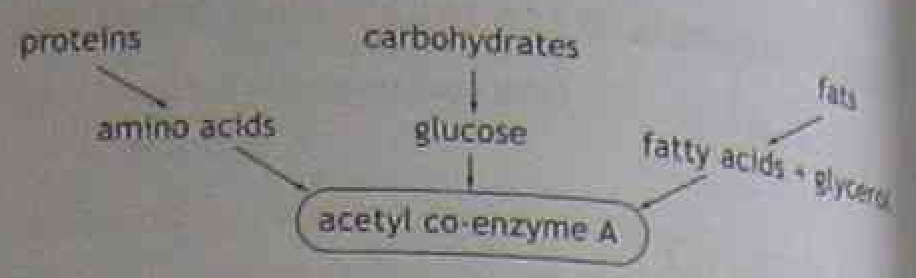


Figure 6.11 Summary of glycolysis

6.8 How fuel molecules enter the cycle

Most fuel molecules enter the cycle as acetyl-CoA. The acetyl group can also be derived from pyruvic acid. The TCA cycle occurs inside mitochondria. The formation of acetyl-CoA is the link between glycolysis and the TCA (Krebs) cycle.



6.9 Krebs cycle

The Krebs cycle (or tricarboxylic acid (TCA) cycle) is a pathway for carbohydrate metabolism and is the main source of metabolic energy as ATP.

Steps in Krebs cycle (TCA cycle)

Step 1. Oxaloacetic acid (4C) condenses with acetyl-CoA (2C) to form citric acid (6C).

Step 2. Citric acid forms the isomer isocitric acid (6C).

Step 3. Isocitrate (6C) is oxidised and CO_2 is lost, forming a ketoglutaric acid (5C). Hydrogen ions are released.

Step 4. Succinyl-CoA (4C) is formed and CO_2 is lost.

Step 5. Succinyl-CoA generates a high energy bond (P_i) and ATP is produced. Succinic acid (4C) is formed.

Step 6. Succinic acid (4C) loses two hydrogen ions and is oxidised to fumaric acid (4C).

Step 7. Water is added across the double bond of fumaric acid to yield malic acid (4C).

Step 8. Oxidation of malic acid occurs, producing oxaloacetic acid (4C).

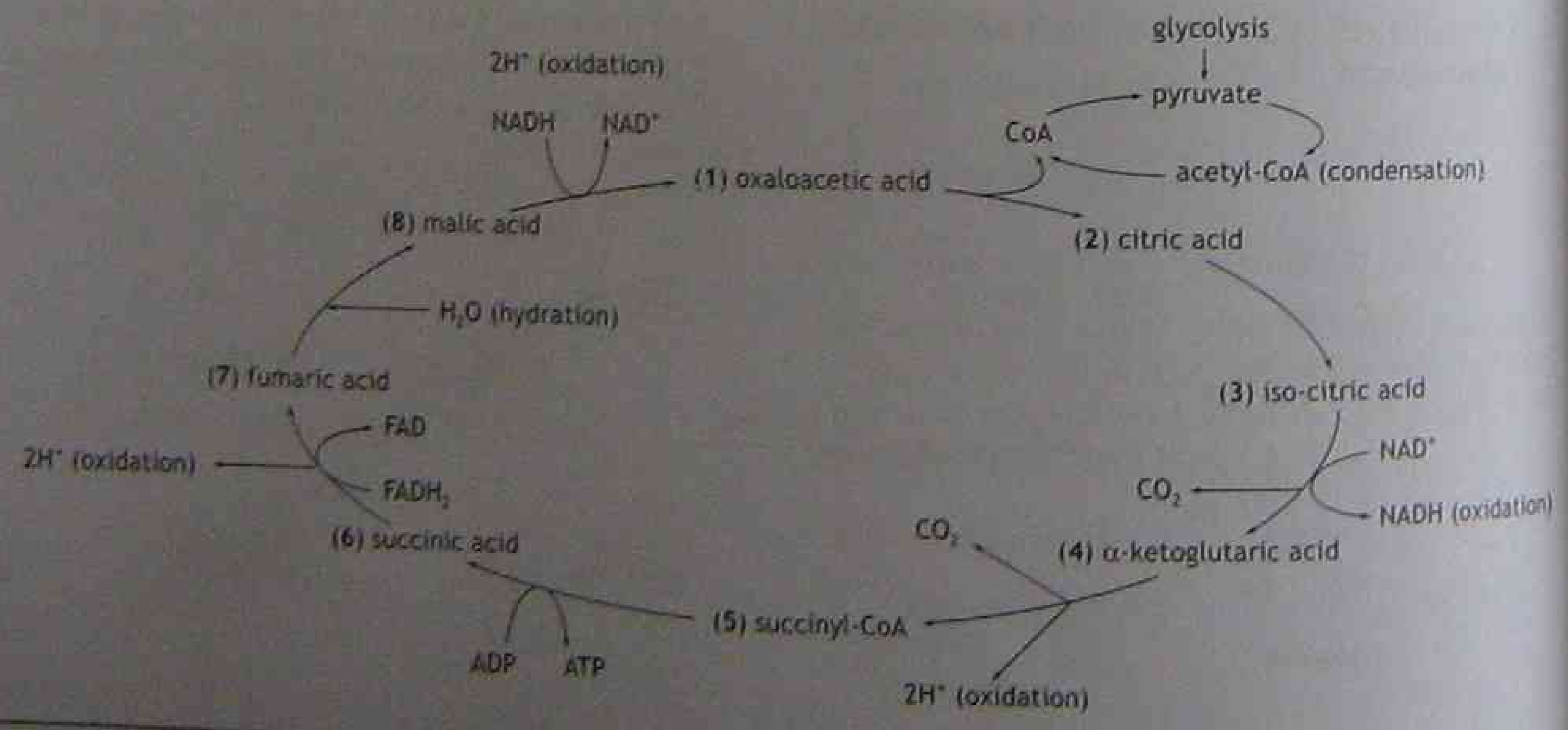


Figure 6.12 Krebs cycle

This reaction is catalysed by specific enzymes. Co-enzymes are involved in electron transfer, for example:

NAD^+ (oxidised form)
NADH (reduced form)

and

FAD (oxidised form)
$FADH_2$ (reduced form)

The Krebs cycle can be reduced to three simple steps:

(a) Pyruvate is converted to acetate which is bonded to co-enzyme A.

(b) Acetyl-CoA then combines with oxaloacetate to form citrate.

(c) Citrate is broken down by various enzymes producing two molecules of CO_2 and two molecules of ATP per molecule of glucose. Hydrogen atoms are lost and then used in the respiratory chain. Oxaloacetate is regenerated.

The importance of the Krebs cycle is that it is a source of molecules which are used up in the respiratory chain. These respiratory chain reactions allow the formation of 34 more molecules of ATP.

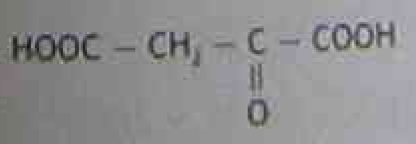
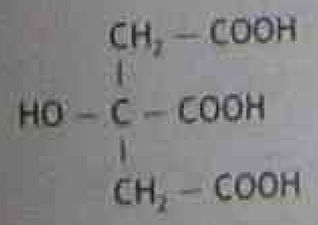
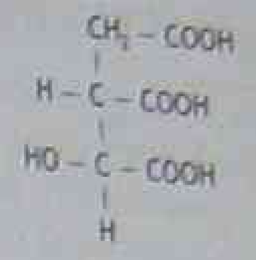
Twenty-four hydrogen ions come from the series of reactions of every molecule of glucose in cell respiration. At the end of a chain of reactions, energy is gradually lost and an electron is transferred to oxygen. Water is formed in the cell (see Section 6.10).

The overall equation for the metabolism of one molecule of glucose is

$$C_6H_{12}O_6 + 6H_2O + 6O_2 + 38ADP + 38\ \text{phosphates}\ (P_i)$$
$$\rightarrow 6CO_2 + 12H_2O + 38ATP$$

Of the 38 molecules of ATP produced, two result from glycolysis, two come from the Krebs cycle and the remaining 34 are produced in the respiratory chain.

Chemical formulae of acids involved in the Krebs cycle

Oxaloacetic acid	 $HOOC-CH_2-\underset{\underset{O}{\Vert}}{C}-COOH$
Citric acid	 $\begin{array}{c} CH_2-COOH \\ \vert \\ HO-C-COOH \\ \vert \\ CH_2-COOH \end{array}$
Isocitric acid	 $\begin{array}{c} CH_2-COOH \\ \vert \\ H-C-COOH \\ \vert \\ HO-C-COOH \\ \vert \\ H \end{array}$
α-ketoglutaric acid	$HOOC-CO-CH_2-CH_2-COOH$
Succinic acid	$HOOC-CH_2-CH_2-COOH$
Fumaric acid	$HOOC-CH=CH-COOH$
Malic acid	$HOOC-CH_2-CHOH-COOH$

Each turn around in the Krebs cycle uses up one acetyl group and regenerates a molecule of oxaloacetic acid ready to begin the sequence again. In the course of these steps, some of the energy released by the oxidation of the carbon-carbon and carbon-hydrogen bonds is used to convert ADP to ATP (one molecule per cycle).

$$ADP + P_i \rightarrow ATP$$

where P_i indicates inorganic phosphate available as a phosphate ion in solution in the cytoplasm. A high-energy bond is formed.

Some energy is used to produce NADH from NAD^+ (NAD is nicotinamide adenine dinucleotide). Three molecules of NADH are formed per cycle. In addition, some energy is used to reduce a second electron carrier (flavin adenine dinucleotide). One molecule of $FADH_2$ is formed from FAD per turn of the cycle. The high energy compounds NADH and $FADH_2$ are involved in respiration. Oxygen (O_2) is required for the Krebs cycle. The electrons and protons removed in the oxidation of carbon are all accepted by NAD^+ and FAD. The NADH/$FADH_2$ reduction with ATP production can be seen as a redox process, so the ATP used in muscle is continually regenerated.

Summary of the Krebs cycle

$$\text{oxaloacetic acid} + \text{acetyl CoA} + ADP +$$
$$P_i + 3NAD^+ + FAD \rightarrow$$
$$\text{oxaloacetic acid} + 2CO_2 + CoA + ATP +$$
$$3NADH + FADH_2 + 3H^+ + H_2O$$

The energy yield of the Krebs cycle is one molecule of ATP, three molecules of NADH and one molecule of $FADH_2$.

For one molecule of glucose, the Krebs cycle would yield double the energy yield shown above (2ATP, 6NADH and $2FADH_2$ molecules).

6.10 Aspects of electron transport

The carbon atoms of the glucose molecules are now completely oxidised. Some of the energy of glucose has been used to produce ATP from ADP. Most of its energy remains in electrons removed from C–C and C–H bonds and is passed stepwise to the electron carriers NAD^+ and FAD. These electrons are still at a high energy level. In the final stage of oxidation of glucose, these carriers form the electron transport chain.

This chain consists of a series of steps, many of which involve iron-containing enzymes called cytochromes. Each iron atom alternately accepts and releases an electron along to the next cytochrome at a slightly lower energy level until the electrons are combined with oxygen. In these processes, the iron (III) is reduced to iron (II) in receiving an electron and oxidised from iron (II) to iron (III) in transferring an electron. Cytochrome oxidase, the last of the enzymes in the chain, transfers an electron to form the reduced cytochrome. This reacts with molecular oxygen and hydronium ions (H_3O^+) in the cell to form water. The chain of electron carriers and enzymes is embedded in the inner membranes of the mitochondria. Each time a pair of electrons passes down the electron transport chain, ATP molecules are formed from ADP and P_i (phosphate).

The use of electron energy released by NADH and $FADH_2$ during cellular respiration to phosphorylate (add a phosphate group onto) ADP to yield energy-rich ATP is called *oxidative phosphorylation*. Oxidative phosphorylation is regulated by supply and demand. Electrons flow along the electron transport chain only if ADP is available to be converted to ATP. (See further discussion in Section 6.32.)

Overall energy harvest for each molecule of glucose

Glycolysis

$$2NADH \rightarrow \begin{matrix} 2ATP \\ 6ATP \end{matrix} \rightarrow 8ATP$$

Respiration

pyruvic acid → acetyl CoA 1NADH →
3ATP (×2) 6ATP

Krebs cycle

→ 1ATP
3NADH → 9ATP → (×2) 24ATP
$1FADH_2$ → 2ATP

How energy metabolism works

- Organisms extract energy from compounds by oxidising them to CO_2 and H_2O.
- NAD^+ is the main oxidising agent.
- NADH gives up its electrons to the electron acceptors in the electron transport chain.
- The electrons are passed down the chain ultimately to oxygen.
- The energy released by the electron acceptors of the electron transport chain is used to phosphorylate ADP, converting it to ATP.
- ATP is used to drive the endergonic reactions of the organism.
- NADH and ATP are used in cyclic fashion. The need for a constant supply of these molecules explains why deprivation of oxygen causes rapid death.
- Most organisms do not feed directly on glucose. In humans, glycogen is converted to glucose and phosphorylate to glucose 6-phosphate before entering the glycolytic pathway. Fats are first split into fatty acids and glycerol and then are chopped into two-carbon fragments before entering the Krebs cycle as acetyl-CoA. Proteins are broken down into their amino acids, then deaminated (i.e. amino groups are removed) before the carbon skeleton may enter the Krebs cycle. These pathways are called catabolic pathways.
- Each mole of glucose oxidised in the cell yields 2.87×10^3 kJ, of which about 1.27×10^3 kJ is stored (in the 38 ATP molecules produced per molecule of glucose). Cellular oxidation of glucose leads to the storage of about 44% of the available energy. The stored energy can be used in muscular work and other energy demanding processes.

Overall reaction for metabolism of glucose in humans

$$C_6H_{12}O_6 + 6H_2O + 6O_2 + 38ADP + 38\text{ phosphates }(P_i) \rightarrow$$
$$6CO_2 + 12H_2O + 38ATP$$

Glycolysis sequence

$$C_6H_{12}O_6 \rightarrow$$
$$2CH_3COCOOH + 2ATP + 4e^- \text{ to chain} + 4H^+$$

Krebs or TCA cycle

$$6H_2O + 2CH_3COCOOH \rightarrow$$
$$6CO_2 + 2ATP + 20e^- \text{ to chain} + 20H^+$$

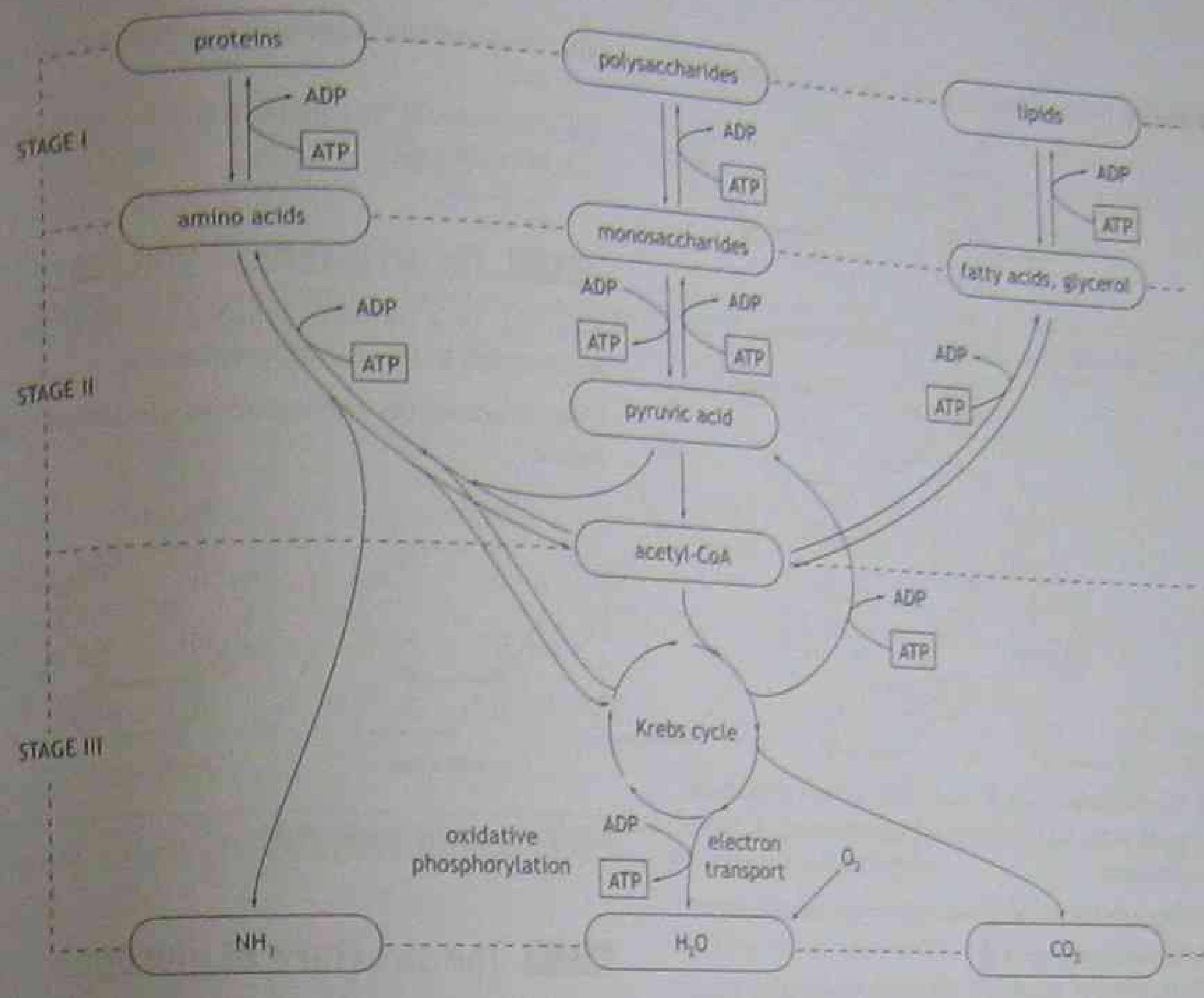


Figure 6.13 Major metabolic pathways in cells

Electron-transport chain

$$24e^- + 6O_2 + 24H^+ \rightarrow 12H_2O + 34ATP$$

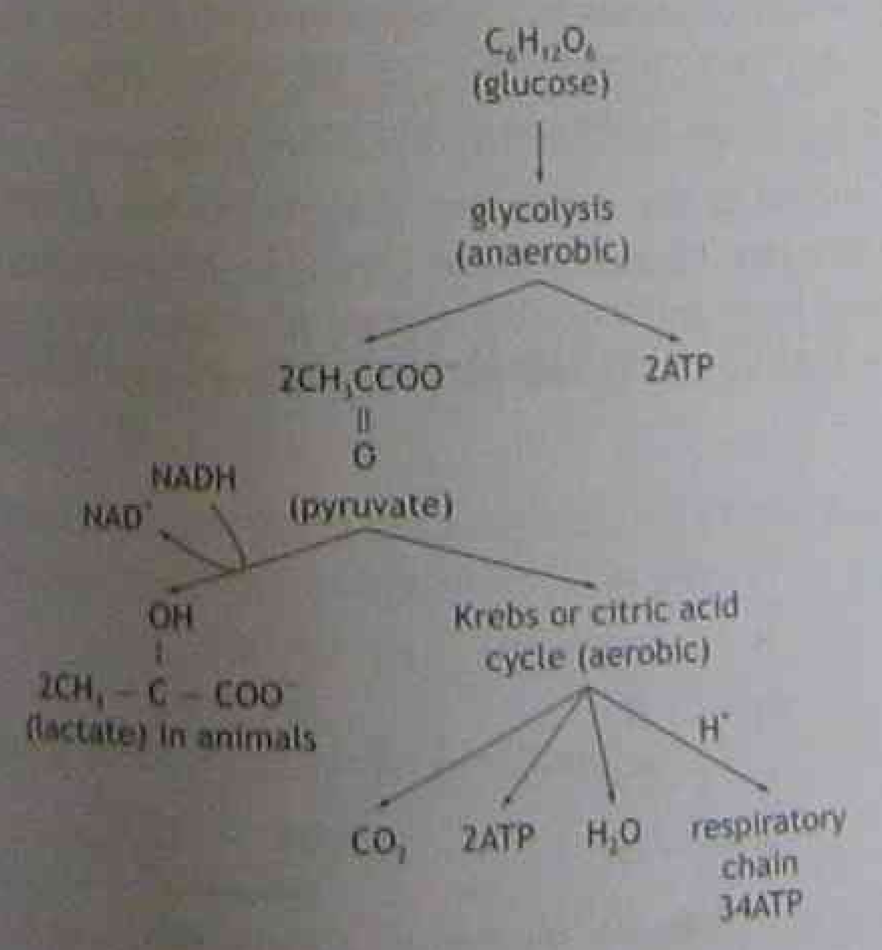


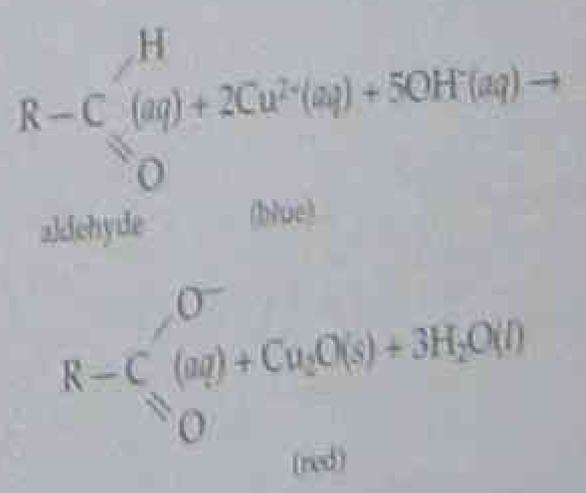
Figure 6.14 The metabolism of glucose in humans

Test for a reducing sugar (glucose)

This test involves the use of *Benedict's solution* (a complex copper II basic salt with citric ions).

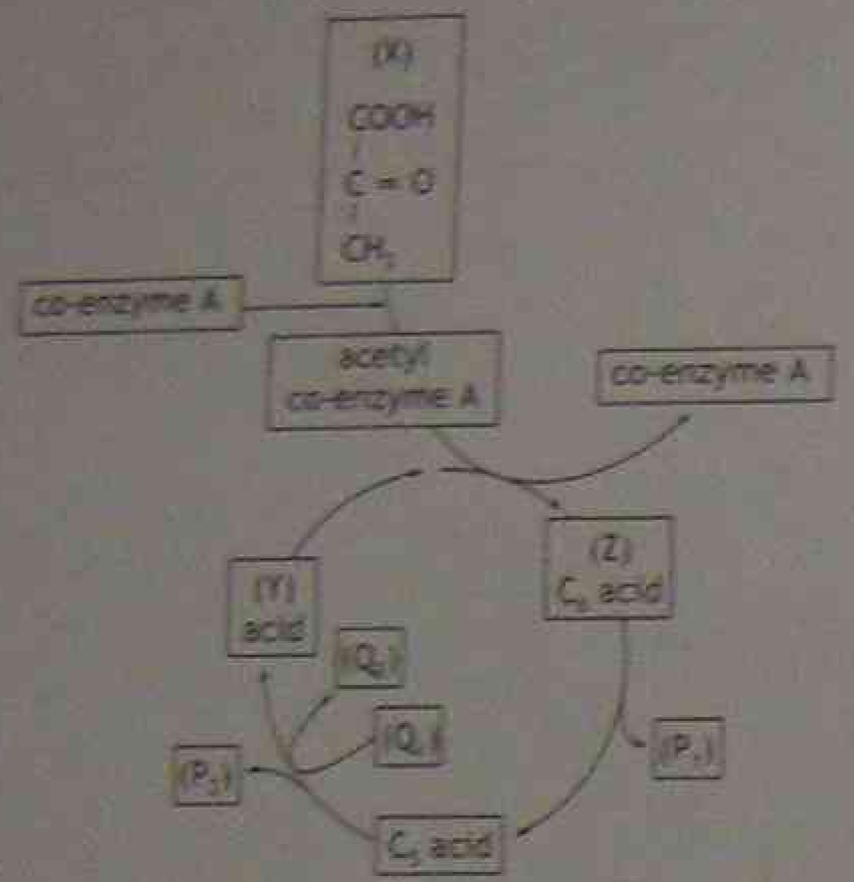
A sample is heated in a water bath with the Benedict's solution (containing blue Cu^{2+} ions). Copper (II) ions are reduced to copper (I) ions which form red copper (I) oxide as a precipitate in alkaline solution.

Reducing sugars in solution contain some open-chain aldehydes.



$$R{-}CHO(aq) + 2Cu^{2+}(aq) + 5OH^-(aq) \rightarrow R{-}COO^-(aq) + Cu_2O(s) + 3H_2O(l)$$

Exercise 6.1



(a) Name substance X and state which metabolic pathway has produced compound X from glucose.

(b) Explain why acid Y has only four carbon atoms.

(c) Name compound Z.

(d) Products P_1 and P_2 are the same substance. How is it removed from the body?

(e) This reaction is catalysed by specific enzymes. Name possible co-enzymes Q_1 and Q_2 and state their function in living cells.

(f) (i) Name the modified cycle shown in the diagram above.
  (ii) Where does the reaction occur?
  (iii) Is the reaction aerobic or anaerobic?

6.11 Carbohydrates

The general formula for carbohydrates is $C_x(H_2O)_y$. Carbohydrates are found in large amounts in living systems. They are important as

(a) sources of energy;

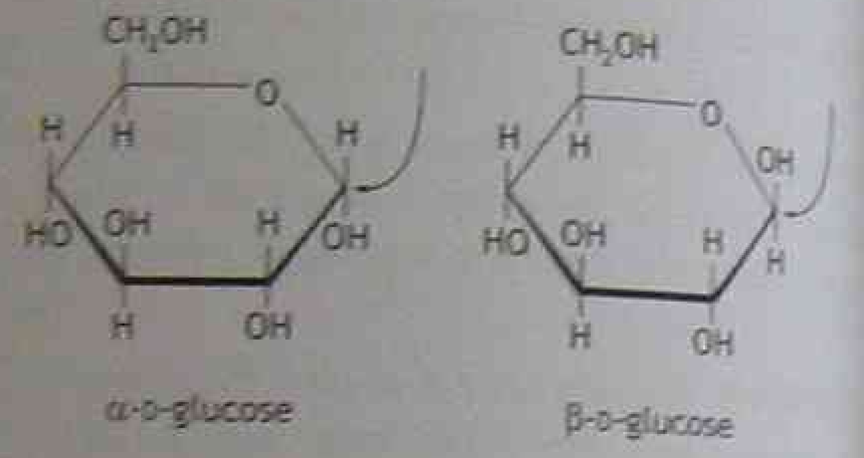
(b) structural and supportive components of cells and

(c) components in genetic control of growth and development.

6.12 The structure of glucose

Glucose is a monosaccharide which can be represented in several different ways.

Optical isomerism also occurs in glucose as shown below.



α-D-glucose β-D-glucose

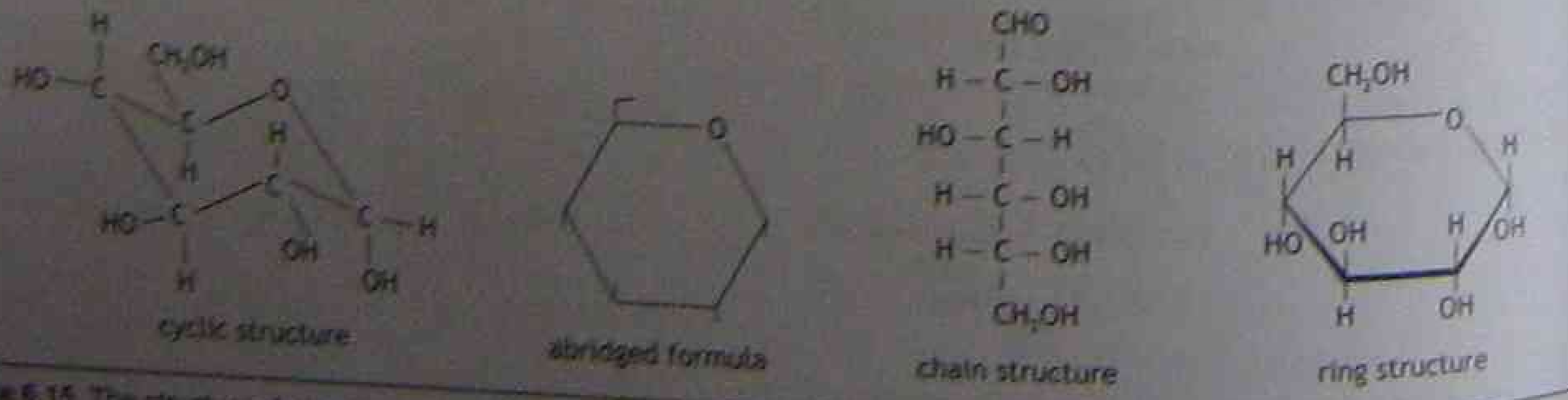
Figure 6.16 Optical isomers of glucose

6.13 The structure of glycogen

The presence of five hydroxyl (OH) groups allows condensation polymers to form. The backbone of the polymers is between the first carbon atom on one glucose molecule and the fourth carbon atom on the second molecule (see Figure 6.17).

Such condensation may occur with α-D-glucose or β-D-glucose. In addition, there may be branching. The branch points in glycogen involve the first atom on one glucose molecule and the sixth carbon atom in a glucose molecule in the backbone.

Glucose is the monomer that forms the polymer glycogen. Humans store glycogen as granules in their liver and muscles. Stored glycogen can easily be hydrolysed to release glucose (see Figure 6.18).



cyclic structure abridged formula chain structure ring structure

Figure 6.15 The structure of glucose

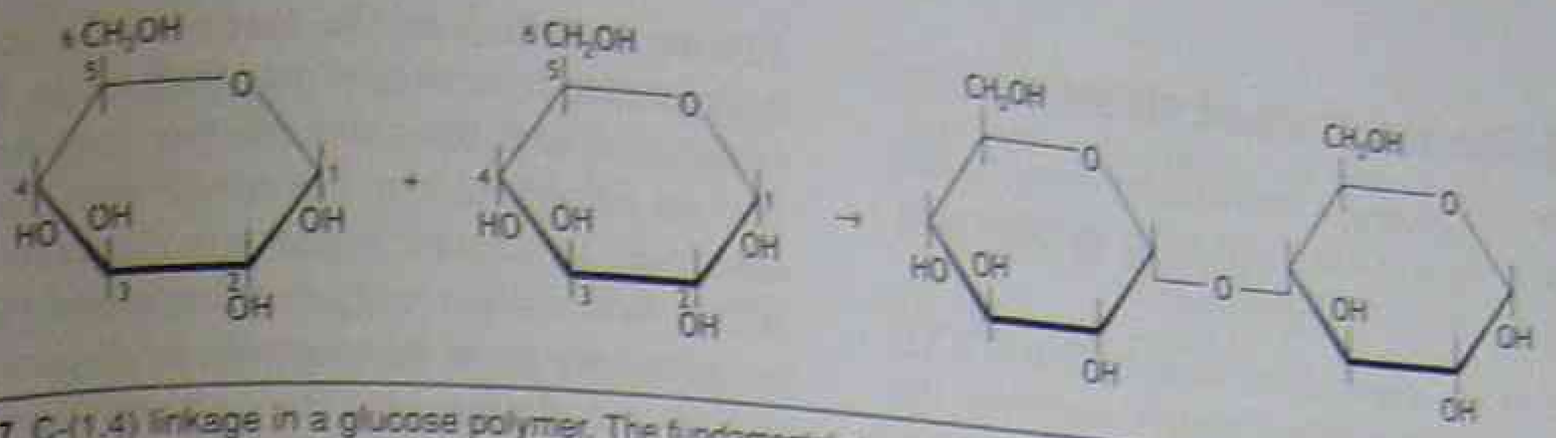


Figure 6.17 C-(1,4) linkage in a glucose polymer. The fundamental structure of glycogen is this 'amylose chain'.

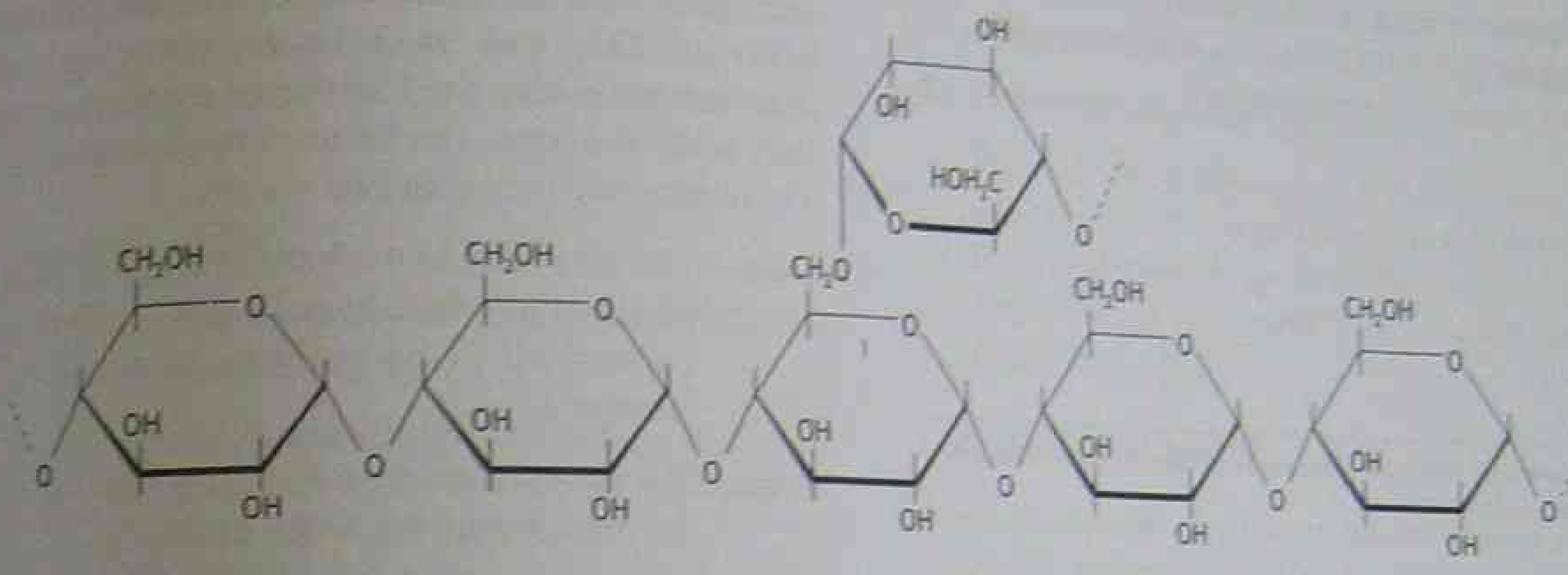


Figure 6.18 Branched structure of glycogen with α(1 → 6) branches on every fourth glucose residue

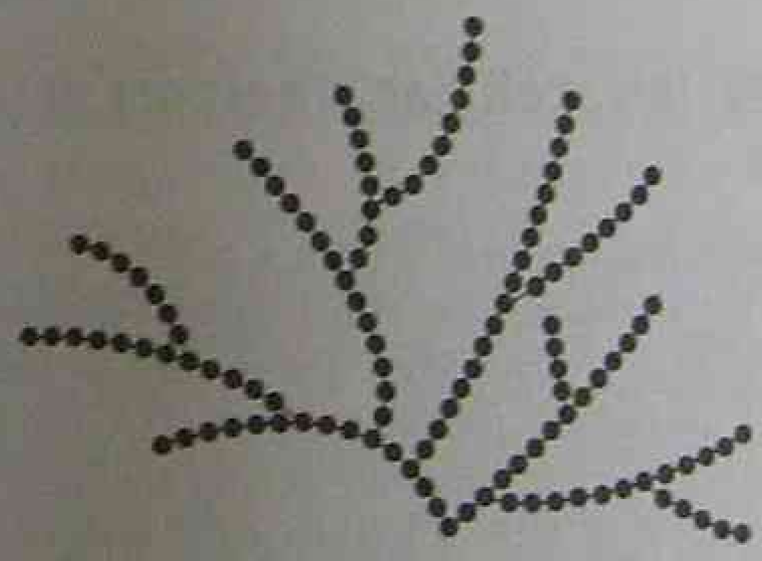
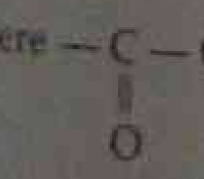


Figure 6.19 A cross section of glycogen shows a tree-like structure created by branched amylose chains (each • represents a glucose molecule).

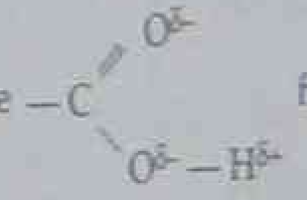
6.14 Fats and oils (lipids) as fuel for cells

Saturated fatty acids are long-chain alkanoic acids with the general molecular formula

$$CH_3(CH_2)_nCOOH$$



where $-\underset{\underset{O}{\|}}{C}-OH$ is the functional group.

- Over 70 fatty acids have been isolated from cells and tissues.
- Nearly all fatty acids have an even number of carbon atoms (usually 16–20) in an unbranched chain.
- Unsaturated fatty acids have lower melting points than their saturated equivalents.
- The  $-C\begin{smallmatrix} \diagup\!\!\!\!= O^{\delta-} \\ \diagdown O^{\delta-}-H^{\delta+} \end{smallmatrix}$ functional group is highly polar so that in a very polar solvent, e.g. a large volume of water, it is possible that a mono-molecular layer could form.

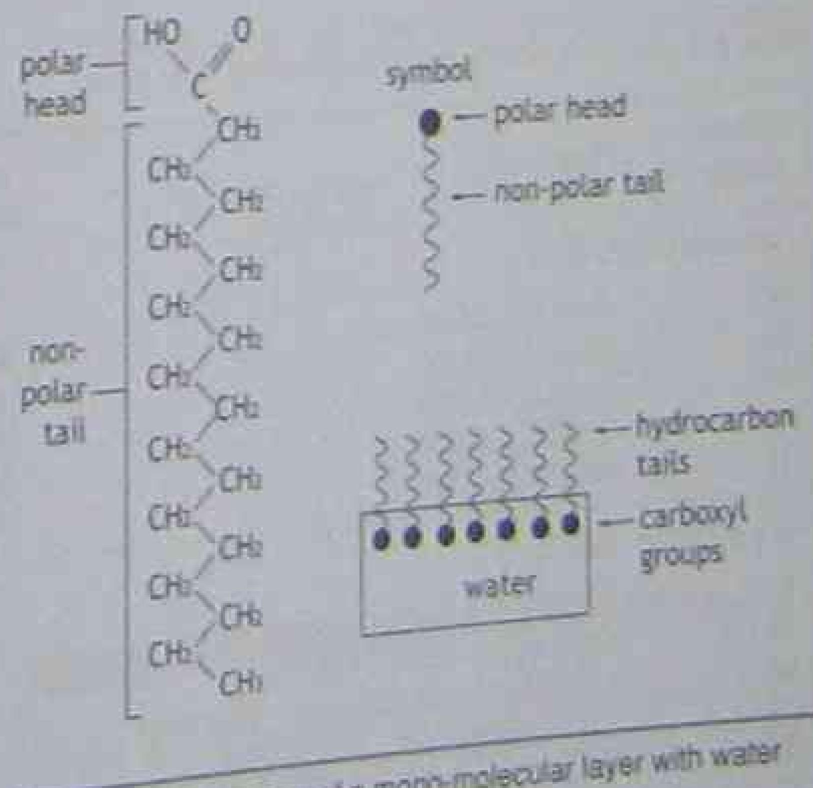


Figure 6.20 Formation of a mono-molecular layer with water

6.15 The structure of glycerol

$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Glycerol, a sweet-tasting syrupy liquid, is an alkane triol hence its systematic name 1,2,3-propanetriol.

Because of the presence of three hydroxyl (OH) groups on such a small carbon skeleton, the molecule will be highly polar. This accounts for its extremely high melting point (290°C), its high specific gravity (1.26) and its miscibility with water and ethanol in all proportions.

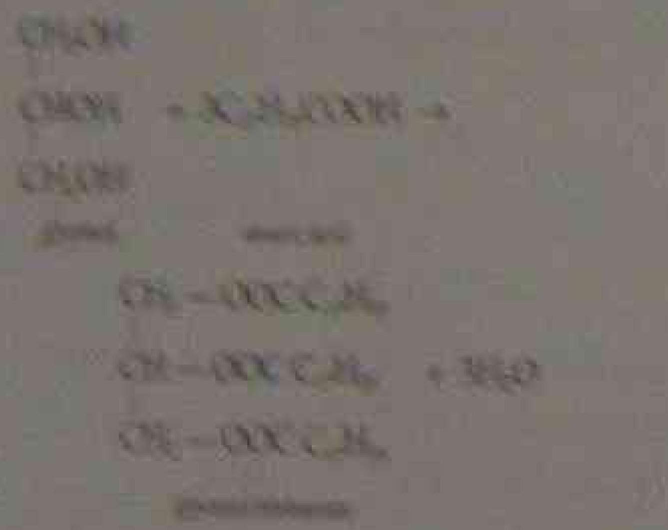
Figure 6.21 Hydrogen bonding between a glycerol molecule and a water molecule

6.16 Esters of fatty acids

Common neutral fats and oils are called triesters of glycerol, or more correctly triacylglycerols (TAGs). In the formation of fats:

glycerol + fatty acids → fat + water

Example



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \quad + 3C_{17}H_{35}COOH \rightarrow \\ | \\ CH_2OH \end{array}$$

$$\begin{array}{l} CH_2-OOCC_{17}H_{35} \\ | \\ CH-OOCC_{17}H_{35} \quad + 3H_2O \\ | \\ CH_2-OOCC_{17}H_{35} \end{array}$$

Fats are formed from the reaction of glycerol with hydrophobic (water-repelling) fatty acids. The water is removed and the product, fat, is hydrophobic. Fats are soluble in non-polar solvents. Fats are an energy-dense source for humans and provide about 30% of their daily energy requirements. Fatty acids are necessary fuels for animals and stored within cells as triacylglycerols. They are released through the bloodstream to meet tissue demands (especially from muscles). The complete combustion of fatty acids to CO_2 and H_2O takes place in the mitochondria where the transfer of electrons from fatty acids to oxygen can be used to generate ATP. The combustion occurs in two stages:

Stage 1: The fatty acid, in the form of a highly polar co-enzyme A thiol ester, is first oxidised to convert all of its carbons to acetyl co-enzyme A.

Stage 2: The acetyl co-enzyme A is then oxidised by the reactions of the Krebs cycle.

Both stages generate ATP by oxidative phosphorylation.

6.17 Intracellular transport of fatty acids

Free fatty acids appear within a cell by absorption from the extracellular fluid or by intracellular hydrolysis of triglycerides. Those used as fuels are mainly long-chain compounds (16–18 C) with 0–2 double bonds. The fatty acid is first combined with co-enzyme A to form a highly polar water-soluble thiol ester. These compounds are called acyl co-enzyme A products and are like acetyl co-enzyme A in structure except that they are made from long-chain fatty acids instead of two-carbon acetic acid. The fatty acids are converted to acyl co-enzyme A at two locations, the endoplasmic reticulum and the mitochondria. When the molecules of acyl co-enzyme A reach the inner surface of the mitochondria, oxidation can occur which results in the liberation of an acetyl co-enzyme A molecule and the formation of a new acyl co-enzyme A compound that is two carbons shorter than the original. The whole process is repeated until the entire long-chain acyl group has been chopped into two-carbon acetyl groups which can then be oxidised by the Krebs cycle.

Table 6.1 Some important naturally occurring fatty acids

Carbon atoms	Structure	Systematic name	Common name	Melting point (°C)
Saturated fatty acids				
12	$CH_3(CH_2)_{10}COOH$	dodecanoic	lauric	44
14	$CH_3(CH_2)_{12}COOH$	tetradecanoic	myristic	58
16	$CH_3(CH_2)_{14}COOH$	[illegible]	palmitic	63
18	$CH_3(CH_2)_{16}COOH$	[illegible]	stearic	70
20	$CH_3(CH_2)_{18}COOH$	[illegible]	arachidic	77
Unsaturated fatty acids				
16	[illegible]	[illegible]	palmitoleic	−1
18	[illegible]	[illegible]	oleic	16
18	[illegible]	[illegible]	linoleic	−5
[illegible]	[illegible]	[illegible]	linolenic	−11
[illegible]	[illegible]	[illegible]	arachidonic	−49

Digestion of fat

1. Bile, produced in the liver and stored in the gall bladder, emulsifies fats.
2. The lipases break down fats to fatty acids and glycerol in the small intestine. Lipases are produced in the pancreas.

6.18 Glycolysis and fatty acids

Glycolysis is the first stage of respiration and involves the anaerobic decomposition of glucose to release energy. The enzymes of glycolysis are found in the cytoplasm of cells and the end product is 2-oxopropanoate (pyruvate). One result of the cell's energy requirements being met, as a result of the oxidation of fatty acids, is an accumulation of acetyl co-enzyme A. This increase in the amount of acetyl co-enzyme A leads to an increase in the conversion of pyruvate to oxaloacetate then diverts the carbons of pyruvate to glucose. (See also the detailed discussion of glycolysis in Section 6.7.)

6.19 Proteins

All proteins contain certain atoms of the elements carbon, hydrogen, oxygen and nitrogen and may also contain small amounts of sulfur. Living organisms are constantly building up and breaking down proteins. The body mass of mammals, for example, contains a large percentage of protein. Foods containing animal proteins include milk, meat, fish and eggs whereas plant proteins can be found in nuts, legumes and soya beans. Proteins are made up of amino acid chains and of the 20 amino acids needed by humans, ten can be synthesised starting from carbohydrate and lipid residues, a source of nitrogen and enzyme catalysts. The remaining proteins must be ingested and are called 'essential' amino acids.

Functions of proteins

(a) Structural proteins

These are 'fibrous' proteins and may be elastic or coiled proteins, for example, keratin found in hair or wool, or inelastic proteins, for example, collagen found in skin, tendons and cartilage.

(b) Physiologically-active proteins

These include enzymes, some hormones, nucleoproteins and blood proteins. Proteins therefore can be used as both structural molecules and as enzymes to catalyse metabolic reactions.

Composition of proteins

Proteins consist of various combinations of a relatively small number of amino acids.

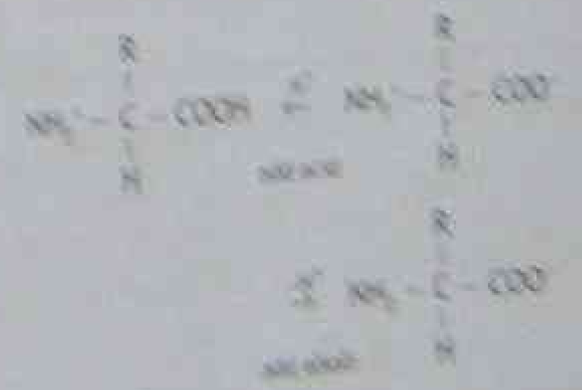
Structure of amino acids

All contain at least one primary amino group ($-NH_2$) and one or more carboxylic acid groups.

General formula

(R = side chain)

It is the side chain that makes the amino acid unique and determines the specific properties of each protein. The dual basic-acidic (amphoteric) character of amino acids gives rise to their ionic behaviour.



6.20 Linkages found in proteins

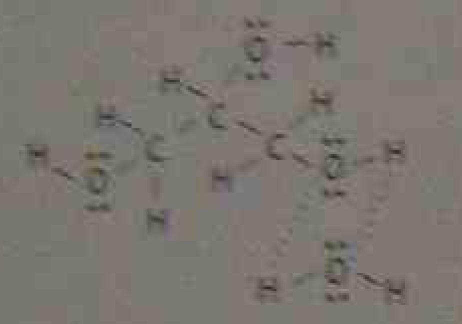
There are a number of reactive points in the structure of amino acids which make possible a

6.15 The structure of glycerol

$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Glycerol, a sweet-tasting syrupy liquid, is an alkane triol hence its systematic name 1,2,3-propanetriol.

Because of the presence of three hydroxyl (OH) groups on such a small carbon skeleton, the molecule will be highly polar. This accounts for its extremely high melting point (290°C), its high specific gravity (1.26) and its miscibility with water and ethanol in all proportions.



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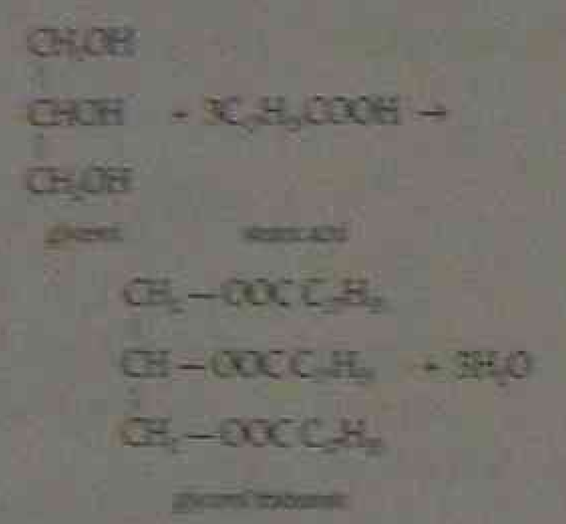
Example



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + 3C_{17}H_{35}COOH \rightarrow \begin{array}{l} CH_2-OOCC_{17}H_{35} \\ | \\ CH-OOCC_{17}H_{35} \\ | \\ CH_2-OOCC_{17}H_{35} \end{array} + 3H_2O$$

glycerol stearic acid

glycerol tristearate

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Both stages generate ATP by oxidative phosphorylation.

6.17 Intracellular transport of fatty acids

Free fatty acids appear within a cell by absorption from the extracellular fluid or by intracellular hydrolysis of triglycerides. Those used as fuels are mainly long-chain compounds (16–18 C) with 0–2 double bonds. The fatty acid is first combined with co-enzyme A to form a highly polar water-soluble thiol ester. These compounds are called acyl co-enzyme A products and are like acetyl co-enzyme A in structure except that they are made from long-chain fatty acids instead of two-carbon acetic acid. The fatty acids are converted to acyl co-enzyme A at two locations, the endoplasmic reticulum and the mitochondria. When the molecules of acyl co-enzyme A reach the inner surface of the mitochondria, oxidation can occur which results in the liberation of an acetyl co-enzyme A molecule and the formation of a new acyl co-enzyme A compound that is two carbons shorter than the original. The whole process is repeated until the entire long-chain acyl group has been chopped into two-carbon acetyl groups which can then be oxidised by the Krebs cycle.

Table 6.1 Some important naturally occurring fatty acids

Carbon atoms	Structure	Systematic name	Common name	Melting point (°C)
Saturated fatty acids				
12	$CH_3(CH_2)_{10}COOH$	dodecanoic	lauric	44
14	$CH_3(CH_2)_{12}COOH$	tetradecanoic	myristic	58
16	$CH_3(CH_2)_{14}COOH$	hexadecanoic	palmitic	63
18	$CH_3(CH_2)_{16}COOH$	octadecanoic	stearic	70
20	$CH_3(CH_2)_{18}COOH$	eicosanoic	arachidic	77
Unsaturated fatty acids				
16	$CH_3(CH_2)_5CH=CH(CH_2)_7COOH$		palmitoleic	−1
18	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$		oleic	16
18	$CH_3(CH_2)_4CH=CHCH_2CH=CH(CH_2)_7COOH$		linoleic	−5
18	$CH_3CH_2(CH=CHCH_2)_3(CH_2)_6COOH$		linolenic	−11
20	$CH_3(CH_2)_3(CH_2CH=CH)_4(CH_2)_3COOH$		arachidonic	−49

Digestion of fat

1. Bile, produced in the liver and stored in the gall bladder, emulsifies fats.
2. The lipases break down fats to fatty acids and glycerol in the small intestine. Lipases are produced in the pancreas.

6.18 Glycolysis and fatty acids

Glycolysis is the first stage of respiration and involves the anaerobic decomposition of glucose to release energy. The enzymes of glycolysis are found in the cytoplasm of cells and the end product is 2-oxopropanoate (pyruvate). One result of the cell's energy requirements being met, as a result of the oxidation of fatty acids, is an accumulation of acetyl co-enzyme A. This increase in the amount of acetyl co-enzyme A leads to an increase in the conversion of pyruvate to oxaloacetate then diverts the carbons of pyruvate to glucose. (See also the detailed discussion of glycolysis in Section 6.7.)

6.19 Proteins

All proteins contain certain atoms of the elements carbon, hydrogen, oxygen and nitrogen and may also contain small amounts of sulfur. Living organisms are constantly building up and breaking down proteins. The body mass of mammals, for example, contains a large percentage of protein. Foods containing animal proteins include milk, meat, fish and eggs whereas plant proteins can be found in nuts, legumes and soya beans. Proteins are made up of amino acid chains and of the 20 amino acids needed by humans, ten can be synthesised starting from carbohydrate and lipid residues, a source of nitrogen and enzyme catalysts. The remaining proteins must be ingested and are called 'essential' amino acids.

Functions of proteins

(a) Structural proteins

These are 'fibrous' proteins and may be elastic or coiled proteins, for example, keratin found in hair or wool, or inelastic proteins, for example, collagen found in skin, tendons and cartilage.

(b) Physiologically-active proteins

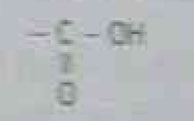
These include enzymes, some hormones, nucleoproteins and blood proteins. Proteins therefore can be used as both structural molecules and as enzymes to catalyse metabolic reactions.

Composition of proteins

Proteins consist of various combinations of a relatively small number of amino acids.

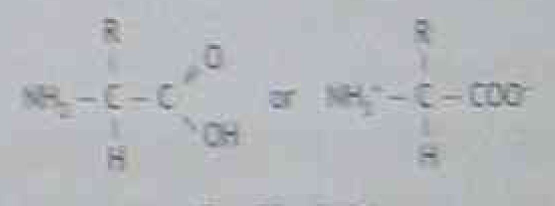
Structure of amino acids

All contain at least one primary amino group ($-NH_2$) and one or more carboxylic acid groups.



$$-\underset{\underset{\displaystyle O}{\|}}{C}-OH$$

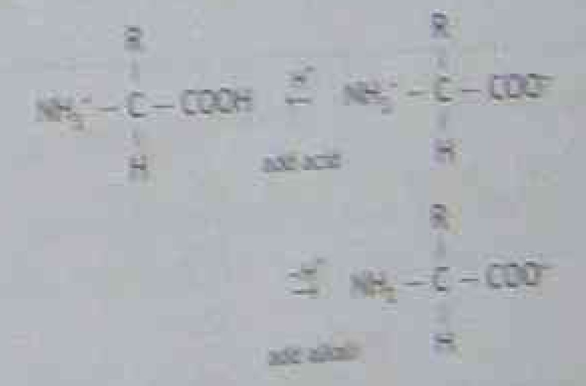
General formula



$$NH_2-\underset{H}{\overset{R}{\underset{|}{\overset{|}{C}}}}-C\begin{array}{l}{}^{\nearrow O}\\{}_{\searrow OH}\end{array} \quad \text{or} \quad NH_3^+-\underset{H}{\overset{R}{\underset{|}{\overset{|}{C}}}}-COO^-$$

(R = side chain)

It is the side chain that makes the amino acid unique and determines the specific properties of each protein. The dual basic-acidic (amphoteric) character of amino acids gives rise to their ionic behaviour.

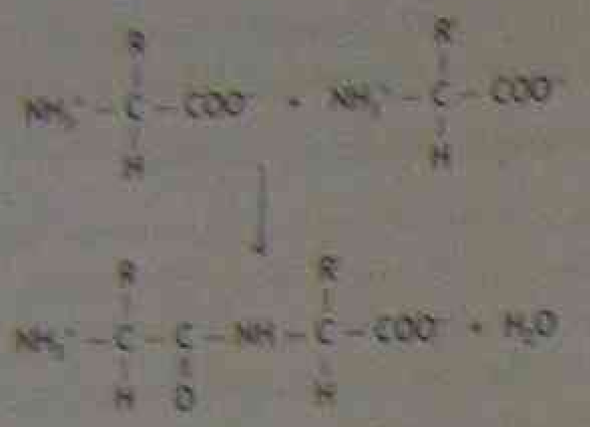


$$NH_3^+-\underset{H}{\overset{R}{\underset{|}{\overset{|}{C}}}}-COOH \underset{\text{add acid}}{\overset{H^+}{\rightleftharpoons}} NH_3^+-\underset{H}{\overset{R}{\underset{|}{\overset{|}{C}}}}-COO^- \underset{\text{add alkali}}{\overset{OH^-}{\rightleftharpoons}} NH_2-\underset{H}{\overset{R}{\underset{|}{\overset{|}{C}}}}-COO^-$$

6.20 Linkages found in proteins

There are a number of reactive points in the structure of amino acids which make possible a variety of linkages. Proteins are made by the linking of amino acids and the main links may be called *amide links* or *peptide bonds*. This linkage involves a condensation reaction between the anion (COO^-) of one amino acid and the cation NH_3^+ of another with the elimination of a water molecule.

Example



$$NH_3^+-\underset{H}{\overset{R}{C}}-COO^- + NH_3^+-\underset{H}{\overset{R}{C}}-COO^- \rightarrow NH_3^+-\underset{H}{\overset{R}{C}}-\underset{\underset{O}{\|}}{C}-NH-\underset{H}{\overset{R}{C}}-COO^- + H_2O$$

where R and R′ are side chains and

$-\underset{\underset{O}{\|}}{C}-NH-$ is the peptide link.

Proteins readily undergo hydrolysis across the peptide link.

$$-\underset{\underset{O}{\|}}{C}-NH- + H-OH \rightarrow -\underset{\underset{O}{\|}}{C}-OH + -NH_2$$

Amino acids are formed. Other types of linkages are subsidiaries of the peptide linkage but are important in determining protein structure.

Disulfide linkage

If the R group forming the side chain contains sulfur atoms, for example, cysteine (see Figure 6.23) a disulfide bridge (–C–S–S–C) may be formed with the other cysteine molecules where S–S is a covalent bond.

Example

This is a section of the structural representation of insulin which was one of the first proteins to have its primary structure determined. It shows part of two polypeptide chains linked by disulfide bridges.

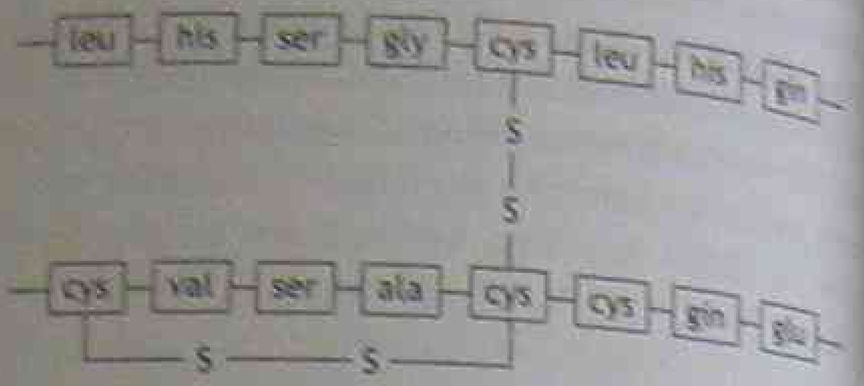


Figure 6.23 Structure of insulin

Electrostatic linkages

These can occur if pH conditions are suitable between adjacent ionised amino (NH_3^+) and carboxylate (COO^-) groups which are present.

Ionic bonds occur in proteins that have acidic and basic groups in their side chains. If the attached groups are in a position along the chain where bending allows them to come together, they remain forming a folded structure.

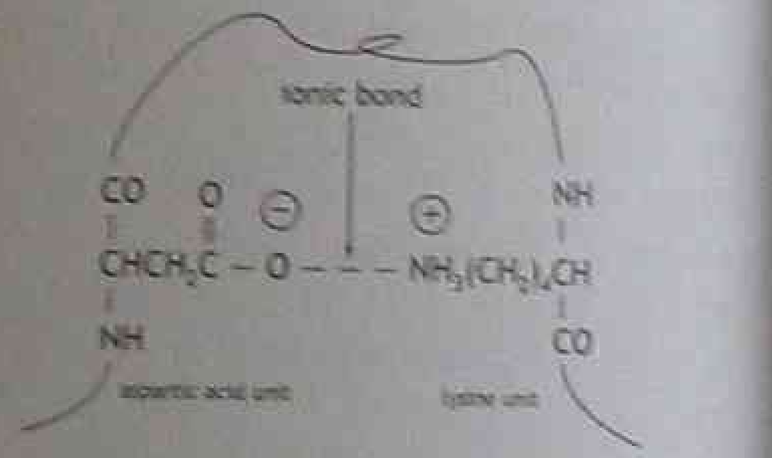


Figure 6.24 Ionic bonding in lysosomes

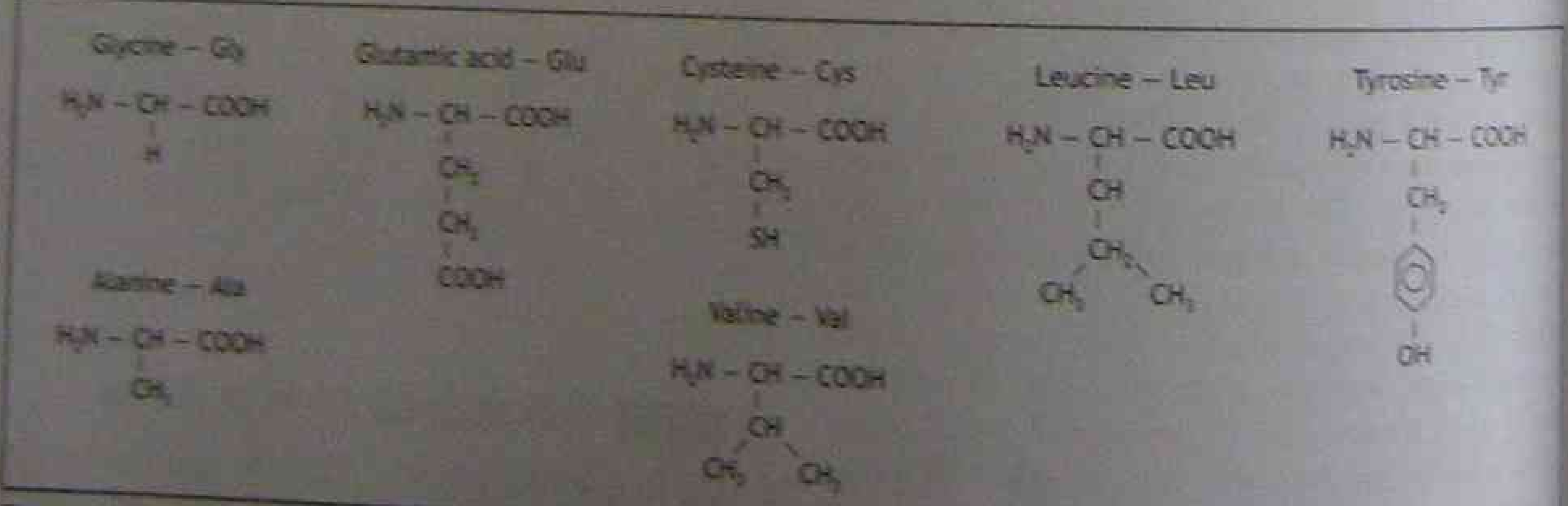


Figure 6.22 Formulae of some simple amino acids

Hydrogen bonds

These also result in folded protein structures and form between the N–H groups on side chains and carbonyl groups from the amide link (or peptide bond).

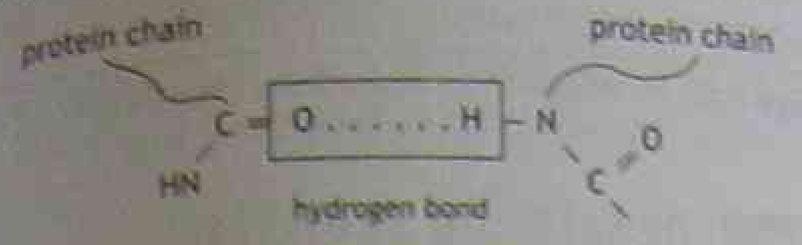


Figure 6.25 Hydrogen bonding between N–H groups and carbonyl groups from amide links or peptide bonds

Hydrogen bonds can also form between hydroxyl groups and peptide linkages.

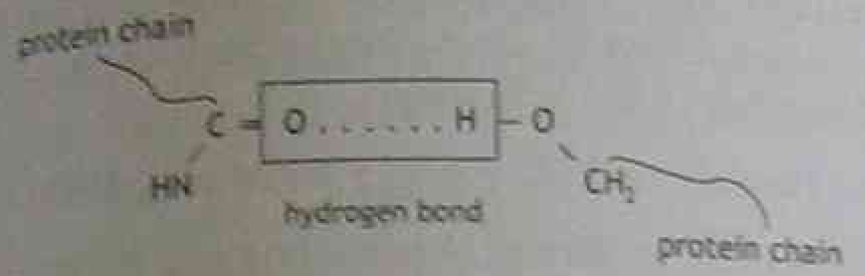


Figure 6.26 Hydrogen bonding between hydroxyl groups and peptide linkages

Hydrophobic interaction

Certain foldings of the protein chain may lead to a lower energy arrangement than others, e.g. a protein dissolved in an aqueous solution folds so that the non-polar hydrocarbon portions are tucked within the molecule whereas the more polar acidic and basic side-chain functional groups are projected into the solution. This is an important factor when stabilising proteins of high molecular mass, e.g. haemoglobin.

6.21 Structure of proteins

The occurrence of so many types of bonds between amino acids in proteins can give rise to different structures. These are described below.

Primary structure

This refers to the sequence of amino acid residues along the peptide chains, for example,

Figure 6.27 Amino acid sequence

Secondary structure

The polypeptides tend to form spirals and coils. The type of coil depends partly on the number of hydrogen bonds formed. They can be shown as:

(i) α helix structure as in wool fibres, or

(ii) β sheet structure as in silk.

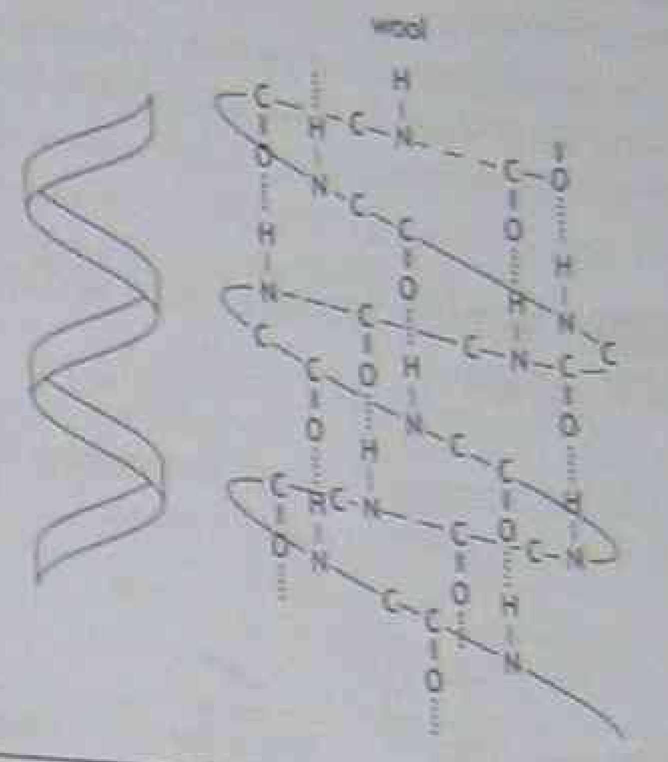


Figure 6.28 α helix structures

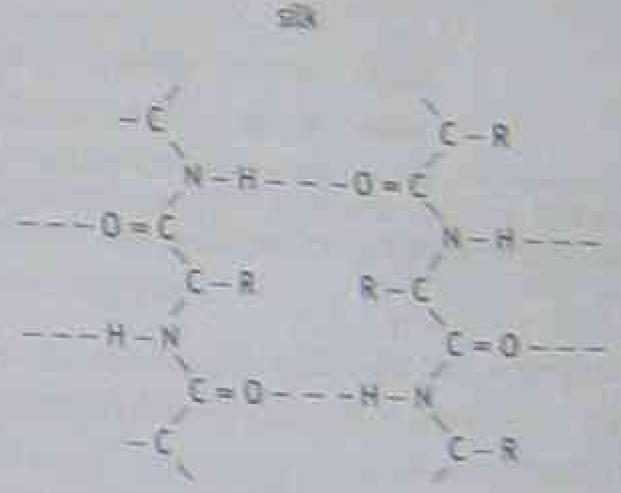


Figure 6.29 β sheet structure

Tertiary structure

This is the complete form of the chain. An important factor in forming this structure is the formation of hydrophobic bonds, for example, lysozyme, an enzyme found in many types of animal cells and body fluids.

Quaternary structure

Two or more polypeptide chains fit together to form a specific structure, for example, haemoglobin.

Figure 6.30 Haemoglobin

Summary

- Chain structure is the basis of proteins.
- Side chains are important in link formation between polypeptide strands, for example, disulfide link.
- The folded structure of protein is stabilised by disulfide bridges, hydrogen bonds and hydrophobic interaction.

6.22 Chemical features of a protein and its shape

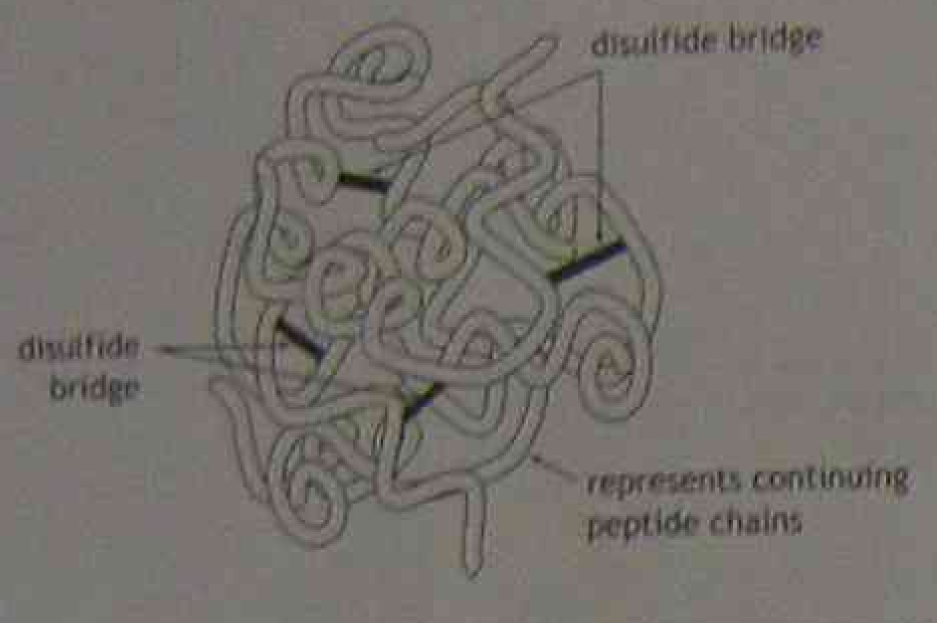


Figure 6.31 A representation of the *lysosome model* which shows the relationship between the chemical feature of a protein and its shape

To produce and stabilise the amount of coiling shown in Figure 6.31, various other intra-chain bonds must also occur in lysosomes. These include hydrogen bonding and ionic bonding. The side chains of lysosomes are hydrophobic (water-repellent) and stay together within the protein rather than become exposed to the water.

Lysosomes are found in the cytoplasm and contain enzymes to digest protein matter, e.g. bacteria and dead cells.

6.23 Enzymes in action

The part of the enzyme at which a reaction occurs is called the active site. Some side chains form bonds with the reactant (substrate) to serve as anchor points which hold the reactant in the active site.

The enzyme must operate specifically to get the right structure to act in the right manner with a special substrate, even though the actual chemistry appears simple, e.g. the hydrolysis of an amide bond (peptide link).

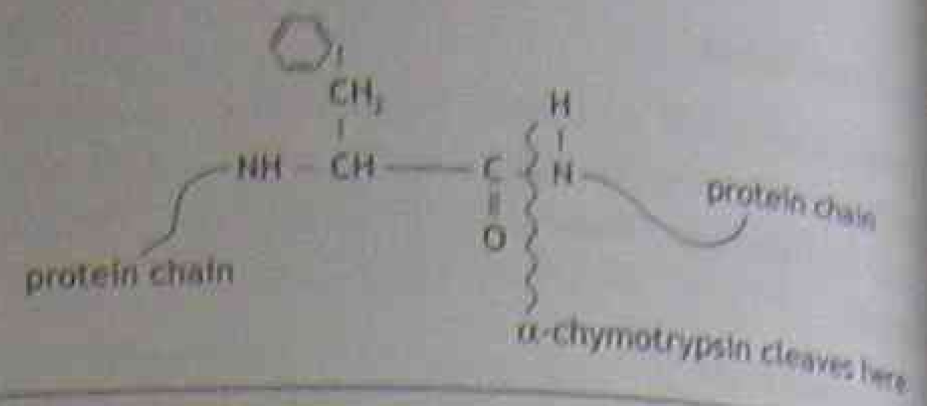


Figure 6.32 Hydrolysis of an amide bond (peptide link)

6.24 Denaturing proteins

Denaturation is a physical or chemical change causing a loss of biological activity. At the molecular level, although the primary structure is not changed, there can be unfolding or alteration of secondary, tertiary and quaternary structures. Globular proteins found in living organisms are readily denatured by the following:

(a) Heat above 60°C, e.g. egg white coagulates.

(b) Shaking or stirring, e.g. beating egg whites.

(c) Changing pH markedly by adding acid or alkali. This disrupts electrostatic bonding between $-COO^- \ldots H_3N^+-$ links

(d) Adding organic solvents, for example, acetone or ether. This disrupts the hydrogen bonds.

(e) Adding detergents such as SDS which exposes the non-polar side chains of the protein to water. In some proteins such as the keratins found in wool or hair, the disulfide bonds may be broken, e.g. curling of hair. Denaturing is often irreversible.

6.25 Tests for proteins (extension work)

(a) Ninhydrin reaction

Amino acids and proteins with an amino group and a free carboxyl $(-\underset{\underset{\displaystyle O}{\|}}{C}-)$ group will produce a blue colour.

(b) Biuret test

Peptides or polypeptides give characteristic pink to purple colours when their alkaline solutions are heated with a dilute solution of copper sulfate.

(c) Xanthoproteic reaction

This produces a yellow colour when concentrated nitric acid comes in contact with protein material. This test should be done as a *demonstration only* as nitric acid reacts with skin.

(d) Using Millon's reagent

When Millon's reagent (a mercury salt in nitric acid) is added to a soluble protein and heated, the substance first coagulates, then a pink colour develops. This test is no longer used in schools because of the presence of a mercury salt.

6.26 The structure of skeletal muscle

Skeletal muscle is used for movement and is anchored to bones by tendons found at both ends of the bulk of the muscle or muscle belly. Muscle cells cause movement by contraction along their length. They consist of 30% protein and 70% water and salts.

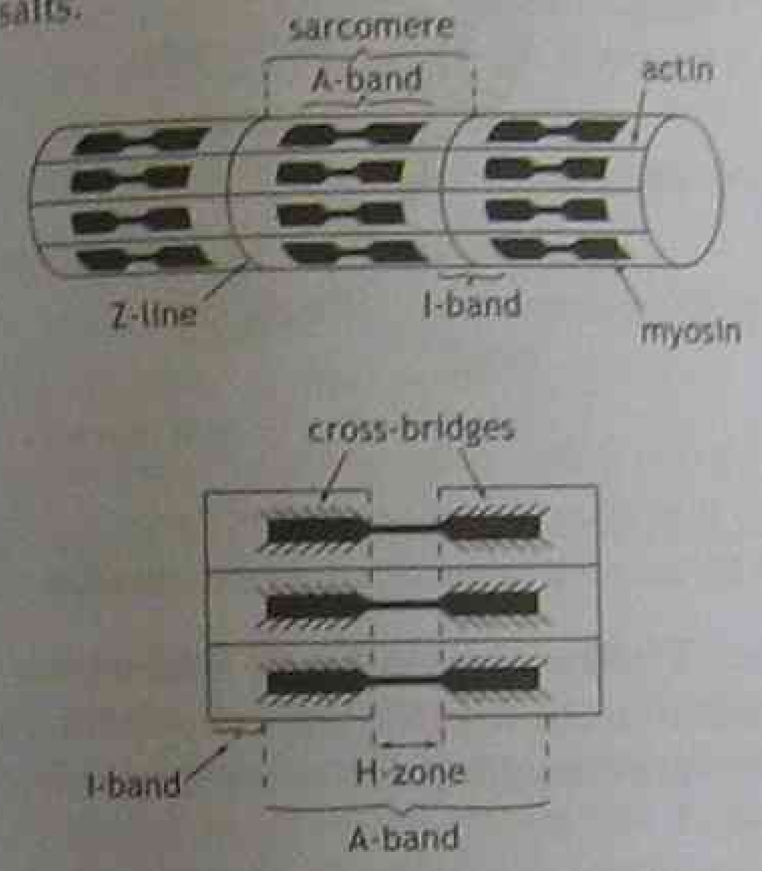


Figure 6.33 Myofilaments

Table 6.2 Build up of skeletal muscle

Muscle component	Appearance
Muscle belly	Made up of thousands of muscle fibres arranged in bundles that run the length of the muscle.
Muscle fibres	These consist of many contractile units called myofibrils which run the length of the fibre and have characteristic dark and light bands.
Myofibrils	Each myofibril is made up of units called sarcomeres.
Sarcomeres	The sarcomere contains two protein filaments: (a) myosin made up from polypeptide chains forming a thick filament; and (b) actin, a thin filament made of globular protein which attaches to the Z-line. Each sarcomere has a Z-line at each end.
Myofilaments	The overlap of myofilaments creates the striped appearance of skeletal (striated) muscle. Only actin fibres are present in the I-band. The A-band is the dark area where myosin and actin overlap. The H-zone in the middle of the A-band contains only thick myosin filaments. The myosin filaments have protein projections which extend towards the actin fibres and are called cross-bridges.

6.27 The sliding filament theory of how muscles contract

- The actin fibres slide across the myosin by the action of cross-bridges that reach out from the myosin fibres and attach themselves to the actin filaments.
- After binding with the actin filaments, the cross-bridges shorten, pulling the actin along the myosin.
- Since the actin is attached to the Z-line, the sarcomere also shortens. Hence the muscle itself shortens and a contraction occurs.

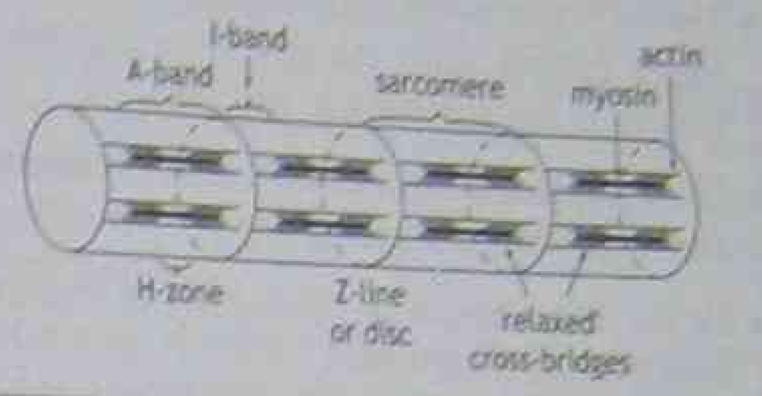


Figure 6.34 Relaxed myofibril

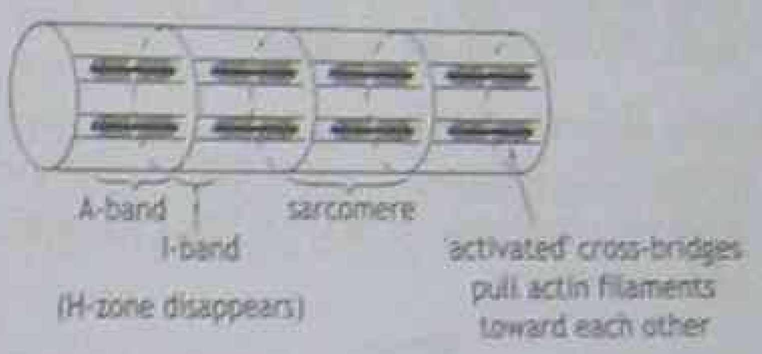


Figure 6.35 Contracted myofibril

6.28 Mechanism for triggering a muscle contraction

- A nerve (electrical impulse) innervates the muscle at the neuro-muscular synapse.
- A motor nerve and the muscle fibres it innervates is called a motor unit.
- The electrical impulse reaches the end of the nerve where it triggers the release of acetyl choline (ACh) from the axon endplate.
- The ACh stimulates another electrical impulse which travels along the sarcolemma down T-tubules to the sarcoplasmic reticulum.
- The endoplasmic reticulum releases calcium ions over the actin and myosin.
- On the actin filament are two regulatory proteins, troponin and tropomyosin.
- Once the calcium ions are released from the sarcoplasmic reticulum, the tropomyosin moves away to allow the cross-bridge of the myosin to make contact with the troponin.
- Once the cross-bridge and the troponin make contact, an enzyme (myosin ATP-ase) allows adenosine triphosphate (ATP) to break down and release energy

$$\text{Adenosine} - P_i - P_i \overset{\text{ATP-ase}}{\wr} P_i \qquad (\text{ATP} \rightarrow \text{ADP} + P_i)$$

$$\downarrow$$

$$\text{energy} \rightarrow \text{muscular activity}$$

- This energy allows the cross-bridge to shorten, pulling the actin filaments across and shortening the muscle.

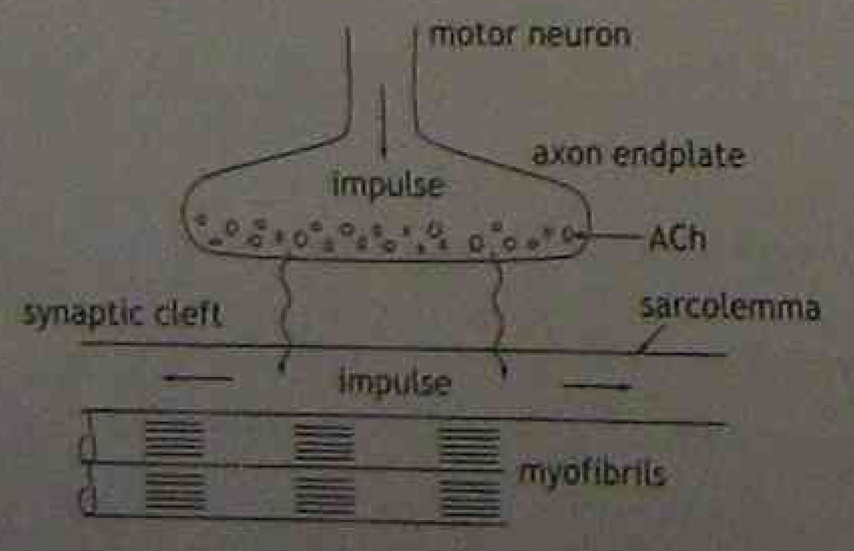


Figure 6.36 Structure of the neuromuscular synapse

6.29 Types of striated muscle cells

Muscle fibres are not identical. Generally two types are recognised (see Table 6.3).

Table 6.3 Types of muscle fibre (extension work)

Type 1 (red fibres)	Type 2 (white fibres)
• slow twitch • contracts relatively slowly • many mitochondria • many capillaries • fewer contractile filaments • slight glycogen stores • carries out aerobic respiration	• fast twitch • contracts relatively rapidly • few mitochondria • few capillaries • many contractile filaments • great glycogen stores • carries out mainly anaerobic respiration
• used for light endurance exercise and distance runnning	• used for heavy exercise and sprinting

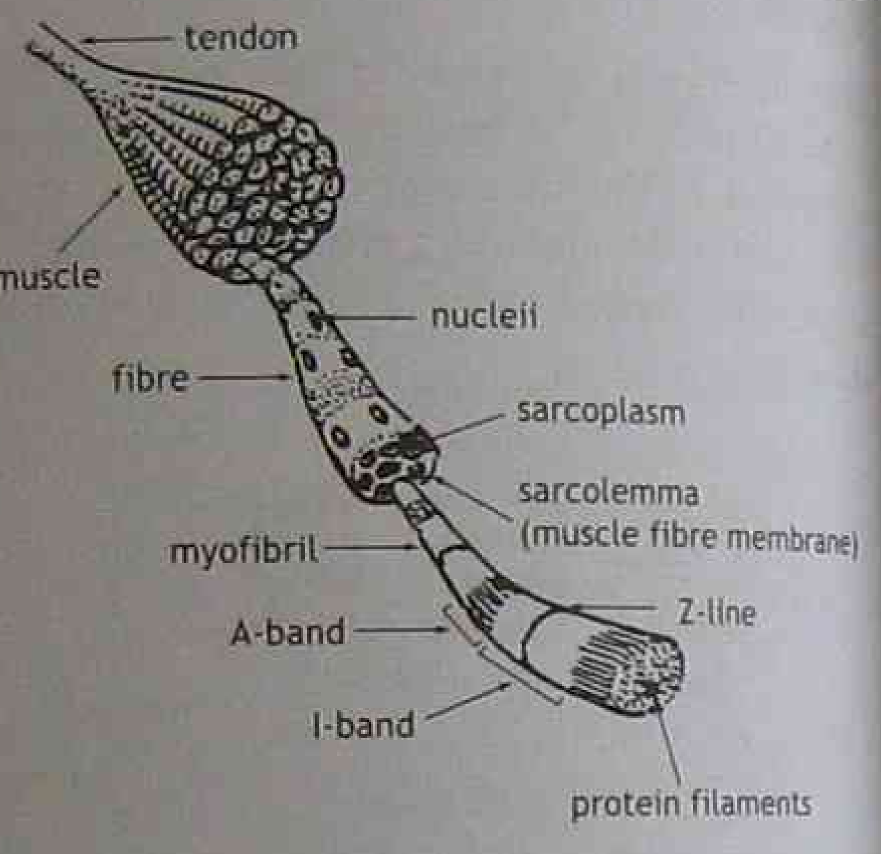


Figure 6.37 Structural design of human skeletal muscle

Each muscle cell is surrounded by a membrane (the sarcolemma) inside which is the sarcoplasm, a jelly-like substance consisting of the substances listed in Table 6.4.

Table 6.4 Contents of sarcoplasm

Substance	Use
Actin and myosin filaments	muscle contraction
Adenosine triphosphate (ATP)	energy production
Creatine phosphate	energy production
Enzymes	energy production and muscle growth
Fat	energy production
Glycogen	energy production
Mitochondria	involved in the release of energy
Myoglobin	a substance which stores and carries oxygen from the blood to the mitochondria

Table 6.5 Usage of different muscles in different situations

Situation	Type 1	Type 2
% in typical leg muscles	45	16
% in leg muscles of a distance runner	80	5
% in leg muscles of sprinter	23	48

Differences in the two types of muscle cell infer that different fuels are needed and that different strategies be used to obtain energy for muscular activity.

6.30 Replenishing ATP in muscles

Since the store of ATP in the muscle is so small (enough for 1–2 seconds), the body must replenish ATP almost as quickly as it is broken down. This is achieved by resynthesising ATP through the breakdown of reserve fuels, namely creatine phosphate, carbohydrates, fats and proteins. The energy for rebuilding comes from three separate but interrelated systems:

- The ATP-PC or phosphate system (an anaerobic system).
- The lactic acid system (an anaerobic system).
- The oxygen or aerobic system.

The major factors determining which energy system to use for an activity are the intensity and duration of the activity.

Fuel comes from the food groups, proteins, fats and carbohydrates. In *aerobic systems* if sufficient oxygen is available, pyruvic acid (from glycolysis) from the formation of acetyl-CoA enters the Krebs cycle which occurs in mitochondria (aerobic). ATP is formed by oxidative phosphorylation during electron transport. This system releases much more energy than the other two systems.

6.31 The electron transport chain

Aspects of electron transport have been discussed in Section 6.10. In the Krebs cycle, the acetyl group is oxidised and the electron acceptors NAD^+ and FAD are reduced to NADH and $FADH_2$. The co-enzymes NADH and $FADH_2$ then transfer their electrons to the series of cytochromes and other electron carriers that make up the electron transport chain. Each electron carrier is successively reduced and then reoxidised. Each electron transfer involves the oxidative phosphorylation of ADP to create ATP. At the end of the chain, reduced cytochrome c reacts with molecular oxygen with the formation of water:

$$2 \text{ reduced cytochrome c} + 2H^+ + {}^1/_2O_2 \rightarrow$$
$$2 \text{ cytochrome c} + H_2O + (\text{high energy bond P})$$

6.32 The phosphate (ATP-PC) system

- This system is anaerobic since the body is unable to deliver oxygen for energy production in time (10–20 s).
- No lactic acid is produced.
- It is not mitochondria based.
- ATP stored in muscles can produce enough energy for about two seconds of muscular activity. The muscles can resynthesise ATP using another fuel called creatine phosphate which is also stored in the muscle.
- Creatine phosphate is broken down into creatine and phosphate releasing energy so that ADP and P_i form ATP.
- After exercise, it takes about two minutes to replenish the creatine phosphate. Oxygen is used for this process.
- The primary use for the ATP-PC system is in sprinting which involves muscles contracting powerfully and rapidly, and utilises Type 2 muscle.

6.33 The lactic acid system

Once the creatine phosphate stores are depleted and high intensity exercise continues, the muscles generate energy for ATP resynthesis by the lactic acid method.

- The system is anaerobic.
- Glycogen is converted to glucose by enzymes, e.g. glycogen phosphorylases.
- Glucose by a process of glycolysis produces pyruvic acid.
- If insufficient oxygen is present to meet the needs of an activity lasting about one minute, e.g. a 400 metre run, the body has no time to deliver oxygen to the muscle to react with the increased amount of pyruvic acid present.
- 'Fast energy' is provided by anaerobic glycolysis.
- Lactic acid is produced (see Figure 6.38).
- The system is fast but inefficient. Only three moles of ATP are produced from anaerobic breakdown of three moles of glycogen.
- The accumulated lactic acid lowers the pH of the

muscle and reduces the capacity of the muscle fibres to contract producing muscle soreness and fatigue.

- The lactic acid diffuses into the blood and is carried to the liver where it is resynthesised to pyruvic acid, then to glucose or glycogen.

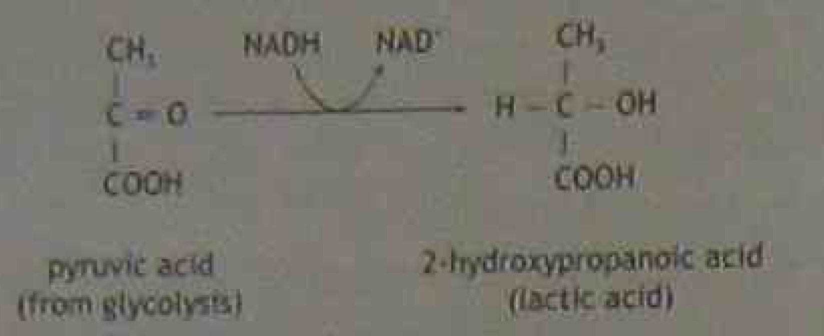


Figure 6.38 Lactic acid production

Overall pathway

$$\text{glucose} + 2NAD^+ + 2(ADP + P_i) \rightarrow$$
$$2\ \text{pyruvate} + 2NADH + 2ATP$$

Note: Glycogen is also a source of glucose for mammalian cells.

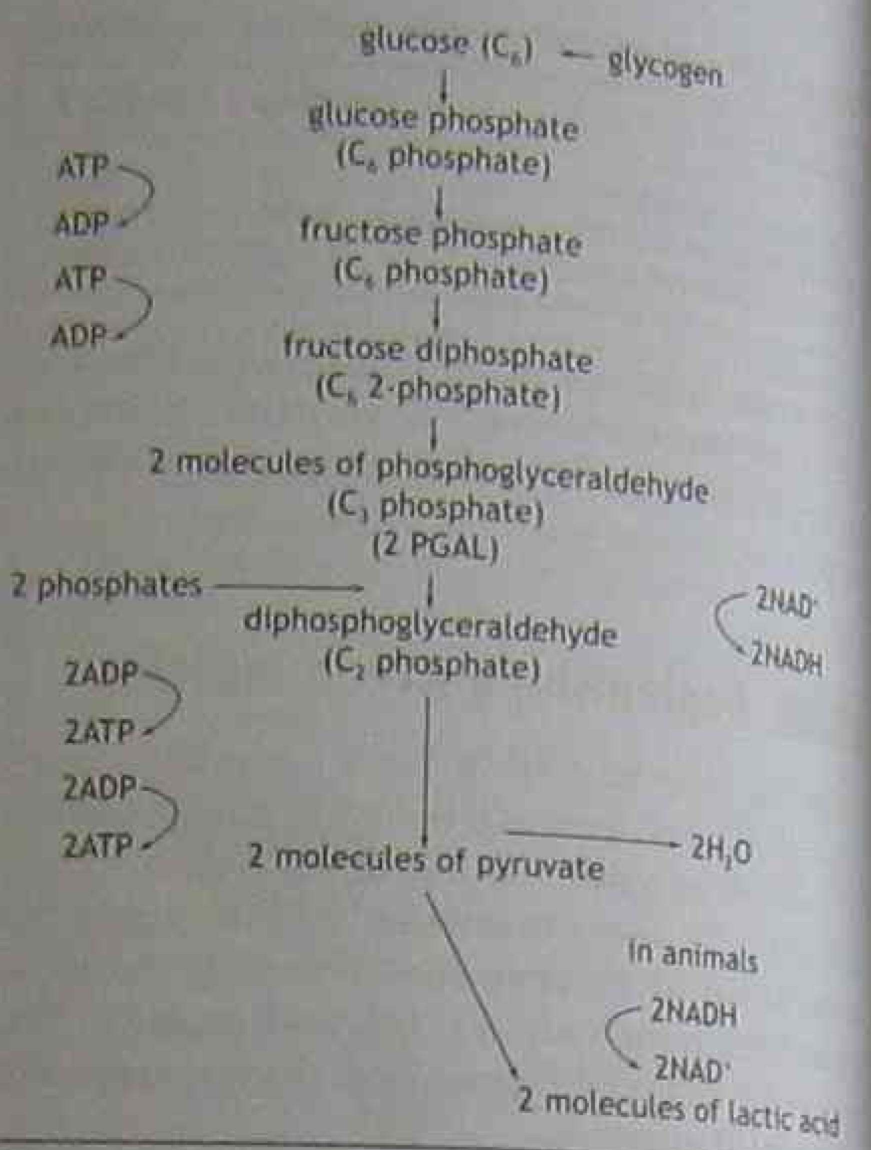


Figure 6.39 Summary of glycolysis — for one molecule of glucose

6.34 Characteristics of systems which replenish ATP in muscles

The following table summarises the characteristics of the ATP-PC or phosphate system, the lactic acid system and the oxygen system for a number of body conditions.

Table 6.6 Characteristics of systems which replenish ATP in muscles

Activity	ATP-PC or phosphate system	Lactic acid system	Oxygen system
Use of oxygen	anaerobic	anaerobic	aerobic
Speed of reaction	very fast	fast	slow
ATP production	very limited	limited	unlimited
Fuel	chemical creatine phosphate	food glycogen	food glycogen, fats and protein
Resulting muscle fatigue	very limited muscle stores	by-product, lactic acid causes muscle fatigue	no lactic acid formed
Primary use	any high-powered, short-duration activity of up to 20 s, e.g. sprinting	intense activities of 30 s to 2 min duration, e.g. a 400 m run	in endurance of long-duration activities, e.g. a marathon event lasting over 2 hours
Muscle fibres	type 2 (fast twitch fibres)	fast twitch fibres are better adapted to produce lactic acid	type 1 fibres are used in endurance exercises

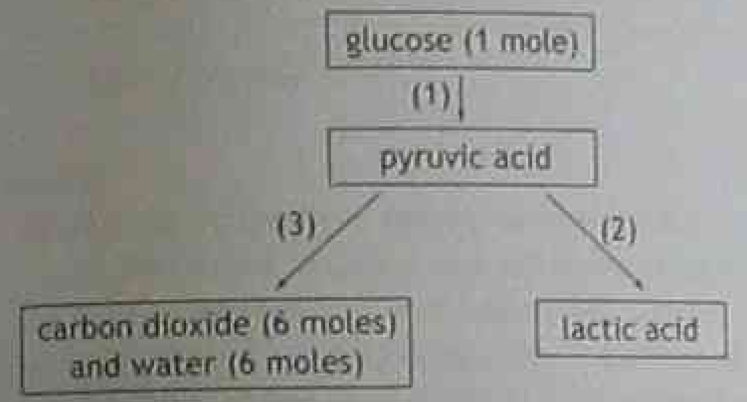
Answers

Answers for Exercise 6.1

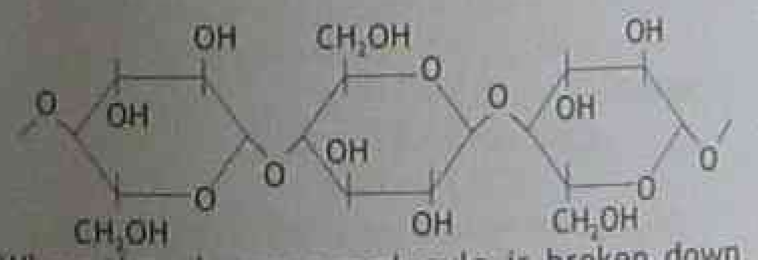
(a) X is pyruvic acid. It is produced by glycolysis.
(b) Because a molecule of CO_2 has been removed from the C_3 acid.
(c) Citric acid.
(d) The CO_2 is removed from the body by the lungs when exhaling.
(e) $NAD^+ \rightarrow NADH$ or $FAD \rightarrow FADH_2$
Their function is to transfer hydrogen atoms.
(f) (i) Krebs cycle, citric acid cycle or tricarboxylic acid cycle.
(ii) In the mitochondria.
(iii) Aerobic.

Test on Chapter 6 – (option 3) The Biochemistry of Movement

1. [10 marks]
The following diagram shows the products of various metabolic reactions occurring in living cells under different conditions. Some of the reactions produce a net yield of ATP, Adenosine triphosphate.

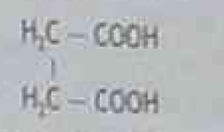


(a) Which reaction(s) occur in the absence of molecular oxygen (O_2)?
(b) How many moles of pyruvic acid are produced from one mole of glucose?
(c) While sprinters are running a race, reactions 1 and 2 are occurring in their muscle tissue, producing a large build-up of lactic acid. The diagram below represents part of a glycogen molecule found in liver and muscle tissues in humans.



When the glycogen molecule is broken down, glucose molecules are formed. Muscle cramp after strenuous exercise is caused by a build-up of lactic acid in the muscles. Outline how the glucose molecules from glycogen are changed into lactic acid.
(d) How do the sprinters' bodies remove this lactic acid after the race?
(e) State two characteristics which differ between type 1 and type 2 muscle cells.
(f) In the leg muscles of a sprinter, would you expect to find a higher percentage of type 1 or type 2 muscle cells?

2. [7 marks]
(a) A diagram of the Krebs cycle is given.
(i) The enzyme Z, succinic acid dehydrogenase, converts succinic acid



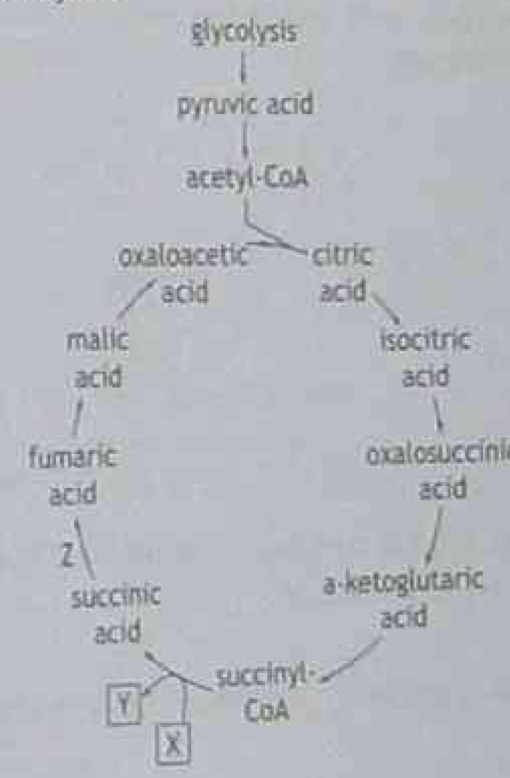
$$\begin{array}{l} H_2C-COOH \\ \quad | \\ H_2C-COOH \end{array}$$

to fumaric acid. This enzyme will not act on malonic acid.

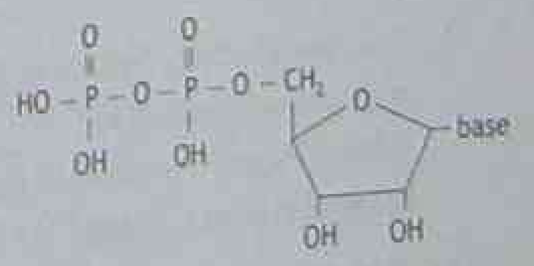
$$H_2C\begin{array}{l} \diagup COOH \\ \diagdown COOH \end{array}$$

(malonic acid)

Explain this in terms of the structure of the enzyme.



(ii) The conversion of succinyl-CoA to succinic acid is accompanied by the conversion of chemical X into chemical Y.
The structure of chemical X is



Draw the probable structure of chemical Y.

(iii) Is the conversion of X of Y an exergonic (exothermic) or endergonic (endothermic) process? Explain.

(b) Only a few swimmers in the world have broken the 15 minute barrier for the 1500 m freestyle. Such a swimmer would require hydrolysis of about 10^{-3} mol of ATP per gram of muscle per minute. The overall equation for the metabolism of one molecule of glucose is

$$C_6H_{12}O_6 + 6H_2O + 6O_2 + 38ADP + 38P_i \rightarrow 6CO_2 + 12H_2O + 38ATP + \text{energy}$$

(i) How many grams of glucose must be used per kilogram of muscle in swimming 1500 m in 15 minutes?

(ii) What is the end product formed in the swimmer's muscles? Draw its structural formula.

3. [3 marks]

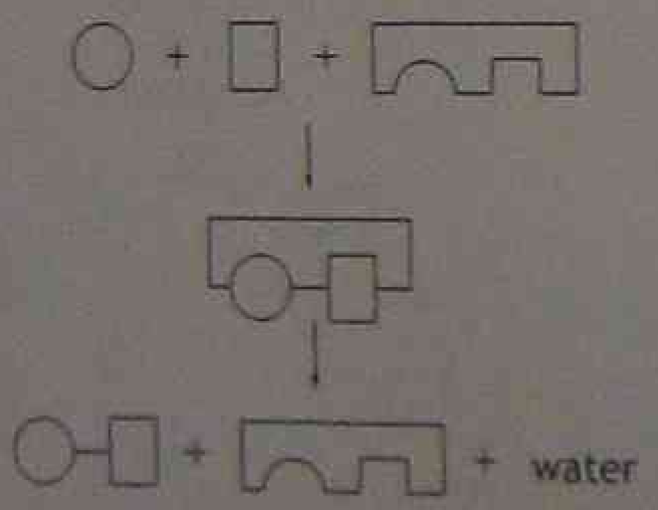
(a) Explain what you understand by the term 'anaerobic power'.

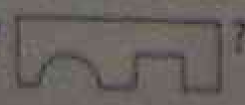
(b) For what types of activities is anaerobic power needed? Give one example.

(c) Muscular power is often defined as 'the ability to develop and apply force (strength) quickly'. On what does the muscular power that you can produce depend?

4. [5 marks]

The following equation is written by a chemist to explain how a certain biochemical is synthesised in a living cell:



(a) What is the biochemical nature of the compound represented by ?

(b) Suppose ○ represents H_2NCH_2COOH

and □ represents $H_2N\overset{CH_3}{\overset{|}{C}}HCOOH$

(i) To what class of compounds do ○ and □ belong?

(ii) Draw the structural formula of the molecule represented by ○-□ showing clearly the nature of the linkage between ○ and □.

Answers for test on Chapter 5 – Option 3 The Biochemistry of Movement

1. [10 marks]

(a) (i) 1 and 2.

(ii) 2 moles.

(iii) 

(iv) After exercise and enough oxygen is available, lactic acid is reconverted to pyruvic acid which is further broken down to carbon dioxide and water with more ATP being resynthesised.

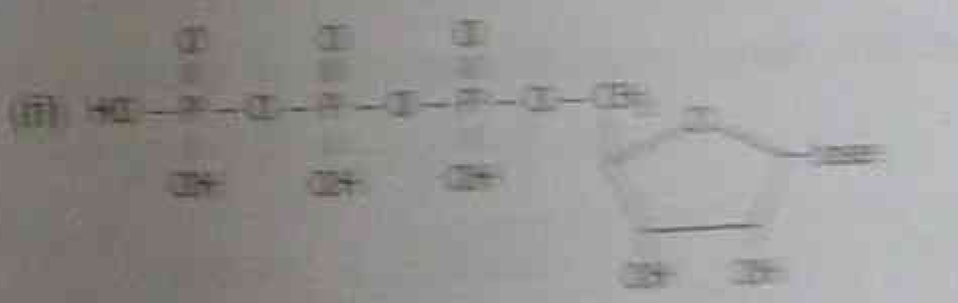
(v)

Type 1 muscle	Type 2 muscle
Contracts relatively slowly	Contracts relatively rapidly
Many mitochondria	Few mitochondria

(vi) Type 2 muscle cells.

2. [7 marks]

(a) (i) Enzymes are very selective in their action. A particular enzyme can catalyse reactions only between a very specific group of reactants called its substrate. The active site of the enzyme must exactly fit the opposing surface of the substrate. This is the basis for the 'lock and key' theory.

(ii) 

(iii) Endothermic, since energy is needed to add on the third phosphate group.

(b) (i) 1 mole $C_6H_{12}O_6$ produces 38 mol ATP

Molar mass of glucose = 180 g

Hydrolysis rate = 10^{-3} ATP g/min

= 10^{-3} × 1000 × 15 moles of ATP for the race

= 15 mol ATP

1 mole glucose is needed to metabolise 38 mol ATP

1 mole glucose = 180 g

Glucose needed = (15 ÷ 38) × 180 = 71 g

(ii) lactic acid = 

3. [3 marks]

(a) [illegible]

(b) [illegible]

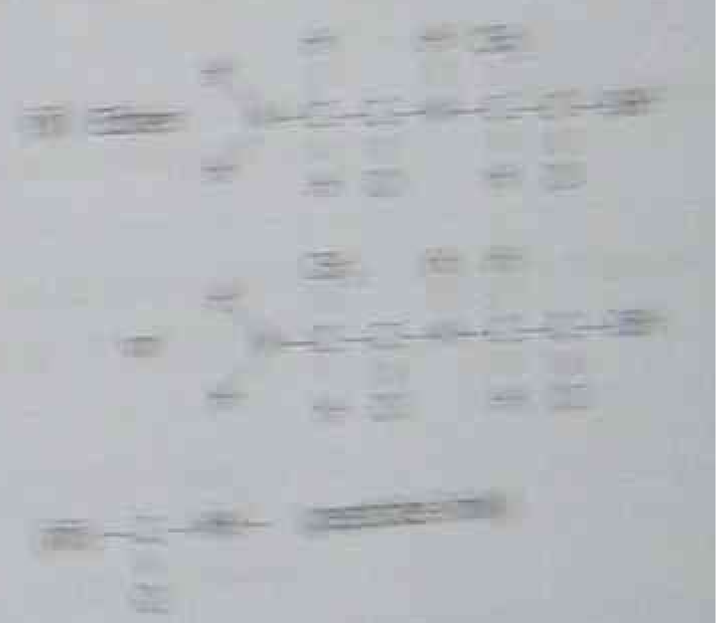
Examples:
- Sprints (100–400 m)
- Gymnastics
- [illegible]
- Weight-lifting

(c) Muscular power depends on the following:
- Anaerobic energy supply
- Muscular strength
- Speed of contraction of muscle

4. [5 marks]

(a) enzyme/protein

(b) (i) amino acids

(ii) 

Total: 25 marks

Draw the probable structure of chemical Y.

(iii) Is the conversion of X of Y an exergonic (exothermic) or endergonic (endothermic) process? Explain.

(b) Only a few swimmers in the world have broken the 15 minute barrier for the 1500 m freestyle. Such a swimmer would require hydrolysis of about 10^{-3} mol of ATP per gram of muscle per minute. The overall equation for the metabolism of one molecule of glucose is

$$C_6H_{12}O_6 + 6H_2O + 6O_2 + 38ADP + 38P_i \rightarrow 6CO_2 + 12H_2O + 38ATP + energy$$

(i) How many grams of glucose must be used per kilogram of muscle in swimming 1500 m in 15 minutes?

(ii) What is the end product formed in the swimmer's muscles? Draw its structural formula.

3. [3 marks]

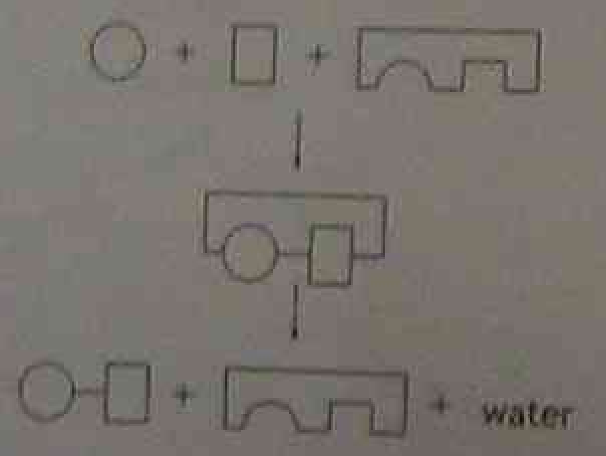
(a) Explain what you understand by the term 'anaerobic power'.

(b) For what types of activities is anaerobic power needed? Give one example.

(c) Muscular power is often defined as 'the ability to develop and apply force (strength) quickly'. On what does the muscular power that you can produce depend?

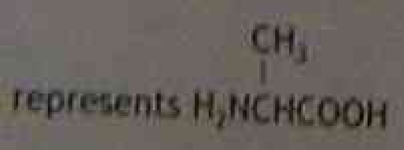
4. [5 marks]

The following equation is written by a chemist to explain how a certain biochemical is synthesised in a living cell:



(a) What is the biochemical nature of the compound represented by ?

(b) Suppose ○ represents H_2NCH_2COOH

and □ represents  $H_2N\overset{\overset{CH_3}{|}}{C}HCOOH$

(i) To what class of compounds do ○ and □ belong?

(ii) Draw the structural formula of the molecule represented by ○–□ showing clearly the nature of the linkage between ○ and □.

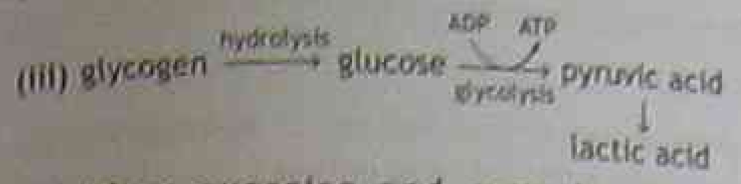
(iii) What do biochemists call this linkage?

Answers for test on Chapter 6 – (option 3) The Biochemistry of Movement

1. [10 marks]

(a) (i) 1 and 2.

(ii) 2 moles.

(iii) 
$$\text{glycogen} \xrightarrow{\text{hydrolysis}} \text{glucose} \xrightarrow[\text{glycolysis}]{\text{ADP}\ \ \text{ATP}} \text{pyruvic acid} \downarrow \text{lactic acid}$$

(iv) After exercise and enough oxygen is available, lactic acid is reconverted to pyruvic acid which is further broken down to carbon dioxide and water with more ATP being resynthesised.

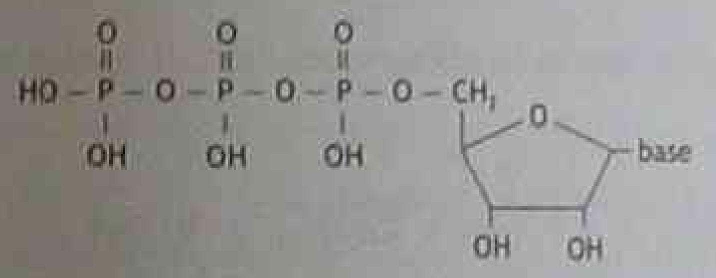
(v)

Type 1 muscle	Type 2 muscle
Contracts relatively slowly	Contracts relatively rapidly
Many mitochondria	Few mitochondria

(vi) Type 2 muscle cells.

2. [7 marks]

(a) (i) Enzymes are very selective in their action. A particular enzyme can catalyse reactions only between a very specific group of reactants called its substrate. The active site of the enzyme must exactly fit the opposing surface of the substrate. This is the basis for the 'lock and key' theory.

(ii) 

(iii) Endothermic, since energy is needed to add on the third phosphate group.

(b) (i) 1 mole $C_6H_{12}O_6$ produces 38 mol ATP

Molar mass of glucose = 180 g

Hydrolysis rate = 10^{-3} ATP/g/min

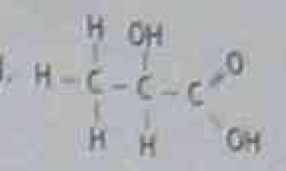
= $10^{-3} \times 1000 \times 15$ moles of ATP for the race

= 15 mol ATP

1 mole glucose is needed to metabolise 38 mol ATP.

1 mole glucose = 180 g

Glucose needed = $(15 \div 38) \times 180 = 71$ g

(ii) Lactic acid.  $H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{OH}{C}}-C\begin{smallmatrix}\nearrow O \\ \searrow OH\end{smallmatrix}$

3. [3 marks]

(a) Anaerobic power is the ability to produce energy by either the ATP-PC system or the lactic acid system so that a high-intensity effort is sustained while a lactic acid build-up is tolerated.

(b) Anaerobic power is needed for short-term (less than 2–3 minutes), high intensity speed activities. Examples:

- Sprints (100–400 m).
- Gymnastics.
- Throws, e.g. shot putting, javelin.
- Weight-lifting.

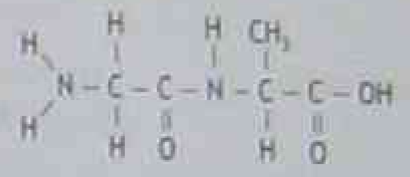
(c) Muscular power depends on the following:

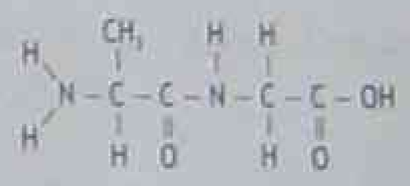
- Anaerobic energy supply.
- Muscular strength.
- Speed of contraction of muscle.

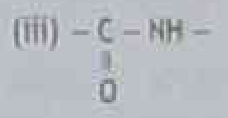
4. [5 marks]

(a) enzyme (protein).

(b) (i) amino acids

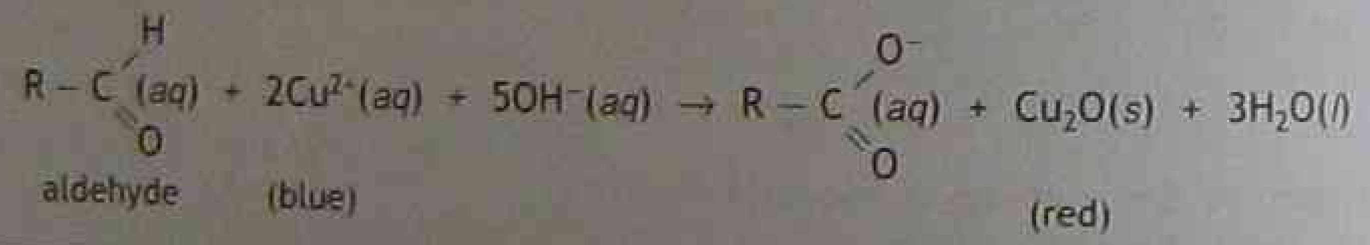
(ii) Either  $H_2N-\underset{H}{\overset{H}{C}}-\underset{\underset{O}{\parallel}}{C}-\overset{H}{N}-\underset{H}{\overset{CH_3}{C}}-\underset{\underset{O}{\parallel}}{C}-OH$

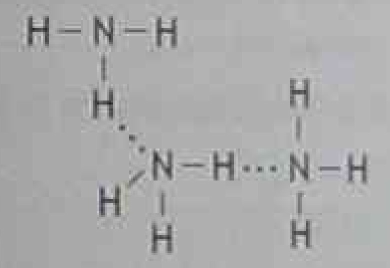
or  $H_2N-\underset{H}{\overset{CH_3}{C}}-\underset{\underset{O}{\parallel}}{C}-\overset{H}{N}-\underset{H}{\overset{H}{C}}-\underset{\underset{O}{\parallel}}{C}-OH$

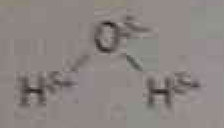
(iii)  $-\underset{\underset{O}{\parallel}}{C}-NH-$ (peptide link)

Total 25 marks

Glossary

Actin fibres	Filaments used for striated muscle contraction.
Active site	The part of an enzyme molecule into which the substrate fits during a reaction where the enzyme acts as a catalyst.
Activation energy	Energy needed by a system before a reaction can occur.
ADP	Adenosine diphosphate. A compound formed by the hydrolysis of an ATP molecule. Energy is released in the process.
Aerobic process	A process needing free oxygen (O_2).
Anabolism	Complex molecules are formed from simple molecules in a metabolic process.
Anaerobic process	A process that occurs without free oxygen.
ATP	Adenosine triphosphate. ATP is formed from ADP + P_i. When energy is needed, ATP reacts with water to give ADP and energy.
Amino acids	Organic compounds containing $-NH_2$ and $-COOH$ bonded to the same carbon atom. They are the building blocks for proteins.
Benedict's solution	A solution containing Cu^{2-} ions and citric ions in an alkaline solution. It is used to detect reducing sugars, e.g. glucose.  $R-C(H){=}O(aq) + 2Cu^{2+}(aq) + 5OH^-(aq) \rightarrow R-C(O^-){=}O(aq) + Cu_2O(s) + 3H_2O(l)$ aldehyde (blue) (red)
Catabolism	Complex molecules are broken down into simple molecules in a simple process which releases energy.
Co-enzymes	A non-protein accessory for an enzyme.
Creatine phosphate (CP)	A phosphate fuel stored in the muscle.
Cytochromes	Haeme-containing proteins that take part in electron transportation.
Carbohydrates	These have a general formula $C_x(H_2O)_y$. They include sugars, starches, glycogen and cellulose.
Denaturation	A physical or chemical change in proteins which results in the loss of biological activity. e.g. heating egg white.

Elimination reaction	The removal of a small molecule, often H_2O, from a molecule. e.g. $CH_3-CH_2Br + NaOH \rightarrow H_2C{=}CH_2 + NaBr + H_2O$
Endergonic reaction	A chemical reaction involving absorption of energy (endothermic reaction).
Enzyme	A protein molecule that acts as a catalyst in a chemical reaction.
Exergonic reaction	A chemical reaction where energy is given out (exothermic reaction).
FAD, $FADH_2$ (reduced form)	Flavin adenine dinucleotide. Acts as a co-enzyme and electron carrier.
Fats	Triacylglycerols (TAGs)
Fatty acids	If saturated they have the general formula $CH_3(CH_2)_nCOOH$, where -COOH is the functional group. If unsaturated, one or more ($-C{=}C-$) groups are present in the molecule.
Glycerol	An alkane triol, 1,2,3-propanetriol.
Glycogen	A complex carbohydrate (polysaccharide) which is converted to glucose by hydrolysis. Humans store carbohydrates as glycogen in their muscles and liver.
Hydrogen bonding	Polar interactions which result when a hydrogen atom, bound to one of three atoms F, O or N, can become attached to one of these atoms in another molecule. Example: 
Hydrolysis	A chemical reaction involving water.
Hydrophobic	Water-repelling.
Hydrophilic	Water-attracting.
Krebs cycle	Stages of cellular respiration in which pyruvates are completely broken down into carbon dioxide. The Krebs cycle is a pathway for carbohydrate metabolism and is the main source of metabolic energy as ATP. (Tricarboxylic acid (TCA) cycle.)
Lactic acid	2-hydroxypropanoic acid produced during anaerobic respiration ($CH_3-CHOH-COOH$).
Lysosome	An enzyme protein that breaks down the cell walls of many bacteria. Lysosomes are also responsible for the breakdown of large molecules in the cell.
Mitochondria	The sites of the aerobic stages of cellular respiration.
Myofibril	The contractile element of a muscle fibre made up of thick and thin filaments arranged in sarcomeres.

Myosin fibres	Filaments used for striated muscle contraction.
NAD **(NADH reduced form)**	Nicotinamide adenine dinucleotide. Acts as a co-enzyme and electron carrier.
Non-polar	Describes a molecule with a symmetrical distribution of charge.
Nucleoside	Composed of ribose and the common bases of nucleic acids.
Nucleotide	Nucleoside phosphates (base-sugar-phosphate).
Oxidative phosphorylation	The process that couples the oxidation of NADH and $FADH_2$ to the production of high energy phosphate bonds in ATP.
Polar	Describes a molecule with a charge that is not evenly distributed so that dipoles (with opposite charges) occur, e.g. water. 
Proteins	Contain the elements carbon, hydrogen, oxygen and nitrogen as well as traces of sulfur in some cases. They are used both as structural molecules and as enzymes to catalyse metabolic reactions.
Saturated fatty acids	Long-chain alkanoic acids with only single C-C bonds.
Sarcomeres	The functional and structural units of contraction in striated muscle.
Striated muscle	A skeletal voluntary muscle. Its striped appearance reflects the arrangement of contractile elements.
Substrate	A substance acted on by an enzyme.
Synapse	The region of a nerve impulse transfer between two neurones
TAG	See 'Fats'.
TCA	See 'Krebs cycle'.
Unsaturated fatty acids	Long-chain alkanoic acids which contain at least one C=C bond.

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7 option four

Forensic Chemistry

Forensic means *applied to the law*, so forensic science is the collection and interpretation of clues to a crime for later presentation in a court of law. Forensic chemists work within the general field of analytical chemistry. They are asked to work through samples, analyse compounds and mixtures to identify trends and draw conclusions from a wide range of investigations. The accuracy of the forensic chemist's analysis is crucial and must be reported in an appropriate manner to communicate the information obtained from the evidence.

Contents

7.1 Planning an experimental investigation using scientific method

Practical investigations are an essential part of this option. Before starting on an investigation, careful planning should be carried out. Consider the following, for example:

Purpose of investigation

- What hypothesis is to be tested?
- What do you predict will happen and why?

Dependent and independent variables

- Which variables will be measured?
- Which factors will be changed?
- Which variables will be kept constant?
- When plotting graphs, use a scale which is as large as possible.
- The independent variable is plotted on the horizontal (x) axis.
- The dependent variable is plotted on the vertical (y) axis.
- Draw the line of best fit, which may be a straight line or a curve.

Observations and results

- What did you observe to be happening?
- Which is the best way to compare and present results: a table, graph, bar chart, flow chart, or data logging and a possible print-out?

Conclusions

- How can the results be interpreted?
- Can you explain the results in terms of chemical ideas?
- Did they fit the original hypothesis?

Evaluation of results

- Are there any improvements needed in the experiment?
- Should multiple measurements be taken to reduce random error?
- Should up-graded apparatus which would allow for greater precision be used?
- Should the experiment be repeated?
- Is the use of a control needed?
- Has the experiment produced any new ideas for further investigation?

The scientific method

A simple analogy can be used to explain the scientific method.

1. You decide that your hair needs cutting. (Problem)
2. At the hairdresser's you look through magazines until you find a style that you think will suit you. (Hypothesis)
3. You have your hair cut. (Experiment)
4. You look in the mirror. (Result)
5. You think that your hair is still too long. (Conclusion)
6. You decide to have your hair cut shorter. (Evaluation)

The scientific method is not a single-structured procedure. It has three objectives that interact with each other:

(a) *To explain*. This involves interaction between observation or activity and theory. Any theory is then tested by further experiments.

(b) *To quantify*. This is an attempt to find a mathematical expression to account for observed data and may involve statistics for example.

(c) *To predict*. For a theory to be successful, it must be able to predict the results of further experiments.

Note: See the Introduction for this book to find additional information on the scientific method, practical skills, information skills, and suggestions on planning first-hand investigations.

7.2 Preventing contamination of the crime scene

Precautions must be taken to ensure accuracy and prevent contamination of samples for analysis by forensic scientists. Forensic means 'applied to the law' so forensic science is the collection and interpretation of clues to a crime for later presentation in a court of law. The work of forensic scientists is based on the belief that someone committing a crime will leave something behind or take something away from the crime scene. Clues may be in any number of forms including fingerprints, hairs, clothing fibres, traces of dirt and bullets. This is called 'the theory of exchange'.

To protect the crime scene, for example in the case of murder, anyone present should wear overalls, hair covering, masks and shoe covers to prevent contamination. If the weather is wet, a tent is usually erected. The hands of the victims are usually bagged before the removal of the corpse in a body bag. Any samples collected must be placed by sterile forceps into sterile sealable plastic bags or containers.

The scene is also photographed and videos are sometimes taken by police photographers. A scientist from a crime laboratory may accompany the pathologist to assist and advise the police team on any material found. The forensic scientist must examine the evidence objectively and all scientific analyses must be accurate and reproducible.

When collecting samples where arson is suspected, because of volatility of flammable or combustible liquids, they must be packed in vapour-tight containers for transmittal to the laboratory. Heat-sealable polyester/polyolefine bags, sold as KAPAK, are used since they are free from contamination.

Extraction and isolation methods in use today are much more sensitive than earlier methods. Even minute traces present a risk of misidentification. Caution must be taken by scene investigators with regard to their tools, clothing and evidence storage facilities, since debris can lead to false positive results if it has been contaminated by dirty tools or gloves.

7.3 Classification of aliphatic carbon compounds

Organic chemistry is the study of the compounds of carbon (excluding the oxides CO and CO_2 and their derivatives). These compounds show remarkable variation in properties and structure. They include hydrocarbons and their derivates as well as organic compounds with reactions that are fundamental to life itself.

Inorganic chemistry is the study of compounds generally not containing carbon (other than CO_2, CO and carbonates). These compounds are very often derived from naturally-occurring minerals.

The diversity of carbon compounds depends on

(a) the unusual strength of the C–C single bond and the ability of carbon to form C=C and $C\equiv C$ bonds;

(b) the four valence electrons on carbon atoms;

(c) the ability of carbon atoms to combine with other non-metal atoms; and

(d) the ability of carbon atoms to bond covalently in chains and rings.

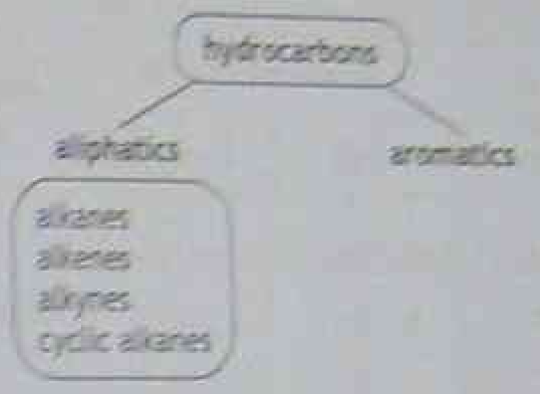


Figure 7.1 Classification of hydrocarbons

Functional group: an atom or group of atoms which gives a homologous series its characteristic chemical properties.

Homologous series: a series in which all the members have the same functional group and the same general molecular formula. Members differ by a $-CH_2$ group.

Table 7.1 Classification of some homologous series

Series	Structural features	Representative members	
Alkanes	hydrocarbons containing single C–C bonds	CH_4 CH_3-CH_3	methane ethane
Alkenes	hydrocarbons containing one C=C double bond	$CH_2=CH_2$ $CH_3-CH=CH_2$	ethene propene
Alkynes	hydrocarbons containing one triple bond	$CH\equiv CH$ $CH_3-C\equiv CH$	ethyne propyne
Alkanols	alkanes with one hydrogen atom replaced by a hydoxyl (OH) group	CH_3CH_2OH $CH_3CH_2CH_2OH$	ethanol 1-propanol
Alkanones	compounds containing the group $C-\underset{O}{\underset{\|}{C}}-C$	$CH_3-\underset{O}{\underset{\|}{C}}-CH_3$	propanone (acetone)
Alkanoic acids	compounds containing the group $-\underset{O}{\underset{\|}{C}}-O-H$	$CH_3-\underset{O}{\underset{\|}{C}}-OH$	ethanoic acid (acetic acid)

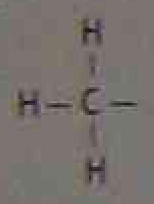
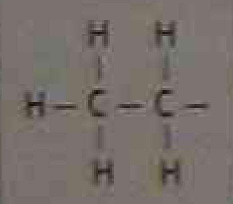
Alkanes

1. Saturated hydrocarbons.
2. Same homologous series.
3. General molecular formula C_nH_{2n+2}.
4. Found in natural gases (C_1–C_4) and liquid petroleum (C_5–C_{17}).
5. Functional group is alkyl group.
6. Contain single C–C bonds only.

Branched-chain hydrocarbons

Alkyl groups are alkane chains minus a hydrogen atom. The suffix -ane of the parent hydrocarbon is dropped and the -yl is added.

Table 7.2 Alkyl groups

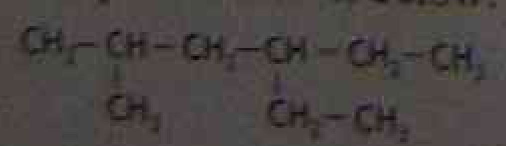
No. of carbon atoms	Structural formula		Alkyl group name
	Full	Condensed	
One	 $$\begin{array}{c} H \\ H-C- \\ H \end{array}$$	CH_3-	methyl
Two	 $$\begin{array}{c} H\;\;H \\ H-C-C- \\ H\;\;H \end{array}$$	CH_3CH_2-	ethyl

Rules for naming branched-chain alkanes

1. Find the longest chain of carbon atoms in the molecule.
2. Name any branch (side) chains as the alkyl groups.
3. Number the side chains from the end of the parent chain which will give them the lowest number.
4. When there is more than one side chain, they are listed alphabetically.
5. If the same side chain occurs more than once, prefixes di-, tri-, tetra- are used.

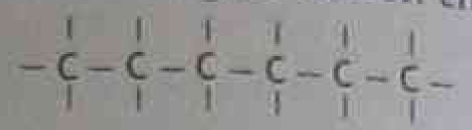
Example 1

To name the compound drawn below:



$$CH_3-\underset{CH_3}{CH}-CH_2-\underset{CH_2-CH_3}{CH}-CH_2-CH_3$$

Step 1. Draw the longest carbon chain



$$-C-C-C-C-C-C-$$

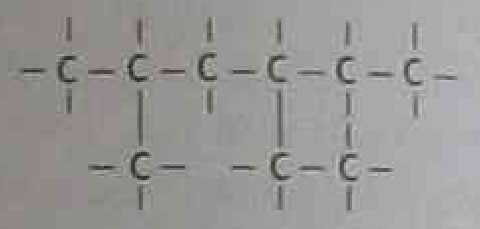
Step 2. Use the chain like a surname .

.... hexane

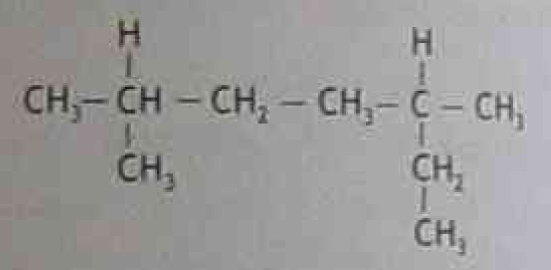
Step 3. Name side chains in alphabetical order.

ethyl-methyl

Step 4. Number from the end of the skeleton to give the lowest number for side chains. Naming of branches is alphabetical before numerical.



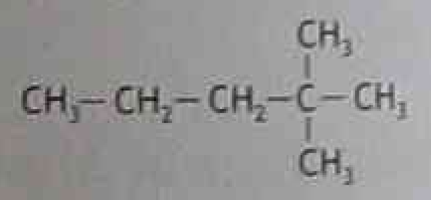
$$\begin{array}{c} -C-C-C-C-C-C- \\ -C-\quad -C-C- \end{array}$$



$$CH_3-\underset{CH_3}{\overset{H}{CH}}-CH_2-CH_3-\underset{CH_2-CH_3}{\overset{H}{C}}-CH_3$$

(*Answer*: 4-ethyl-2-methylhexane)

Example 2



$$CH_3-CH_2-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

When same-name side chains are involved, use prefixes di-, tri- . . .

The compound above is called 2,2-dimethylpentane

Isomerism in alkanes

Isomers are compounds which have the same molecular, but different structural formula.

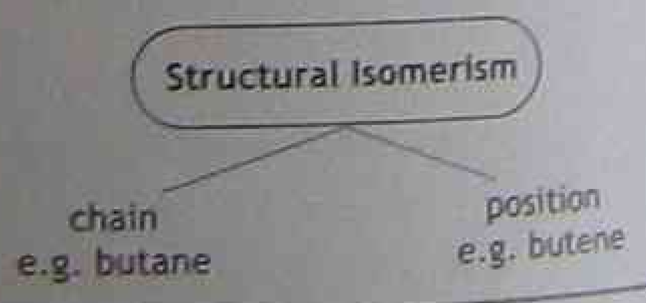
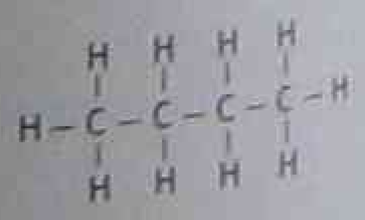


Figure 7.2 Structural isomerism

Isomers of butane

Molecular formula C_4H_{10}

Straight chain

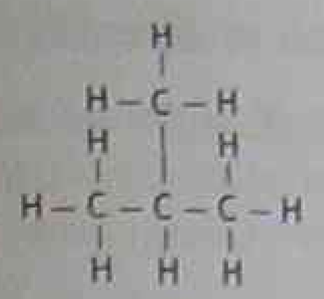


$$\begin{array}{c} H\;\;H\;\;H\;\;H \\ H-C-C-C-C-H \\ H\;\;H\;\;H\;\;H \end{array}$$

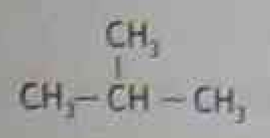
$CH_3-CH_2-CH_2-CH_3$

butane

Branched chain



$$\begin{array}{c} H \\ H-C-H \\ H\quad|\quad H \\ H-C-C-C-H \\ H\;\;H\;\;H \end{array}$$



$$CH_3-\overset{CH_3}{CH}-CH_3$$

2-methylpropane

Alkenes

1. Unsaturated hydrocarbons.
2. General molecular formula C_nH_{2n}.
3. Functional group C=C.

Models

Model kits should be used regularly to show that carbon-carbon covalent bonds may be

single: C–C

double: C=C

or triple: C≡C

Other elements can join these structures, the commonest being hydrogen, oxygen, nitrogen, sulfur, phosphorus and the halogens.

Note: For substances with two alkene groups each is numbered and 'diene' is used. For example,

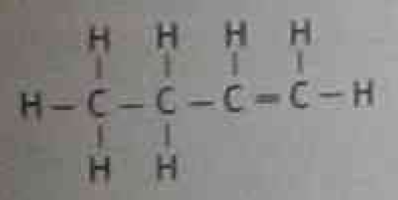
$$CH_2=CH-CH_2-CH=CH_2$$

is 1, 4 pentadiene.

After propene, different isomers are possible by shifting the position of the double bond, so the double bond must be numbered.

1-butene

C_4H_8

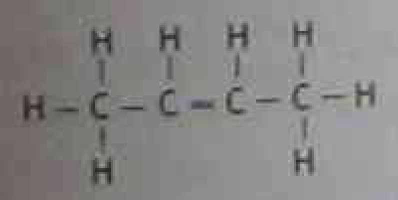


$$\begin{array}{c} H\;\;H\;\;H\;\;H \\ H-C-C-C=C-H \\ H\;\;H \end{array}$$

gas

2-butene

C_4H_8



$$\begin{array}{c} H\;\;H\;\;H\;\;H \\ H-C-C=C-C-H \\ H\qquad\quad H \end{array}$$

gas

Position isomers

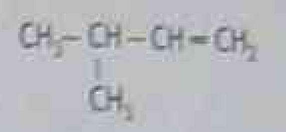
Same homologous series.
Different position of functional group, e.g. alkenes C=C bond. Owing to isomerism, additional naming rules are needed.

Rules for naming alkenes

1. Choose the longest consecutive chain of carbon atoms that includes the double bond, and name it as the parent alkene.
2. Number the chain from the end that gives the double bond its smaller number.
3. Name and number the alkyl groups as with the alkanes.

Example

When side chains are present. Name the compound below:



$$CH_3-\underset{CH_3}{CH}-CH=CH_2$$

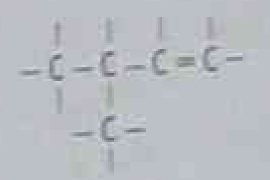
Step 1. Draw the longest carbon chain that contains the double bond.

$$\begin{array}{c} 4\;\;3\;\;2\;\;1 \\ -C-C-C=C- \end{array}$$

Step 2. Use the chain as a surname. Number the chain.

...... 1-butene

Step 3. Name and number any side chains using the same numbering system as for the double bond.



$$\begin{array}{c} -C-C-C=C- \\ -C- \end{array}$$

(*Answer*: 3-methyl-1-butene)

Alkynes

1. Unsaturated hydrocarbons.
2. General molecular formula C_nH_{2n-2}.
3. Functional group C≡C bond.

Cyclic hydrocarbons

Cycloalkanes are saturated hydrocarbons (C_nH_{2n}) where the carbons form a closed ring.

Figure 7.3 Formula for cyclohexane

Cycloalkenes are unsaturated hydrocarbons (C_nH_{2n-2}) where the carbons form a closed ring.

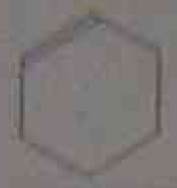


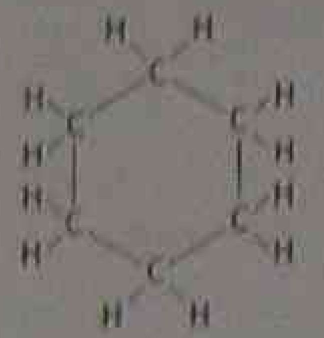
Figure 7.4 Formula for cyclohexene

Rule for naming cyclic hydrocarbons

The prefix 'cyclo-' is added to the corresponding aliphatic hydrocarbon.

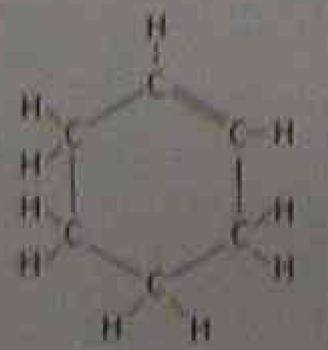
Example 1

Cycloalkane

General molecular formula	C_nH_{2n}
6-carbon ring	cyclohexane
Structural formula	

Example 2

Cycloalkene

General molecular formula	C_nH_{2n-2}
6-carbon ring	cyclohexene
Structural formula	

The alkanols (c.n. alcohols)

General molecular formula is $C_nH_{2n+2}O$ or $C_nH_{2n+1}OH$. Functional group is the hydroxyl (-OH) group.

Rules for naming alkanols

1. Choose the longest consecutive chain of carbon atoms which contain the -OH group.
2. Number the chain from the end that gives the -OH group its smallest number.
3. Name and number the alkyl groups as with the alkanes.

Isomerism in alkanols

After ethanol, different isomers are possible owing to position isomerism. After propanol, both position and branched chain isomerism can occur.

Example

To name the compound drawn below:

$$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

Step 1. The longest chain containing the -OH group contains three carbon atoms.

Step 2. The surname is ..... propanol.

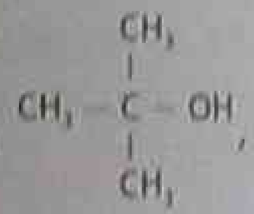
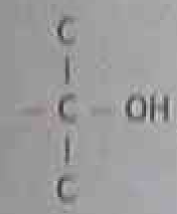
Step 3. The -OH group is on the second carbon atom, so the name is 2-propanol.

1-propanol and 2-propanol are position isomers

$$CH_3-CH_2-CH_2-OH$$

1-propanol is a primary alkanol since the -OH group is attached to a terminal carbon atom ($-CH_2OH$). (-COH group attached to one C-atom)

2-propanol is a secondary alkanol since a  $\overset{\displaystyle C}{\overset{|}{-CHOH}}$ group is present.
(-COH group attached to two C-atoms)

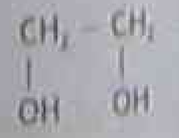
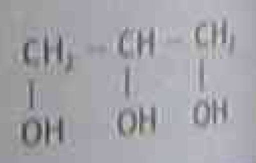
2-methyl-2-propanol,  $CH_3-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-OH$, is an example of a tertiary alkanol since a  $-\overset{\displaystyle C}{\overset{|}{\underset{\displaystyle C}{\underset{|}{C}}}}-OH$ group is present.

(-COH group attached to three C-atoms)

Diols and triols

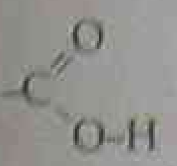
Diols are compounds which contain two hydroxyl groups. Triols are compounds which contain three hydroxyl groups.

Table 7.3 The diols and triols

Name	Molecular formula	Structural formula
1,2-ethanediol (c.n. ethylene glycol)	$C_2H_6O_2$	 $\underset{\displaystyle OH}{\underset{\mid}{CH_2}}-\underset{\displaystyle OH}{\underset{\mid}{CH_2}}$
1,2,3-propanetriol (c.n. glycerol or glycerine)	$C_3H_8O_3$	 $\underset{\displaystyle OH}{\underset{\mid}{CH_2}}-\underset{\displaystyle OH}{\underset{\mid}{CH}}-\underset{\displaystyle OH}{\underset{\mid}{CH_2}}$

Alkanoic acids (carboxylic acids)

General formula is R–COOH, where R is an alkyl group (except for HCOOH).

Functional group is 

$$-C\overset{\displaystyle O}{\underset{\displaystyle O-H}{\Big<}}$$

Alkanoic acids are named by dropping the -e from the corresponding alkane and adding -oic acid.

Examples

HCOOH	methanoic acid (formic acid)
CH_3COOH	ethanoic acid (acetic acid)
CH_3CH_2COOH	propanoic acid

Physical properties

1. The first four members are water soluble liquids.
2. Because of their hydrogen bonding, they have relatively high boiling points.

7.4 Organic analysis

There are laboratory tests which can be carried out to distinguish between certain organic compounds. Safety precautions, e.g. wearing safety glasses, must be observed. Several of these tests are outlined below. Since this is essentially a practical topic, some activities are included which have worked answers for revision purposes.

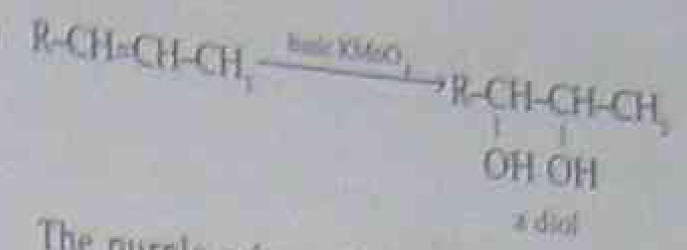
Tests to distinguish between alkanes and alkenes

(a) If an alkene, e.g. cyclohexene, is shaken with bromine water, the red-brown colour of the bromine immediately fades to become colourless. Cyclohexene in an addition reaction with bromine becomes 1,2 dibromo cyclohexane.

$$R\text{-}CH{=}CH_2 \xrightarrow{Br_2} RCHBr\text{–}CH_2Br$$

Cyclohexane does not react immediately with bromine water though if it is allowed to stand, the colour will fade due to the occurrence of a substitution reaction.

(b) *Oxidation* of alkenes by potassium permanganate. Alkenes are readily oxidised, e.g. by potassium permanganate solution. If the $KMnO_4$ solution is basic or neutral, the following reactions will occur:

(i) 

$$R\text{-}CH{=}CH\text{-}CH_3 \xrightarrow{\text{basic } KMnO_4} \underset{\text{a diol}}{R\text{-}\underset{\displaystyle OH}{\underset{|}{CH}}\text{-}\underset{\displaystyle OH}{\underset{|}{CH}}\text{-}CH_3}$$

The purple colour of the $KMnO_4$ solution will form a brown precipitate of MnO_2. Alkanes would produce no change.

(ii) If the alkene is boiled with a concentrated acidified solution of potassium permanganate, further oxidation occurs, and if the alkene has a straight chain, the end products will be alkanoic acids.

General equation: (not for 1-alkenes)

$$R\text{–}CH{=}CH\text{–}CH_3 \xrightarrow[\text{acid } KMnO_4]{H_2O \text{ heat}} R\text{–}COOH + CH_3\text{–}COOH$$

Example 1

$$\underset{\text{2-butene}}{CH_3\text{–}CH{=}CH\text{–}CH_3} \xrightarrow[\text{acid } KMnO_4]{H_2O \text{ heat}} \underset{\text{ethanoic acid}}{CH_3\text{–}COOH + CH_3\text{–}COOH}$$

In this example, the alkene was *symmetrical* so only one product, ethanoic acid, was formed.

Example 2

$$\underset{\text{2-pentene}}{CH_3\text{–}CH_2\text{–}CH{=}CH\text{–}CH_3} \xrightarrow[\text{acid } KMnO_4]{H_2O \text{ heat}} \underset{\text{propanoic acid}}{CH_3\text{–}CH_2\text{–}COOH} + \underset{\text{ethanoic acid}}{CH_3\text{–}COOH}$$

In this example, the alkene is *asymmetrical*, so two different alkanoic acids are formed.

Example 3

For a 1-alkene. Vigorous oxidation causes CO_2 gas to be given off and one alkanoic acid to be formed.

$$\underset{\text{1-propene}}{CH_3\text{–}CH{=}CH_2} \xrightarrow{[O]} \underset{\text{ethanoic acid}}{CH_3\text{–}COOH} + CO_2 + H_2O$$

Note 1. In all the examples in (ii) the carbon chain has shortened.

Note 2. CO_2 is only given off when the double bond is attached to a terminal, that is, an end-of-chain carbon atom.

Note 3. It is possible, by carrying out vigorous oxidation using $KMnO_4$, to distinguish between 1-alkenes (where the C=C bond is found at the end of the carbon chain) and the other alkenes.

If a gas is given off during this oxidation and, when bubbled into limewater it turns milky, a 1-alkene is present.

Tests for alkanols

(a) Reaction with sodium metal

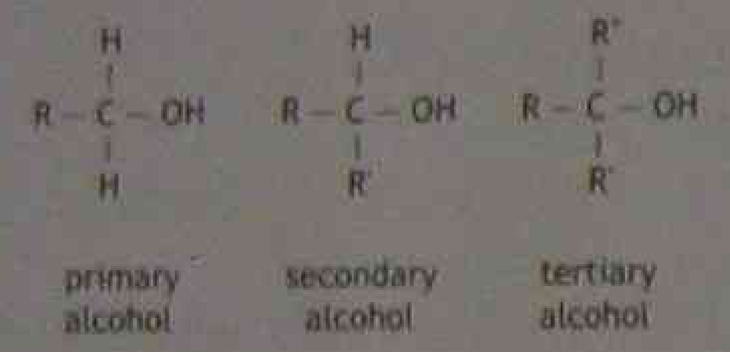
This is a very important reaction for alcohols since it shows that one hydrogen atom, the one in the -OH group, is bonded differently from the other hydrogen atoms in the alcohol molecule.

$$2ROH(l) + 2Na(s) \rightarrow 2RONa(l) + H_2(g)$$

An alkanol reacts with sodium metal but not with sodium hydrogen carbonate (which distinguishes alkanols from alkanoic acids).

(b) Oxidation

Type formulae for alcohols



where R, R′, R″ are any alkyl groups.

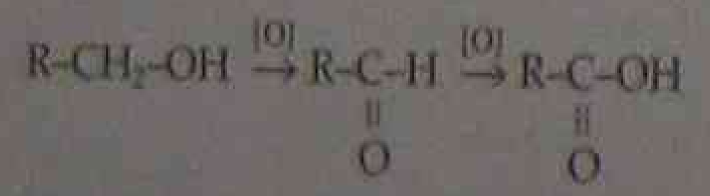
Primary alcohols

These have an -OH group on a terminal carbon atom, $R\text{-}CH_2OH$, for example

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH \text{ (1-butanol).}$$

On oxidation by acidified potassium permanganate or potassium dichromate, they first form the alkanals which are readily oxidised in turn to alkanoic acids.

General equation



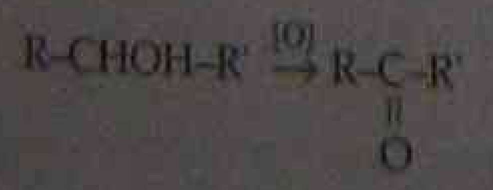
$$R\text{-}CH_2\text{-}OH \overset{[O]}{\rightarrow} R\text{-}\underset{\underset{O}{\|}}{C}\text{-}H \overset{[O]}{\rightarrow} R\text{-}\underset{\underset{O}{\|}}{C}\text{-}OH$$

Secondary alcohol

These are oxidised by potassium permanganate and potassium dichromate in acid solutions. They contain a -CHOH-R group which cannot be on a terminal carbon atom.

$$\text{secondary alkanols} \xrightarrow{[O]} \text{alkanones}$$

General equation:



$$R\text{-}CHOH\text{-}R' \overset{[O]}{\rightarrow} R\text{-}\underset{\underset{O}{\|}}{C}\text{-}R'$$

Note: Colour changes are

$K_2Cr_2O_7 \rightarrow Cr^{3+}$ (orange → green)

$KMnO_4 \rightarrow Mn^{2+}$ (purple → colourless)

Tertiary alkanols

These are not oxidised under normal conditions, so they can be distinguished from primary and secondary alkanols.

(c) Preparation of esters

Esters are prepared by the reaction of an alkanoic acid and an alkanol in the presence of concentrated H_2SO_4 which acts as a catalyst. After warming, the fruity smell of the ester can be detected.

Table 7.4 Characteristic odours of some esters

Name	Odour
ethyl butanoate	pineapple
pentyl ethanoate	banana
octyl butanoate	orange
ethyl ethanoate	nail-polish remover
ethyl methanoate	rum

Some specific reactions to identify organic substances

Table 7.5 pH and solubility tests

Acid functional groups	Basic functional groups	Neutral functional groups
Alkanoic acids Phenols	aliphatic amines aromatic amines	alkenes alkynes haloalkanes
Form bubbles of CO_2 with $NaHCO_3(aq)$	turn red litmus blue turn blue litmus red	alkanols alkanals alkanones

Tests for alkanoic acids

(a) Alkanoic acids are weak acids so they turn blue litmus red.

(b) Alkanoic acid + sodium hydrogen carbonate will release CO_2 which, when bubbled into limewater, turns it milky and then clear.

(i) $R\text{-}COOH(aq) + NaHCO_3(aq) \rightarrow R\text{-}COONa(aq) + CO_2(g) + H_2O(l)$

(ii) $CO_2(g) + Ca(OH)_2(aq) \rightarrow CaCO_3(s) + H_2O(l)$

(iii) $CaCO_3(s) + CO_2(g) + H_2O(l) \rightarrow Ca(HCO_3)_2(aq)$

(c) Active metal + alkanoic acid → salt + hydrogen
(Ca or Mg)

Note: Do not use Na in this reaction (DANGER).

Example

$$\underset{\substack{\text{ethanoic acid}\\\text{(acetic acid)}}}{2CH_3\text{-}COOH} + Ca \rightarrow \underset{\substack{\text{calcium ethanoate}\\\text{(calcium acetate)}}}{2(CH_3 - COO)_2Ca} + H_2$$

(d) Alkali + alkanoic acid → salt + water

Example

$$KOH + \underset{\text{acetic acid}}{CH_3\text{-}COOH} \rightarrow \underset{\text{potassium acetate}}{CH_3\text{-}COOK} + H_2O$$

(e) Alkanoic acid + alkanol → ester + water

Example

$$R\text{-}COOH + HOR' \xrightarrow{\text{conc. } H_2SO_4} R\text{-}COOR' + H_2O$$

Activity 7.1

Testing hydrocarbons

Procedure

Using clean dry test tubes labelled A–D:

(a) Test small amounts (about 1 mL) of

(i) cyclohexane, and (ii) cyclohexene

with about 1 mL of bromine water. Note any colour changes.

Care: Hydrocarbons and bromine are toxic substances and must not be spilt or inhaled.

(b) Test small amounts of

(i) cyclohexane, and

(ii) cyclohexene

with 2–3 mL of acidified potassium permanganate solution. Note any colour changes.

Activity 7.2

Testing alkanols

Procedure

Using clean dry test tubes labelled A–C:

(a) Add about 2 mL of

(i) 1-butanol to test tube A

(ii) 2-butanol to test tube B, and

(iii) methyl-2-propanol to test tube C.

Add 2–3 mL of acidified potassium permanganate ($KMnO_4$) to each of the test tubes A–C. Shake the test tube gently and observe any colour changes over the next 10 minutes.

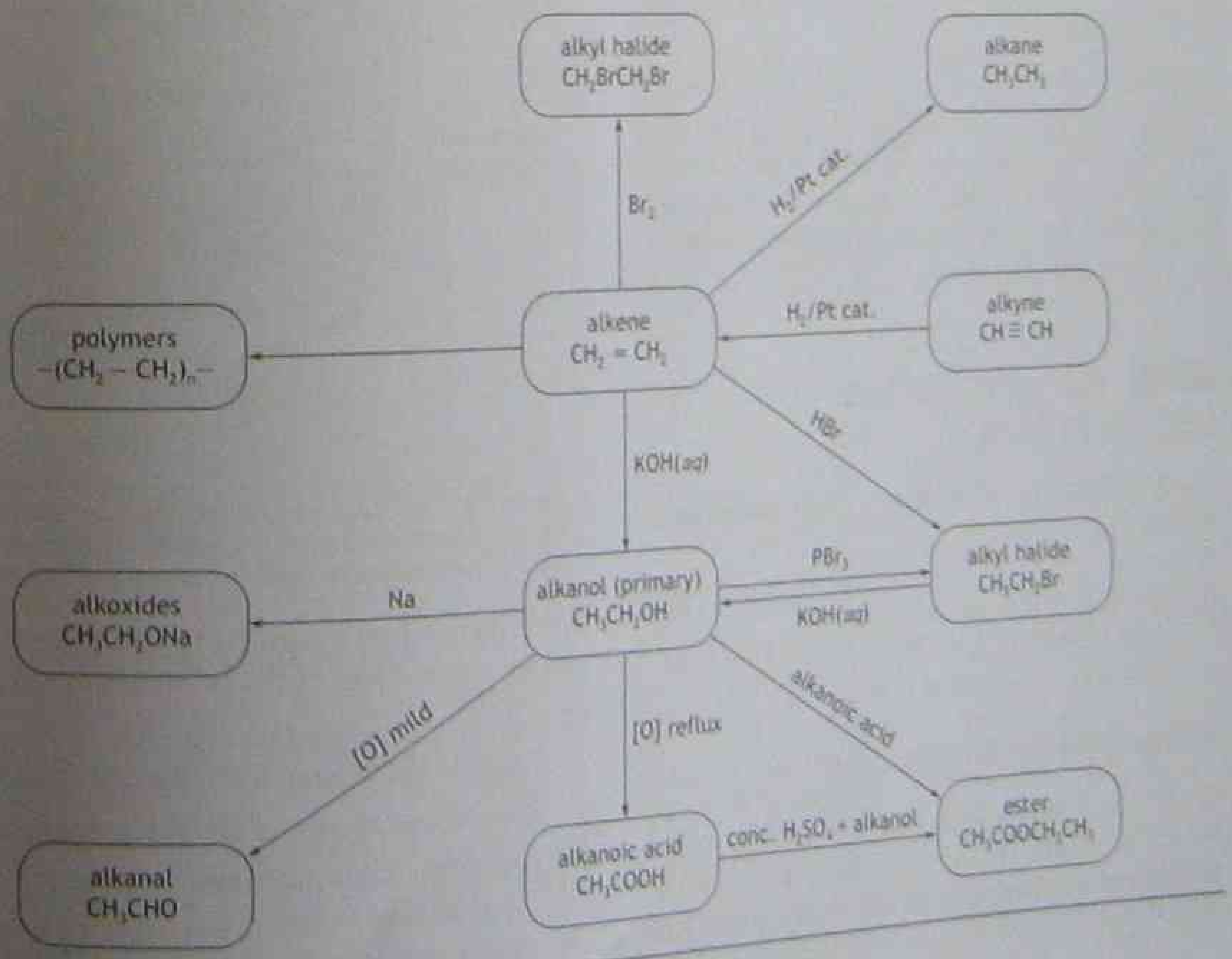


Figure 7.5 Flow chart of common aliphatic reactions

(b) Write appropriate equations, using structural formulae. State which of the alkanols (C_4H_9OH) is tertiary.

Activity 7.3

Testing alkanoic acids

Procedure

Using clean dry test tubes A–D, add about 5 mL of 2 M acetic (ethanoic) acid solution (CH_3COOH):

- To A add a few small pieces of cleaned magnesium ribbon.
- To B add a marble chip ($CaCO_3$).
- To C add about 3 mL of 2 M sodium hydroxide solution (NaOH).
- To D add a few drops of Universal Indicator (or use UI paper).

Write down any evidence of a chemical reaction and write any appropriate equations, with states, for test tubes A–C. Record the pH for test tube D.

The next reaction involves very corrosive liquids and a strong-smelling vapour. It should be carried out as a demonstration test in a fume cupboard. To a clean dry test tube carefully add 2 mL of glacial acetic acid (17 M CH_3COOH), 1 mL of ethanol (C_2H_5OH) and three drops of concentrated sulfuric acid (H_2SO_4).

Lightly stopper the test tube and place it in a water bath in the fume cupboard for about 15 minutes. Allow the test tube to cool and unstopper it. Carefully smell the vapour and describe it. Is there evidence of a new compound being formed? Write an equation for the reaction.

7.5 Inorganic analysis (extension work)

Inorganic analysis is considered here in terms of testing for

(a) gases,
(b) anions (negative ions),
(c) cations (positive ions), and
(d) complex transition metal ions.

Qualitative analysis

Qualitative analysis allows us to determine which substance is present. The aim here is to test the suitability of certain reagents and techniques for the detection of the following anions and cations:

Anions	SO_4^{2-}, Cl^-, NO_3^-, CO_3^{2-}, OH^- (extension S^{2-}, Br^- and I^-)
Cations	Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Zn^{2+}, Pb^{2+}, Ag^+, Cu^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+}, NH_4^+, H

The accumulated evidence obtained in submitting an unknown sample to several reagents could be expected to lead to either a unique identification or at least to identification of the anion or cation as being within a small group.

Various techniques are employed:

1. Appearance — including colour and whether powder or crystalline.
2. Solubility — in water (hot or cold). Test soluble substances with pH paper.
   — in dilute acids and alkalis.
3. Actions of acids and alkalis.
4. Action of heat.
5. Precipitation reactions.
6. Action of oxidising and reducing agents.

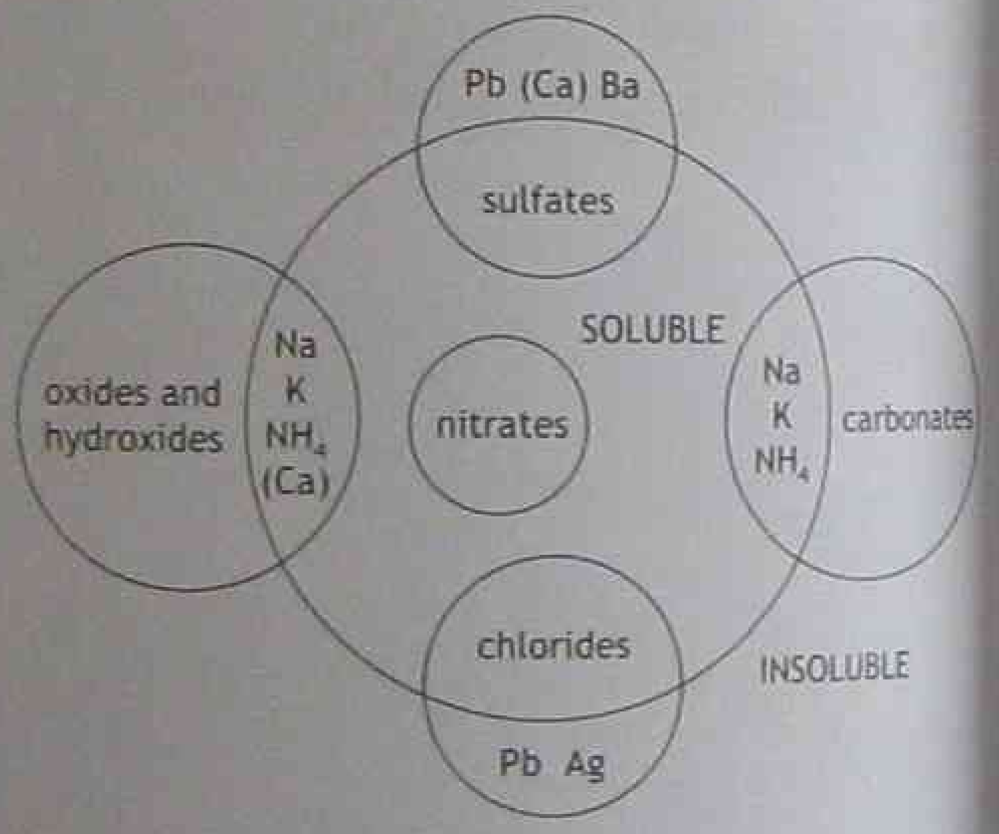


Figure 7.6 Solubility of inorganic compounds. Substances within the large central circle have a solubility > 1 g L^{-1} and are called soluble. Insoluble compounds lie outside the large circle

After general tests, special tests can be carried out using one or more of the following:

1. Specific precipitation agents (e.g. in spot tests).
2. Specific oxidising or reducing agents.
3. Specific colour reactions (e.g. in spot tests).
4. Paper chromatography.
5. Flame testing.

EXTENSION ACTIVITIES

Activity 7.4

Tests on gases

1. *Oxygen.* Hold a glowing splint to the mouth of the test tube.
2. *Acidic or basic gases.* Hold a piece of moist litmus to the mouth of the test tube.
3. *Nitrogen dioxide.* Brown colour in air. Gives acidic reaction to moist litmus.
4. *Hydrogen gas.* Colourless gas. Use a glowing splint.
5. *Hydrogen chloride gas.* When a glass rod moistened with ammonia solution is held near the mouth of the test tube, dense white fumes form. Hydrogen chloride gas is also acidic to litmus.
6. *Carbon dioxide gas.* Acidic to litmus. Forms a white precipitate when first bubbled into a solution of limewater. If CO_2 is bubbled into limewater for some time, the solution eventually becomes clear due to the formation of soluble calcium hydrogen carbonate, $Ca(HCO_3)_2$.
7. Complete the following table.

Gas	Formula	Moist litmus	Special tests	Equations
Oxygen				
Nitrogen dioxide				
Hydrogen				
Hydrogen chloride				
Carbon dioxide				

Activity 7.5

Tests for identifying anions by dilute acids

Problem

Is the reaction of dilute acids of value in identifying anions?

Method

1. Examine the action of dilute acids (2 M HCl and 2 M H_2SO_4) on a representative range of solid carbonates, nitrates, chlorides and sulfates.
2. Test all gases evolved.
3. Tabulate results and write equations where possible.

Anion	Action of dilute acids	Some equations
CO_3^{2-}		
Cl^-		
NO_3^-		
SO_4^{2-}		

Conclusion . . .

Activity 7.6

Tests for identifying halide ions by precipitation reactions

Explanation

We can look up solubility tables to find which salts of the halides are insoluble (see Figure 7.6).

Method

1. Decide on a suitable salt to add to the halide solutions.
2. Make up about a 0.01 M solution of this salt, using distilled water.
3. Compare the following table.

Anion	Salt added	Colour of precipitate	Equation
Cl^-			
Br^-			
I^-			

Conclusion . . .

Activity 7.7

Tests for identifying cations by precipitation reactions

Problem

What use are precipitation reactions in identifying cations?

Explanation

Precipitation reactions can be particularly useful if

(b) if most of the salts of the cation are soluble (e.g. most chlorides are soluble except those of silver, mercury and lead; lead chloride is soluble in hot water but not in cold).

We could add a dilute solution of hydrochloric acid to our unknown solution and if a precipitate formed, we could say that any of the above metal ions could be present. We could then carry out other precipitation reactions to narrow the field even further.

Example 1

Reactions of the lead ion (Pb^{2+})

Take lead nitrate or lead acetate solutions.

Using separate test tubes
(a) add potassium iodide solution,
(b) add potassium chromate solution, and
(c) add dilute sulfuric acid solution.

Lead salt	Solution added	Colour of precipitate	Equation
(a)			
(b)			
(c)			

Example 2

Reactions of the silver ion (Ag^+)

Take a dilute solution of silver nitrate solution.

Care: Stains hands and clothing.
(Suggest demonstration.)

Using separate test tubes
(a) add potassium chromate solution, and
(b) add potassium iodide solution.

Silver salt	Solution added	Colour of precipitate	Equation
(a)			
(b)			

Example 3

Reactions of the barium ion (Ba^{2+})

Take a solution of barium chloride.

Using separate test tubes
(a) add potassium chromate solution, and

Barium salt	Solution added	Colour of precipitate	Equation
(a)			
(b)			

Activity 7.8

Use of hydroxide reactions for distinguishing between cations

Method

1. In each case, 0.1 M sodium hydroxide and about 3 M ammonia solution are separately added to the soluble salts of the cations in the table at the top of the next page.
2. Write equations where possible.

Conclusion . . .

Activity 7.9

Tests involving complex ions

Problem

Can complex ions be used to detect metals in mixtures?

Explanation

The transition metals form many complexes, and coloured complexes are particularly useful in detecting the metals present.

(a) Complex thiocyanates

The thiocyanate ion is the NCS^- ion.

Method

1. A 0.1 M solution of ammonium thiocyanate is added to a solution of an iron (III) compound (e.g. $FeCl_3$).
2. Note any colour change.
3. Record your observation.
4. Repeat the test with an iron (II) salt.

Note: Because iron (II) salts are readily oxidised to iron (III) salts, it is necessary to prepare a fresh solution of iron (II) sulfate. To do this, add dilute sulfuric acid and zinc to the solution of the iron (II) salt before use. Decant off 2–3 mL of the reduced solution and test with ammonium thiocyanate. Record the result.

Cation	Hydroxide	Precipitation by NaOH		Precipitation by NH_4OH		Coloured precipitation (State colour)
		Sol. in excess	Insol.	Sol. in excess	Insol.	
Na^+	NaOH					
K^+	KOH					
Mg^{2+}	$Mg(OH)_2$					
Ba^{2+}	$Ba(OH)_2$					
Zn^{2+}	$Zn(OH)_2$					
Al^{3+}	$Al(OH)_3$					
Pb^{2+}	$Pb(OH)_2$					
Ag^+	Ag_2O					
Cu^{2+}	$Cu(OH)_2$					
Fe^{3+}	$Fe(OH)_3$					
Ca^{2+}	$Ca(OH)_2$					
NH_4^+	NH_4OH					

Ion	Reagent	Observations
Fe^{3+}	ammonium thiocyanate	
Fe^{2+}	ammonium thiocyanate	

Conclusion . . .

Extension

Add a small quantity of sodium fluoride solution to the thiocyanate complex formed with Fe^{3+} ions. Record your result and look up the scientific literature on complex ions to suggest an explanation.

(b) Complex amines

A coloured amine is formed by the Cu^{2+} ion.

Method

1. Half fill a test tube with a 0.5 M $CuSO_4.5H_2O$.
2. Add a small amount of 1 M sodium hydroxide and then an excess.
3. Record the result.
4. Repeat using 7 M ammonia solution, dropwise at first then in excess.
5. Record your observations.

Ion	Reagent	Observations
Cu^{2+}	NaOH	
Cu^{2+}	ammonia solution	(i) (dropwise) (ii) (excess)

Conclusion . . .

7.6 Forensic evidence from soils

Soils can offer importance evidence in a crime investigation. In Sydney, after the drawing of the first Opera House Lottery the winner's 8-year-old son (G.T.) was kidnapped for ransom. Several days later, the child's body was found in a bushy hollow. Geologists investigating soil samples found traces of pink mortar on the boy's clothes which matched mortar on a building site owned by the suspected kidnapper. This geological evidence was used in the trial of the murderer.

- A forensic scientist carries out a preliminary separation using a stereoscopic microscope. Extraneous materials, e.g. insect parts or plant matter, are mechanically separated.
- A mineral examination by means of polarised light microscopy may be attempted.
- Particle size distribution may be carried out (particles of sand are much larger than clay particles).
- Colour comparison of soils depends on the

chemical substances present, e.g. light-coloured soils can contain silica or lime; iron compounds produce brown, red or yellow coloured soils.

- pH testing of soils can be easily determined using either a soil pH meter kit or Universal Indicator (UI) in liquid or paper form.
- If $pH > 7$, the soil is alkaline; if $pH = 7$, the soil is neutral; and if $pH < 7$, the soil is acidic.
- Other groundwater tests can be used to determine hardness, sulfate or salt content.
- Humus content of soil can be determined by ignition loss found by heating oven-dried soil at about 700°C for 30 minutes. The humus is burnt off as CO_2 and H_2O.
- Examination of soil for pollen and other biochemical factors can reduce areas of investigation.

7.7 Facial reconstruction techniques

Whether applied to modern criminal investigations or to archaeological and anthropological studies, facial reconstruction brings together the work of numerous specialists ranging from dentists to geneticists and from archaeologists to radiologists.

These techniques are used for a number of reconstruction tasks:

- To identify skeletal remains thought to be of historical importance.

  Example

  The Case of the 'Carian Princess'

  A tomb was uncovered in Caria (Turkey) in 1989, the sarcophagus revealed a full female skeleton strikingly dressed with gold jewellery. She was nicknamed the 'Carian Princess'. From the jewellery, it was established that she was buried about 340–320 BC. Forensic dental techniques helped to establish her age when she died. Eventually, with the help of historical records, she was identified as Ada I. The forensic scientists were asked to carry out a *whole body* reconstruction which is now displayed in Bodrum Museum.
- To provide a reconstructed facial model that would be acceptable to show to the public, using papers and/or television.

  Example

  The body of Karen Price was found by workmen when laying new drains in 1989. She had disappeared nine years previously. Forensic dentists established her age as about 15.5 years. The skull was cast and the rebuilding of the head took two days. After a television appearance on *Crimewatch (UK)*, the model was identified and her killers were convicted one year after the showing of the program.
- New technology is now being used in facial reconstruction. An optical laser scanning system can gather all data on a skull in a matter of minutes. It can then reproduce it in a three-dimensional image on a computer.

These advances indicate how changes in technology can enhance or alter the outcome of a forensic investigation.

Forensic dentistry

Forensic dentistry/odontology is an important means of identifying victims of crime, accidents or disasters, and the perpetrators. It also has significant applications in the field or archaeology and anthropology.

Archaeology/Anthropology

Important facts about remains can be gleaned from examinations of the teeth of the skeleton. Accurate estimates of the age and sex of such remains can be made, as illustrated by the case of the 'Carian Princess'. In this case, a technique devised by Dr David Whittaker of the University of Wales was applied. The technique measures the ratio of sclerotic apical dentine to non-sclerotic coronal dentine, thus helping to determine more accurately the age at time of death of the 'Princess' thus providing more clues to her actual identity when compared to historical records. The teeth can also provide information about diet by looking at such things as attrition and staining, and also information about health status, diseases and even cultural practices such as symbolic filing, grinding or the removal of teeth.

Another technique for examining human dental structure can be used to determine age. Analysis of spherical structures in dentine made of calcium phosphate has shown that by counting them and noting their state of fusion, correlation exists between the state of fusion of calciospherites and age.

Identification

In cases of disaster or accident, forensic dentistry can be used to discover or confirm the identity of victims. In such circumstances, remains may be severely affected by trauma or fire, making identification difficult. A case in France involving a collision between a passenger train and a petrol tanker made use of forensic dental techniques (namely a specific odontostomatological technique of craniomandibular disarticulation with bone samples) resulting in identification of 92% of the heavily carbonised remains, with only one case needing molecular biology for positive identification.

Another example of identification by forensic odontology is the determination of gender from a sample of the dental pulp. Capillary gel electrophoresis with amelogenin locus as marker is used.

Dental records may also be used to identify unknown living or dead persons in cases of accident or disaster but also increasingly in the investigation of crime. Victims may be identified by comparison of ante-mortem and post-mortem records, most commonly X-rays, but also dental models, prostheses or unique features. If dental records are not available, other records may provide samples of DNA (e.g. from cytological smears such as the PAP smear used for routine cervical cancer checks in women) which may be compared to DNA derived from the teeth by cryogenic grinding.

Not only victims may be identified by forensic odontology. Perpetrators may also be identified by analysing bite marks and saliva samples. One case saw determination of a burglar's DNA profile from saliva left in a bitten piece of cheese. Saliva samples may even be collected from within bite wounds and DNA profiles compared to those of suspects. The bite mark itself may be compared with models, photographs or such other records of the bite to help implicate or exculpate an accused person.

7.8 Progress in analytical chemistry

Technological change in analytical chemistry can significantly alter the outcome in the forensic investigation of blood stains. Until the 1970s, analysis of bloodstains was limited to three basic types of testing:

1. Identifying the stain as blood (using ninhydrin).
2. Identifying the stain as being of human or animal origin.
3. Identifying the blood group.

(i) The ABO system divides blood into four basic groups. The groups are identified by analysing protein molecules called antigens and antibodies. Individuals with protein A have blood type A; those with protein B have blood type B; those with both proteins have blood type AB; and those with neither protein have blood group O. Each person's blood type is determined by the two inherited genes (one from each parent).

(ii) The Rh protein system depends on the fact that about eight in every ten people have Rh protein in their cells. People with this protein are called Rh positive and those who lack it are called Rh negative.

Note: The performance of blood tests in schools or colleges is forbidden because of concern about transmitting blood diseases.

Table 7.6 Percentage frequency in the Australian population of the eight main blood groups

Blood group	% frequency	Blood group	% frequency
O positive	40	B positive	8
O negative	9	B negative	2
A positive	31	AB positive	2
A negative	7	AB negative	1

More recently, in the USA, it was found that the enzyme phosphoglucomutase (PGM) could be detected in dried blood stains. This was useful to the forensic investigator since the enzyme is polymorphic. Since then, several genetic markers have been found to be polymorphic in a specific racial group, e.g. transferrin is a serum protein which is rare in white populations but occurs in 8–10% of African-Americans and other black communities.

Advances in genetic technology

- provide genetic profiles of both victim and suspect;
- increase the discrimination potential of a specific bloodstain since it lowers the frequency of occurrence of the stain within a given population;
- provide an ability to distinguish between two persons of the same blood group; and
- in some cases, can indicate the possible racial origin of the bloodstain.

The value of this advanced technology can be illustrated in the following case histories which took place in the United States of America.

Case 1: E.S. homicide

A woman (E.S.) was raped and murdered. Blood from a cut on the perpetrator's hand was left on the victim's nightgown. Both the victim's blood and the blood stain on the nightgown was Group O, but the bloodstain did not originate from the victim because the other genetic marker phenotypes were different. The murderer was seen leaving the crime and was a black male, possibly of African-American origin. Calculation of the frequency of occurrence in the black population of blood group O and the genetic markers identified in the bloodstain indicated that 0.3% of the black male population in the United States could be expected to have these phenotypes; so 99.7% of the black male population was eliminated as being the source of the bloodstain.

Case 2: A.C. homicide

Two weeks after the E.S. homicide, a second woman (A.C.) was found brutally murdered and her car and credit cards stolen. Two days later, police identified the woman's car and a black suspect (K.A.) was arrested. His clothing was blood-stained and genetic markers showed that the blood could have originated from A.C. The blood from the victim's nightgown in the E.S. case were compared with the suspect's blood. Both the blood group and markers were the same, indicating that K.A. could have committed both murders. Fingerprints on a telephone which was found ripped from the wall in the A.C. case were also identified as belonging to K.A. The suspect was subsequently convicted of both homicides. In each case, bloodstain analysis played an integral part in the identification of the victim's assailant.

Case 3: Poison analysis

Forensic chemists now make use of powerful molecular and biochemical techniques. Immunoassay techniques can be used to detect the traces of poison months or even years after a murder has been committed. Biological molecules (antibodies) can bind to specific proteins (antigens). In radioimmunoassays (RIA), radioactively labelled antigens that selectively react with the substance in question are added to a sample. If the substance's antibodies are present, they attach themselves to the labelled antigens. After the antibody-antigen complexes are separated, a measure of the radioactivity of the solution is taken to see whether the substance is present.

Forensic chemists from the London Metropolitan Police Forensic Laboratory carried out radioimmunoassays and high performance liquid chromatography (HPLC) on year-old routine samples taken from the body of a landscape gardener. The samples had been preserved in formalin and abnormalities were noticed by a medical student. The forensic chemists were able to detect the presence of paraquat, a poisonous water-soluble ammonium compound used in some weedkillers. The gardener's widow admitted adding weedkiller to her husband's drink and was convicted of murder.

Cases of suspected arson

Gas chromatography-mass spectroscopy (GC-MS) has, as a result of recent advances in technology, become more affordable and easier to use. Definitive information on compound information is provided and the technique is increasingly used in analysis of fine debris samples. Several substances can be identified which are found in the following major classes of petroleum products:

1. Saturated aliphatic hydrocarbons
2. Alicyclic and unsaturated aliphatic hydrocarbons
3. Alkylbenzenes
4. Monoterpenes

The GC-MS scheme is based on the identification of chemical composition of a material by mass spectroscopy carried out within the boiling point range. Analysis of organic material can also be used to distinguish between plant and animal material.

7.9 Carbohydrates

General formula: $C_x(H_2O)_y$.

Carbohydrates are found in large amounts in living systems. They are important as

(a) sources of energy;

(b) structure and supportive components of cells; and

(c) components in genetic control of growth and development.

Classification

Carbohydrates are usually classified by the number of monomer units they contain.

Group I – Monosaccharides

These are simple sugars with a carbon chain that usually contains five carbon atoms (pentoses) or six carbon atoms (hexoses).

Pentoses e.g. ribose (present in RNA), deoxyribose (present in DNA).

Hexoses e.g. glucose, fructose.

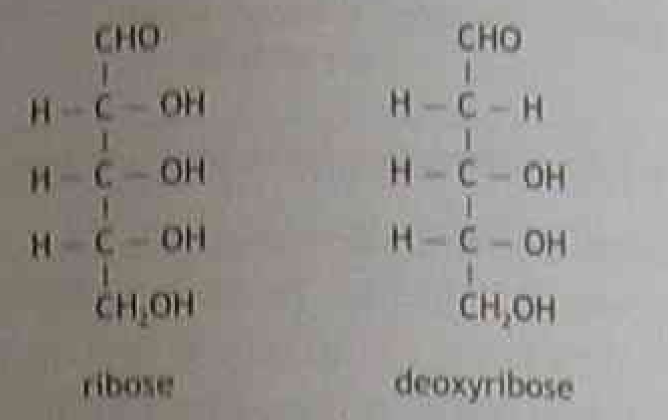


Figure 7.7a Monosaccharides — simple sugars (pentoses)

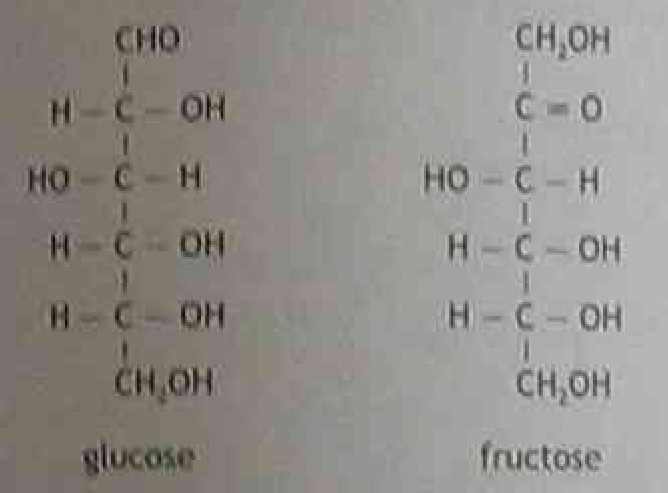


Figure 7.7b Monosaccharides — simple sugars (hexoses)

Functional groups present

In addition to -OH groups, a second functional group may be present. If an aldehyde group

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

is present, the sugar is called an aldose. Glucose is an example of an aldohexose. If a ketone group

$$-\underset{\underset{O}{\|}}{C}-$$

is present, the sugar is called a ketose. Fructose is an example of a ketohexose.

Properties of monosaccharides

(a) They do not undergo hydrolysis.

(b) Some hexoses contain functional groups which can be oxidised to carboxylic acids.

$$-\underset{\underset{O}{\|}}{C}-H \xrightarrow{[O]} -\underset{\underset{O}{\|}}{C}-OH$$

A suitable oxidising agent is Benedict's solution, an alkaline solution containing Cu^{2+} ions complexed as citrate ion. On warming gently with a monosaccharide, blue Benedict's solution will be reduced to form a brick-red precipitate of Cu_2O.

$$RCHO(aq) + 2Cu(OH)_2(aq) + NaOH(aq) \rightarrow RCOO^-Na^+(aq) + Cu_2O(s) + 3H_2O(l)$$

Note: Fructose, although a ketose, is changed to an aldose in the presence of alkali, so all the common monosaccharides give the test. Sugars which reduce Benedict's solution are called reducing sugars. Indicator paper, such as Clinitest paper or Multistix test strips, can also be used to detect reducing sugars.

(c) They are all soluble in water and their solutions can be tasted to compare their sweetness. Fructose (found in honey) is the sweetest of the naturally-occurring sugars.

(d) They can rotate a beam of polarised light when it is passed through the sugar solution. The beam of light may rotate to the right (dextrorotatory) or to the left (laevorotatory). Examples are D-glucose (commonly found) and L-glucose (very rare in nature).

(e) Hexose sugars can be changed to ethanol and carbon dioxide by fermentation using yeast as a catalyst. Yeast contains the enzyme zymase.

$$\underset{\text{glucose}}{C_6H_{12}O_6(aq)} \xrightarrow{\text{zymase}} \underset{\text{ethanol}}{2C_2H_5OH(aq)} + \underset{\text{carbon dioxide}}{2CO_2(g)}$$

(f) Chromatography methods may be used to identify monosaccharides using suitable solvents.
The formulae of monosaccharides can be represented in several different ways. (See Figure 7.8 over page.)

Group II – Disaccharides

General formula: $C_{12}H_{22}O_{11}$.

A disaccharide contains two monomer units and is formed as a result of acetal linkage. This is a condensation reaction which involves the elimination of water.

Example

$$\underset{\text{glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{fructose}}{C_6H_{12}O_6(aq)} \xrightarrow{-H_2O} \underset{\text{sucrose}}{C_{12}H_{22}O_{11}(aq)}$$

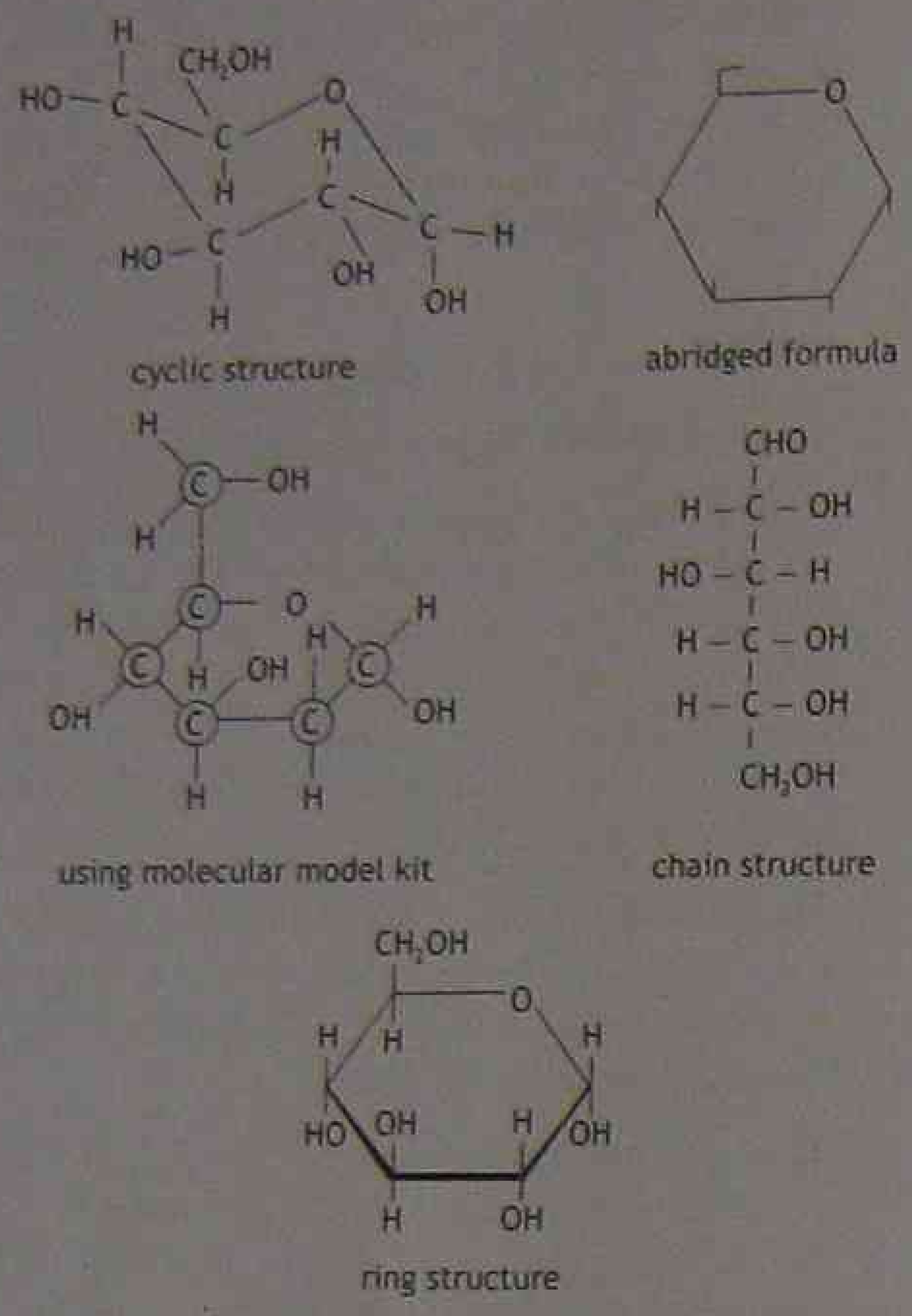


Figure 7.8 Structure of glucose

The most abundant disaccharides found in nature are sucrose (cane or beet sugar), lactose (milk sugar) and maltose (malt sugar).

Properties of disaccharides

(a) All are water-soluble.
(b) All are sweet-tasting. Sucrose is the sweetest of the disaccharides.
(c) They can be broken down into their monosaccharide units by acid hydrolysis or by the use of specific enzymes.
  Sucrose + water → fructose + glucose
  Maltose + water → 2 glucose
  Lactose + water → galactose + glucose
(d) Reduction reactions, for example with alkaline Benedict's solution only occur with lactose and maltose but not with sucrose. Residues from hydrolysis reactions can also be tested. After boiling a sucrose solution with a dilute mineral acid (HCl), a positive test will be given, indicating that the non-reducing disaccharide has been broken into smaller monosaccharides which are reducing sugars.
(e) Paper chromatography can be used to identify unknown disaccharides or their monosaccharide products after hydrolysis by using standard sugar solutions.

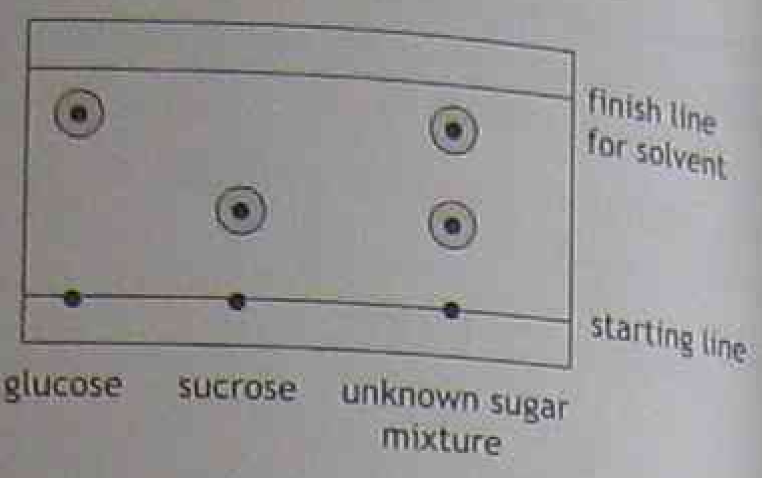


Figure 7.9 Separation of sugars by paper chromatography

The unknown sugar mixture would contain both sucrose and glucose. This conclusion is reached by comparing the distance that the different molecules travel in the solvent in the time taken for the solvent to reach the finish line.

Structure formulae for disaccharides

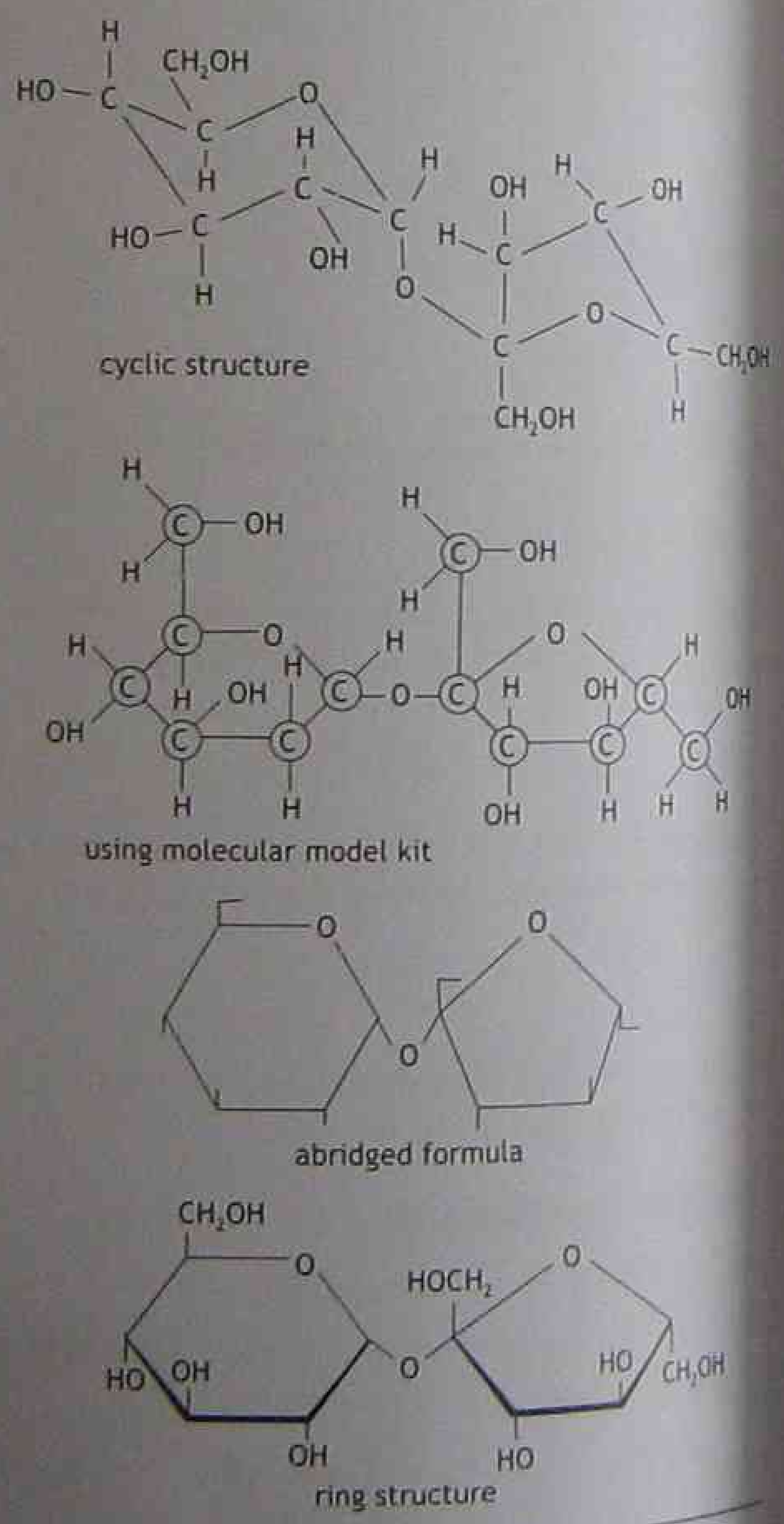
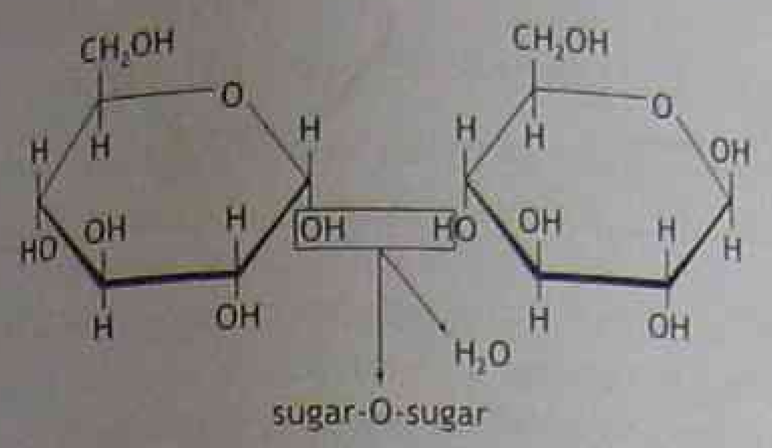


Figure 7.10 Structure of sucrose

The sugar-O-sugar or *glycoside bond in disaccharides* involves the elimination of water.



A *condensation reaction* to show this dehydration synthesis reaction is shown, where glucose and fructose forms sucrose.

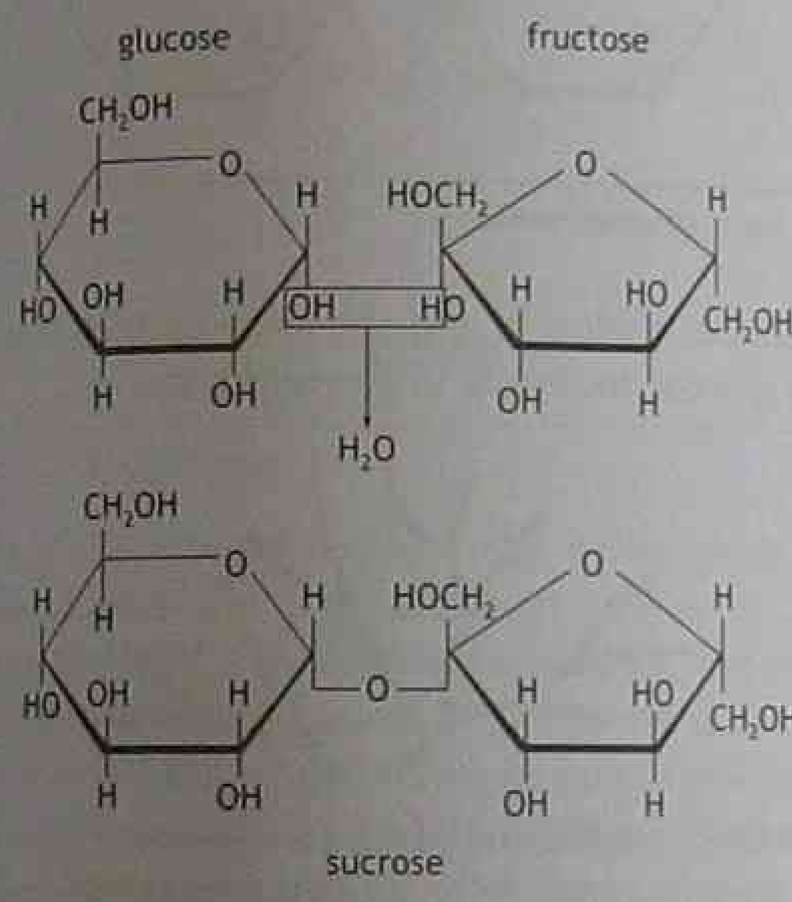


Figure 7.11 Glucose + fructose = sucrose

Group III – Polysaccharides

The most commonly found polysaccharides in living systems are cellulose, glycogen and starch. All are made up of many glucose units.

Structure

Cellulose contains β-D-glucose molecules linked by β(1 → 4) glycosidic bonds. A linear polymer of glucose is formed containing about 3000 units. Chains are linked by hydrogen bonding.

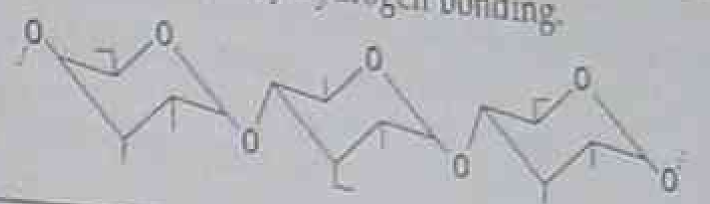


Figure 7.12 Cellulose

Starch contains two components:
(a) A small amount of amylose which has a linear structure linked by α(1 → 4) glycosidic bonds.
(b) Amylopectin, a branched chain structure, forming the major quantity.

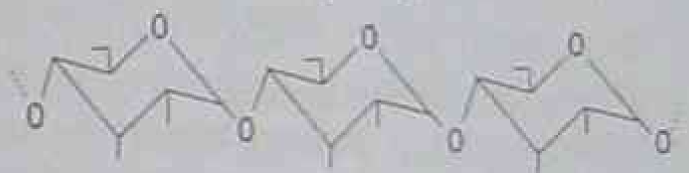


Figure 7.13 Starch (amylose chain)

Glycogen forms a highly branched chain structure.

Condensation reactions for polysaccharides

Many monosaccharides are joined to form a polysaccharide.
(a) Cellulose
(b) Starch molecule

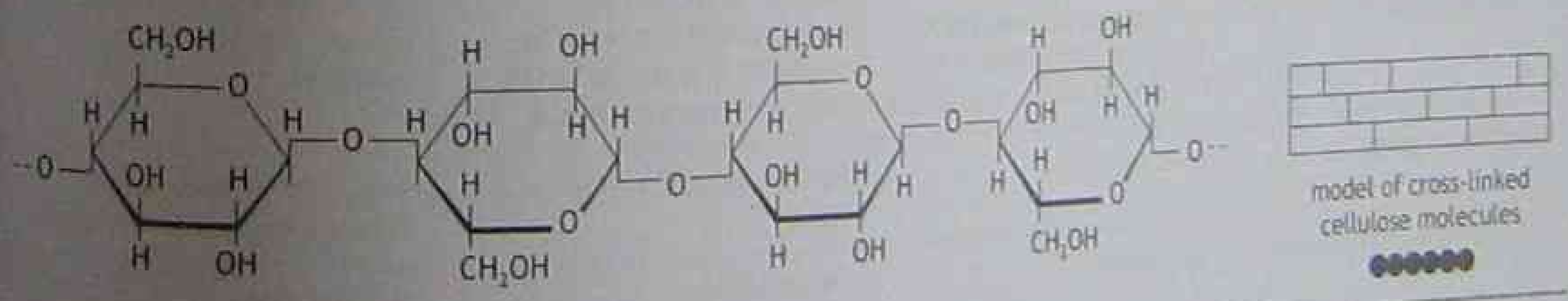


Figure 7.14 Cellulose molecule

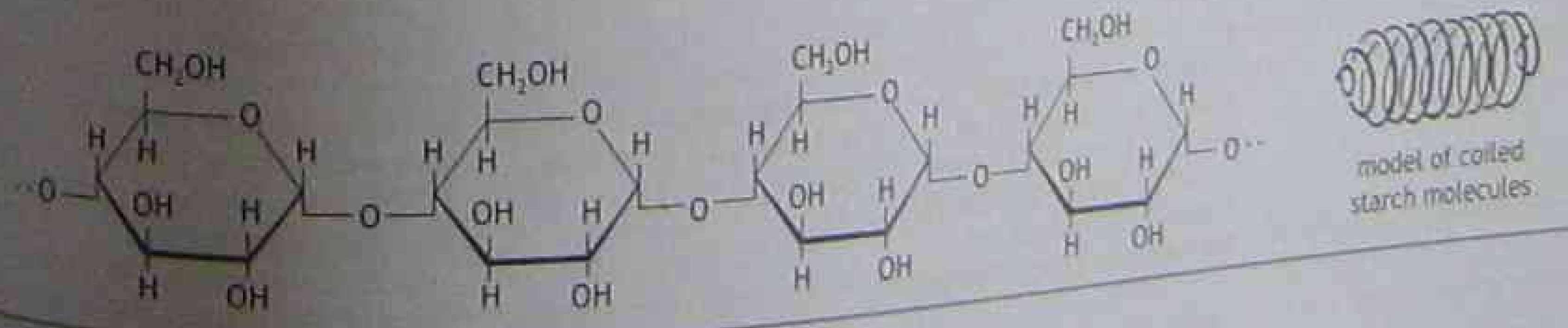


Figure 7.15 Starch molecule

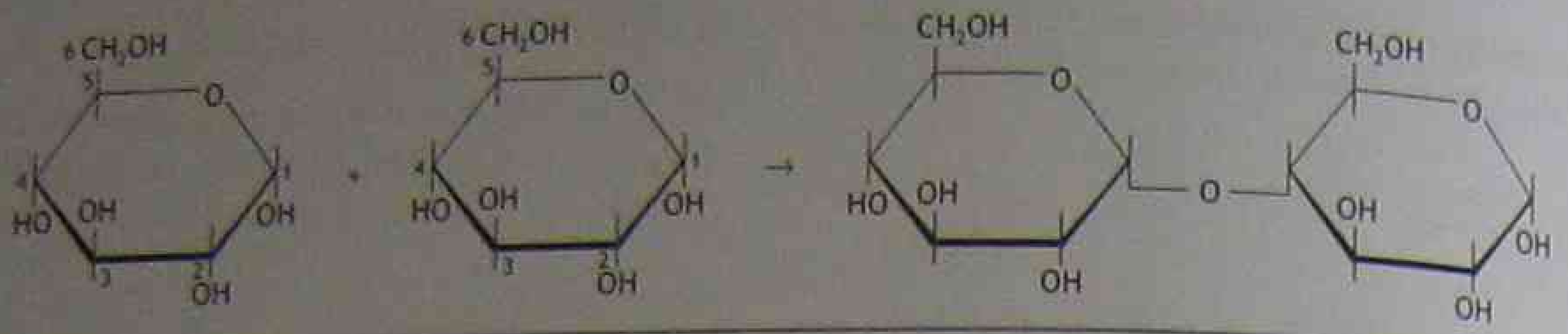


Figure 7.16 (1:4) linkage in a glucose polymer

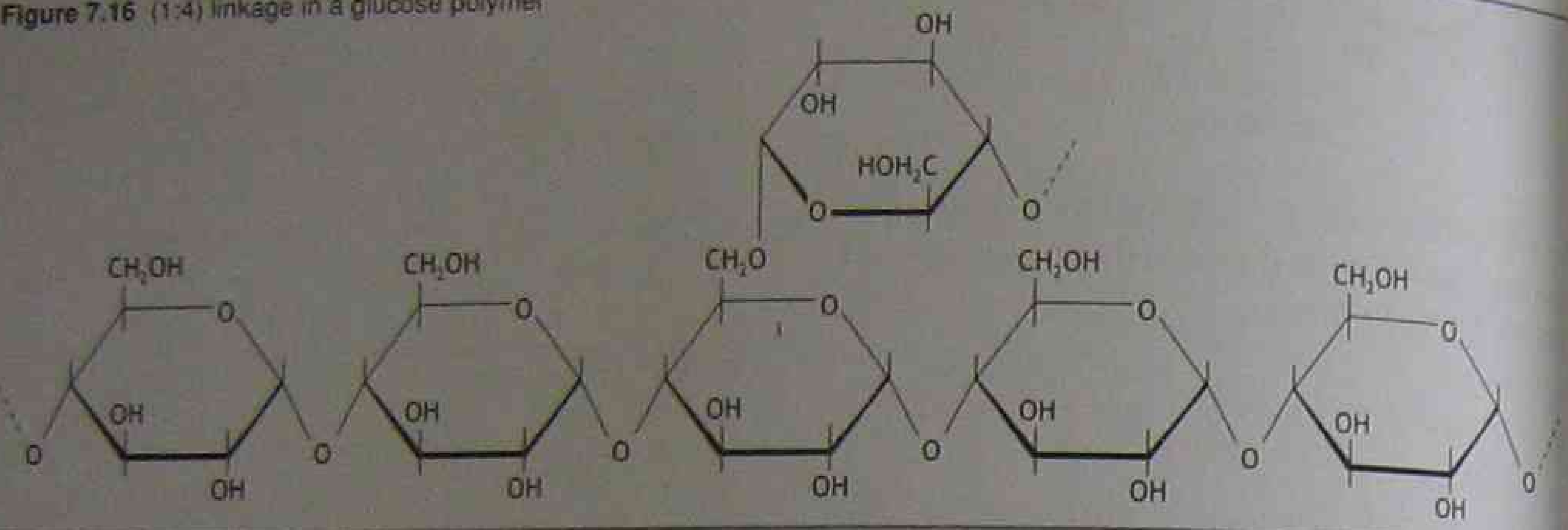
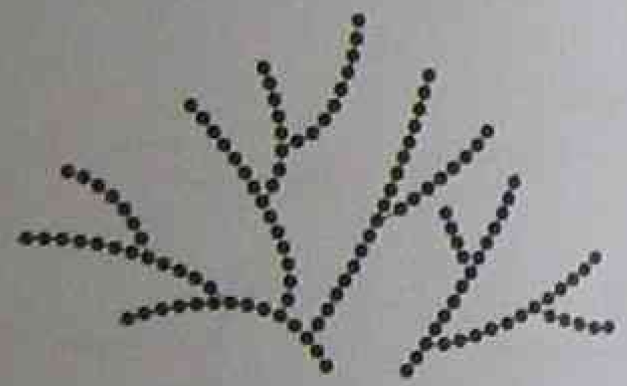


Figure 7.17 Branched structure of glycogen with α(1 → 6) branches on every fourth glucose residue

(c) Glycogen molecule

The presence of five hydroxyl (OH) groups allows condensation polymers to form. The backbone of the polymers is between the first carbon atom on one glucose molecule and the fourth carbon atom on the second molecule.

This 'amylose chain' is the fundamental structure of glycogen. Condensation such as this may occur with α-D-glucose or β-D-glucose. In addition, branching may occur. The branch points in glycogen involve the first atom on one glucose molecule and the sixth carbon atom in a glucose molecule in the backbone.



A cross section of glycogen shows a tree-like structure created by branched amylose chains (each • represents a glucose molecule).

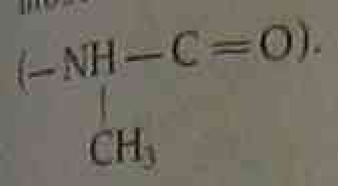
Table 7.7 Comparison of the properties of major polysaccharides

Aspect	Cellulose	Glycogen	Starch
Biological role	Most abundant naturally-occurring compound. Main structural component of the cell wall of plants. e.g. cotton.	Form in which animal carbohydrate is stored. In mammals it is stored in the liver and in muscle tissue.	Carbohydrate stored form for plants, e.g. wheat, rice, potatoes.
Solubility in water	Insoluble	Forms a colloid in cold water.	Insoluble in cold water. Forms a colloid in hot water.
Test with Benedict's solution	No reaction	No reaction	No reaction
Test with iodine solution	No reaction	Red-brown colour	Blue-black colour with amylose. Red-violet colour with amylopectin.
Products of digestion	Humans and many higher animals cannot break the β(1 → 4) bonds of cellulose to obtain glucose (no specific enzyme). Ruminants use bacteria to attack cellulose.	Stored glycogen can readily be hydrolysed to release glucose.	Main source of energy in human diet. In mouth: • Starch → enzyme maltose (salivary amylase). • Pancreatic amylase breaks α(1 → 4) bonds releasing glucose.

All polysaccharides under suitable conditions using an acid or specific enzyme(s) can undergo a hydrolysis reaction:

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6$$

Another most important polymer which consists of repeated modified monosaccharides is chitin. The monomer is a six-carbon sugar, like glucose, to which a nitrogen-containing group has been added. Several naturally-occurring amino sugars are formed, D-glucosamide being the most common. In most cases, the–NH_2 groups are acetylated



$$(-\underset{\displaystyle CH_3}{\underset{|}{NH}}-C=O).$$

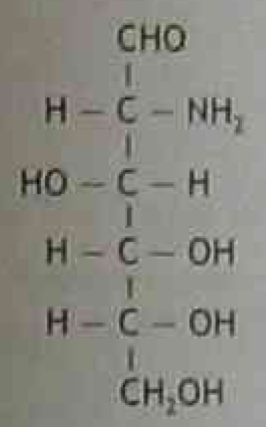


Figure 7.18 D-glucosamine

Of all the invertebrates, the arthropods and especially the insects are the most successful. Chitin forms the hard waterproof exoskeleton and makes possible the development of the finely articulated appendages. Chitin also forms an integral part of the cell wall structure of certain bacteria. Fungal cell walls also contain chitin rather than cellulose.

The discovery of chitin in a forensic sample can indicate the presence of material from the phylum Arthropoda, certain bacteria and the presence of fungal material.

7.10 Proteins

All proteins contain atoms of the elements of carbon, hydrogen, oxygen and nitrogen. They may also contain small amounts of sulfur.

Functions of proteins

Structural proteins

These are 'fibrous' proteins and may be elastic or coiled proteins, for example, keratin found in hair or wool or inelastic proteins, for example, collagen found in skin, tendons and cartilage.

Physiologically-active proteins

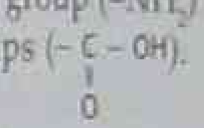
These include enzymes, some hormones, nucleo-proteins and blood proteins.

Composition of proteins

Proteins consist of various combinations of a relatively small number of amino acids.

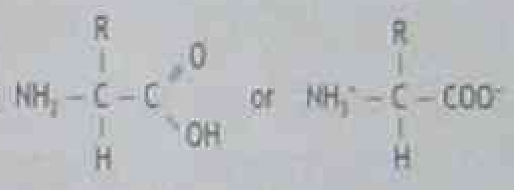
Structure of amino acids

All contain at least one primary amino group (–NH_2) and one or more carboxylic acid groups



$$(-\underset{\displaystyle O}{\underset{\|}{C}}-OH).$$

General formula



$$NH_2-\overset{\displaystyle R}{\overset{|}{\underset{\displaystyle H}{\underset{|}{C}}}}-C\begin{matrix}\nearrow O \\ \searrow OH\end{matrix} \quad \text{or} \quad NH_3^+-\overset{\displaystyle R}{\overset{|}{\underset{\displaystyle H}{\underset{|}{C}}}}-COO^-$$

(R = side chain)

Twenty fundamental amino acids occur frequently in proteins. It is the side chain that makes the amino acid unique and determines the specific properties of each protein.

The dual basic-acidic (amphoteric) character of amino acids gives rise to their ionic behaviour.

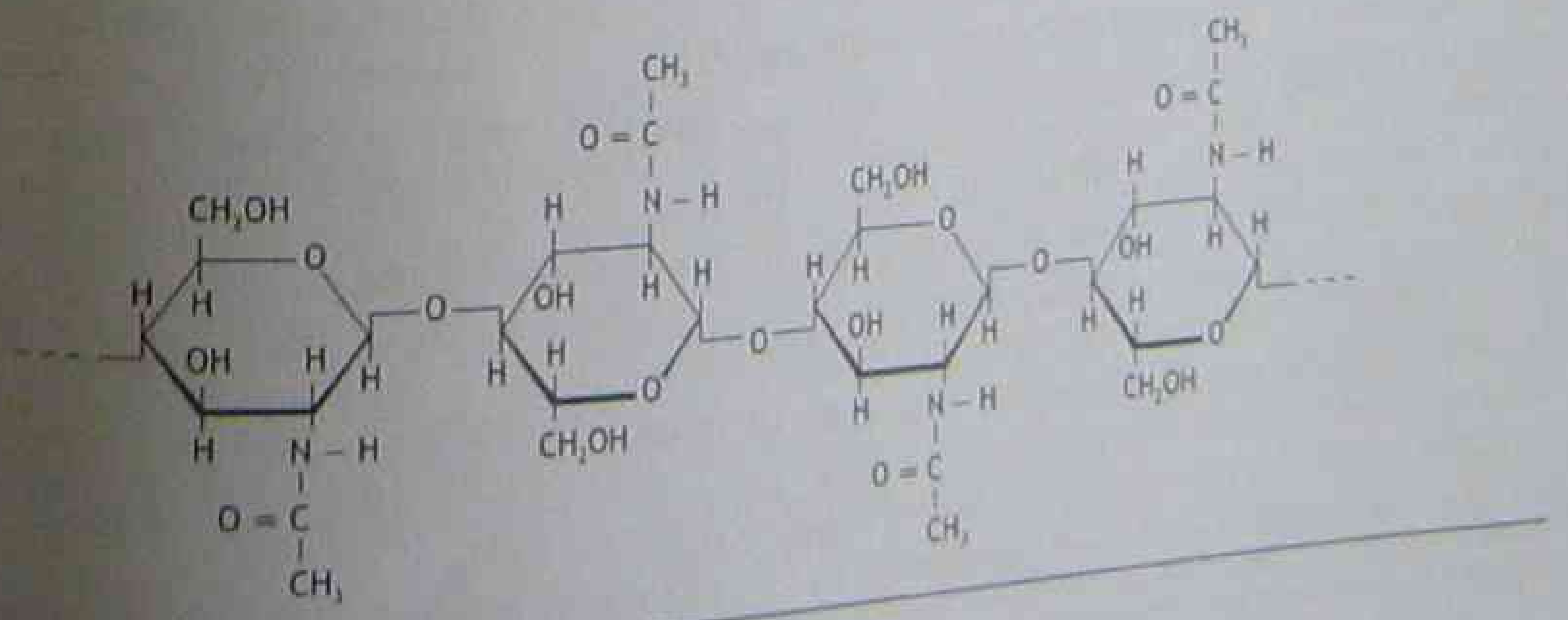
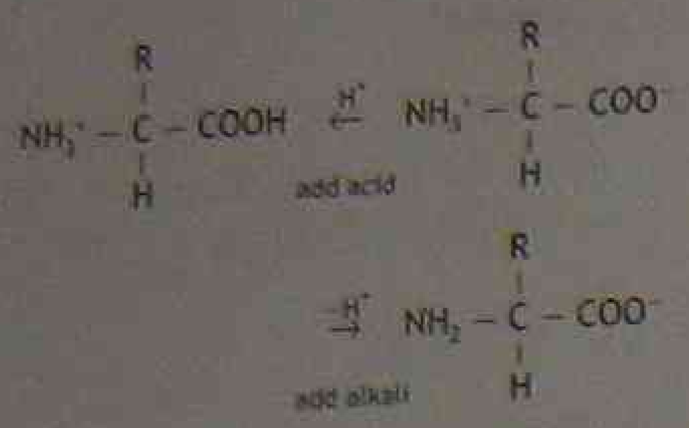


Figure 7.19 Chitin



$$NH_3^+ - \overset{\overset{R}{|}}{\underset{\underset{H}{|}}{C}} - COOH \underset{\text{add acid}}{\xleftarrow{H^+}} NH_3^+ - \overset{\overset{R}{|}}{\underset{\underset{H}{|}}{C}} - COO^-$$

$$\underset{\text{add alkali}}{\xrightarrow{-H^+}} NH_2 - \overset{\overset{R}{|}}{\underset{\underset{H}{|}}{C}} - COO^-$$

Linkages found in proteins

There are a number of reactive points in the structure of amino acids which make possible a variety of linkages. Proteins are made by the linking of amino acids and the main links may be called *amide links* or *peptide bonds*. This linkage involves a condensation reaction between the anion (COO^-) of one amino acid and the cation (NH_3^+) of another with the elimination of a water molecule. A covalent C–N bond is produced from the peptide linkage.

Structure of proteins

The occurrence of so many types of bonds between amino acids in proteins gives rise to four different structures.

Primary structure

This refers to the sequence of amino acid residues along the peptide chains, for example,

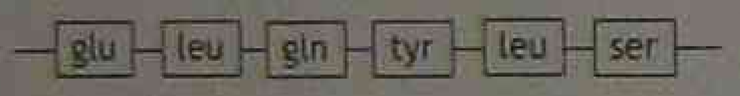


Figure 7.20 Amino acid sequence

Secondary structure

The polypeptides tend to form spirals and coils. The type of coil depends partly on the number of hydrogen bonds formed. They can be shown as

(a) α helix structures, for example, in wool fibres, or

(b) β sheet structures as in silk.

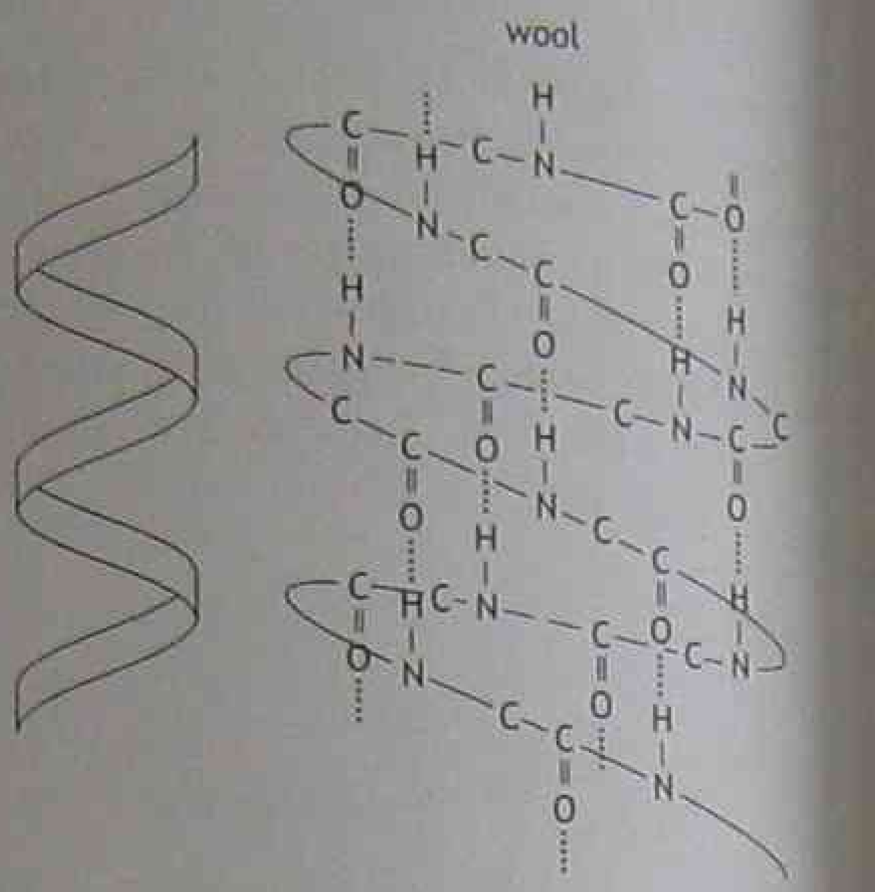


Figure 7.22a α helix structures

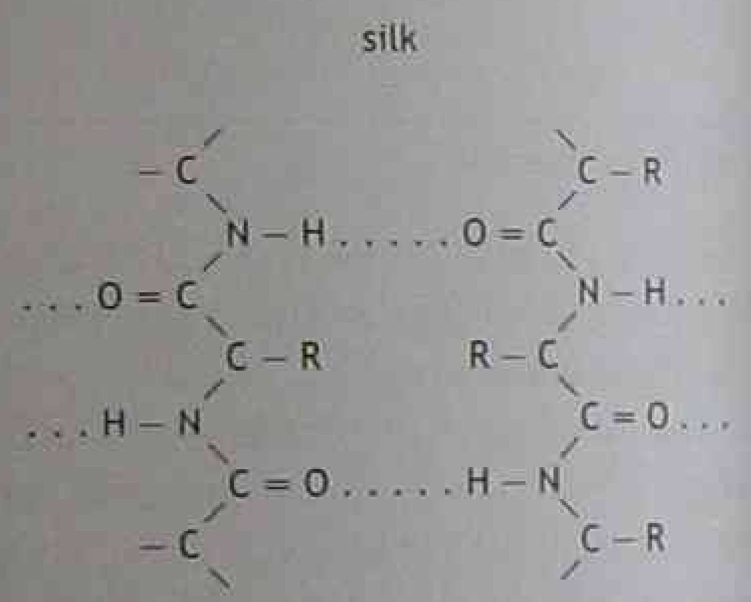


Figure 7.22b β sheet structure

Tertiary structure

This is the complete form of the chain. An important factor in forming this structure is the formation of hydrophobic bonds, for example, lysozyme, an enzyme found in many types of animal cells and body fluids.

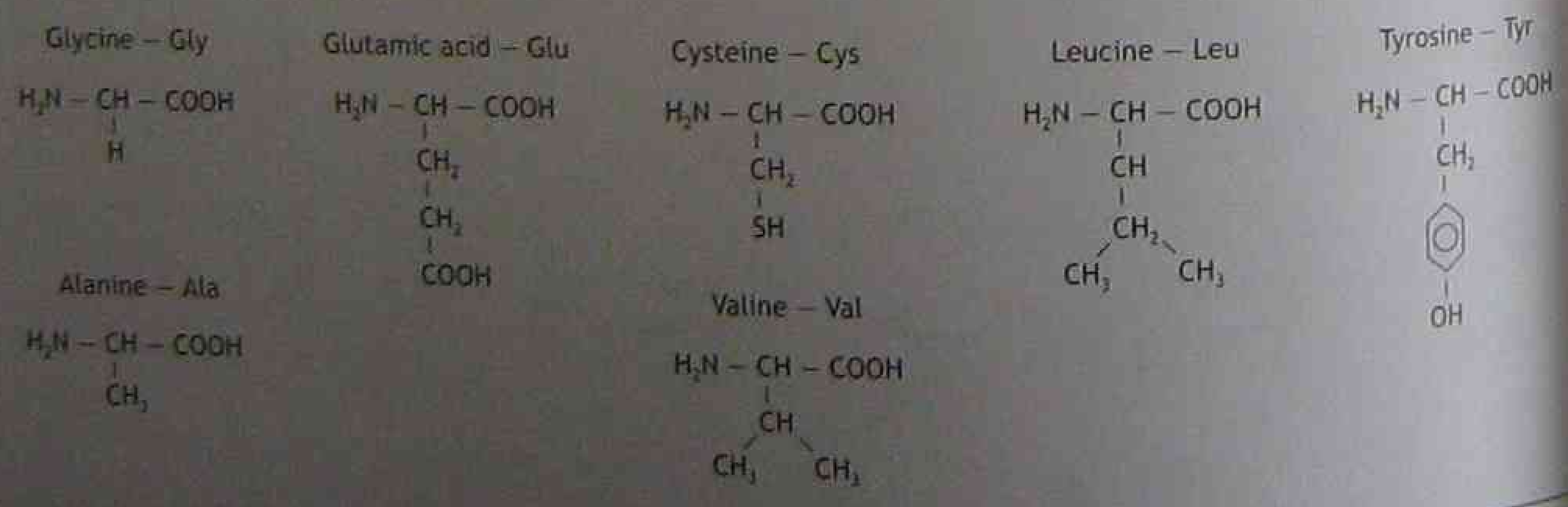


Figure 7.21 Formulae of some simple amino acids

Quaternary structure

Two or more polypeptide chains fit together to form a specific structure, for example, haemoglobin.

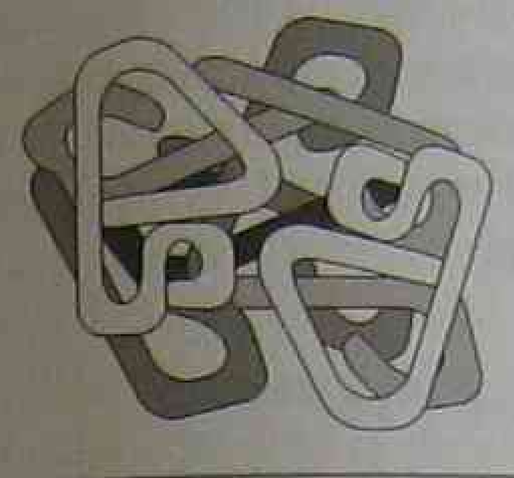


Figure 7.23 Haemoglobin

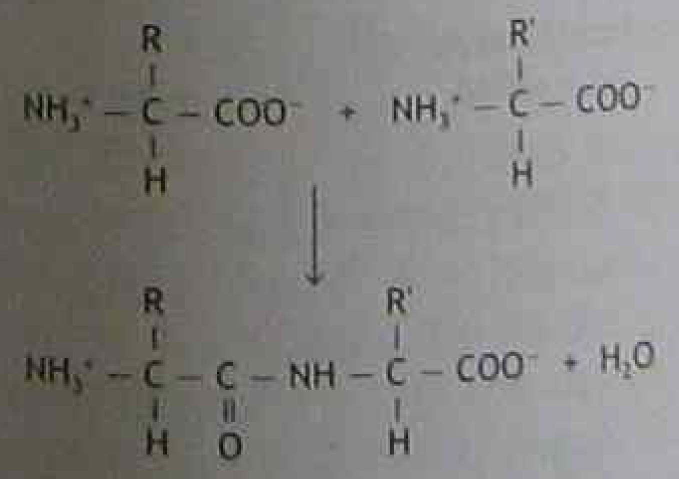
Summary

- Chain structure is the basis of amino acids.
- Side chains are important in link formation between polypeptide strands, for example, disulfide link.
- The folded structure of protein is stabilised by disulfide bridges, hydrogen bonds and hydrophobic interaction.
- Proteins can be broken into different lengths by the choice of enzymes.

Enzymes

- Enzymes are physiologically active proteins which have specific functions. Often enzymes work in conjunction with each other, e.g. in glycolysis.
- Enzymes are protein bio-catalysts. A catalyst increases the rate of a chemical reaction but undergoes no permanent change.
- The section of the enzyme in which reaction occurs is called the *active* site. Some side chains form bonds with the reactant (*substrates*) to serve as anchor points to hold the reactant in the active site.

Example

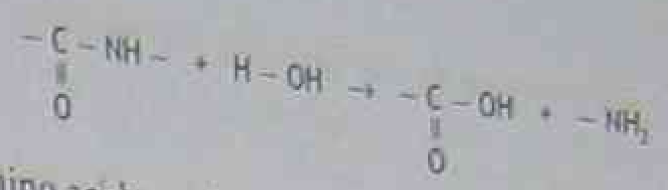


$$NH_3^+ - \overset{\overset{R}{|}}{\underset{\underset{H}{|}}{C}} - COO^- + NH_3^+ - \overset{\overset{R'}{|}}{\underset{\underset{H}{|}}{C}} - COO^-$$

$$\downarrow$$

$$NH_3^+ - \overset{\overset{R}{|}}{\underset{\underset{H}{|}}{C}} - \underset{\underset{O}{\|}}{C} - NH - \overset{\overset{R'}{|}}{\underset{\underset{H}{|}}{C}} - COO^- + H_2O$$

Proteins readily undergo hydrolysis across the peptide link.



$$-\underset{\underset{O}{\|}}{C} - NH - + H - OH \rightarrow -\underset{\underset{O}{\|}}{C} - OH + -NH_2$$

Amino acids are formed. Other types of linkages are subsidiaries of the peptide linkage but are important in determining protein structure.

Tests for protein

(a) *Biuret Test*. Peptides or polypeptides give characteristic purple-pink colour when their alkaline solutions are heated with a solution of copper sulfate.

(b) *Millon's reagent* (a mercury salt in nitric acid). When Millon's reagent is added to a soluble protein and heated, the substance first coagulates, then a pink colour develops. (This test is not used in schools.)

(c) *Ninhydrin reagent*. Reacts with amino acids to produce a blue colour.

(d) *Xanthroproteic reaction*. Produces a yellow colour when concentrated nitric acid comes in contact with protein material. **Demonstration only** as nitric acid reacts with the skin.

7.11 Principles of chromatography

Chromatography is a technique used to separate substances which have similar physical and chemical properties. A range of techniques includes paper, thin layer, column, gas and high pressure liquid chromatography.

Paper chromatography

A piece of absorbent paper (filter paper can be used) represents the stationary phase. The mobile phase is the liquid which flows over the stationary phase to separate the components of the mixture. The substance to be separated is loaded about 2 cm above the edge of the paper. The position of this spot, which is kept as small as possible, is called the origin. The paper is then placed in a container so that the edge of the paper below the origin enters the solvent. As the solvent rises up the paper, the components of each sample separate. A pencil line is drawn about 1 cm below the top of the paper to represent the distance the solvent front will travel before the paper is removed to be dried in an oven. The components of a mixture can thus be identified by comparing the distance they travel along the stationary phase to the distance travelled by the solvent front. This is called the R_f value for a component.

$$R_f = \frac{\text{distance moved from origin by component}}{\text{distance moved from origin by solvent}}$$

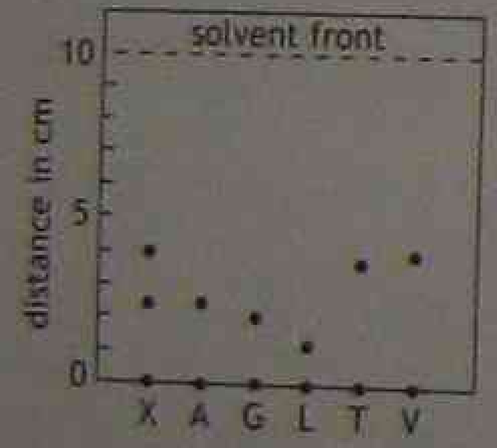
Note:

1. R_f values will always be less than 1.
2. The component most strongly absorbed onto the stationary phase moves the shortest distance and has the lowest R_f value.

(See experiment using food colouring given in Chapter 1, Section 1.6 of the Year 11 text.)

Each component has a characteristic R_f value. By using known substances as standards together with the unknown, the compounds in a mixture can be analysed.

Paper chromatography is useful for separating mixtures of chemical substances such as amino acids because they migrate at different rates. A suitable solvent would be a mixture of n-butanol: acetic acid: water in the ratio of 60 : 15 : 25 parts by volume. In this case, when the paper has been removed and dried, it is sprayed with 0.1% ninhydrin in acetone. When the chromatogram is dry, the purple spots around each amino acid can be marked.



standard amino acid	R_f
alanine (A)	0.24 (2.4÷10)
glycine (G)	0.20
lysine (L)	0.12
tyrosine (T)	0.38
valine (V)	0.40

Figure 7.24 Analysis of fruit juice

An unknown fruit juice contains alanine and valine. Instead of using standards, you could calculate the R_f values for the unknown amino acids and then consult a reference table for amino acids using the SAME solvent system. When the solvent system is changed, the R_f value will also change.

Thin layer chromatography

The TLC system uses the principle of partition chromatography with some absorptive effects. It has the advantages of paper chromatography but can separate non-polar compounds. The liquid sample is spotted onto the granular surface of a gel-coated plate. The plate is placed in a closed chamber containing a liquid. The mixture is separated with substances having the greater affinity for the moving liquid travelling up the plate at a faster speed.

Example

Figure 7.25 shows the chromatogram of a marijuana extract that has been separated into its components by TLC and visualised by spraying it with a chemical reagent.

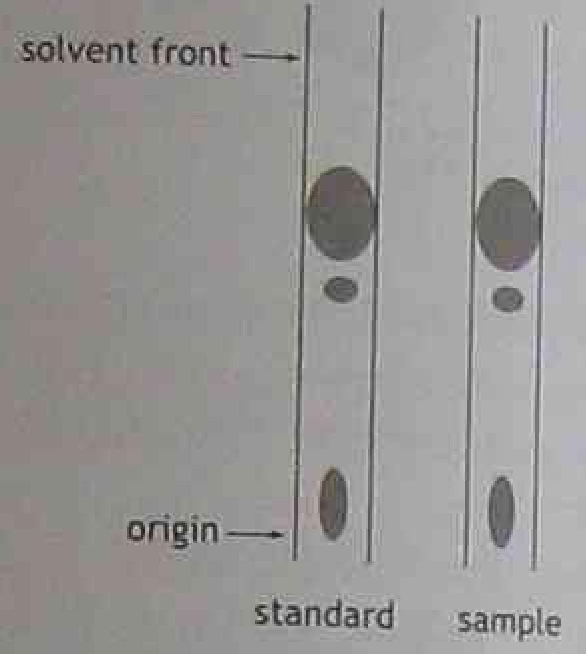


Figure 7.25 TLC chromatogram of marijuana extract

Column chromatography

The stationary phase is a solid packed into a glass column. The sample is added to the top of the column and the solvent, the mobile phase is added dropwise to the top of the column. A tap at the bottom of the column allows the eluent (solvent) to leave at a steady rate.

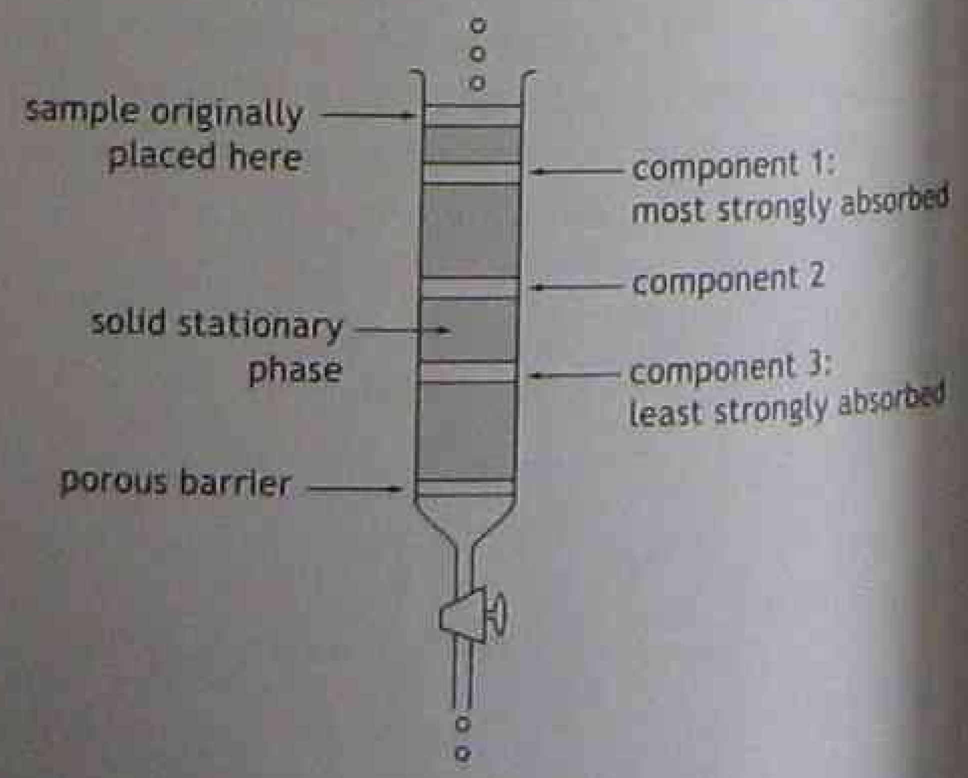


Figure 7.26 Use of column chromatography to separate a mixture

High performance liquid chromatography

The HPLC system was developed from column chromatography. It allows sensitive analysis of a wide range of compounds and is widely used for pharmaceutical analysis. Other uses include analysis of cosmetics, explosives, soft drinks, herbicides and drinking water on a daily basis. When an HPLC system is equipped with a fluorescence detector, illicit drugs, e.g. amphetamines, can be found in picogram amounts in autopsy samples.

Note 1: Components in HPLC can be identified by comparing their retention time with that of known standards under the same conditions.

Note 2: Quantitative information can be obtained from the area under the peak of the chromatogram. This is dependant on the amount of component present and can be determined by comparison with the areas of standards.

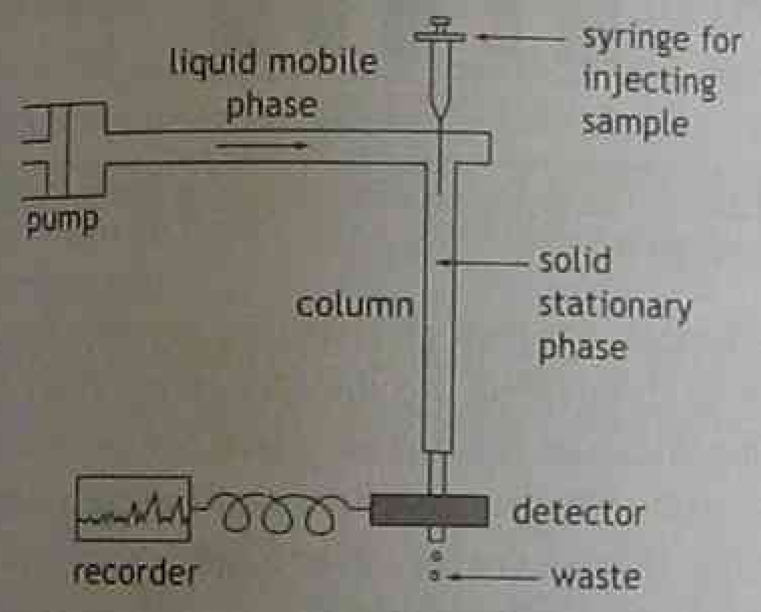


Figure 7.27 A schematic diagram to show HPLC

Gas chromatography

Gas chromatography permits the rapid separation of complex mixtures into individual compounds, and allows identification and quantitative determination of each compound.

The GC system is extremely sensitive and can detect material at a level of 1×10^{-9} g. Urine samples from high profile athletes are tested for illegal performance-enhancing drugs by GC.

As shown in Figure 7.28, a sample is introduced by syringe (1) into the heated injection chamber (2). A constant stream of nitrogen gas (3) flows through its injector, carrying the sample into the column (4) which contains a thin film of liquid. After the sample has been separated in the column, the carrier gas and separated components flow into the detector (5). Signals developed by the detector then activate a recorder (7) which traces a series of peaks on the chromatogram (8). The components present are identified by the elution time, and the peak area defines the concentration.

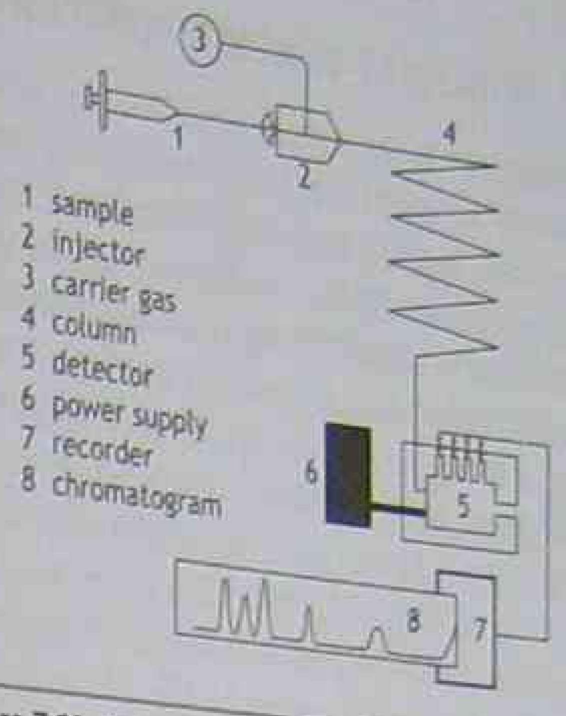


Figure 7.28 A simplified diagram for gas chromatography

Note: An important extension of gas chromatography to forensic science is the technique of *pyrolysis gas chromatography*. Many solid materials, e.g. paint chips, fibres and plastics, cannot be readily dissolved for injection into the gas chromatograph. Materials such as these are therefore pyrolysed (heated) to high temperatures (500–1000°C) before they enter the carrier gas stream and hence into the GC column.

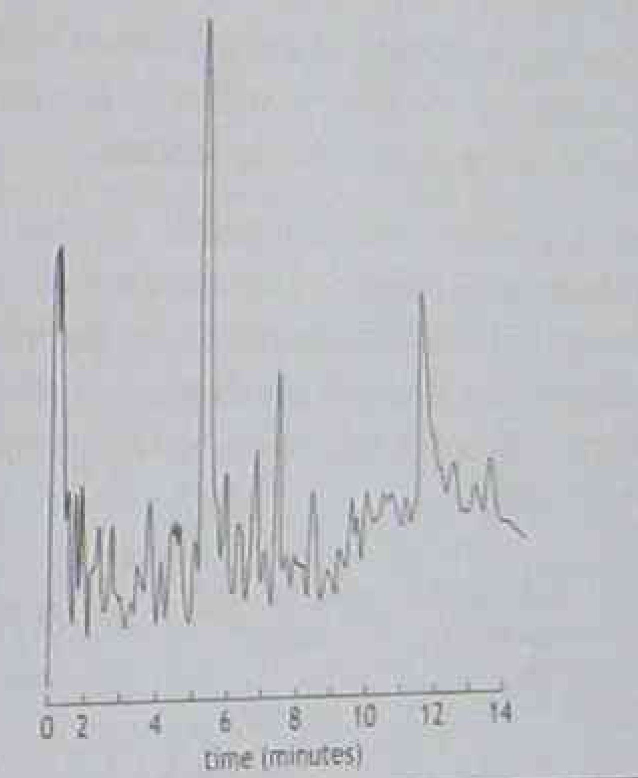


Figure 7.29 Pyrogram of a GM automobile paint

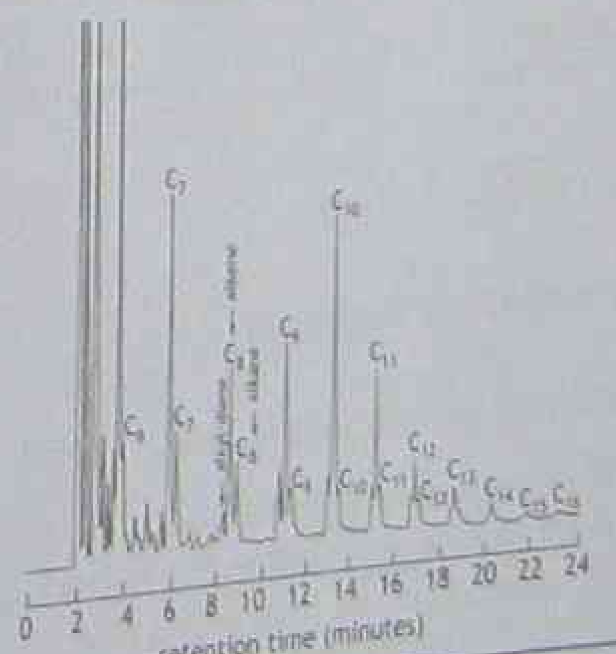


Figure 7.30 Chromatogram of pyrolysis products from polyethylene

7.12 Principles of electrophoresis

Electrophoresis is the separation of molecules by migration in an electric field. The molecules to be separated are applied to a supporting media, e.g. paper, agar gel or cellulose acetate. Most biological molecules are electrically charged, so they will move in an electric field when a current is applied. The net charge of a biological molecule depends on pH. At a low pH, most proteins have a net positive charge and will move towards a negative electrode (cathode). At a high pH, they have a net negative charge and will move towards the positive electrode (anode). The isoelectric point is the pH at which there is no electric charge on the molecule. The molecule will not move in an electric field at this pH. Different molecules differ greatly in their isoelectric points, so they will migrate at different rates at a particular pH.

Example

The isoelectric point of albumin, a serum protein, is 4.7. Another serum protein, gamma-globulin, has an isoelectric point of 7.3. At a pH of 8.6, both proteins will be negatively charged and will migrate towards the anode, but the albumin will move at a greater velocity, so the proteins will be separated.

The materials and equipment needed for electrophoretic separation are a support medium through which the sample is separated; an electrophoresis tank with two chambers in which to place the electrodes and a buffer; and a high voltage power supply.

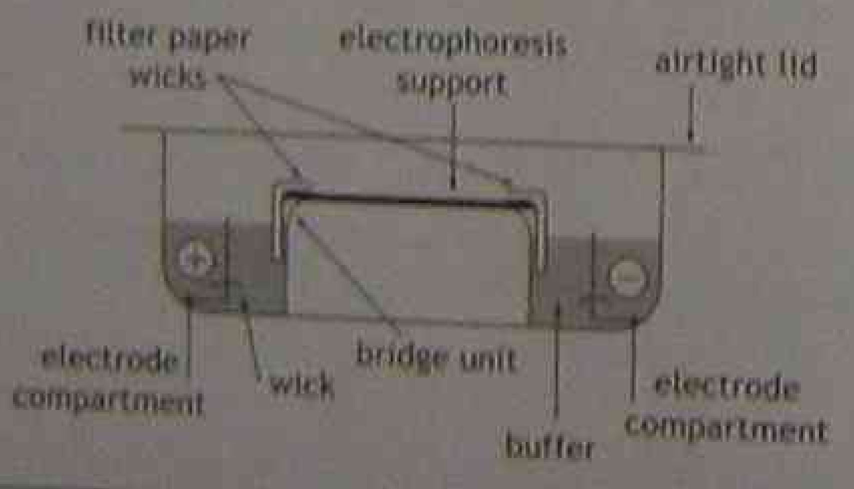


Figure 7.31 Electrophoresis tank

Electrophoresis Technique

Separation of serum proteins on cellulose acetate

Cellulose acetate is a suitable support medium for the separation of serum proteins — albumin, and alpha$_1$, alpha$_2$, beta and gamma globulin.

Electrophoresis is an important tool which can assist the forensic chemist to identify the origins of protein. DNA typing techniques such as the polymerise chain reaction (PCR) involve repeatedly replicating a small area of the DNA molecule so that particular piece is present in greater amounts. Amounts of DNA produced by the PCR are placed in line on a gel. An electrical voltage is applied to the gel. The DNA then travels through the gel because of the electrical charge of the DNA molecules. The larger molecules travel the shorter distance because of hindrance due to the gel molecules. The DNA is then stained and the distance that the DNA replicas have travelled through the gel is compared to the distance that known standards have travelled.

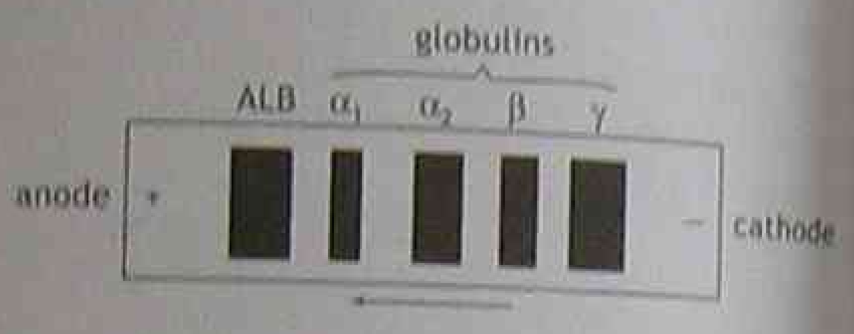
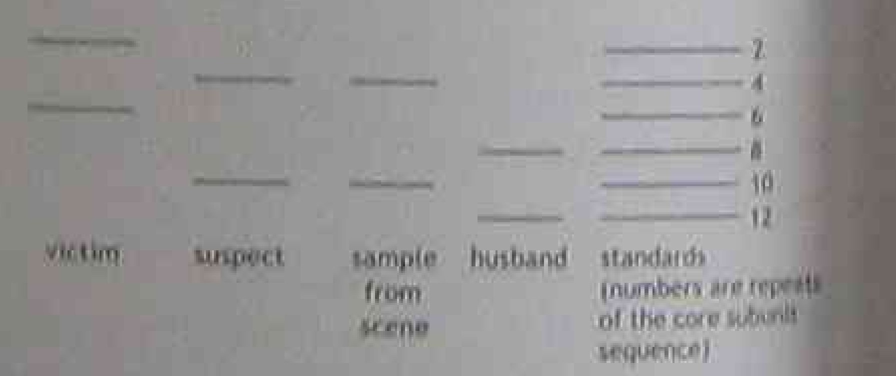


Figure 7.32 Normal electrophoretic pattern of serum proteins in a buffer of pH 8.5

This detection system is required by the forensic scientist to determine the difference between types once amplification has taken place. At present only systems using length variation are routinely used in casework in Australia. Here, the variation is detected using electrophoresis.

The results look like this:

Locus 'C' results



Questions

1. The sample from the scene could not be from ________ .

2. The sample from the scene could be from ________ .

Electrophoresis is the basis of the newly-developed technique of DNA fingerprinting. It is an excellent method for the separation and qualitative analysis of very large molecules such as proteins (see next section on DNA testing).

7.13 Methods and functions of DNA testing

What is DNA?

Deoxyribonucleic acid (DNA) is a compound found in all living things. Inside each of the cells in the human body are strands of material called *chromosomes*. In human cells (except the sex cells) there are 46 chromosomes.

These chromosomes hold as a compact coil a single very long molecule of DNA which is an important nucleic acid. This stores all the coded information that basically determines what you look like and how your body functions. Sections of DNA which contain complete messages are called *genes*. These genes are arranged on chromosomes like a string of beads. The message in a gene is a coded formula needed by the cell to produce one protein.

DNA is polymer found in the nuclei of our cells. It is a long twisted molecule made by linking a series of repeating units called *nucleotides*. Each nucleotide is made up of three groups of atoms: (i) a cyclic sugar (deoxyribose), (ii) a phosphate group, and (iii) a nitrogen base.

A DNA nucleotide can contain any of four nitrogen bases: adenine, thymine, guanine and cytosine.

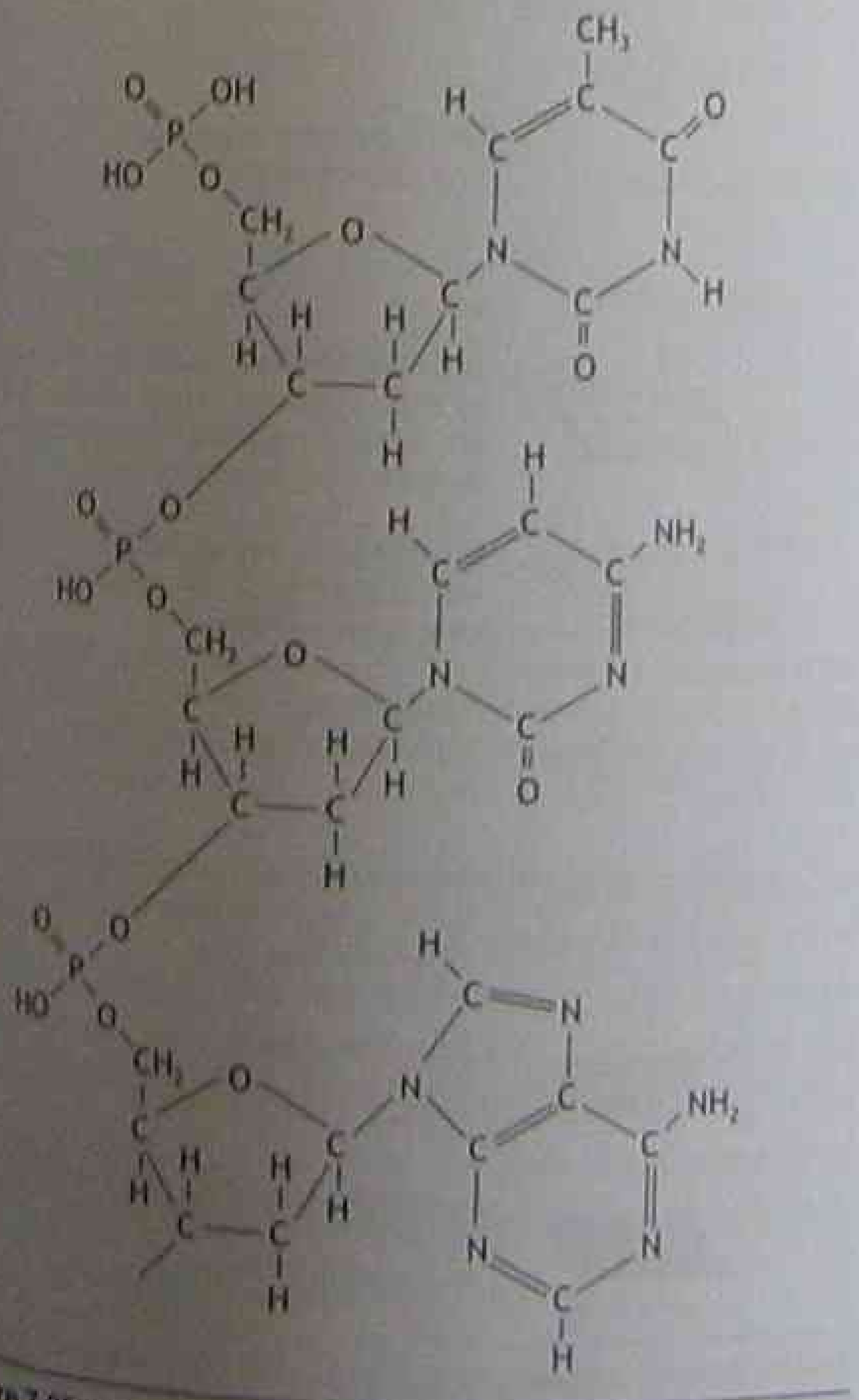


Figure 7.33 Structural formula of part of a nucleic acid molecule

Nitrogen base pairing

Each strand of DNA is composed of linked sugar-phosphate groups. A base is attached to each sugar in the strand. There are four types of bases in DNA; adenine (A), guanine (G), cytosine (C) and thymine (T). The bases along one strand link to the bases of a second strand of DNA. A only joins with T and G only joins with C.

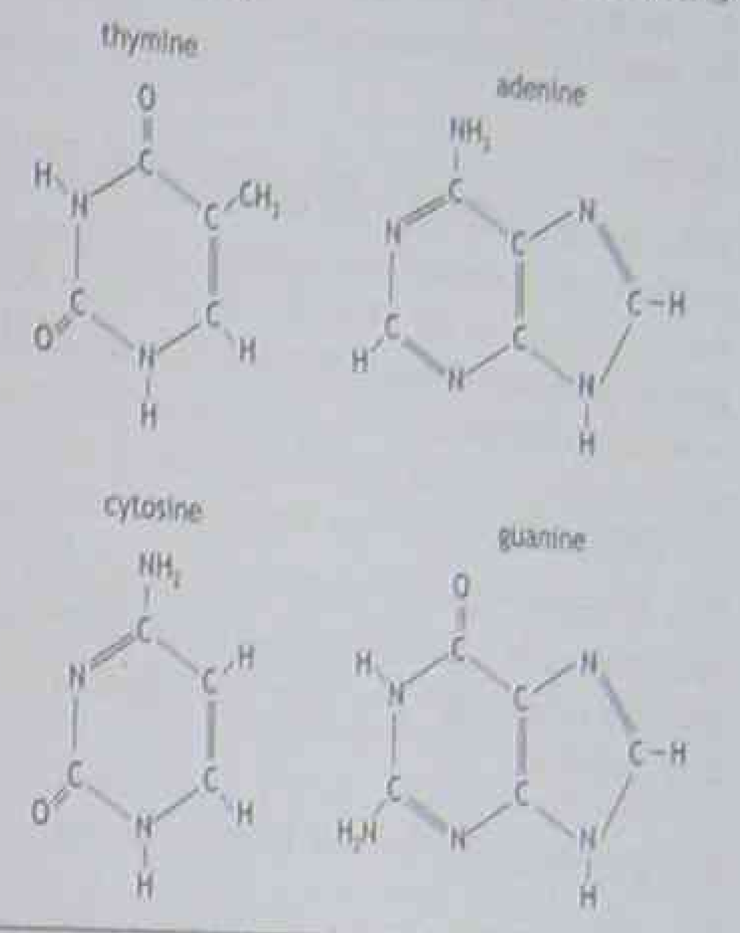


Figure 7.34 Formulae for the four nitrogen bases

The DNA molecule is composed of two DNA strands coiled to form a double helix.

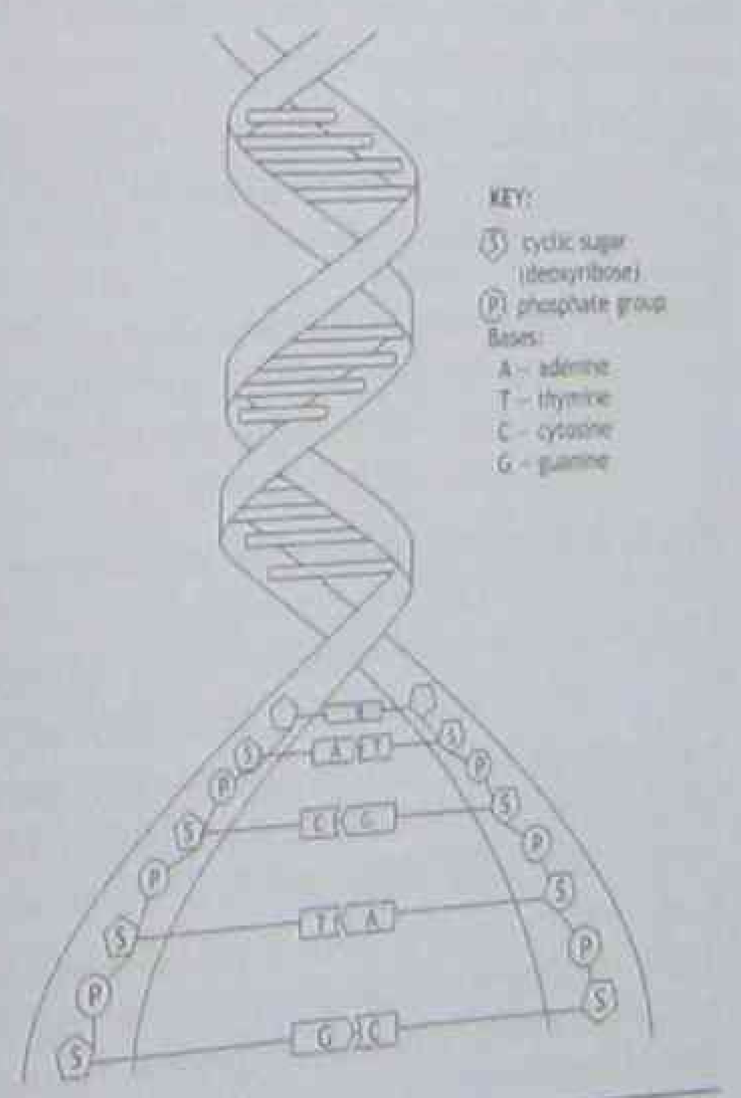


Figure 7.35 Geometric representation of DNA. The rungs are paired nitrogen bases; the sides are phosphate groups and sugars.

Whenever a cell in your body divides and forms two new cells, a copy of DNA must be passed on, as follows:

(a) A special enzyme 'unzips' the two strands.

(b) Free building blocks in the cell attach themselves to the bases on each strand (A with T and C with G) and join together to form a new second strand. The result is two double helices both identical to the original.

Analysis

DNA allows identification of individuals. The only people to share entire DNA sequences are identical twins. Because of the small amounts of samples received, the forensic scientists must allow the DNA to replicate itself.

Extraction of DNA

This is usually done by shaking the sample in a mixture of *water-saturated phenol and water*. The DNA dissolves in the water layer from which the DNA is then recovered.

Making copies of DNA

This will increase the amount of DNA available for testing.

Methods of DNA testing

One process that is used is the polymerise chain reaction (PCR) method.

Step 1. The double-stranded DNA is dissociated into single strands by incubation at 94°C (*template strand separation*).

Step 2. Short pieces of purified DNA, called *primers*, are then added. By lowering the temperature, copies of the primers bond to the DNA (*primer hybridisation*).

Step 3. A heat-stable DNA polymerase (an enzyme) is then added and the sample warmed, causing the primers to synthesise complementary strands of each of the single strands. This process is repeated for about 25 cycles to amplify the original DNA sequence (*primer extension*).

Step 4. The amplified DNA is then digested by adding restriction enzymes. These cut the DNA into a series of fragments of various sizes.

Step 5. The fragments are then separated by gel electrophoresis. The DNA is placed at one end of a plate containing Agarose gel with a positive electrode placed at the other end. The DNA being negatively charged moves towards the positive electrode. The distance that an individual fragment of DNA travels depends on the amount of its electrical charge which is determined by its length and molecular mass.

Step 6. After electrophoresis, the DNA is transferred to a nylon membrane. Radioactive probes are used so that the DNA sequences to which they become attached can be tracked. An X-ray film is placed next to the membrane and is later developed (*autoradiography*).

Step 7. The *autoradiograph* looks something like a 'bar code'. The final step is the band pattern comparison. Genetic difference between individuals will be identified by differences in the location and distribution of the band patterns (see Figure 7.36).

Note: A newer and faster technique for seeing if any binding (hybridisation) has occurred, uses probes which are attached to an easily visible thermo-luminous chemical. This replaces radioactive probes.

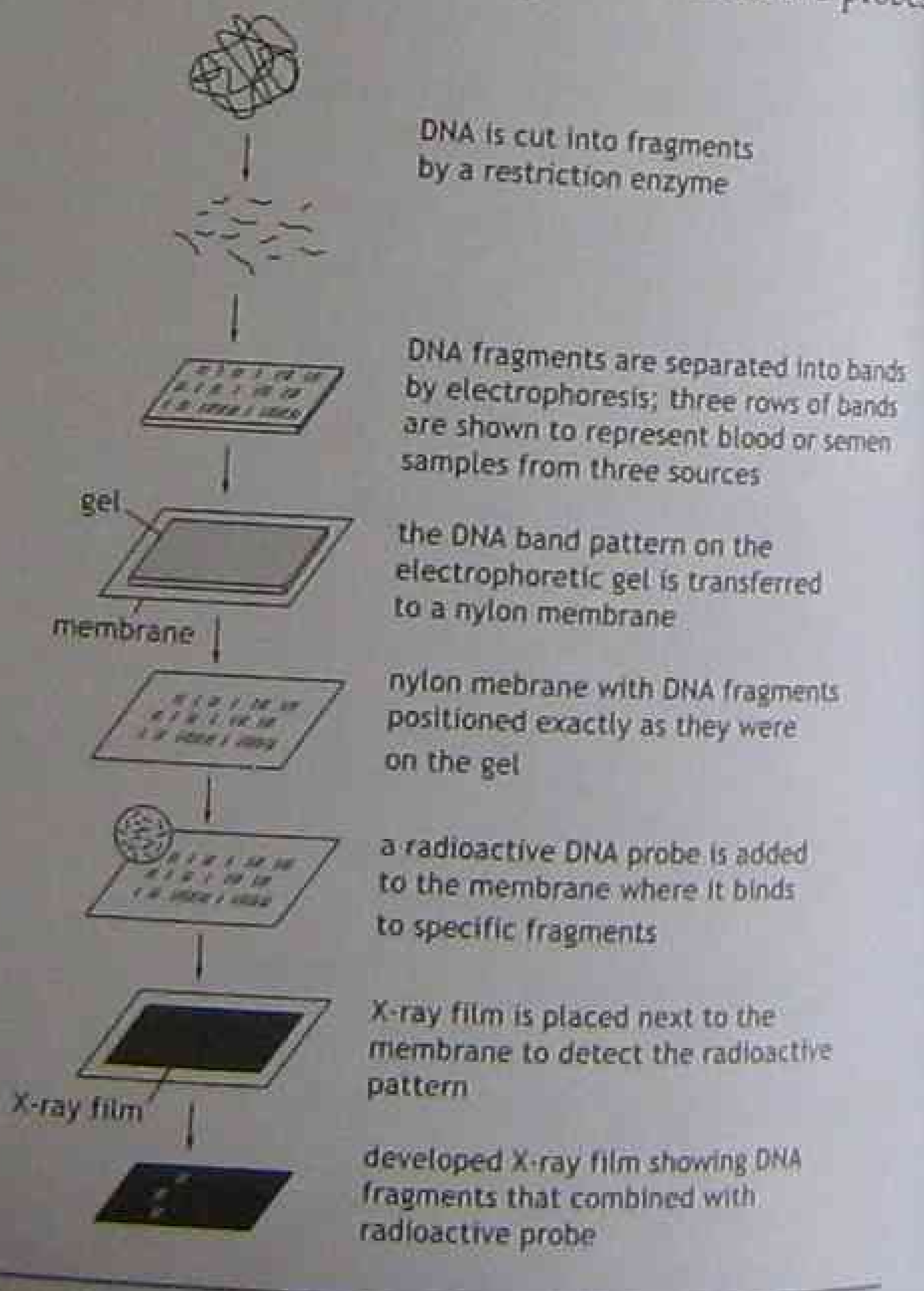


Figure 7.36 The DNA typing process (PCR reaction) using a radioactive DNA probe

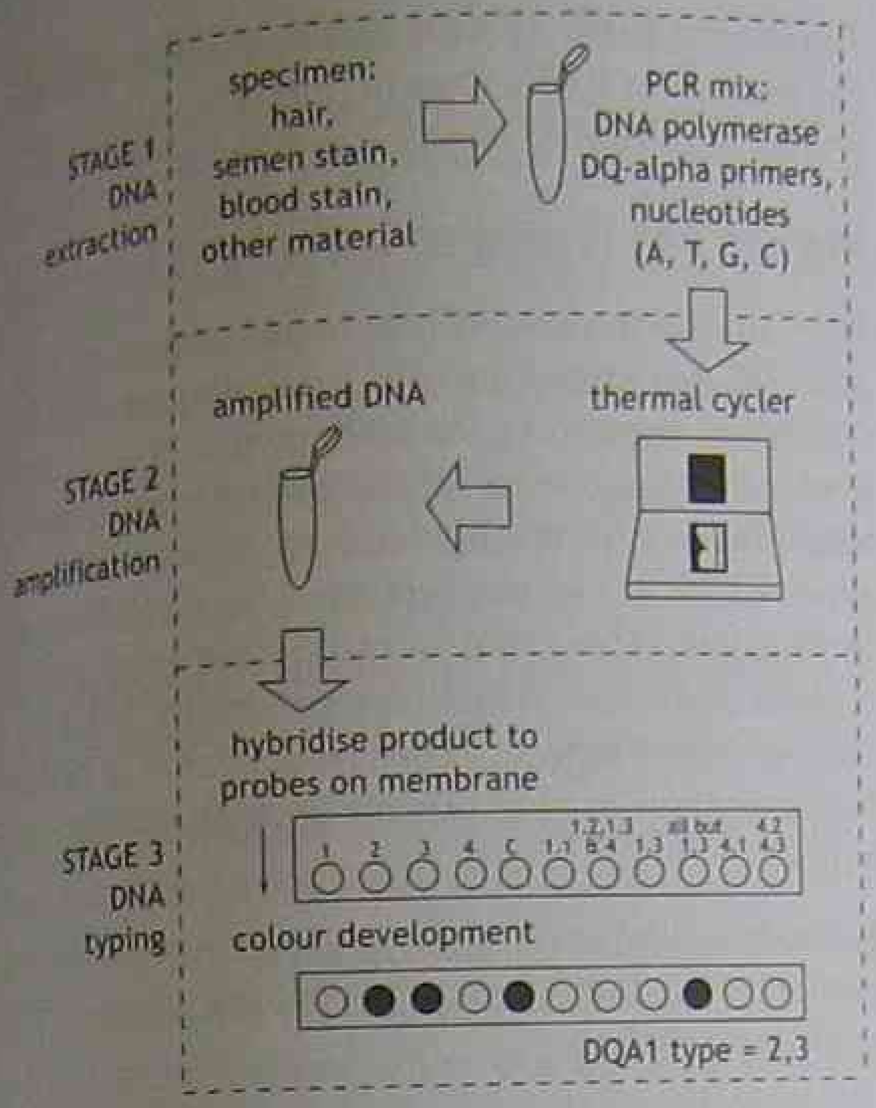


Figure 7.37 The PCR process for typing blood, semen and other materials for DQA1 is a three-stage process. The DQA1 type is obtained by reading the dot pattern on a nylon strip.

DNA amplification

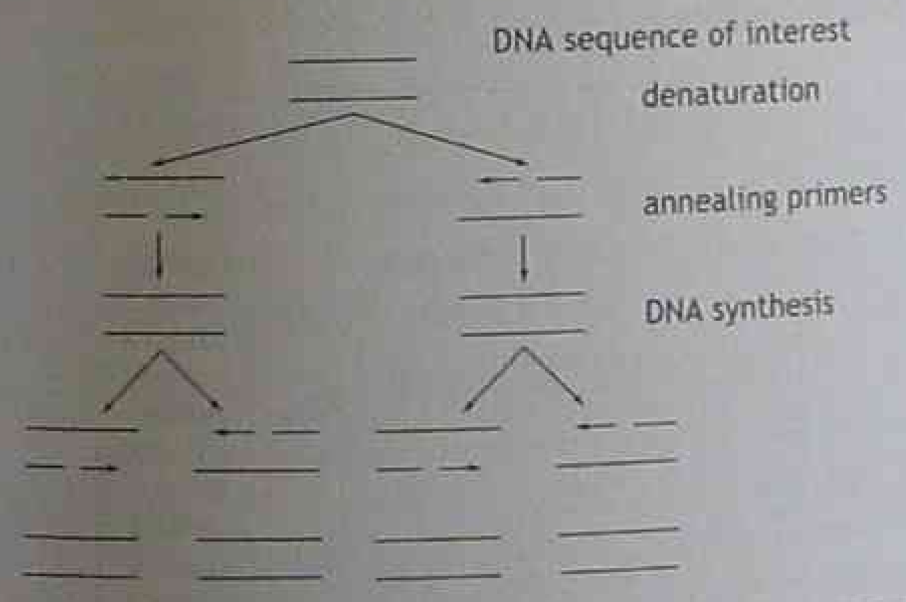


Figure 7.38 Representation of the polymerise chain reaction (PCR) technique, which uses repeated cycles of denaturation, primer annealing and DNA synthesis to selectively amplify the DNA sequence of interest.

The HLA-DQA$_1$ was the first PCR technique used in casework in Victoria. With this method, the variation is detected using probes which recognise only specific variations in the DNA sequence. The probes only attach to the copies of DNA containing particular DNA sequence. A colour reaction detects the presence of copies of DNA bound to the probes on the membrane.

The results are represented in Figure 7.39.

The coloured dots indicate the DNA type, the coloured 'C' dot indicates the test is working correctly.

Figure 7.39 Results of PCR technique

Conclusion

This individual is HLA-DQA1 type 2,4.

Note: This variation is sequence variation, hence the name HLA-DQA1.

Some functions of DNA testing

Identifying relationships

Each chromosome contains nucleotides identical to those of each parent, as well as the nucleotides (units of nucleic acids) that distinguish the individuality of each person. If samples from the child and one of the parents are available, the nucleotides that are different from the known parent's DNA must have come from the unknown parent's DNA. If a sample from the suspected, but as yet unknown, parent supplies all the 'missing' nucleotides without any superfluous nucleotides, then the suspect is the other parent. The DNA testing method is ideal for identifying individuals or tracing the identity of parents.

Identification of individuals

The promise of DNA typing is substantial. Samples of human skin, hair follicles, blood, semen or saliva-containing cells can be examined to identify the DNA pattern. DNA testing requires very small samples; it is durable to heat and moisture, and degrades slowly in a decomposing body. DNA will have the greatest effect on violent crime cases such as murder and rape. It has been used in the United States and the United Kingdom to successfully solve these sorts of cases. Plans are being made to introduce the setting up of a DNA databank in New South Wales. Once this has been done, convicted rapists and murderers will be expected to undergo compulsory DNA testing.

A widespread community testing program involving voluntary DNA testing was set up by the New South Wales police at the small country town of Wee Waa where a 91-year-old woman was brutally bashed and raped. The crime occurred on New Year's Day 1999. The town was outraged, and when 18 months later the police asked the 400 men in the town to submit a salivary swab for DNA testing, the response was 98%. The police promised that all the DNA results which showed the men to be not guilty would be immediately destroyed. Shortly after the sampling, a 44-year-old labourer confessed to the crime.

This style of testing would be more difficult to carry out in large towns with itinerant populations. There is also the problem that if someone refuses the test, he or she could be regarded as a suspect. In this particular case there was very little protest from civil libertarians.

Is DNA testing a technology which is worthwhile?

Civil libertarians claim that DNA samples could be corrupted or swapped, either deliberately or inadvertently. Proposed safeguards include the establishment of an independent institution that will handle all DNA samples. If rules for handling samples are breached, this could lead to a gaol term. The risk of duplication of the DNA code is 149 billion to one. The first case in Britain solved by DNA testing allowed a person to go free as well as conviction of the criminal. Between 1983 and 1986, a double rape and murder occurred in a small country town. After the wrong man had confessed to one of the murders, the police DNA-tested 600 men in the town but found no matches. On checking the men who had refused to be tested, the local baker was again asked for a DNA sample. He agreed and the result led to him serving two life sentences for his crimes. A bill that will allow police to take DNA samples without consent from people suspected of serious crimes, and from prisoners serving terms of more than five years is expected to come into force in New South Wales by 2001.

Although the investigation in Wee Waa resulted in an arrest, voluntary DNA testing of hundreds of taxi drivers in Perth in an attempt to solve the serial killing of two young girls which occurred over three years was unsuccessful.

The setting up of a national database in Britain in 1995 has resulted in a 40% drop in burglary and the clear-up rate for unsolved crimes has increased by 60%.

Why can DNA testing of saliva be so accurate?

DNA is a chemical which is found in the nuclei of cells. DNA is organised into chromosomes, each of which can contain up to 4000 genes. It is not the nucleotide sequence which is used to identify individuals; it is the non-coding regions between genes which are of importance to modern forensic techniques. The DNA sections between genes contain sequences which are constantly repeated. The number of repeats varies from person to person but is unique for that person (except for identical twins).

Forensic scientists target one of these repeated sequences in their tests; this procedure is called *single locus probing*.

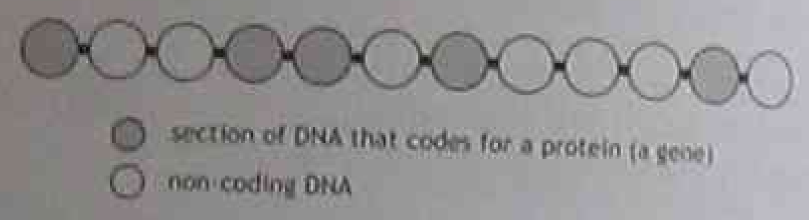


Figure 7.40 Diagrammatic sequence between bases and non-coding sections. The size of the non-coding sections varies between individuals.

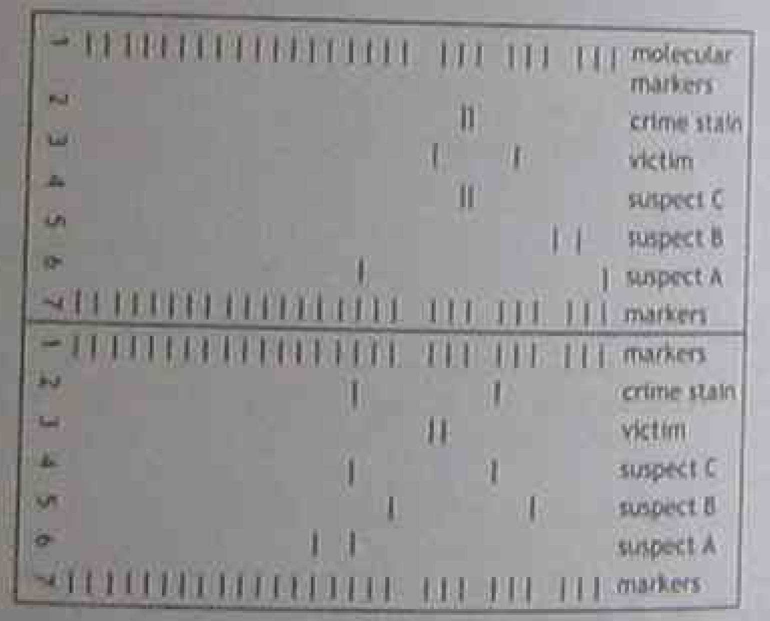
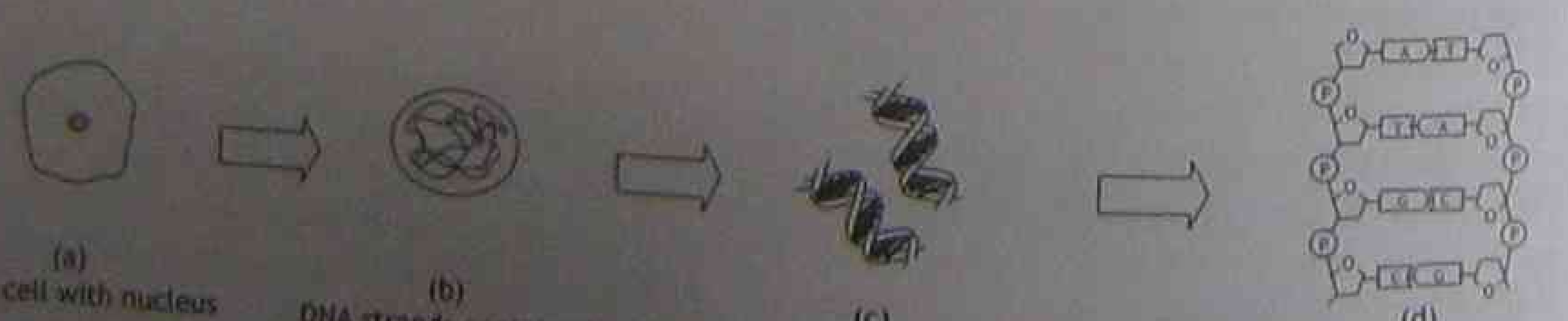


Figure 7.41 Result of saliva testing using two different probes. It is simple to identify the culprit using matching procedures.



(a)
cheek cell with nucleus

(b)
DNA strands contained within the nucleus

(c)
each strand of DNA is a double chain of nucleotides bonded together

(d)
the A–T and C–G sequences of bases determine what protein will be made in the cell

Figure 7.42 Use of saliva in DNA testing

7.14 DNA testing using microscopy

A large amount of forensic evidence consists of very small samples and macroscopic analysis is therefore inappropriate. When the destructive testing of material is used, e.g. determining humus in a soil sample by ignition so that CO_2 and water are driven off, the sample is destroyed. During forensic investigations, the defence may wish to have a sample retested by their own analysts. Some material should be set aside to cope with these inquiries.

The following techniques are used in the analysis of small samples.

Electron spectroscopy for chemical analysis — X-ray photoelectron spectroscopy

- The orderly arrangement of atoms or ions in crystals causes X-rays to be diffracted.
- Diffraction occurs when the distance between reflecting surfaces is about the same magnitude as the wavelength of the radiation.
- X-ray diffraction can be used to discover the arrangement of atoms, ions or molecules in crystals and the spacing between them. It can also produce electron-density contour maps of molecules and ionic crystals, and can also be used for gas molecules.
- Electron density contour mapping has been computerised to help build up structural models.
- The scattering of X-rays by atoms is the result of interaction with electron clouds surrounding the nucleus.

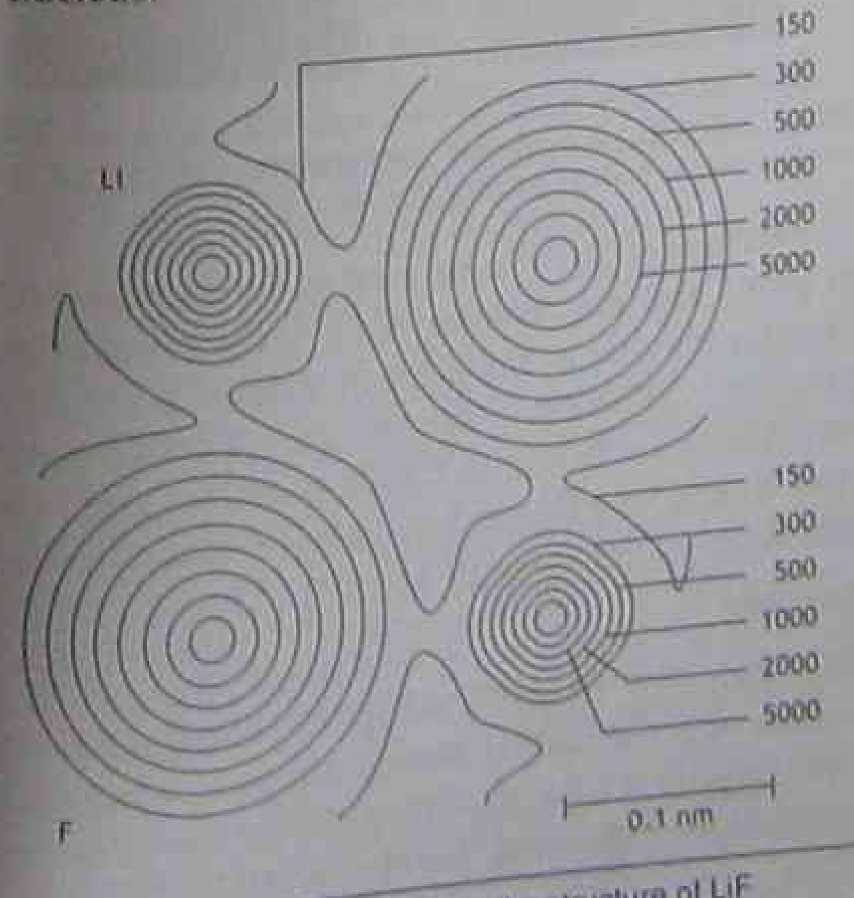


Figure 7.43 Electron map showing the structure of LiF

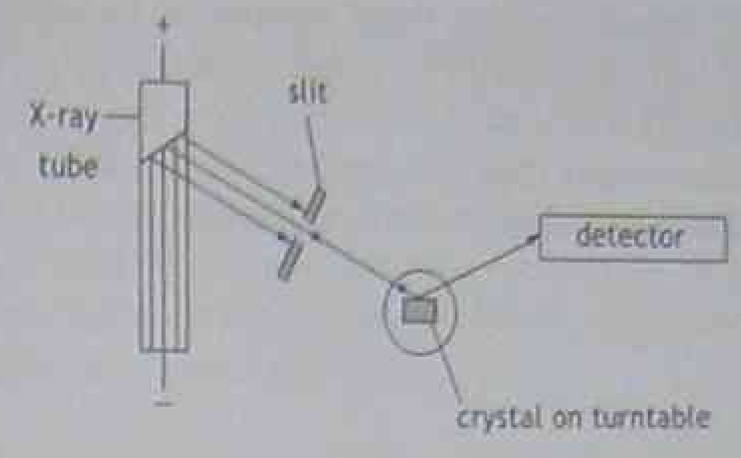


Figure 7.44 Schematic diagram for X-ray diffraction

- Electron diffraction was used in the determination of the double helix structure of DNA.

Atomic-force microscopy

- The atomic-force microscope (AFM) uses a sharp probe moving over the surface of a sample. In this method, the probe is a tip on the end of a cantilever which bends in response to the force between the tip and the sample. As the cantilever flexes, the light from the laser is reflected onto the split photo-diode. By measuring the difference signal (P_1–P_2), change in the bending of the cantilever can be measured. The movement of the tip is performed by a precise positioning device in the form of a tube scanner. The atomic-force microscope is capable of producing faithful topographical imaging. Interactive forces between the tip and sample are the reason for image contrast with the AFM.

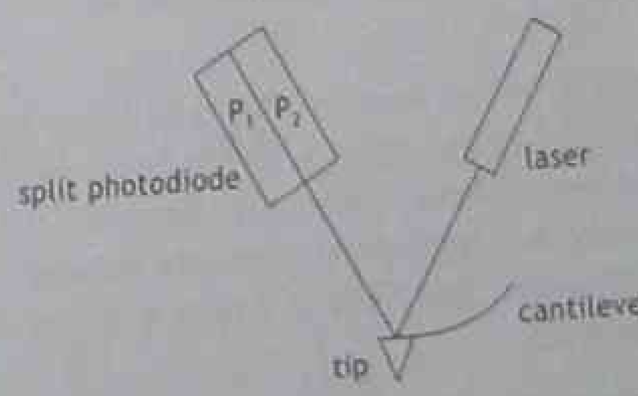


Figure 7.45 Schematic diagram for the atomic-force microscope. Height image data obtained by the AFM are three-dimensional.

Scanning tunnelling microscopy

The operating principle of the scanning tunnelling microscope (STM) takes advantage of an electrical current flowing between two conductors that are separated by extremely small distances. This current, the tunnel current, depends exponentially on the distance between the two conductors. This exponential dependence on the separation between probe and sample allows the atomic resolution. The STM's capacity for high resolution is not restricted to conducting materials. It has recently been used for organic systems (bulk insulators) including polypeptides and other organic material. It was found that it is possible to achieve a tiny tunnel current when they are prepared as thin films on conductive substrates such as graphite.

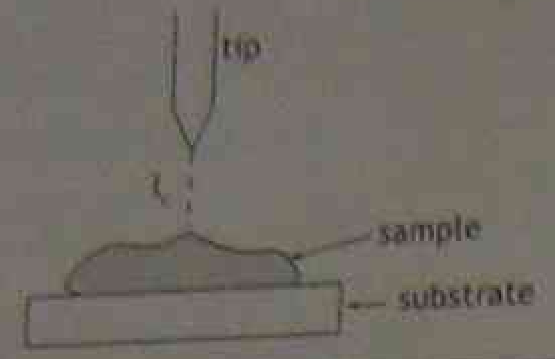


Figure 7.46 Schematic diagram of the STM

Scanning electron microscopy (SEM)

The SEM has found many other applications in the field of crime detection. The instrument's capabilities of high magnification, high resolution and extraordinary depth of field have made it the instrument of choice in many forensic examinations.

In the SEM a focused beam of electrons is scanned over the surface of a specimen and causes secondary electrons to be emitted. These secondary electrons are collected and detected to produce a signal that is displayed on a cathode ray tube (CRT). Magnification is simply the ratio of the size of the CRT scan to that of the sample scan and can be increased by reducing the scanning pattern on the sample. Magnification ranges from 10× to 2 000 000× can be obtained.

The impact of the focused electron beam on the sample surface also causes X-rays to be emitted from the specimen. These X-rays are characteristic and can be used to identify the elements present in the specimen when the SEM is fitted with an X-ray microanalyser.

This elemental analysis technique is most useful in gunshot detection. When a firearm is discharged, a large cloud of gunshot residue is expelled which contains substances evolved from the primer, propellant charge, bullet, cartridge case and lubricants. Particles can be detected which have a unique gunshot residue (GSR) by SEM analysis which can also be used to determine whether a suspect has recently fired a gun. Suspected gunshot particles are transferred to adhesive tape, and then examined under the SEM to validate the presence of particles that may have come from the bullet primer. X-rays emitted during SEM analysis are passed to a detector where they are converted into electrical signals. These signals are displayed according to the energies of the emitted X-rays. The elements lead, antimony and barium found in most primers can be rapidly detected and identified.

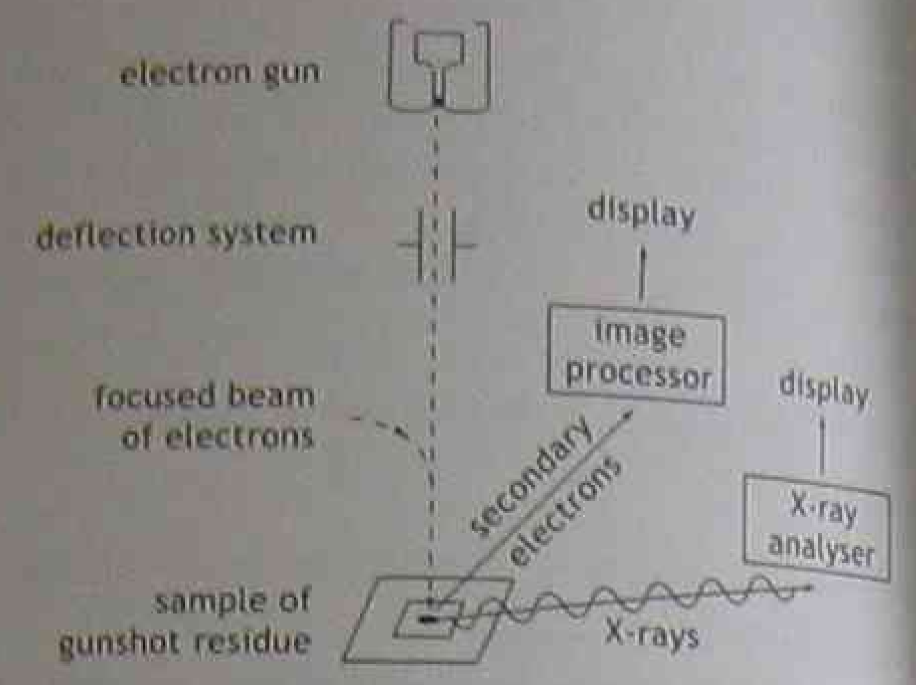


Figure 7.47 A schematic diagram for a scanning electron microscope showing the image of a gunshot residue particle. Simultaneously, an X-ray analyser detects and displays X-ray emissions from the elements lead (Pb), antimony (Sb) and barium (Ba) in the particle.

Scanning electron micrographs are also valuable for identifying and matching fibres found at a crime scene.

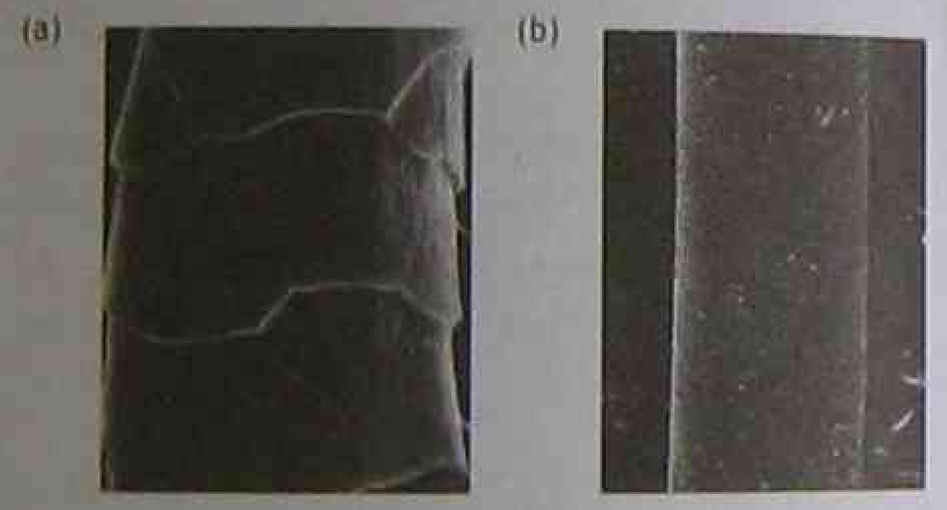


Figure 7.48 Scanning electron micrographs of (a) a wool fibre showing scales and (b) a synthetic fibre

This technique can also be used to detect impurities in paint and contaminants of surface coatings. Samples may be in the form of a dried paint film, powder or paint scrapings. Particles in concentrations as low as 1 microgram per gram can be detected. It could produce useful evidence for the conviction of hit and run drivers.

Example

The definite identification of marijuana by microscopic methods depends largely on observing short hairs that have the shape of 'bear claws' on the upper side of the leaf. These are called cystolithic hairs.

7.15 The use of the mass spectrometer

The mass spectrometer has been called a 'fancy chemical balance'. Mass spectrometers depend on the difference in mass-to-charge ratio (m/e) of ionised atoms or molecules to separate them from each other. The general operating sequence is to create gas-phase ions, then separate the ions based on their mass/charge ratio, and finally to measure the quantity of ions of each mass/charge ratio.

Using the mass spectrometer

Step 1. The sample is vaporised, if necessary, before entering the main body of the mass spectrometer.

Step 2. The vaporised sample passes through a small inlet into the ionising chamber which is at low pressure (10^{-4} Pa). Here an electron beam ionises part of the sample by knocking out electrons from the neutral atoms or molecules to form mainly ions with a single positive charge.

Step 3. The positive ions are accelerated to high speeds by an electric field (present on charged plates).

Step 4. Ions then pass through a perpendicular magnetic field. This field causes the ions to move in curved paths with a radius dependent on the mass-to-charge (m/e) ratio of the ions. For singly-charged ions, their radius depends on their mass.

Step 5. Only ions with a particular radius reach the collector. By changing the electric or magnetic field, different masses can reach the collector.

Step 6. The detector identifies the mass of each particle from its path. The data are recorded as a mass spectrum.

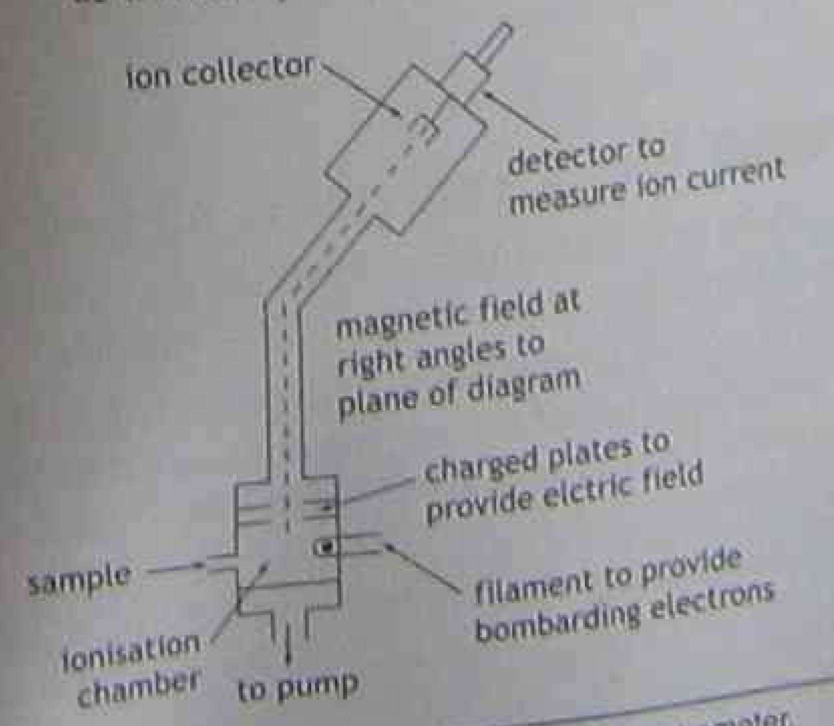


Figure 7.49 Schematic diagram of the mass spectrometer.

Note: There are many different ionising methods used in mass spectroscopy. Some give +ve ions; some give -ve ions.

A mass spectrometer can be used for (a) determining the mass of naturally-occurring isotopes, or (b) for calculating average relative masses for the elements from mass spectrum results.

To calculate average relative masses of elements

$$\text{Av. atomic mass (amu)} = \frac{\Sigma(\text{atomic mass of isotope} \times \%\ \text{abundance})}{\Sigma\ \text{frequency of occurrence}}$$

Example 1

Question

Find the average atomic mass of silver.

Mass no.	Isotopic mass	% present
107	106.91	51.35
109	108.89	48.65

Answer

$$\text{Av. atomic mass} = \frac{(51.35 \times 106.91) + (48.65 \times 108.89)}{100}$$
$$= 107.87\ \text{amu}$$

Table 7.8 Data from the mass spectrum of mercury

Mass no.	Isotopic mass	Fractional abundance
196	195.965	0.0014
198	197.967	0.10039
199	198.967	0.1683
200	199.968	0.2312
201	200.970	0.1323
202	201.970	0.2979
204	203.973	0.0685

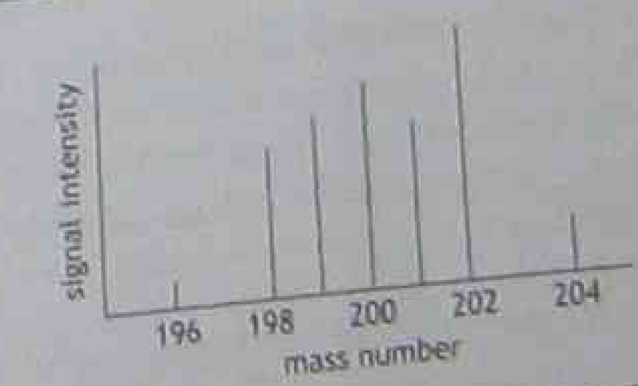


Figure 7.50 The mass spectrum of Hg^+ ions in mercury vapour

Example 2

Question

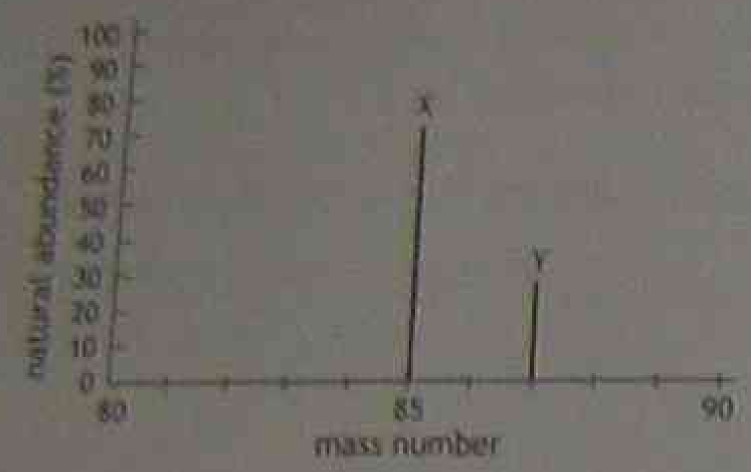
Calculate the average atomic mass for mercury.

Answer

$$\text{Atomic mass} = (0.0014 \times 195.965) + \ldots + (0.0685 \times 203.973)$$
$$= 200.59\ \text{amu}$$

Example 3

The element rubidium occurs naturally as two isotopes (X and Y) whose positions in the mass spectrum are represented below.



Questions

(a) Write down the composition of the nucleus of the isotope Y.

(b) Using the data, calculate the atomic mass in amu of natural rubidium (to 1 decimal place).

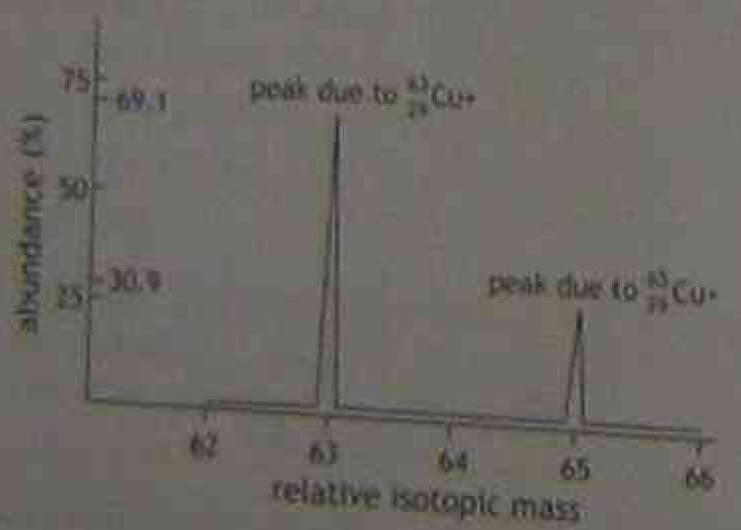
Answers

(a) Y is $^{87}_{37}\text{Rb}$.

(b) $$\text{Atomic mass} = \frac{(72\times85)+(28\times87)}{100}$$
$$=61.2+24.36$$
$$=85.6\,\text{amu}$$

Example 4

The isotopes of naturally-occurring copper are positioned on the mass spectrum shown below.



Question

Calculate the relative atomic mass of copper (to 1 decimal place).

Answer

$$\text{Atomic mass} = \frac{(69.1\times62.9)+(30.9\times64.9)}{100}$$
$$=63.5\,\text{amu}$$

Molecular ion determination

When a molecular substance is injected into the ionisation chamber and bombarding electrons have low energies, the molecules tend to lose just one electron. High resolution mass spectrometers use the molecular ions to allow the relative molecular mass of the compound to be found.

Fragmentation patterns

If higher energy electrons are used to bombard a molecular sample, the molecules break apart, forming a fragmentation pattern which is characteristic of the compound for the given conditions.

Note 1: Computer libraries containing large numbers of known compounds are available for matching with an unknown sample. These mass spectra libraries can be used to identify illegal drugs in the blood of both athletes and race horses.

Note 2: The combination of the gas chromatograph and the mass spectrometer enables forensic toxicologists to separate the components of a drug mixture, and provides for the specific identification of a drug substance.

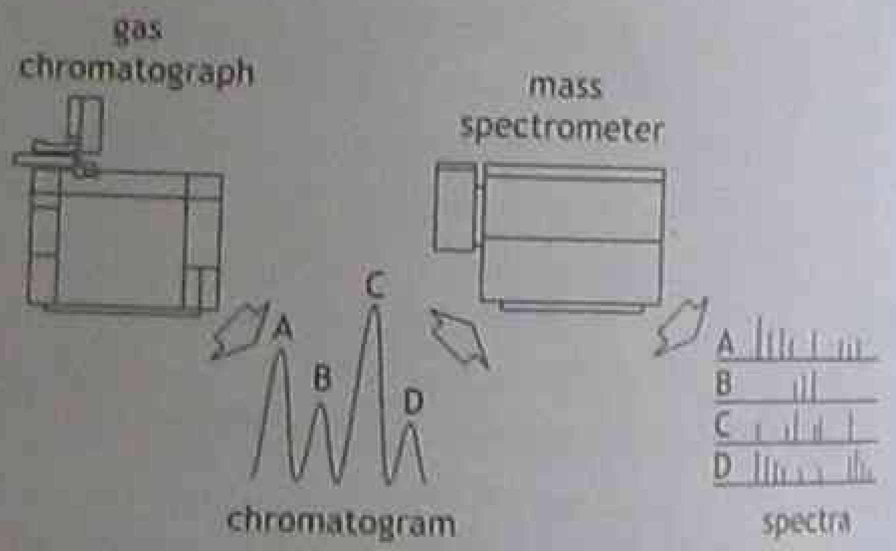


Figure 7.51 Schematic diagram for use of a combined GC-MS method for drug analysis

7.16 Emission spectra of elements

- Each element has its own unique electron configuration, e.g. Na 2,8,1 or $1s^2 2s^2 2p^6 3s^1$.
- The emission spectrum of each individual element occurs as a result of electrons moving between the element's electronic levels, reflecting its electronic structure.
- Light is emitted when an electron in an allowed high energy (excited) orbital falls into a lower energy (ground state) orbital.
- The light emitted is in a single whole quantum ($h\nu$) of energy or a photon of light.

Example

If a sodium atom is excited and falls back to the ground state, then energy will be emitted. For sodium this corresponds to its characteristic wavelength of 0.589 nm and imparts a bright yellow colour.

- Each line in the emission spectra corresponds to a single possible transition between the allowed electron orbitals within the atom.

Activity 7.10

Flame Tests

Introduction

For some elements in Group I and Group II, there is one particular electron transition that occurs far more readily than any other. This means that the emission spectrum of such an element has a very bright line corresponding to this transition. The flame (non-luminous Bunsen flame) in which the excited atoms are produced takes on the colour of that line. This method of identification is very useful in deciding whether Group I elements are present since they do not form precipitates because all of their commonly occurring compounds are soluble.

Aim

To identify characteristic colours that are produced by the samples provided for flame testing.

Method

Care: Use safety goggles for this experiment.

How to clean wire. Dip wire in concentrated HCl and then heat it in the non-luminous Bunsen flame until no colour shows. (**Care:** Do not heat the glass tube as it may shatter.)

Hold the loop of the wire under a gently dripping tap and then dip the tip into the substance you are testing. Introduce the tip of the wire slowly into the edge of the Bunsen flame and record the colour of the flame observed in the record column below.

At the end of each test, the wire should be cleaned until the flame is colourless. Proceed to test the remaining solutions.

When testing potassium salts, if Analar quality reagents are not used, impurities containing sodium salts can mask the delicate lilac colour of potassium. This can be overcome if the Bunsen flame is looked at through a piece of blue (cobalt) glass which will filter out the yellow colour of the sodium flame.

Results

Name of substance	Formula	Cation present	Colour of flame
Sodium chloride			
Potassium nitrate			
Lithium oxide			
Calcium nitrate			
Barium chloride			
Strontium nitrate			

Questions

1. Are there any Group I elements tested?
2. What are they?
3. Are there any Group II elements tested?
4. What are they?
5. How would you carry out an experiment to determine whether the colour present in the flame of the substances tested was due to the cation present or the anion present?

Use of emission spectra to identify trace elements

All elements have identifiable emission spectra which can be used to identify trace elements. When sufficient energy is supplied to an atom it will emit light.

Example 1

When a platinum wire is held in a Bunsen flame, it becomes incandescent and gives off white light. When the incandescent wire is viewed through a spectroscope, a continuous spectrum of colours is observed. This range includes the entire visible spectrum. Light energy of the shortest wavelength (highest frequency) is bent most (deep violet colour) whereas that of the longest wavelength (lowest frequency) is bent least (deep red colour). Between these two extremes there is a gradual blending from one colour to the next (the colours of the rainbow, r.o.y.g.b.v.)

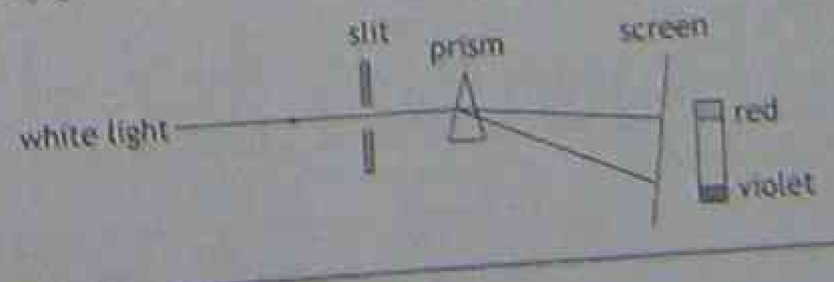


Figure 7.52 Continuous spectrum

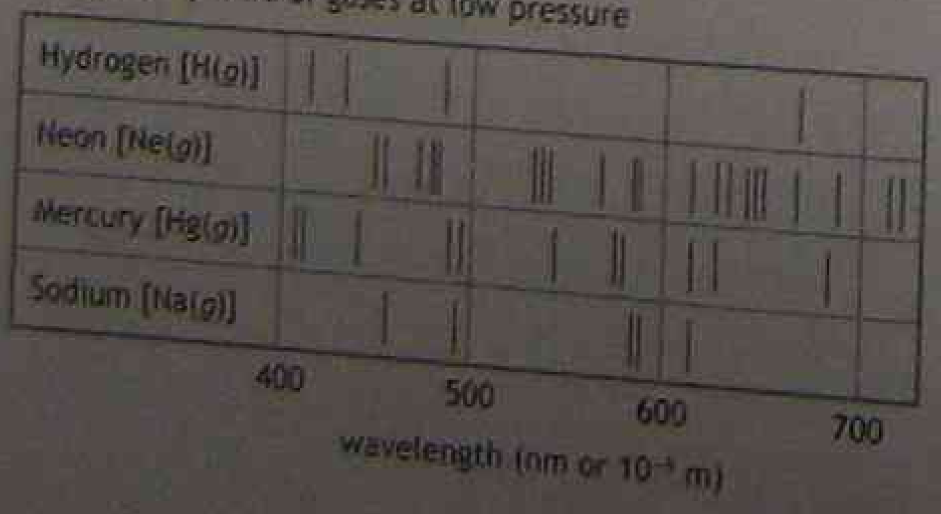
In general, incandescent solids and gases under high pressure give continuous spectra.

Example 2

When substances are vaporised in a flame, electrons are raised to higher energy by heat energy. When these electrons fall back to the lower energy levels available to them, energy is released. The energy released by any substance has wavelengths characteristic of that substance. Different wavelengths produce different spectral lines in the spectroscope, e.g. the two yellow lines for vaporised sodium atoms. The spectrum produced by injecting a substance into a colourless flame is called an emission spectrum. The spectra produced by excited atoms are as different as fingerprints. Bright lines in the visible portion of the spectrum account for the flame colouration produced by various metals (see Activity 7.10). The colour seen is the combination of light energies of the different wavelengths emitted.

- Electrical discharge tubes provide a convenient means of atomising and exciting gaseous or easily volatilised elements, e.g. hydrogen, neon and mercury vapour.
- When a high voltage is passed through a gas or vapour in a glass tube at low pressure (about 1 kPa) the gas will glow.
- The colour of the light is characteristic of the gas, e.g. neon gives the characteristic red colour seen in neon signs, sodium gives the yellow colour of some sodium street lights, whereas mercury vapour gives the characteristic colour seen in mercury lamps.
- If the light from a discharge tube is passed through a prism, a continuous band of colours is replaced by discrete sharp lines at specific wavelengths. These intense lines are called the bright-line emission spectrum of the element.
- No two elements have the same emission spectra. Some spectral lines produced by excited atoms may fall outside of the range of visible wavelengths, e.g. in the ultraviolet and infrared regions.

Table 7.9 Spectra of gases at low pressure

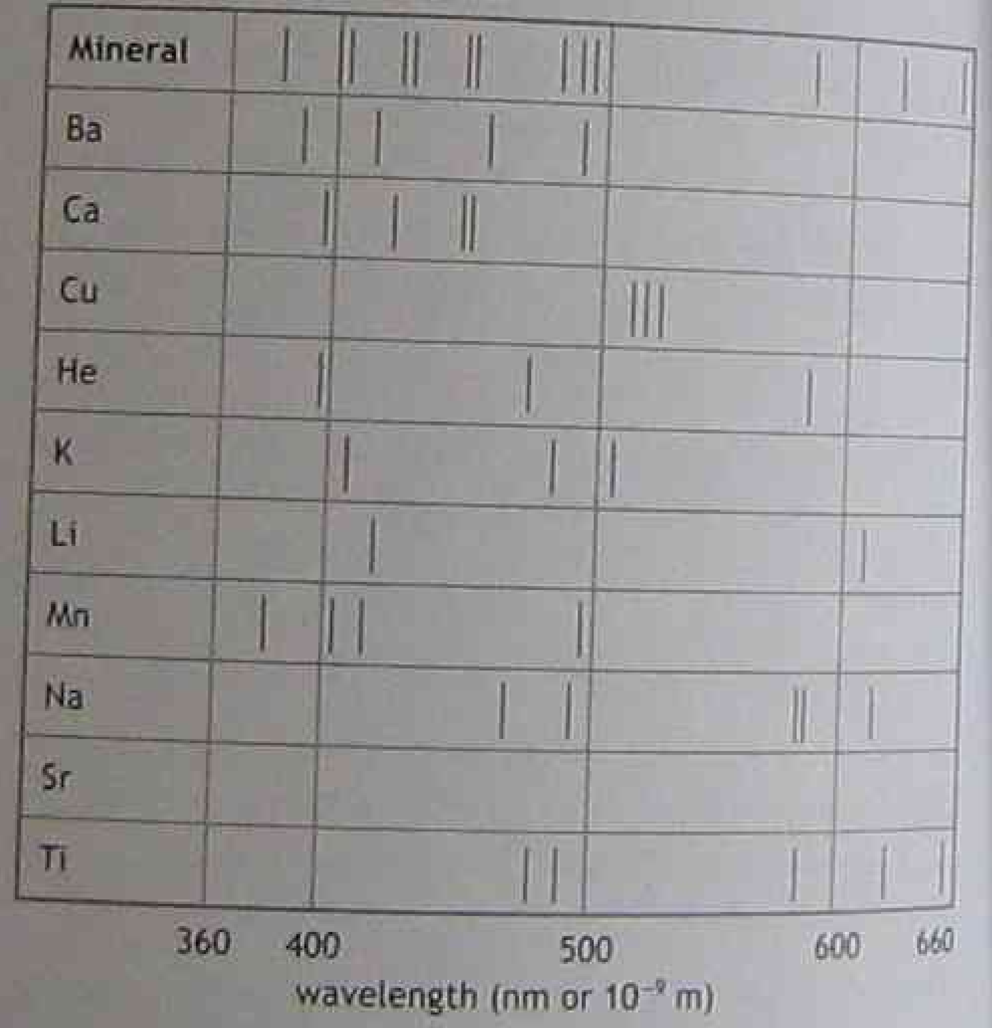


Characteristic emission spectra

These can be widely used to identify elements present in chemicals.

- The presence of a mineral, chemical compounds, or even lunar rock, can be matched against standard samples which have also been put through the spectrograph. A sample of the material is placed in a cup in the lower carbon electrode and the upper graphite electrode is used to complete a high voltage carbon arc. The light from the arc is imaged on a photographic plate which is developed to produce the spectra.
- Copper and copper-based alloys are checked for impurities by this method which is also used for ferrous alloys (steels).
- Aluminium alloys are checked for composition and/or impurities by a similar method, using a spark discharge between rods made from each aluminium melt.

Table 7.10 Some spectroscopic emission lines of certain elements and of a sample of a mineral



7.17 Laboratory use of absorption, ultraviolet and infrared spectroscopy

Absorption spectroscopy

- Light, interacting with invisible atoms and molecules, makes their presence known to us by absorption spectrophotometry.
- When atoms or molecules absorb light, the incoming energy excites a quantised structure to a higher energy level.
- The type of excitation depends on the wavelength of the light. Electrons are promoted to higher orbitals by ultraviolet or visible light. Vibrations are excited by infrared light and rotations are excited by microwaves.
- An absorption spectrum is the absorption of light as a function of wavelength. The spectrum of an atom or molecule depends on its energy level structure so absorption spectra are useful for identifying compounds.

Ultraviolet spectroscopy

The near ultraviolet (UV) region of the electromagnetic spectrum extends from 200–400 nm. Ultraviolet radiation, which is absorbed by outer electrons of atoms, results in the promotion of electrons from one energy level or orbital to a higher one. Electrons from alkanes and other saturated hydrocarbons are not affected and show no absorption between the region 200–700 nm. In reporting UV spectral information, only absorbance maxima (peaks) are reported. A C=O group and an aromatic ring, e.g. benzene (257 nm) is an indication of some type of unsaturation. Any absorbed wavelengths are measured to identify the atoms concerned.

As well as being useful in aiding the determination of molecular structure, ultraviolet spectroscopy is also used for quantitative analysis. The concentration of substance can be determined since the amount of absorption is dependent on the concentration of the absorbing species present in the sample. In addition to its use in the case of unsaturated organic substances, spectrophotometry is also used to determine inorganic ions as simple complexes, e.g. $FeCl_4^-$.

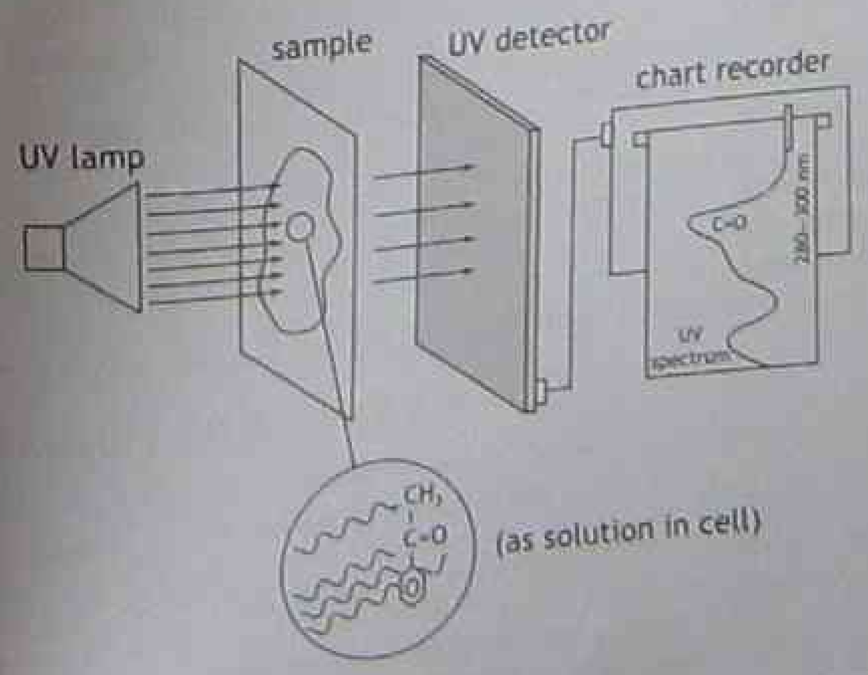


Figure 7.53 Ultraviolet spectroscopy

Infrared spectroscopy

Molecules undergo stretching or bending vibrations. These vibrations become excited by infrared (IR) radiation. Each group of atoms has its own characteristic set of vibrational frequencies. These can be measured by passing an infrared light through them and recording at what wavelengths such absorptions occur. By comparing the IR spectrum produced by the sample with the results from a known compound, the identity of the unknown sample may be shown. Infrared spectroscopy can be used to analyse solids, liquids and powders in order to

- identify the contaminant in a sample,
- detect the presence of a certain pigment, e.g. in a paint sample, and
- use a database which is computerised for matching samples.

Tables and databases can be created because a particular chemical bond absorbs at a particular wave number no matter what compound the bond is in.

Example 1

Alcohols show characteristic absorption of infrared radiation due to O–H and C–O stretch.

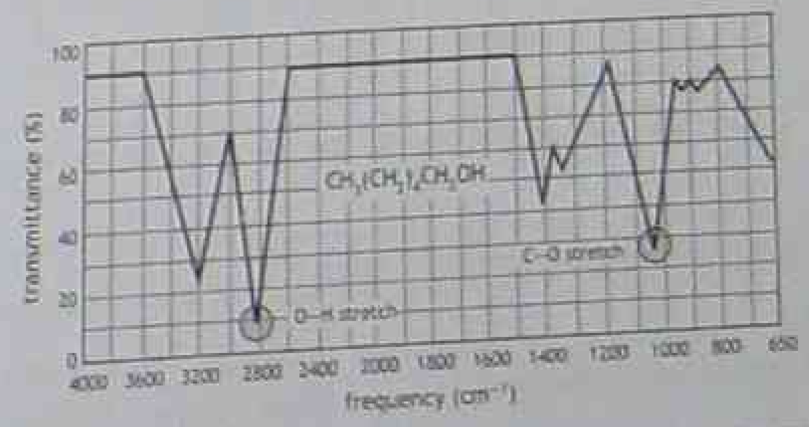


Figure 7.54 An IR spectrum of hexanol

Example 2

Infrared absorption between 1700–1800 cm^{-1} is a reliable means of confirming the presence of a C=O group because few other bond vibrations absorb energy in this region.

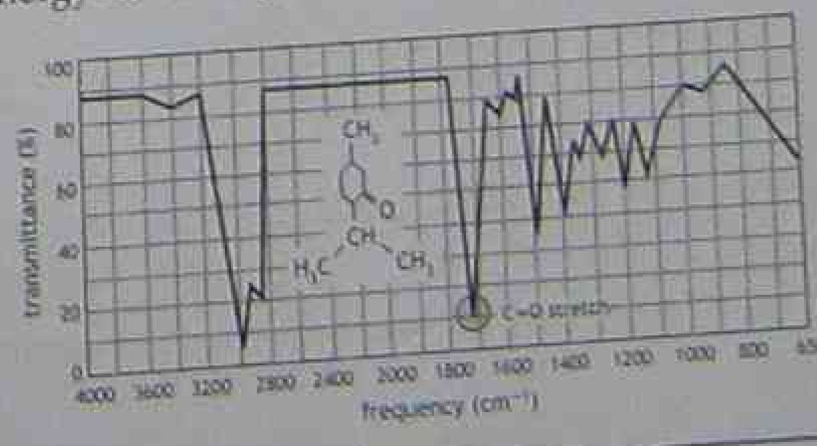


Figure 7.55 An IR spectrum of a C=O group

Infrared spectrophotometry analysis

This technique is known as frustrated internal reflectance spectroscopy (FIRS) and is used extensively for analysing coatings, pastes and paints.

Different compounds absorb different wavelengths within the infrared spectrum, therefore reducing the transmittance of infrared light. In the case of FIRS, direct analysis of the surface can be carried out.

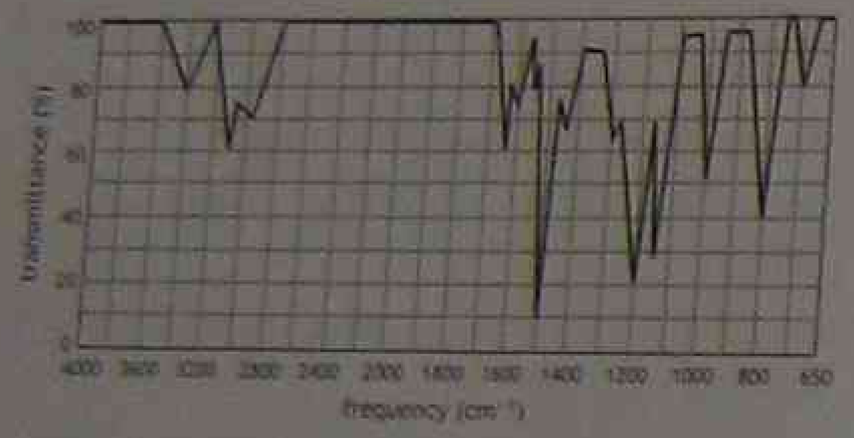


Figure 7.56 IR spectrum of epoxy paint

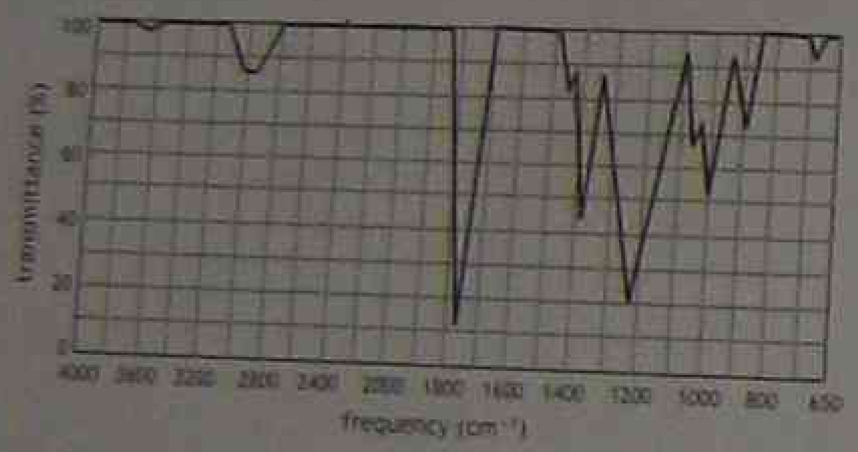


Figure 7.57 IR spectrum of vinyl paint

Note: Frequency (cm^{-1}) equals wave number, or $^1/_\lambda$ (λ in cm) or the number of waves cm^{-1}.

Answers

Answers for Activity 7.1

(a) (i) No immediate change in the colour of the brown bromine water with cyclohexane.

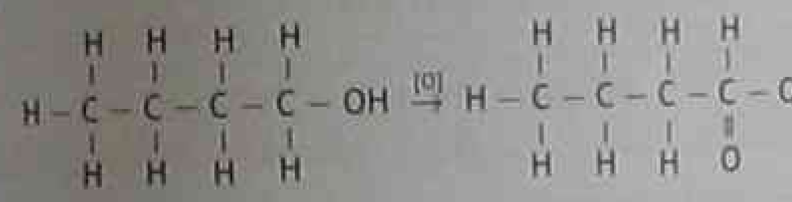
(ii) Bromine water was decolourised instantly with cyclohexane (colour change from brown to colourless).

(b) (i) No colour change with acidified potassium permanganate and cyclohexane.

(ii) Acidified permanganate was decolourised by cyclohexane (colour change from purple to colourless).

Answers for Activity 7.2

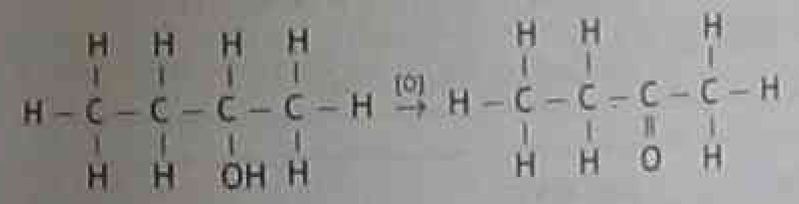
(a) (i) Primary alkanol



$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & OH \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array} \xrightarrow{[O]} \begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & OH \\ & & | & & | & & | & & \| & & \\ & & H & & H & & H & & O & & \end{array}$$

1-butanol butanoic acid

(ii) Secondary alkanol

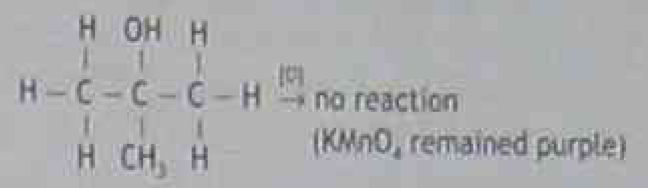


$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & OH & & H & & \end{array} \xrightarrow{[O]} \begin{array}{ccccccccccc} & & H & & H & & & & H & & \\ & & | & & | & & & & | & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & \| & & | & & \\ & & H & & H & & O & & H & & \end{array}$$

2-butanol 2-butanone

In (a) (i) and (ii), purple acidified $KMnO_4$ was reduced to colourless Mn^{2+} ions.

(iii) Tertiary alkanol



$$\begin{array}{ccccccccc} & & H & & OH & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & CH_3 & & H & & \end{array} \xrightarrow{[O]} \text{no reaction } (KMnO_4 \text{ remained purple})$$

methyl-2-propanol

Answers for Activity 7.3

Test tube A:
Gas evolved (H_2) – can use 'pop' test.
$2CH_3COOH(aq) + Mg(s) \rightarrow (CH_3COO)_2Mg(aq) + H_2(g)$

Test tube B:
Gas evolved (CO_2) – can bubble into limewater.
$2CH_3COOH(aq) + CaCO_3(s)$
$\rightarrow (CH_3COO)_2Ca(aq) + H_2O(l) + CO_2(g)$

Test tube C:
$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$

Test tube D:
State colour and pH of your solution.

Test tube E:
The product had a pleasant smell (like nail polish remover). This is an esterification reaction.
$CH_3COOH(aq) + CH_3CH_2OH(aq)$
$\xrightarrow{\text{conc } H_2SO_4} CH_3COOCH_2CH_3(aq) + H_2O(l)$

Answers for Activity 7.4

Gas	Formula	With moist litmus	Special tests	Equations
Oxygen	O_2			
Oxides of nitrogen (any NO → NO_2 in air)	NO_2	acidic		
Hydrogen	H_2		'pop' test using lighted taper	$2H\ (g) + O\ (g) \rightarrow H\ O(l)$
Hydrogen chloride	$HCl(g)$	acidic	white fumes with ammonia solution	$HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$
Carbon dioxide	CO_2	acidic	precipitate when bubbled into limewater; soluble bicarbonate can then form	$CO_2(g) + Ca^{2+}(aq) + 2OH^-(aq) \rightarrow CaCO_3(s) + H_2O(l)$ $CaCO_3(s) + CO_2(g) + H_2O(l) \rightarrow Ca(HCO_3)_2(aq)$

Answers for Activity 7.5

Anion	Action of dilute acids	Some equations
CO_3^{2-}	all carbonates liberated CO_2	$Na_2CO_3(s) + 2H^+(aq) + 2Cl^-(aq) \rightarrow 2Na^+(aq) + 2Cl^-(aq) + CO_2(g) + H_2O(l)$
Cl^- NO_3^- SO_4^{2-}	no decomposition of the anion; may get precipitate as in sample equation	$AgNO_3(s) + H^+(aq) + Cl^-(aq) \rightarrow AgCl(s) + H^+(aq) + NO_3^-(aq)$

Answers for Activity 7.6

Anion	Salt added	Colour of precipitate	Equation
Cl^-	$AgNO_3$ $Pb(NO_3)_2$	white-purple on exposure to light white	$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$ $Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s)$
Br^-	$AgNO_3$ $Pb(NO_3)_2$	cream white	$Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$ see chloride
I^-	$AgNO_3$ $Pb(NO_3)_2$	yellow yellow	$Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$

Answers for Activity 7.7

Lead salt	Solution added	Colour of precipitate	Equation
$Pb(NO_3)_2$ or $(CH_3COO)_2Pb.3H_2O$	KI	yellow	$Pb^{2+}(aq) + 2I^-(aq) \rightarrow PbI_2(s)$
$Pb(NO_3)_2$ or $(CH_3COO)_2Pb.3H_2O$	K_2CrO_4	yellow	$Pb^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow PbCrO_4(s)$
$Pb(NO_3)_2$ or $(CH_3COO)_2Pb.3H_2O$	H_2SO_4 (dilute)	white	$Pb^{2+}(aq) + SO_4^{2-}(aq) \rightarrow PbSO_4(s)$

Silver salt	Solution added	Colour of precipitate	Equation
$AgNO_3$	K_2CrO_4	red	$2Ag^+(aq) + CrO_4^{2-}(aq) \rightarrow Ag_2CrO_4(s)$
$AgNO_3$	KI	yellow	$Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$

Barium salt	Solution added	Colour of precipitate	Equation
$BaCl_2.2H_2O$	K_2CrO_4	yellow	$Ba^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow BaCrO_4(s)$
$BaCl_2.2H_2O$	dil. H_2SO_4	white	$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$

Answers for Activity 7.8

Cation	Hydroxide	Precipitation by NaOH		Precipitation by NH_4OH		Coloured precipitation
		Sol. in excess	Insol.	Sol. in excess	Insol.	(State colour)
Na^+	NaOH					
K^+	KOH					
Mg^{2+}	$Mg(OH)_2$		✓		✓	
Ba^{2+}	$Ba(OH)_2$		✓		✓	
Zn^{2+}	$Zn(OH)_2$	✓		✓		
Al^{3+}	$Al(OH)_3$	✓			✓	
Pb^{2+}	$Pb(OH)_2$	✓			✓	
Ag^+	Ag_2O*		✓	✓		
Cu^{2+}	$Cu(OH)_2$		✓	✓ deep blue		pale blue $[Cu(OH)_2]$
Fe^{3+}	$Fe(OH)_3$		✓		✓	red-brown
Ca^{2+}	$Ca(OH)_2$					
NH_4^+	NH_4OH					

* AgOH is unstable

Conclusion:
In some cases (e.g. Cu^{2+} with ammonia solution) the colour of the complex ion can be used to identify the cation.

Answers for Activity 7.9

Ion	Reagent	Observations
Fe^{3+}	ammonium thiocyanate	red colour in water
Fe^{2+}	ammonium thiocyanate	no red colour

If a fluoride is added to the blood-red complex ion $FeSCN^{2+}$ the red colour is destroyed due to the formation of a more stable fluoride complex.

Ion	Reagent	Observations
Cu^{2+}	NaOH	pale blue precipitate of $Cu(OH)_2$
Cu^{2+}	ammonia solution	deep blue complex ion $[Cu(NH_3)_4]^{2+}$

Answers for Activity 7.10

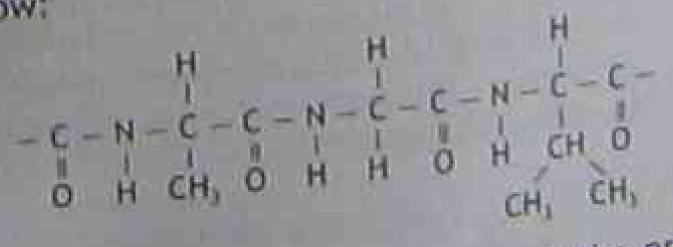
1. Yes.
2. Sodium, potassium and lithium.
3. Yes.
4. Calcium, barium and strontium.
5. To determine whether the colour of the flame was due to the cation or anion present, a variety of salts with the same cation would be tested, e.g. NaCl, $NaNO_3$, $NaSO_4$. If all the salts containing the Na^+ ion gave a yellow colour in the flame it could be assumed that, in this case, the cation determined the flame colour. The experiment should be repeated for the other substances tested.

Name of substance	Formula	Cation present	Colour of flame
Sodium chloride	NaCl	Na^+	yellow
Potassium nitrate	KNO_3	K^+	lilac
Lithium oxide	Li_2O	Li^+	crimson
Calcium nitrate	$Ca(NO_3)_2$	Ca^{2+}	brick-red
Barium chloride	$BaCl_2$	Ba^{2+}	apple-green
Strontium nitrate	$Sr(NO_3)_2$	Sr^{2+}	scarlet

Test on Chapter 7 – (option 4) Forensic Science

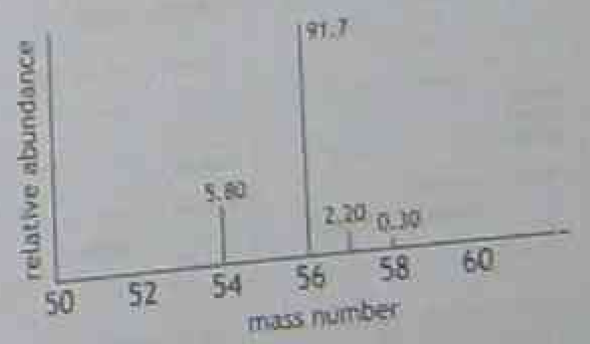
1. **[5 marks]**
   Condensation reactions are used in the formation of polysaccharides.
   (a) (i) Name a plant polymer which cannot be digested by humans.
   (ii) Draw a graphic formula for the monomer used in the manufacture of the plant polymer and name this monomer.
   (b) Name the polysaccharide molecule found in humans. Where in the body is it stored?
   (c) State one difference in fundamental structure between the polysaccharide molecules in 1(a) and (b).
   (d) (i) Name the polysaccharide used by the largest of the invertebrate phyla.
   (ii) What is the significance to this invertebrate phylum, relating to its evolution, of its unique polysaccharide molecule?
   (iii) What is the special chemical group present in the polysaccharide?

2. **[3 marks]**
   The structure for part of a protein molecule is given below:



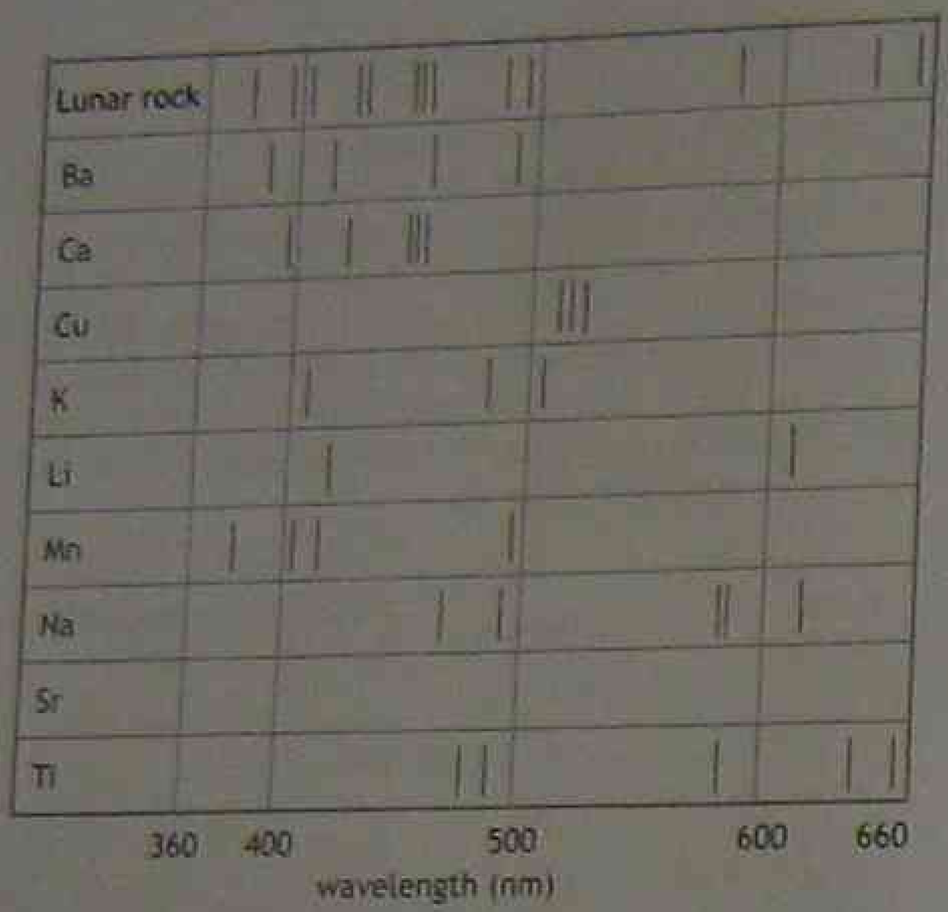
When this protein is hydrolysed and the products examined by paper chromatography, three spots are developed, using ninhydrin.
(a) Write the condensed structural formulae for two monomers of the above protein.
(b) Why is paper chromatography useful for separating amino acid mixtures?

3. **[2 marks]**
   A sample of the element iron is analysed in the mass spectrometer. The result is given in the mass spectrum.

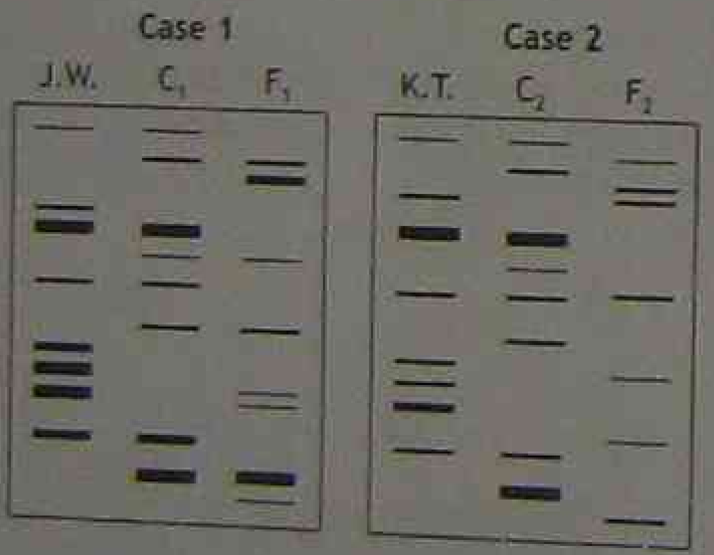


Use the information from this mass spectrum to calculate the relative atomic mass of iron (correct to 1 decimal place).

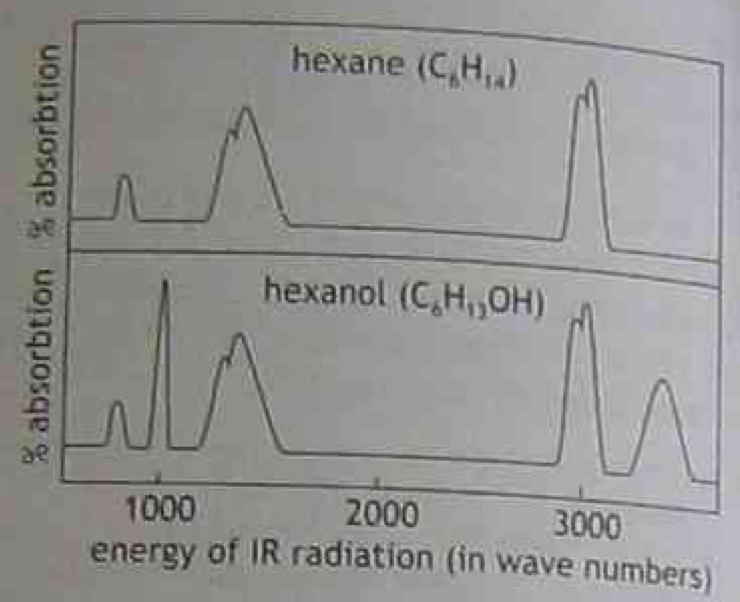
4. **[4 marks]**
   A sample of lunar rock was subjected to spectroscopic analysis (as shown in the diagram below). Also shown are spectroscopic emission lines from selected elements.
   (a) Identify the elements present in the lunar rock sample.
   (b) Explain why each element has its own unique set of emission lines.



5. [5 marks]
In making a DNA 'fingerprint', DNA fragments are separated into bands during gel electrophoresis under strict pH control.
   (a) Explain why the DNA moves to the positive electrode.
   (b) Why don't the DNA fragments all travel at the same rate towards the positive electrode?
   (c) The DNA prints shown below were used as evidence in two court cases where the women (J.W. and K.T.) claimed that particular men (F_1 and F_2) were the respective fathers of their children (C_1 and C_2). State from the DNA fingerprints what the outcome of each case should be regarding paternity.



6. [2 marks]
   (a) Explain what you understand by the term 'absorption spectrum'.
   (b) The infrared spectra of hexane (C_6H_{14}) and hexanol ($C_6H_{13}OH$) are given below:

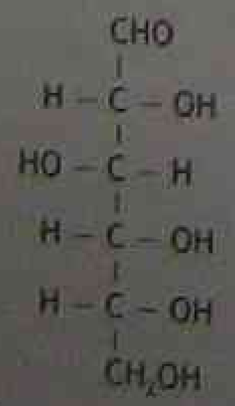


      (i) What is the cause of absorption peaks in spectra?
      (ii) Why are there two additional peaks in the infrared spectrum of hexanol?

7. [4 marks]
   (a) Account for the differences in the volume of $KMnO_4$ used in the reactions of glycerol, 1,2-propanediol and 1-propanol with cold, dilute potassium permanganate. Use structural formula in your answer.
   (b) What differences in rate of reaction would you expect to find?
   (c) In carrying out practical titrations with 0.1 M cold potassium permanganate on primary alkanols, acidified permanganate is used. State a reason for this.
   (d) Draw a structure for the triglyceride formed between glycerol and stearic acid, $CH_3(CH_2)_{16}COOH$, to show clearly the ester links.

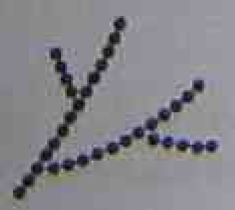
Answers for test on Chapter 7 – (option 4) Forensic Science

1. [5 marks]
   (a) (i) cellulose (ii) glucose



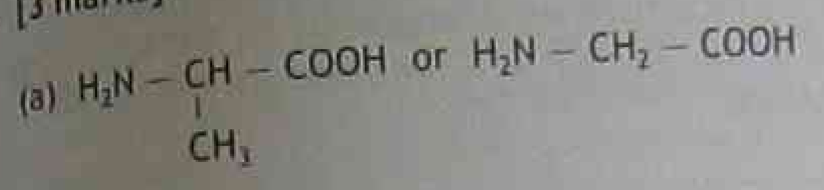
$$\begin{array}{c} CHO \\ | \\ H-C-OH \\ | \\ HO-C-H \\ | \\ H-C-OH \\ | \\ H-C-OH \\ | \\ CH_2OH \end{array}$$

   (b) Glycogen. It is stored in the liver.
   (c) Cellulose shows some cross linkage and monomer is glucose. The fundamental structure of glycogen is the 'amylose chain' made up of glucose monomers. The branched amylose chains create a tree-like cross-section.



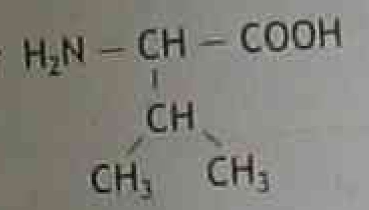
   (d) (i) Chitin.
      (ii) Chitin forms hard waterproof exoskeletons and makes possible the development of the finely articulated appendages.
      (iii) The $-NH_2$ group is present in the monomer as a naturally-occurring amino sugar, e.g. as D-glucosamide.

2. [3 marks]
   (a)



$$H_2N-\underset{\underset{\displaystyle CH_3}{|}}{CH}-COOH \quad \text{or} \quad H_2N-CH_2-COOH$$

or



$$H_2N-\underset{\underset{\displaystyle CH_3 \quad CH_3}{\diagup \quad \diagdown}}{\underset{\underset{\displaystyle CH}{|}}{CH}}-COOH$$

   (b) Paper chromatography is useful for separation mixtures of amino acids because they migrate at different rates in a particular solvent.

3. [2 marks]

$$A_r = \frac{(5.80\times54)+(91.7\times56)+(2.2\times57)+(0.30\times58)}{100}$$
$$= \frac{5591.2}{100}$$
$$= 55.9 \text{ (relative atomic mass of iron)}$$

4. [4 marks]
   (a) Elements are calcium (Ca), manganese (Mn) and titanium (Ti).
   (b) Each element has a unique electronic configuration. The emission spectrum of each element results from electrons moving between the element's electronic levels. The emission of radiation in quanta occurs when electrons jump from higher to lower energy levels. The electron transitions between all the available energy levels for each element results in each element giving rise to the unique emission spectra.

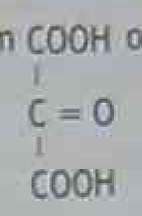
5. [5 marks]
   (a) DNA is negatively charged, so will move towards the positive electron.
   (b) The distance that an individual fragment of DNA travels depends on the amount of its electrical charge, which is determined by its length and molar mass.
   (c) Case 1 – F_1 is the father of the child C_1.
   Case 2 – F_2 is not the father of the child C_2.

6. [3 marks]
   (a) An absorption spectrum is the absorption of light as a function of wavelength.
   (b) (i) Absorption of energy into the molecular motion.
      (ii) Hexanol has two extra bonds (O–H) and (C–O) compared with hexane.

7. [4 marks]
   (a)

$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

has two primary alkanol (CH_2OH) groups and one secondary alkanol (CHOH) group present in the molecule so would be expected under the conditions given to form



$$\begin{array}{c} COOH \\ | \\ C=O \\ | \\ COOH \end{array}$$

on complete oxidation.

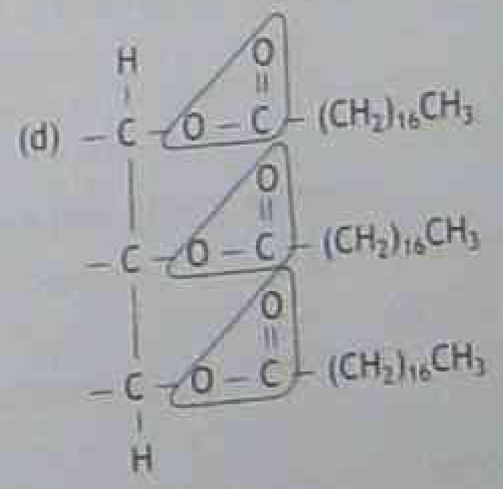
$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_3 \end{array}$$

would form

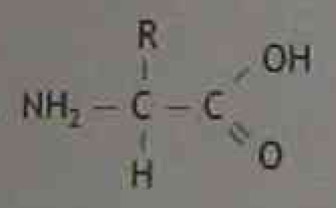
$$\begin{array}{c} COOH \\ | \\ C=O \\ | \\ CH_3 \end{array}$$

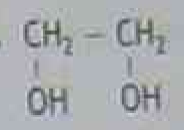
on complete oxidation.

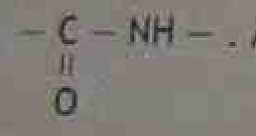
$CH_3-CH_2-CH_2OH$ would form CH_3-CH_2COOH on complete oxidation.
If two volumes of cold, dilute $KMnO_4$ were required to oxidise a primary alkanol and one volume of cold, dilute $KMnO_4$ was required to oxidise a secondary alkanol, the volume ratios needed for glycerol : 1,2 propanediol : 1-propanol would be 5 : 3 : 2.
   (b) Glycerol would require the most bonds to be broken and reformed in the oxidation reaction, so this reaction would be the slowest and the oxidation of 1-propanol would be the most rapid reaction.
   (c) Acidified $KMnO_4$ prevents the precipitation of brown MnO_2 which could obscure the end point of the titration.
   (d)



Glossary

Absorption spectrum	For an element, it is a line spectrum which is complementary to the emission spectra. It results from the selective absorption of characteristic wavelengths by an element when white light is passed through the vapour of the element at a temperature too low to excite the electrons atomic force microscopy.
AFM	Atomic force microscopy.
Alkanes	C_nH_{2n+2} – saturated hydrocarbons.
Alkenes	C_nH_{2n} – unsaturated hydrocarbons containing a double bond (C=C).
Alkynes	C_nH_{2n-2} – unsaturated hydrocarbons containing a triple bond (C≡C).
Alkanols	$C_nH_{2n+1}OH$ – they contain an –OH functional group.
Amino acids	Organic molecules containing nitrogen in the form $-NH_2$ and a $-COO^-$ group bonded to the same carbon atom.  $NH_2-\underset{H}{\overset{R}{C}}-C\overset{OH}{\underset{O}{}}$
Anthropological studies	Scientific studies that examine nature of human cultural development.
Archaeological studies	Scientific studies of prehistoric antiquities.
Arthropod	An invertebrate animal with jointed appendages, e.g. insects or crabs.
Carbohydrates	General formula $C_x(H_2O)_y$. They include sugars, starches, glycogen and cellulose.
Chitin	A polysaccharide with a six-carbon sugar to which a nitrogen-containing group has been added, acting as the monomer. Chitin forms the waterproof exoskeleton of arthropods.
Chromatography	A general name for the process which separates the components of a mixture by selective removal of these components from a moving fluid.
Complex ion	A charged species where ligands are bound, e.g. $[Ni(CN)_4]^{2-}$.
CRT	Cathode ray tube.

Diols	Organic compounds containing two hydroxyl groups, e.g. ethanediol.  $\underset{OH}{CH_2}-\underset{OH}{CH_2}$
Disaccharide	Formed by a condensation reaction between two monomers with water being eliminated, e.g. sucrose ($C_{12}H_{22}O_{11}$).
DNA	A very long molecule of deoxyribonucleic acid. It stores all the coded information and is a polymer found in our cells. DNA is found in all living things.
DNA sequence of bases	Adenine (A) – Thymine (T); Cytosine (C) – Guanine (G).
Electrophoresis	The separation of molecules by migration in an electric field.
Electron spectroscopy	X-ray photoelectric spectroscopy.
Emission spectra	Each element has a unique electronic configuration. The emission spectrum of each element results from electrons moving between the element's electronic levels. The emission of radiation in whole quanta occurs when electrons jump from higher to lower energy levels. Each element has a distinct set of frequencies.
Enzyme	A physiologically active protein. They are protein biocatalysts.
Ester	Compound formed from the reaction of an organic acid and an alkanol (RCOOR').
FIRS	Frustrated internal reflectance spectroscopy.
Forensic	A term meaning 'applied to the law'.
Genetic markers	Specifically inherited traits that can be analysed, e.g. protein in blood.
Genotype	The type and arrangement of genes in an organism.
Glycerol	An alkane triol called 1,2,3-propanetriol.
Glycogen	A polysaccharide which stores animal protein. It is composed from glucose monomers and in cross-section shows a tree-like structure created by branched amylose chains.
HPLC	High performance liquid chromatography.
Infrared spectroscopy	Each group of atoms has its own characteristic set of vibrational frequencies. These can be measured by passing infrared radiation through them and recording the wavelengths at which absorptions occur. The IR spectrum produced by the sample is computer-matched for identification.
Isomers	Compounds with the same molecular but different structural formulae.
Mass spectrometer	This instrument depends on the difference in mass-to-charge ratio (m/e) of ionised atoms or molecules to separate them from each other.

Monosaccharide	A simple sugar containing a five- or six-carbon ring, e.g. glucose $C_6H_{12}O_6$.
Nucleic acids	The largest and most complicated molecules in living things. They carry information about the control and reproduction of cells. They are made up of units called nucleotides.
Nucleotides	Nucleotides consist of three parts, a phosphate group, a simple sugar and a nitrogen base.
Organic chemistry	The study of carbon compounds excluding the oxides CO and CO_2 and their derivates.
PCR	Polymerise chain reaction, which is a DNA typing technique.
Peptide bond	Proteins are made by linking aminoacids, with the peptide bond being the main link, e.g.  $-\underset{\underset{\displaystyle O}{\parallel}}{C}-NH-$. Also known as 'amide link'.
Phenotype	A physical characteristic produced by the genotype.
Polymers	Large molecules made up of smaller units called monomers, e.g. glycogen is a polymer of glucose.
Polymorphic trait	Indicates that several distinct types of features are specifically inherited, e.g. blood groups.
Polysaccharide	A polymer made up of monomers, e.g. starch, cellulose, glycogen and chitin.
Proteins	They are used both as structural molecules and as enzymes to catalyse metabolic reactions. They contain the elements carbon, hydrogen, oxygen and nitrogen as well as traces of sulfur in some cases.
Saponification	The process used in soap making. Fat + alkali → salt of fatty acid + glycerol.
Scientific method	The logical way in which a scientist goes about trying to solve a problem.
SEM	Scanning electron microscope.
Single local probing	A method of DNA typing.
Spectroscopy	The science dealing with spectrum analysis.
STM	Scanning tunnelling microscope.
TLC	Thin layer chromatography.
Unsaturated fatty acids	Long-chain alkanoic acids which contain at least one C=C bond.

8 option five

The Chemistry of Art

From prehistoric times, humans have been fascinated by colour. The colours of prehistoric, Egyptian and Roman painting reflect the rituals and symbols of those diverse cultures as well as the limited range of materials that were then available. Studies of the origin of colour in chemicals have led to a greater understanding of chemistry, especially in the transition elements and their coloured compounds.

Contents

8.1 Ancient pigments

- The earliest pigments were made from naturally occurring earths — white chalk, the reds, browns and yellows from ochres, the darker umbers and charred wood.
- The pigments were suspended in a vehicle which could be water, saliva or even urine. These pigments needed to be insoluble so that they would remain in place when the vehicle evaporated.
- The brilliant colours of the ground minerals did not fade in light as did many of the plant dyes also used.

Table 8.1 Some ancient pigments

Mineral	Colour	Chemical composition
*Red ochre powder	red	$Fe_2O_3.H_2O$ (red iron oxide-haematite)
*Yellow ochre	yellow	$Fe_2O_3.H_2O$ (geothite) + clay
Burnt yellow earth produced from early paleolithic times by heating yellow earth	red	$Fe_2O_3.H_2O$ (red iron oxide-haematite)
Chalk	white	$CaCO_3$
*White clay (kaolinite)	white	$Al_2O_3.2SiO_2.2H_2O$
*Charcoal black	black	C
*Bone black	black	$C + Ca_3(PO_4)_2$

* Pigments used by Australian Aborigines

8.2 Early uses of pigments in cave paintings

Europe

The prehistoric cave paintings at Lascaux in south-west France are world famous. The main pigments are red ochre (signifying life) and black (symbolising death). Yellow ochre was sometimes used and calcite crystal ($CaCO_3$) lined the walls of the cave. The pigments were mixed with animal fats and warmed to make them workable.

Australia

By far the most prolific works of prehistoric art by Australian Aborigines are those engraved on rock surfaces. This art style extended over the whole continent, wherever suitable rock was available in the locality of tribal activity. Most were located near Aboriginal ceremonial sites or corroboree grounds near permanent waterholes. Some caves are decorated only with stencilled images of hands. The pigments, usually white pipe clay or gypsum, or red ochre, were mixed in the mouth then 'spluttered' or sprayed with the lips around the object held against the rock. Black was used for drawing outlines and, in areas where black manganese oxide was available, the works were more permanent than those done with charcoal. A number of ochre mines producing mainly red and yellow colours have been discovered. Trading from such abundant sources is evident. In some cases iron ore concentrations in rock outcrops and cliff faces provided a range of colours from red through purple to brown. Much of Australia's earliest cave art is in the form of schematic drawing, where men (not animals) were depicted as stick-like images. Among the most ancient paintings are the human stick figures Mimi (Arnhem land) and Bradshaw (North Kimberley) said by local Aborigines to belong to the distant Dreamtime. The Aborigines are more interested in works related to their inherited mythology, e.g. paintings of north-western Australia often show the Wandjina (who could control the elements such as monsoons) in the company of a snake or rock python. These snakes are said to have powers that control weather and fertility. The rockface is customarily prepared by applying an all-over wash of white clay.

North America

The first Ancestral Pueblo people settled at Mesa Verde (Colorado, USA) about 400 AD. *Petroglyphs* or rock art, are found throughout the Southwest. There are many examples from Mesa Verde National Park. The symbols have been partially interpreted as representing the Pueblo history of emergence, migration and trail settlement.

The Pueblo people are responsible for the famous cliff dwellings, some villages having 200 rooms. Many rooms were plastered on the inside and decorated with painted designs. By 1400 AD, the people of Mesa Verde had left and travelled into New Mexico and Arizona.

8.3 Self decoration

Ceremonial art

The Koori people of coastal New South Wales painted themselves with ochre. The initiated men were painted like Biami, the Dreamtime creator. Red and yellow ochres, white pipe clay and charcoal were applied with fingers or brushes to produce symbols representing ancestral history and myths. The females were painted in white with water symbols, e.g. three half ovals on their breasts. Newly-born children had their bodies painted with white clay. Major ceremonial occasions include the Intichuma fertility ritual corroboree and initiation ceremonies when Koori boys become adults.

Facial decoration among the people of Papua New Guinea is colourful and dramatic. For festivals the Mount Hagen men paint their faces with black charcoal and outline features with white, red, blue or yellow river clays. Women and boys paint their faces red and use touches of brighter colours as decoration. Black paint represents male aggression and hidden strengths whereas red, for females, signifies magic, material wealth and fertility.

Cosmetics

Body and face painting continued to affect attitudes of early Middle Eastern and Mediterranean civilisations in their use of facial cosmetics. Early peoples accentuated the eye as the main facial feature. In ancient Egypt it was the symbol of the sungod Ra. This dominance of the eye as a symbol is seen in Egyptian frescoes. Egyptian eye make-up consisted of the raw materials listed in Table 8.2 which were prepared by grinding on a stone slab. It was applied in powder form over a base of ointment.

In addition, local oxides of copper, iron and manganese were used. For face make-up, white lead $[2PbCO_3.Pb(OH)_2]$ was used to give a paler skin colour. Red phosphorus was used as a rouge while cinnabar (HgS) was imported from China during the 12th dynasty and used to brighten the lips. Red ochre was also used to colour cheeks and lips. Some of the cosmetics used contained metallic poisons such as lead, mercury, arsenic and antimony; they posed a potential health hazard in early Egyptian and Roman cultures. White lead was still being used as a base for face powder in 18th century Europe.

In the 19th century, some of the toxic properties of metallic-based paints had been discovered when chemical analysis showed, for example, the presence of As and Pb. Talc replaced white lead as a face blanche. In the 21st century, natural cosmetic ingredients have so far not been completely replaced by synthetic substitutes. Colouring ingredients are still manufactured from the basic earth pigments, iron oxides, charcoals and various ochres.

8.4 Preparation of the dead for burial

Central to Egyptian mortuary practices was the belief that life continued after death. The Egyptians believed that the living, the dead and the gods all had the same basic needs— shelter, food and drink.

In tomb paintings the typical Egyptian colours of white, black, red and yellow ochre were used as well as ultramarine blue (shipped from Afghanistan).

Mummification was used so that the spirit could recognise its body. This intentional method of preserving a corpse was developed by the ancient Egyptians c.2600 BC. The main purpose was to dehydrate body tissues and thus prevent rapid decomposition. There were two main stages of mummification.

(a) *Evisceration* of the body (the viscera were placed in Canopic jars). The brain was never kept. The heart was considered the most important organ.

(b) *Dehydration* of the body using natron (a mixture of Na_2CO_3 and $NaHCO_3$ which contained a high percentage of impurities (NaCl and Na_2SO_4).

After removal from the natron bed, packing and resinous paste was applied before the body was

Table 8.2 Egyptian eye make-up

Ore	Chemical composition	Colour	Source
Malachite	$CuCO_3.Cu(OH)_2$	green	Sinai and eastern desert
Chrysocolla	$CuSiO_3.H_2O$	greenish-blue	locally found
Galena	PbS	dark grey	Aswan and Red Sea
Stibnite	Sb_2S_3	black	Asia Minor, Persia
Orpiment	As_2S_3	yellow	

wrapped in linen cloths and bandages. Coffins were used to protect the dead from the earliest recorded times and were usually made of wood.

The mummiform figures often had headcloths, false beards, 'broad collars' and body wrappings decorated with geometric designs that imitate textiles. A vertical column of inscription supplied a funerary message to ensure the continued survival of the owner.

Some royal burials were in pyramids, though the use of rock tombs cut into cliffs became widespread, e.g. in the Valley of the Kings, where inscriptions were displayed as a monument. A sarcophagus or outer stone coffin bearing sculpture or inscriptions was used as a monument.

8.5 Techniques used to attach pigments to surfaces

Frescoes

The art of fresco was revived in medieval times by the great Florentine master, Giotto (c.1267-1337). Frescoes are built up in layers on a dry wall. The fresco is offered to a surface as follows:

- A mortar layer of coarse sand, loam and water is applied followed by a coarse plaster layer of three parts sand: one part lime.
- The arricio, another rough plaster, is then applied.
- The next layer, the sinopia (made from sinoper, a red earth), functions as the base on which the fresco design is drawn.
- The smooth final layer, the intonaco, is only 3–5 mm thick. It is made of sand or marble dust and fine lime in equal quantities.
- As the lime dries and the water evaporates, a hard crystalline surface is formed in which the colour is bound. The pigments must then be applied rapidly or the hues will darken.

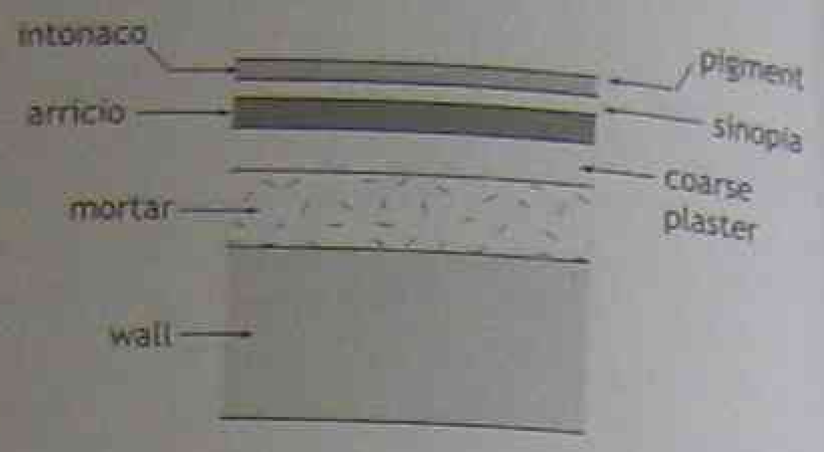


Figure 8.1 Fresco layers

- Since pigments derived from plants were sensitive to the alkali in the lime, earth colours were the staple pigments used in frescoes.
- Some pigments could not be used in frescoes, e.g. lead white ($PbSO_4.PbO$) which turns black (PbS forms), and vermilion (HgS) which is oxidised and turns black.
- Giotto's innovative fresco technique relied on the 'dish system'. Pure powdered colours were mixed in separate dishes to his specifications as follows:
  - (i) Pure colour + water for shadows.
  - (ii) The same colour + white for mid-tones.
  - (iii) More white was used for the lights.
  - (iv) Fresco was worked in daily sections, so batches of colour had to be matched.
  - (v) Frescoes were to lighten on drying.

Egg tempera painting

The colours of early medieval panel paintings (13th – mid 15th century) are often very well preserved. This is because egg tempera methods were used. The wet pigment (powdered colour in water) was bound in the medium of a whole egg or egg yolk. As the protein in the egg hardened, the colours were given a sheen and a tough skin. The watery content of the egg limits the range of pigments since, as the water evaporates, the paints begin to set almost at once. The colours must be mixed beforehand and the paint must be applied very thinly in layers to prevent shrinking and cracking. Lead white can be added to provide the highlights. The wooden panel (often made of white poplar) was first covered with a coating of animal glue called size so that the wood did not absorb the paint.

Table 8.3 Pigments used in frescoes

Colour group	Pigment	Formula
Reds	sinopia (red earth) raw sienna (goethite) red umber	Fe_2O_3 $Fe_2O_3 + H_2O$ + clay, etc. $Fe_2O_3 + MnO_2 + H_2O$ + clay, etc.
Greens	green earth (celodonite + glauconite)	Fe, Mg, Al, K hydrosilicates
Blues	*azure blue (applied to dry plaster making the layer more vulnerable)	$2CuCO_3.Cu(OH)_2$ (basic copper carbonate)
White	slaked lime Giotto's paste (dried ground lime + vinegar) chalk	$Ca(OH)_2$ $CaCO_3$

* Pigment has 'greened' due to high levels of CO_2

Pigment selection depended to some extent on their cost. Some commonly used pigments are given below:

- *Ultramarine blue* ($Na_{8-10}Al_6Si_6O_{24}S_{2-4}$) was extracted from lapis lazuli, a stone that was brought from Afghanistan. Because of its cost, it was reserved for the most significant figures, e.g. Christ and the Virgin.
- *Vermilion* (HgS), the brightest red used, was imported from China. An artificial vermilion was developed by heating sulfur and mercury.
- *Pure gold* was also used. Gold and red were associated with the worship of the Trinity, saints and angels.
- *Azurite or German blue* [$2CuCO_3.Cu(OH)_2$] was commonly used for the sky or the frame owing to its relative cheapness.

Pigments may be spread on a surface layer to produce colour, e.g. as paints, or mixed with the bulk of material, e.g. glass colours.

Glass

Commercial glass can be made by heating lime (CaO), sodium carbonate (Na_2CO_3) and sand (SiO_2) to produce an amorphous substance.

Table 8.4 Some substances which can be used to produce colour

Oxide	Resulting colour
Chromium	dark-green
Manganese	blue-violet
Copper	greenish-blue
Iron	green
Cobalt	blue (deep)
Uranium	yellow

Glass is a fused mixture of sodium and calcium silicates with various amounts of insoluble silicates and other substances which will produce colour. Colloidally suspended metals or their oxides can colour glass.

8.6 Constituents of paints

Paint consists of *pigment* dispersed in a liquid called the *vehicle*.

Pigment

- The pigment is a solid material composed of very fine particles which are insoluble in the vehicle.
- The pigment provides the colour to the paint film.
- It must remain suspended in the paint and not settle to form a hard sediment.
- Pigments may be mixed with extenders, e.g. talc or china clay is usually added to decrease cost.
- Titanium oxide (TiO_2) is the most common white pigment now used, since it shows greater opacity than zinc oxide (ZnO) and is safer to use than white lead [$2PbCO_3.Pb(OH)_2$].
- The pigment is chosen because it confers some or all of the following properties to the paint film:
  - (i) Colour.
  - (ii) Hiding power (opacity).
  - (iii) Strength and adhesion.
  - (iv) Durability and weathering properties.
  - (v) Reduced gloss.
  - (vi) Corrosion resistance.
- Pigments may be organic, inorganic or metallic. Inorganic pigments, e.g. certain metal oxides and salts, are more stable to light, resistant to heat and provide better corrosion resistance on metals.

Vehicle

- 'Vehicle' is the name given to the liquid portion of the paint because it 'carries' the pigment.
- When spread out thinly, the vehicle changes in time to an adherent dry film, e.g. when a liquid like linseed oil is a constituent.

Table 8.5 Some vehicle components

Vehicle component	Nature and function
Thinner	usually a solvent (e.g. turpentine, water) added to facilitate application
Resin or polymer	used to be natural (e.g. shellac) but now is synthetic (e.g. vinyl, alkyl, polyurethane and PVA polymer) which hardens on exposure to air and gives bulk, gloss and toughness to the paint film
Drier	a metal soap (e.g. manganese linoleate) which speeds up the drying of an alkyl-based paint
Plasticiser	a solvent for the resin which improves flexibility and adhesion of the hardened paint film

- A chemical reaction occurs between the constituents of the vehicle to produce a dry paint film.
- The vehicle should have the following properties:
  - (i) Ability to wet the particles of the pigment.
  - (ii) Sufficient viscosity to hold the particles in suspension when the paint is drying, yet sufficient fluidity to make application easy.
  - (iii) Capacity to form a tough adherent film on the surface to which it is applied.

8.7 Increase in availability of pigments

Over time, more pigments and vehicles became available to artists as a result of:

(a) the discovery of new mineral deposits;
(b) improved extraction methods for useful minerals; and
(c) increased trading with distant communities.

This can be illustrated by a historical example, the discovery of the whitest substance on earth, titanium dioxide. This compound is now widely used in paint pigments, sunscreens and cosmetics. Rutile and ilmenite are the major raw materials. Mineral sands produced in Western Australia provide over 70% of the world's synthetic rutile requirements.

- In 1791, William Gregor, a Cornish chemist, examined sand from his local river and discovered the reactions which were to form the basis of the production of TiO_2 up to 1960.
- In 1795, M.H. Klaproth, a German chemist, discovered the same oxide in rutile and named the element titanium.
- Mineral sands were first mined in Australia at Byron Bay in 1934.
- By 1960, mineral sands were being mined commercially in Queensland, New South Wales, Victoria and Western Australia.
- Ilmenite, the major mineral in Western Australian deposits, was increased in value by upgrading secondary ilmenite (58% TiO_2) to synthetic rutile (90% TiO_2) in the early 1960s. This was done by the two-stage Becher process.
- In the Becher process, secondary ilmenite, coal and sulfur are fed into a rotary kiln at 1200°C. This removes oxygen from the ore and produces metallic iron in the ilmenite. Ilmenite grains are converted to porous synthetic rutile grains with metallic iron and other impurities. In the second stage, iron is drawn out as hydrated iron oxide from the synthetic rutile grains. These grains are given a mild acid treatment to dissolve impurities, and then washed, filtered, dried and transported to white pigment manufacturing plants in Australia or exported for further processing.

Some plants, such as that at Kwinana in Western Australia, use the newer chlorination process to produce white pigment by heating a mixture of synthetic rutile (95% TiO_2), coke and chlorine to form gaseous titanium tetrachloride.

$$(TiCl_4).3TiO_2(s) + 4C(s) + 6Cl_2(g)$$
$$\rightarrow 4TiCl_4(g) + 2CO(g) + 2CO_2(g)$$

The $TiCl_4(g)$ is condensed to $TiCl_4(l)$ and most impurities separate as solids. The titanium tetrachloride is then reheated to a gas with hot oxygen to form very fine crystalline rutile. The displaced $Cl_2(g)$ is recycled to the start of the process.

$$TiCl_4(l) + O_2(g) \rightarrow TiO_2(s) + 2Cl_2(g)$$

Note: Pigments listed in Tables 8.1 to 8.4 mostly have their metallic colour component in the first transition series of the Periodic Table.

For Zn group,	Zn	ZnO	Zn^{2+}	(white)
	Cd	CdS	Cd^{2+}	(yellow)
	Hg	HgS	Hg^{2+}	(vermilion red)

8.8 Light emission by atoms

Early in the history of chemistry it was observed that when elements were heated in the flame, and later when they were excited in a discharge tube, colours of light characteristic of the element used were seen. Sodium ions in a non-luminous Bunsen flame appear yellow; the sodium vapour used in some street lights is also yellow. When an atom is not heated in a flame or excited in a discharge tube, it adopts the lowest state of energy — the *ground state*. Electrons which acquire enough energy, e.g. by heating, move to higher energy levels and an atom containing such electrons is said to be *excited*.

Atoms of Group I metals are comparatively easily excited to higher energy states, e.g. by energy supplied from a non-luminous Bunsen flame. Compounds of these metals show characteristic colours in the flame and are often used as simple identification tests. Flame colour is due to the release of energy by excited electrons as they move

back to a lower energy level. The emission spectrum of sodium, for example, has two very strong yellow emission lines at 589 nm and 616 nm, so the flame colour is yellow. These lines are very close together.

Excited atoms only emit certain frequencies of radiation because

- atoms with many electrons have sets of energy levels;
- each energy level can only accommodate a certain number of electrons; and
- the ground state has its electrons located in the lowest available energy levels.

Since the electron configuration of a sodium atom is 2,8,1, it follows that the simplest way of exciting the sodium atom is to move the outer electron into the next available higher energy level.

Note: A fully worked experiment is included in Activity 8.1, and is only useful for elements that have a major emission in the visible spectrum.

Activity 8.1

Flame tests

Introduction

For some elements in Group I and Group II there is one particular electron transition that occurs far more readily than any other. This means that the emission spectrum of such an element has a very bright line corresponding to this transition. The flame (non-luminous Bunsen flame) in which the excited atoms are produced takes on the colour of that line. This method of identification is very useful in deciding whether Group I elements are present since they do not form precipitates because all their commonly occurring compounds are soluble.

Aim

To identify characteristic colours that are produced by the samples provided for flame testing.

Method

CARE: Use safety glasses for this experiment.

How to clean wire

Dip the wire in concentrated HCl, then heat in the non-luminous Bunsen flame until no colour shows.

CARE: Do not heat the glass tube as it may shatter.

Step 1. Hold the loop of the wire under a gently dripping tap and then dip the tip into the substance you are testing. Introduce the tip of the wire slowly into the edge of the Bunsen flame and record the colour of the flame observed in the record column below.

Step 2. At the end of each test, the wire should be cleaned until the flame is colourless.

Step 3. Proceed to test the remaining solutions, except for the copper sulfate solution.

Step 4. Copper salts will attack the platinum wire, so test this solution using a clean stainless steel spatula.

Step 5. When testing potassium salts, if analytical quality reagents are not used, impurities containing sodium salts can mask the delicate lilac colour of potassium. This can be overcome if the Bunsen flame is looked at through a piece of blue (cobalt) glass which will filter out the yellow colour of the sodium flame.

Results

Name of substance	Formula	Cation present	Colour of flame
Sodium chloride			
Potassium nitrate			
Lithium oxide			
Calcium nitrate			
Barium chloride			
Strontium nitrate			
Copper sulfate			

Questions

1. Are there any Group I elements tested?
2. What are they?
3. Are there any Group II elements tested?
4. What are they?
5. State the group of elements to which copper belongs.
6. Carry out a series of experiments to determine whether the cation or the anion imparts colour to the flame.

8.9 A study of the atomic spectra

To understand how a study of atomic spectra led to an informed theory for the arrangement of electrons in atoms, the nature and origin of light must first be considered:

- Light is part of the electromagnetic spectrum.
- Electromagnetic radiation is a type of wave motion where different types have different wavelengths.
- Electromagnetic radiation travels at a velocity of 3×10^{8} ms^{-1}.

When white light passes through a prism, it is broken up into a mixture of wavelengths from blue to red (the colours of the rainbow), forming a continuous spectrum.

- The operation of a spectroscope is based on this principle. If observations are made by eye, it is called *spectroscopy*, and *spectrography* if photographic plates are used.
- If a colourless flame is used and a substance such as a pure sodium salt is introduced, sharp images of the slit will appear at certain wavelengths. The images are called 'spectral lines', e.g. Na at 589 nm and 616 nm which are yellow lines.
- The spectrum of light emitted by a substance is called an *emission spectrum*.

8.10 Interpreting the hydrogen spectrum

- The spectrum of atomic hydrogen can be seen by passing an electric current through hydrogen gas at low pressure. The gas has a deep violet glow, as some H_2 molecules are broken up into H atoms.

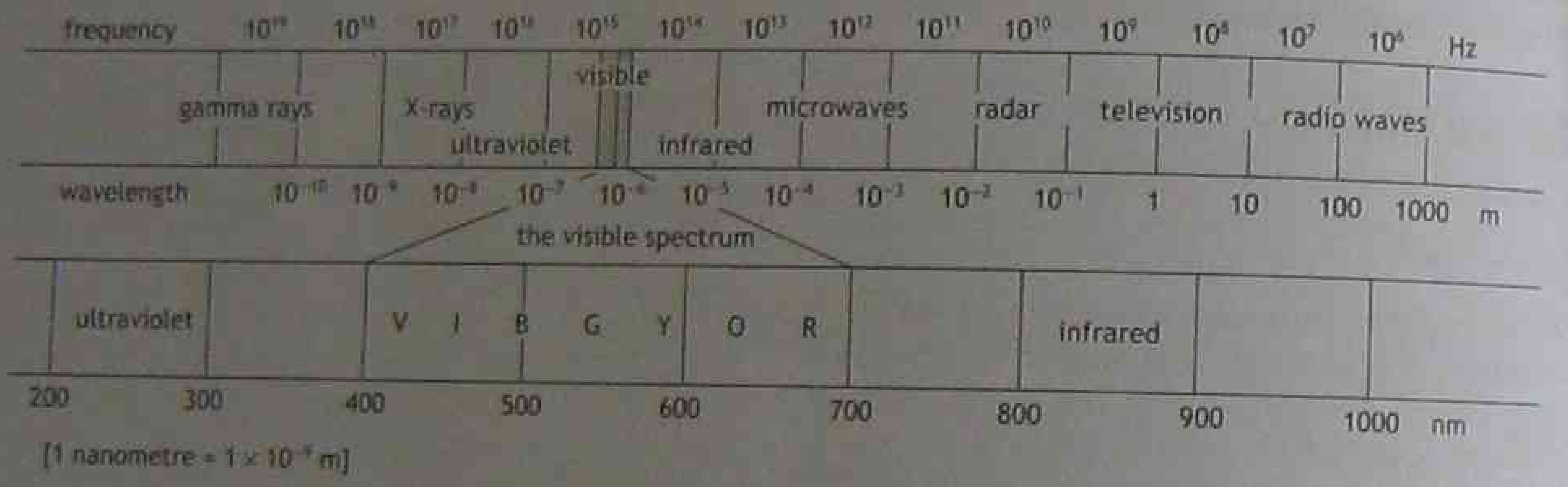


Figure 8.2 The electromagnetic spectrum

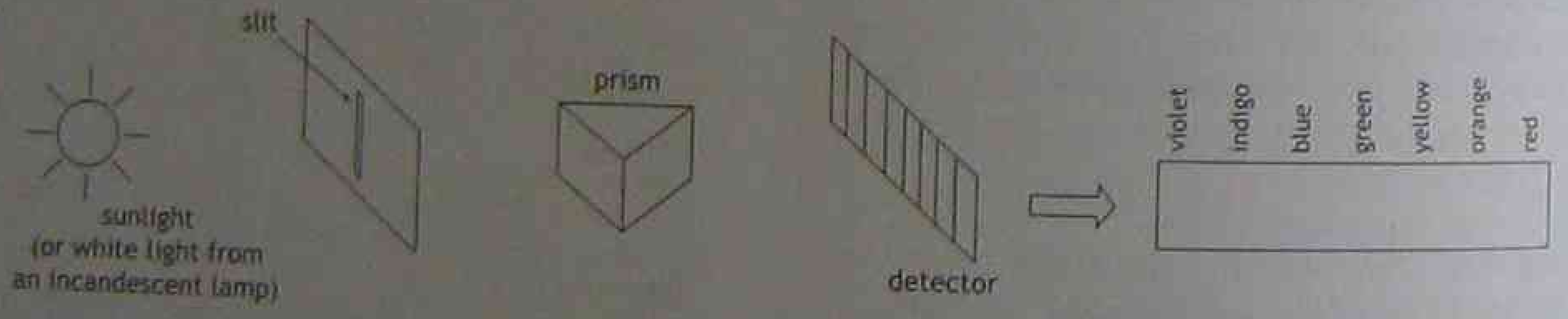


Figure 8.3 A continuous visible spectrum

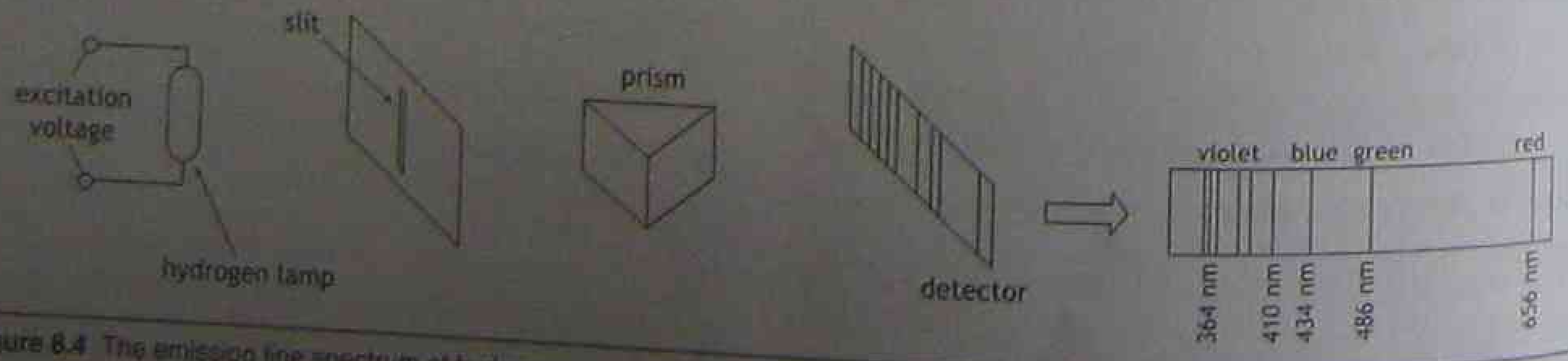


Figure 8.4 The emission line spectrum of hydrogen

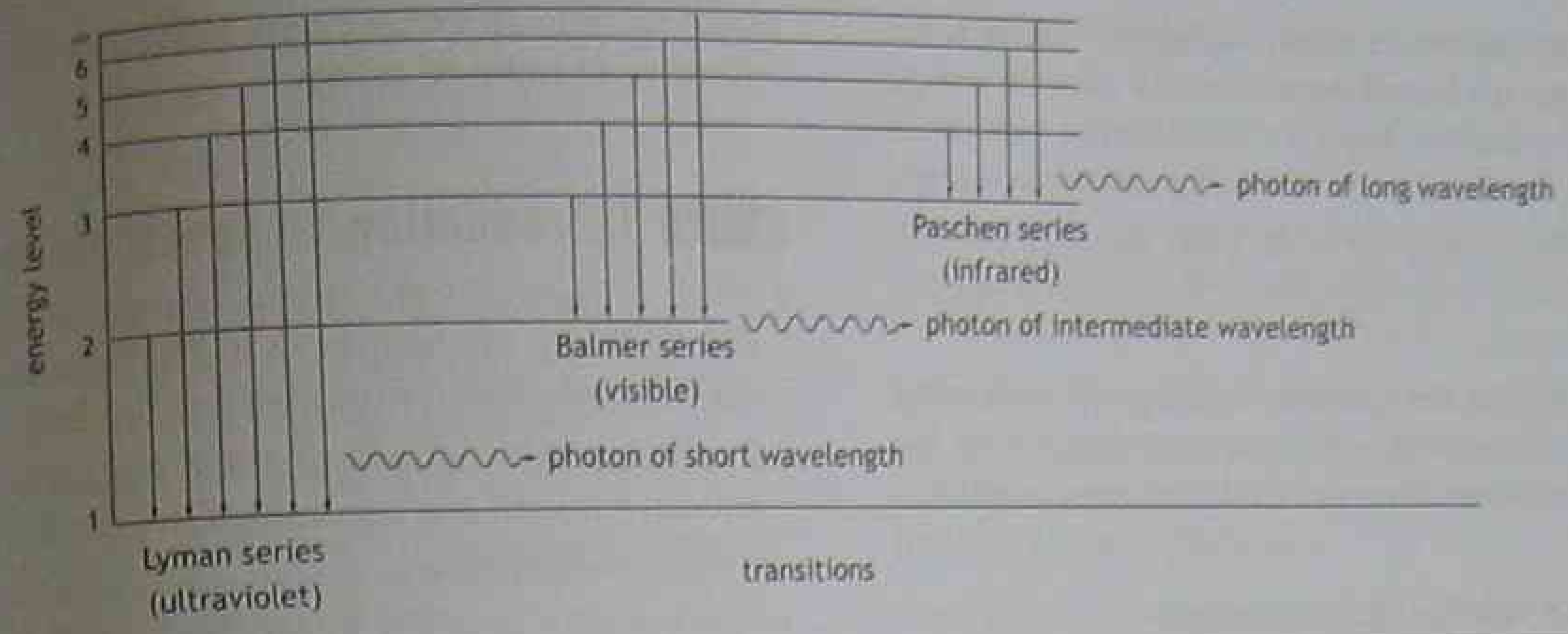


Figure 8.5 Energy level transitions for hydrogen

- The hydrogen spectrum has sets of lines in the infrared, visible and ultraviolet regions, which are usually detected by photography (see Figure 8.5).
- In a sample of hydrogen gas there are countless atoms.
- Individual atoms absorb and emit different amounts of energy.
- Atoms which drop from the fourth to the second energy level and emit energy by their transition contribute to the green line in the visible hydrogen spectrum.
- In other hydrogen atoms, an electron may drop from the third level to the second level. This transition represents a smaller energy gap, so the atoms emit radiation of a longer wavelength which is seen as a red line in the visible hydrogen spectrum.
- These visible lines make up the Balmer series. They are the lines produced when an electron jumps from the 3rd, 4th, 5th or 6th level to the 2nd energy level.
- The intensity of colour of a particular line depends on the number of electrons simultaneously making the transition represented by the line.

8.11 The Bohr theory of the hydrogen atom

In 1913, the Danish physicist Neils Bohr took up the challenge to construct a theory to explain the hydrogen spectrum. Max Planck had found, in 1900, that if an electron fell from a state of energy E_1 to E_2, then the energy of the photon emitted would be $E_1 - E_2 = h\upsilon$, where υ is the frequency and h is Planck's Constant.

Bohr's model took into account Ernest Rutherford's experiments which established the nuclear nature of the atom and Albert Einstein's work showing radiant energy to be discrete bundles of energy called photons. Bohr applied Planck's concept of the quantisation of energy to explain the hydrogen spectra.

Bohr's postulates are as follows:

(a) The electron of the hydrogen atom moves about the central proton in a circular orbit. For an electron in an atom, only orbits of certain energies and radii are allowed (this is an extension of Planck's concept of quantisation of energy).

(b) In the absence of radiant energy, an electron in an atom stays in one of the allowed *energy states*. If an atom absorbs radiant energy, the electron can change from one allowed energy state to another, thus $\Delta E = h\upsilon$.

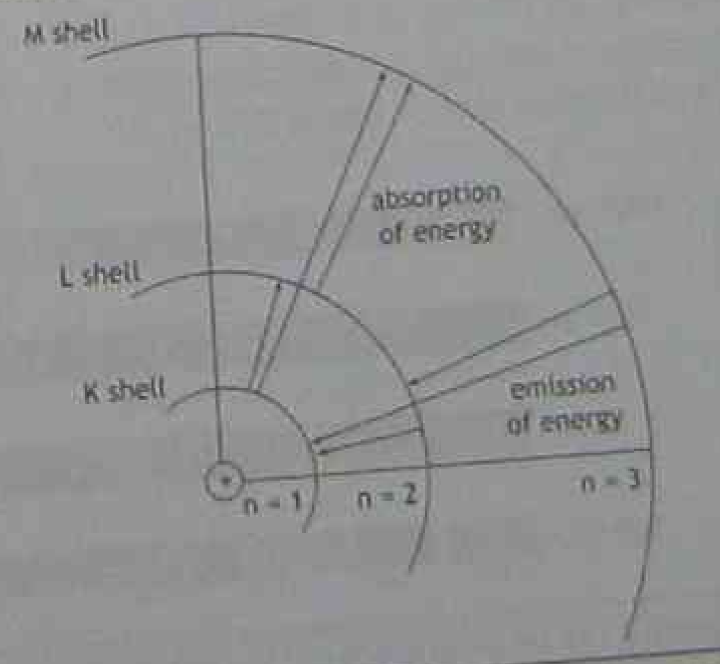


Figure 8.6 The three lowest energy orbits in the Bohr model of the hydrogen atom

Note 1: The arrows shown in Figure 8.6 refer to the transitions of an electron from one allowed energy state to another. Light is only absorbed or emitted when an electron moves between allowed orbits.

Note 2: The number of electrons that each electron shell can contain depends on the quantum number of the shell.

Note 3: The Bohr atomic model predicts that the chemical reactivity of an element depends on the number of electrons present in the outer or valence shell.

Table 8.6 Maximum number of electrons when $n = 1, 2$ or 3

Quantum number	Principal energy levels (shells)	Number of subshells	Electron capacity
1	K = 1	1	2
2	L = 2	2	8
3	M = 3	3	18

Bohr determined that the atomic radius for an atom is directly proportional to the square of the principal quantum number and inversely proportional to the atomic number.

He was able to calculate theoretically the wavelength of the known lines in the hydrogen spectra and also predicted the existence of undiscovered lines in the ultraviolet region of the hydrogen spectrum. The discovery of the Lyman series supported his theory. In his model, Bohr also showed that the absorptions or emissions in the line spectra corresponded to transitions of the electron from one orbit to another.

The Bohr model successfully explained the hydrogen spectrum but failed to account for the lines observed in the atomic spectra of atoms containing more than one electron. A new model of the atom, called the quantum mechanics or wave mechanics model, was developed. The concept of quantised energy levels introduced by Bohr was incorporated into the new theory.

Figure 8.7 The emission spectra of four chemical elements

Note: Emission spectra are the result of electrons returning from an excited state to the ground state following an input of energy.

8.12 Introduction to spectroscopy

- When a beam of light strikes a material object, several things can happen to it. The light may be emitted, reflected, transmitted or absorbed.
- By shining light on an object and measuring the amount reflected and transmitted, we can tell how much was absorbed.
- Spectroscopy uses the absorption, emission or scattering of electromagnetic radiation by atoms or molecules (or their ions) to study qualitatively or quantitatively the atoms or molecules or to study physical processes. It is used to study the way in which light is absorbed or emitted from the atoms or molecules of a substance.
- *Absorption* is a transition from a lower level to a higher level with transfer of energy from the radiation field to the atom or molecule.
- *Emission* involves the transition from a higher level to a lower level when energy is transferred to the radiation field.
- *Scattering* is the redirection of light as a result of its interaction with matter. The scattering is caused by random emissions of atoms when electrons go from higher to lower energy levels.

8.13 Absorption spectra

If a beam of white light is passed through a coloured substance, photons of certain wavelengths are absorbed but those of other wavelengths pass through. When the *transmittance* or *absorbency* of a sample is measured and plotted as a function of wavelength, an absorption spectrum is obtained.

In most quantitative analytical work, a calibration (standard) graph, usually linear, is prepared (Figure 8.8). The absorbency of the sample is read directly from the measuring circuit of the spectrophotometer. The absorption spectrum (Figure 8.9) shows that the sample transmits the least light at 410 nm and most around 700 nm.

Unit equivalents in spectroscopy

1 nanometre (nm) = 1 millimicron (mμ) = 10 Ångstroms (Å). Although each of these units is still in use, the SI preferred term for Australian usage is the nanometre.

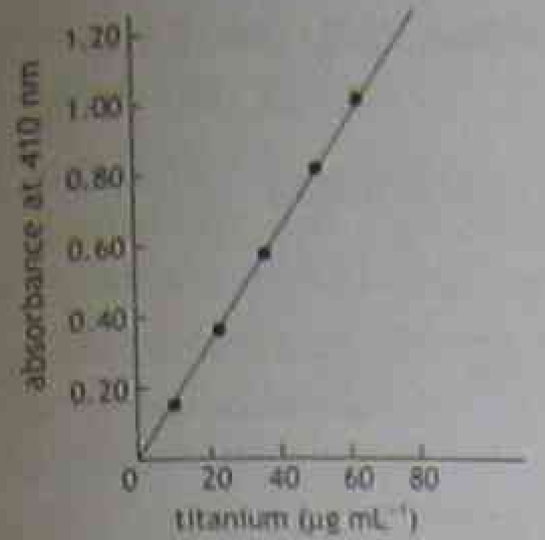


Figure 8.8 Calibration curve for determination of titanium by its colour formed with hydrogen peroxide

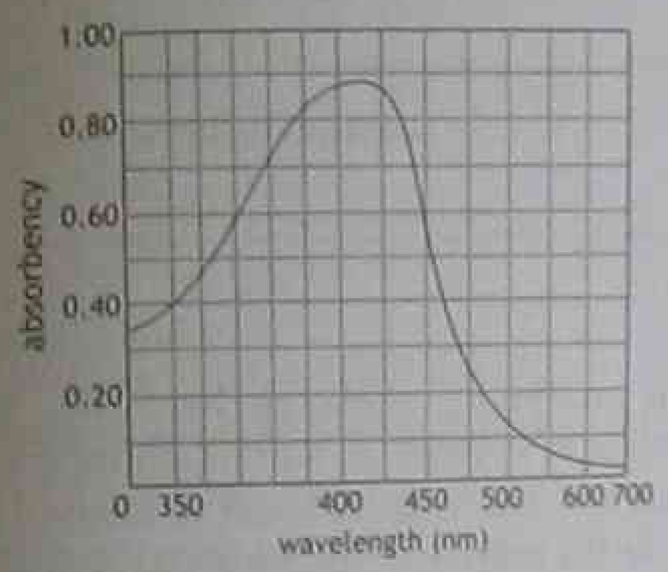


Figure 8.9 Absorption spectrum of the peroxytitanate complex in region 340–700 nm

Note 1: This is an example of visible light spectrophotometry.

Note 2: The ion absorbs light below 400 nm, that is blue, violet and green light, and transmits red and orange light.

Absorption spectra of some aqueous transition metal ions

When atoms or molecules absorb light, the incoming energy causes excitation to a higher energy level. The type of excitation depends on the wavelength of the light. Electrons are promoted to higher orbitals by ultraviolet or visible light. Vibrations are excited by infrared light.

An absorption spectrum is the absorption of light as a function of wavelength. The spectrum of an atom or molecule depends on its energy level structure. Absorption spectra therefore are useful in the identification of compounds (Figure 8.10).

8.14 Reflectance spectra

In opaque samples such as solids or highly absorbing solutions, the radiation reflected from the surface of the sample may be measured and compared with the radiation reflected from a non-absorbing or white sample. If the reflectance intensity is plotted as a function of wavelength, it gives a reflectance spectrum. Reflectance spectra are most often used in the paint industry for matching and identifying colours in pigments.

In *infrared reflectance spectroscopy*, the crystals used are ionic compounds such as sodium chloride or potassium bromide. Both materials are clear and transmit infrared (IR) light.

In *ultraviolet reflectance spectroscopy*, a material which does not absorb ultraviolet light (UV) such as quartz (crystalline SiO_2 often called silica) should be used.

It should be realised that materials that are useful for one type of spectroscopy are not necessarily useful for other types. Different materials are transparent to different wavelengths of the electromagnetic spectrum.

8.15 Infrared spectroscopy

Molecules undergo stretching or bending vibrations. These vibrations become excited by infrared radiation. Each group of atoms has its own characteristic set of vibrational frequencies. These can be measured by passing infrared light through them and recording at which wavelengths

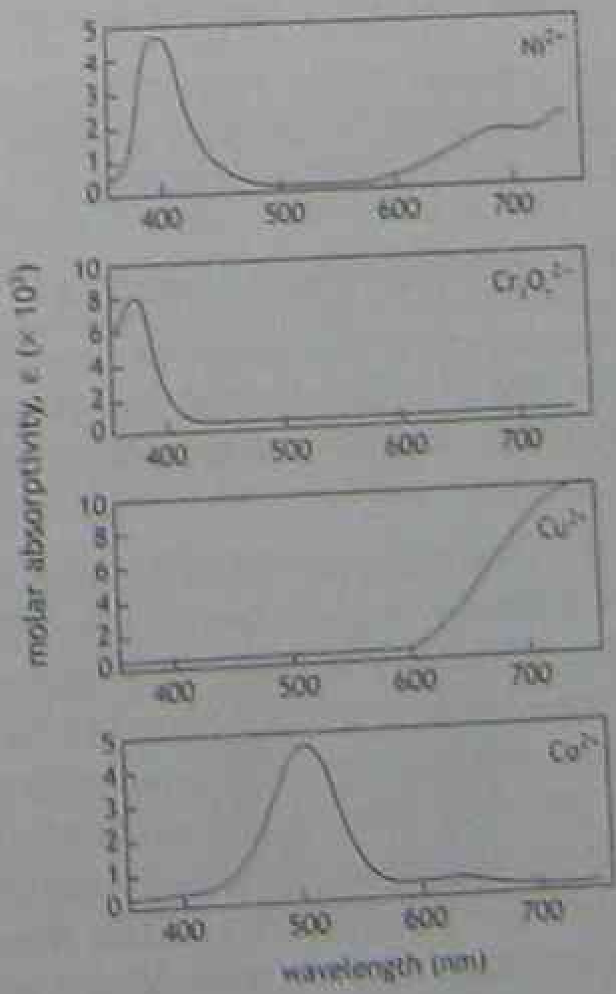


Figure 8.10 The absorption spectra of aqueous solutions of some transition metal ions

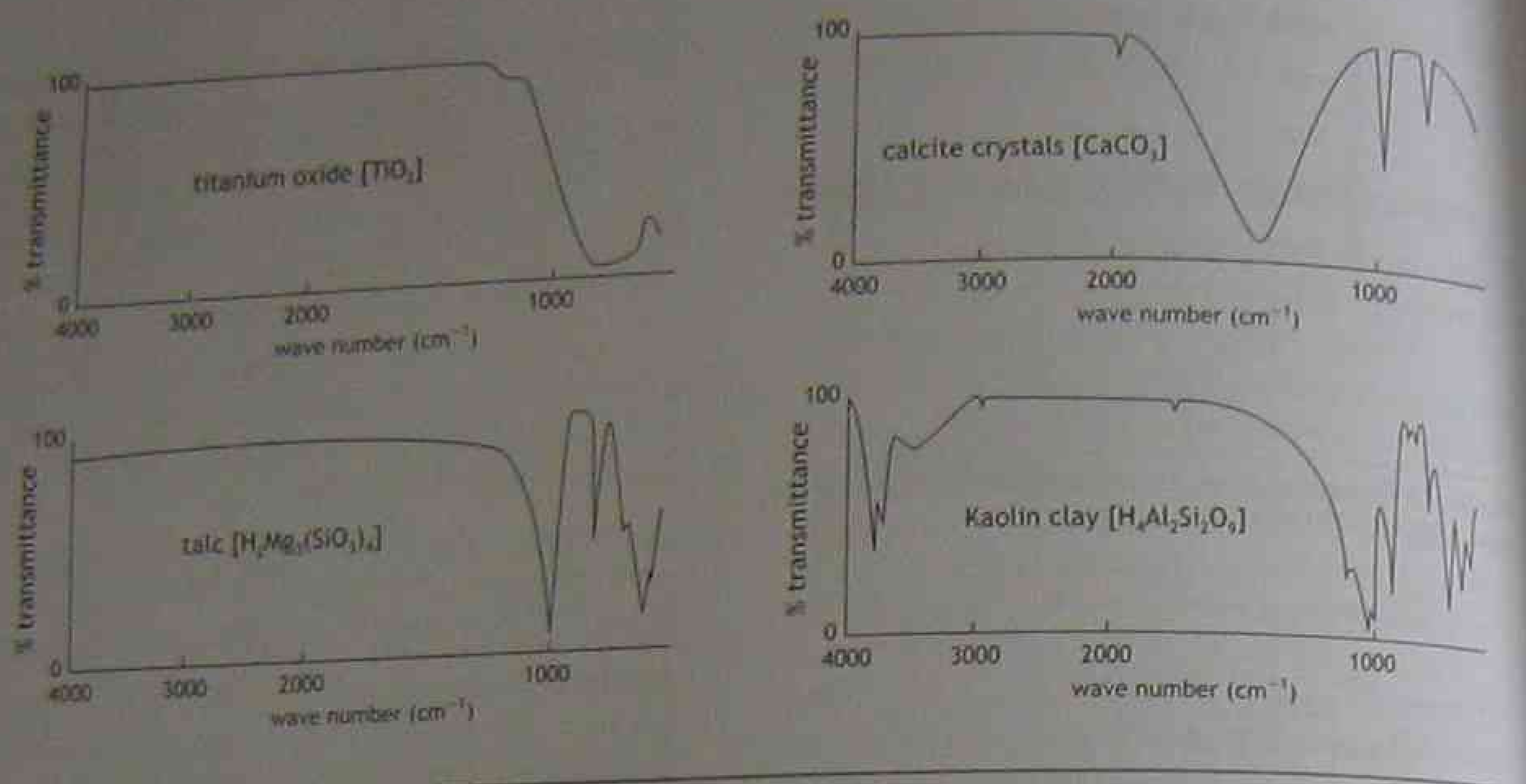


Figure 8.11 Printouts of some paint additives using IR analysis

absorptions occur. By comparing the IR spectrum produced by the sample with the results from a known compound, the identity of the unknown sample can be shown. Infrared spectroscopy can be used to analyse solids, liquids and powders in order to

(a) identify the contaminant in a sample; or

(b) detect the presence of a certain pigment, e.g. in a paint sample.

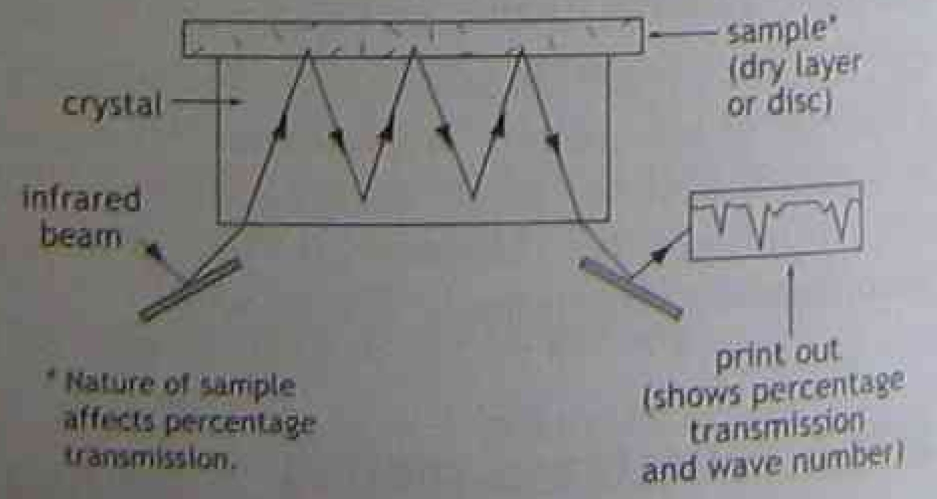
The white pigment TiO_2 is not affected by ultraviolet light, so IR spectroscopy is used for its analysis.

A database consists of the absorption spectra of known samples which is compiled (computerised) and used for matching unknown samples.

Infrared spectrophotometry analysis

- Solid samples for analysis can be prepared by pressing a disc of an intimate mixture of the solid with potassium bromide (KBr) which has few infrared bands.
- *Attenuated total reflectance* (ATR), also called *frustrated internal reflectance spectroscopy* (FIRS) is a useful technique. The sample to be analysed is put on a reflectance prism and placed in the light path of the infrared source. The beam of infrared energy is absorbed at the wavelengths where the sample normally absorbs. At other wavelengths the infrared energy is reflected. The resulting spectra is similar to that of a transmission spectra for the material. This technique is used extensively for analysing coatings, pastes and paints.
- When analysing surfaces by FIRS, a large rectangular crystal of KBr is clamped to the surface and the infrared beam is focused on one edge of the crystal, so that the beam is reflected internally within the crystal. As the beam reflects off the inner surface of the crystal, it penetrates the surface being examined by a few micrometres (μm).

The transmission of the infrared beam is affected since different compounds absorb different wavelengths within the infrared spectrum. When the infra-red beam emerges from the crystal, the results are displayed as a series of *peaks* and *troughs* on a graph. Each surface type produces a series of characteristic peaks which can then be matched against standard sample graphs for compound identification. This method allows the direct analysis of surfaces with no preparation. Computerised data can be used to compare reference spectra.



* Nature of sample affects percentage transmission.

Figure 8.12 FIRS analysis

8.16 The quantum-mechanical description of the atom

- There is a probability that an electron will be in a certain region of space at a given instant (this gives rise to electron density mapping).
- The term *orbital* denotes an allowed energy state for the electron. An orbital has characteristic energy and characteristic shape.
- Three quantum numbers, *n*, *l* and m_l are used to describe an orbital.
- The principal quantum number (*n*) can have integral numbers of 1, 2, 3, etc (as in the Bohr model). The quantum number relates to the average distance of the electron from the nucleus.
- The second quantum number (*l*) defines the shape of the orbital.

l	0	1	2	3
Orbital shape	s	p	d	f

- A collection of orbitals with the same value of *n* is called an *electron shell*.
- One or more orbitals with the same set of *n* and *l* values is called a *subshell*.
- The third quantum number (m_l) is called the *magnetic quantum number* and describes the orientation of the orbital in space.
- Electron spin adds a fourth quantum number. The presence of electron spin is important in determining the electronic structure of atoms.
- The four quantum numbers identify the energy level of the electron.
- The Pauli Exclusion Principle states that no two electrons in an atom can have the same set of four quantum numbers. This means that each orbital can hold a maximum of two electrons.
- Hund's Rule states that electrons must occupy degenerate orbitals (orbitals with the same energy) one at a time, until all orbitals have at least one electron before the pairing of electrons in the orbitals occurs.
- Electron configuration of an atom can be built up by adding electrons to orbitals of successively higher energy in accordance with the Pauli Exclusion Principle and Hund's Rule.

8.17 Organisation of the Periodic Table in terms of shells

The distribution of electrons within shells can be predicted from the Periodic Table.

Principal shells

Electrons are arranged into principal energy levels or shells around the nucleus as shown in Table 8.7. The maximum number of electrons in each energy level is $2n^2$ where *n* is the number of the level.

Quantum mechanics theory shows that each energy level consists of one or more sublevels or subshells. The number of subshells into which each energy level is divided corresponds to the number of the energy level.

Table 8.7 Electron arrangement in atoms

Principal energy levels (shells)	Number of subshells	Name of subshells	Max. no. of electrons in subshells	
K = 1	1	s	2	= 2
L = 2	2	s p	2 6	= 8
M = 3	3	s p d	2 6 10	= 18
N = 4	4	s p d f	2 6 10 14	= 32

Hence electron configuration may be shown as electrons (a) in shells, or (b) in subshells.

Example

Sulfur (a) S — 2, 8, 6

(b) S — $1s^2 2s^2 2p^6 3s^2 3p^4$

Energy subshells are further divided into orbitals. Quantum mechanics shows that each orbital represents a region in space where a pair of electrons is most likely to be found. Orbitals that make up a particular subshell are all of equal energy.

The s subshell consists of only one spherically shaped orbital. The axes *x*, *y* and *z* are used to show the orientation of the orbital in space.

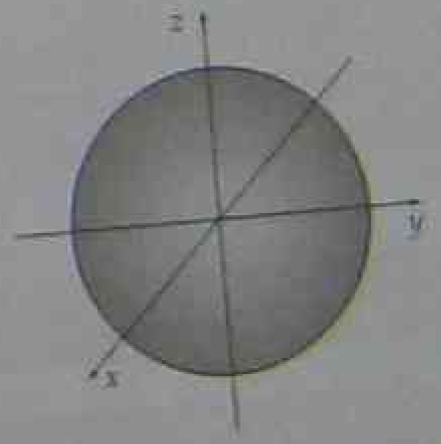


Figure 8.13 The s subshell

The p subshell has three dumbbell shaped orbitals. Each orbital is of equal energy. Each orbital does not have a definite boundary. The electron density probability decreases outside the area indicated by the dumbbell shaped illustration.

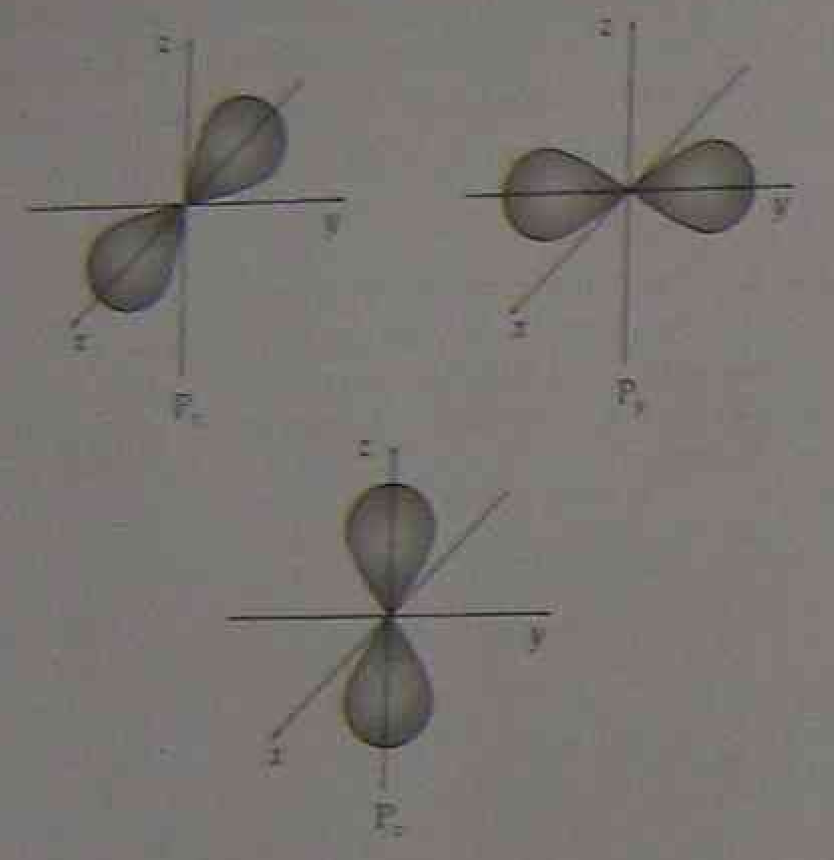


Figure 8.14 The three orbitals of the p subshell

Practical work

Sausage-shaped balloons can be used to illustrate the three-dimensional effect.

8.18 Electron spin

The Pauli Exclusion Principle states that there can be no more than two electrons in any given orbital and that these must have opposing spins. This sets the maximum number of electrons in subshells (see Table 8.8).

In filling a particular subshell, electrons occupy orbitals of equal energy one at a time before there is any pairing (Hund's rule).

Electron spin can be represented by using a square to indicate an orbital and an arrow to indicate an electron. The direction of the arrow indicates the spin direction.

Example

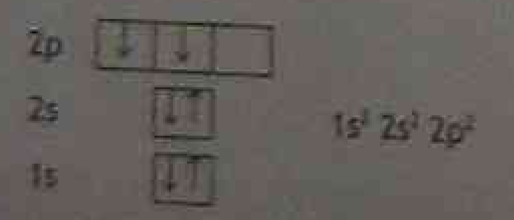


Figure 8.15 Carbon atom showing electron spin

Table 8.8 To show the electron spin orbital diagrams for the first ten elements

Atom	Electron spin orbital diagram			Electron configuration
$_1H$	↓			$1s^1$
$_2He$	↓↑			$1s^2$
$_3Li$	↓↑	↓		$1s^2\ 2s^1$
$_4Be$	↓↑	↓↑		$1s^2\ 2s^2$
$_5B$	↓↑	↓↑	↓ | |	$1s^2\ 2s^2\ 2p^1$
$_6C$	↓↑	↓↑	↓ | ↓ |	$1s^2\ 2s^2\ 2p^2$
$_7N$	↓↑	↓↑	↓ | ↓ | ↓	$1s^2\ 2s^2\ 2p^3$
$_8O$	↓↑	↓↑	↓↑ | ↓ | ↓	$1s^2\ 2s^2\ 2p^4$
$_9F$	↓↑	↓↑	↓↑ | ↓↑ | ↓	$1s^2\ 2s^2\ 2p^5$
$_{10}Ne$	↓↑	↓↑	↓↑ | ↓↑ | ↓↑	$1s^2\ 2s^2\ 2p^6$
	1s	2s	2p	

Elements with higher energy are said to be in their excited state.

Variations in the filling order of electronic configurations in the Periodic Table

(a) *d-orbitals*. In the first transition series, examples where the electron configuration ends in $4s^1$ rather than $4s^2$ are

Element 24: chromium (Cr)
$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

Element 29: copper (Cu)
$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^1$

In the case of copper, greater stability results from the complete filling of the 3d orbitals.

(b) *f-orbitals*. There are marked variations in the series in which the f-orbitals are filling since the sublevels are very close together.

Examples are

Element 64: gadolinium (Gd)
$4s^2\ 4p^6\ 4d^{10}\ 4f^7\ 5s^2\ 5p^6\ 5d^1\ 6s^2$

Element 65: terbium (Tb)
$4s^2\ 4p^6\ 4d^{10}\ 4f^9\ 5s^2\ 5p^6\ 5d^0\ 6s^2$

In Figure 8.16, it is seen that since electrons will occupy the lowest available energy level, the 4s subshell is filled before the 3d subshell.

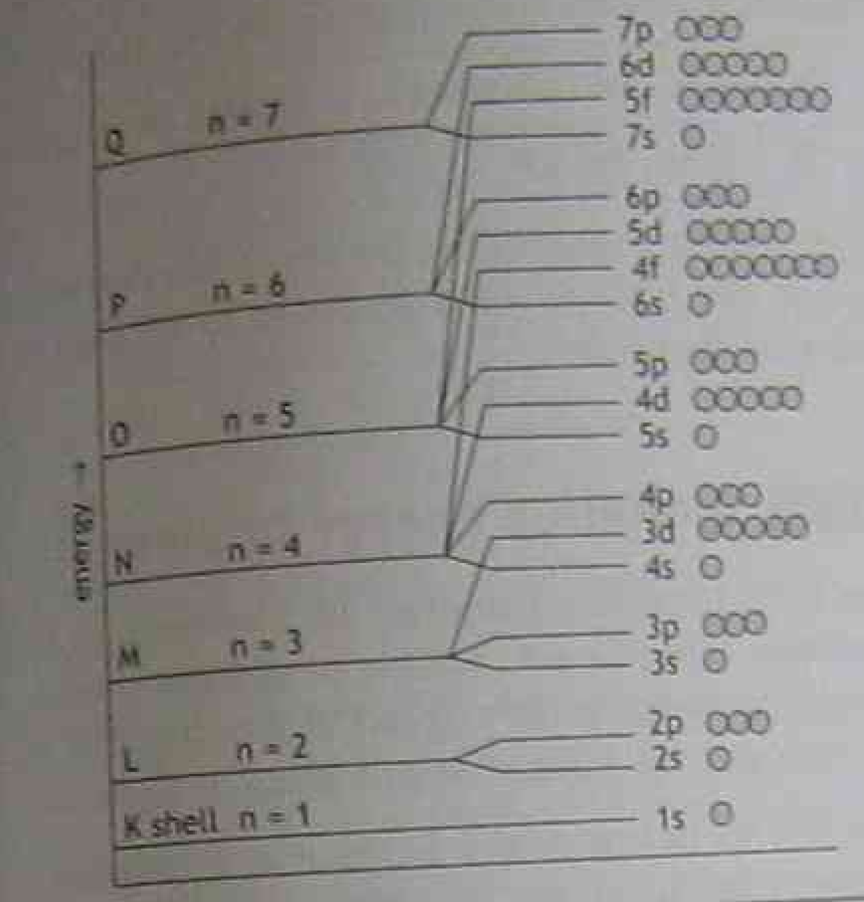


Figure 8.16 Energy level diagram showing shells, subshells and orbitals

Electronic energy levels in atoms

Orbitals are filled in order of increasing energy. This can be shown in different ways. In Figure 8.17, the *aufbau* (building up) order for the occupancy of subshells is shown (from head to tail).

Use of the *aufbau* order gives the electron arrangement of electrons in atoms in their ground state (lowest energy). See the filling of subshells for the first 20 elements in Table 8.11 and s, p, d and f block elements in Table 8.9.

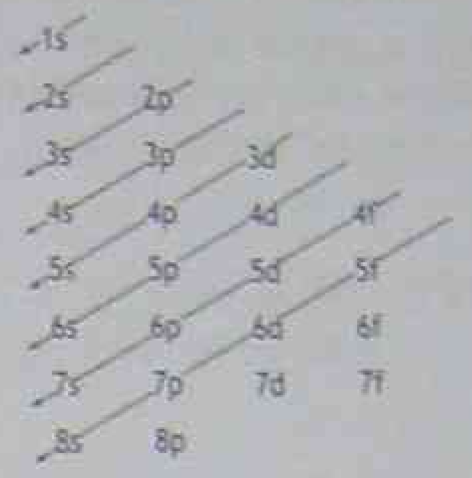


Figure 8.17 Aufbau order

The ten elements following calcium make up the first transition series. The inner d-orbitals are occupied only after the s-orbitals in the next higher energy level is filled.

Example

The transition series (Sc → Zn) fills the 4s and then the inner 3d subshell. As a result of their electron configuration

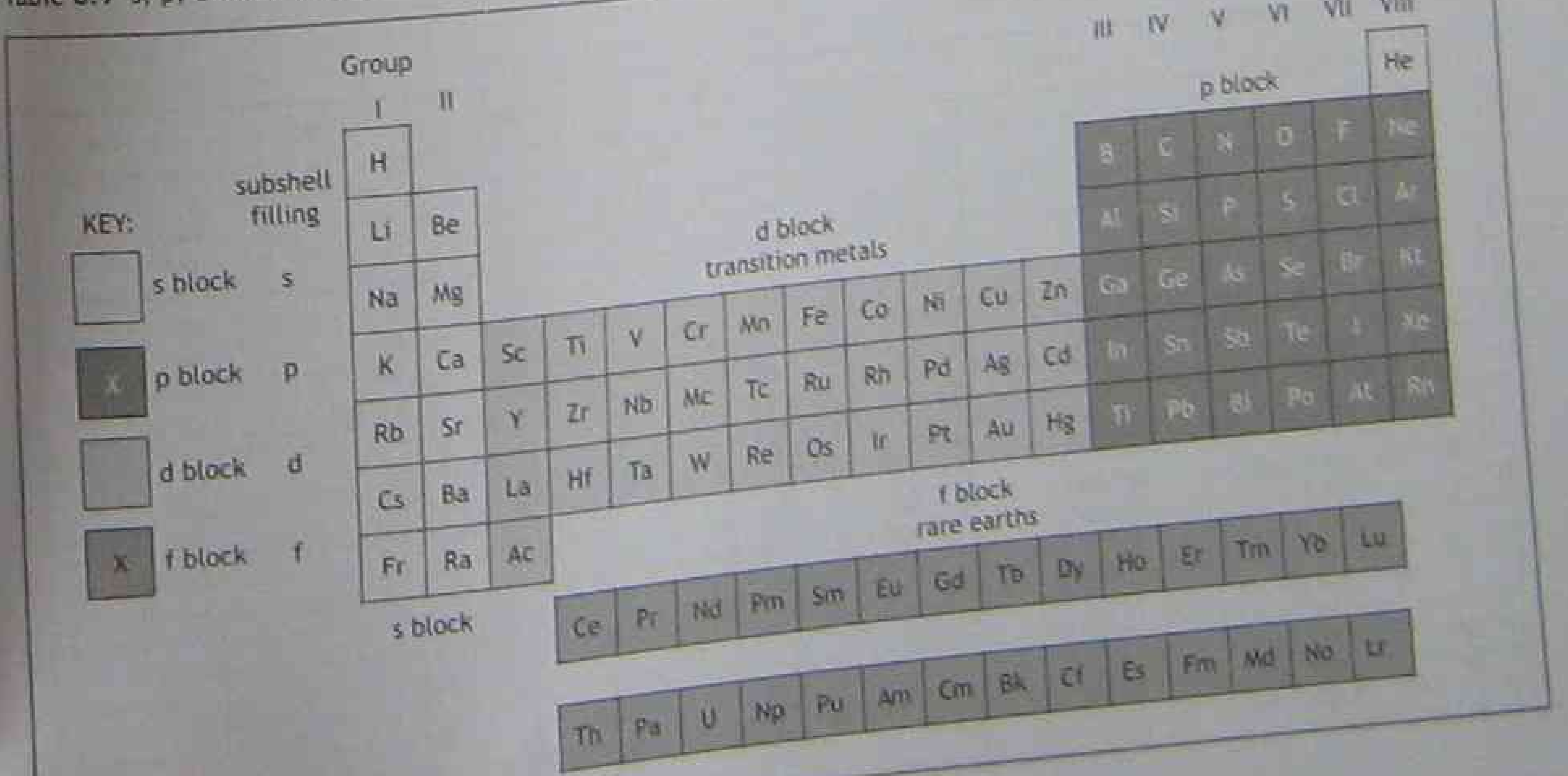
(a) transition metals have similar atomic radii (s level in outer shell is always filled); and
(b) transition metals can form ions by losing electrons from both the 3d and 4s subshells.

Example

Fe — $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$

Fe^{2+} ion is formed by the loss of two 4s electrons.
Fe^{3+} is formed by the loss of two 4s electrons and one 3d electron.

Table 8.9 s, p, d and f block elements



KEY: subshell filling
☐ s block s
▨ p block p
☐ d block d
▨ f block f

Group

I	II											III	IV	V	VI	VII	VIII
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

s block

d block
transition metals

p block

f block
rare earths

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

The fifth period also contains 10 transition metals. The sixth period consists of 32 elements. In addition to 10 transition elements there are 14 rare earth elements forming the lanthanide series.

Example

Cerium Ce (58) — $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$
$4s^2\ 4p^6\ 4d^{10}\ 4f^2\ 5s^2\ 5p^6\ 6s^2$

8.19 Organisation of the Periodic Table in terms of s, p, d and f blocks

In the Periodic Table, elements are arranged in order of atomic number. This corresponds to the number of electrons in the atoms so that structures of the elements in each block are related to the order of filling the energy sublevel.

Table 8.10 Filling of sublevels

Period	Sublevels being filled
1	1s
2	2s 2p
3	3s 3p
4	4s 3d 4p
5	5s 4d 5p
6	6s 4f 5d 6p
7	7s 5f 6d 7p

Methods of writing electron configurations

An abbreviated form, using the appropriate noble gas configuration, is often used.

Example

1. Na $1s^2\ 2s^2\ 2p^6\ 3s^1$ can be written as $[Ne]3s^1$
2. Ti $[Ar]\ 4s^2\ 3d^2$

After calcium (element 20), the set of 3d orbitals fills and so the table is split in order to fit these 10 elements (Sc to Zn).

8.20 Ionisation energy of elements

The first ionisation energy of elements in the Periodic Table is a function of atomic number. Ionisation energy is the product of the charge on the electron and the ionisation potential.

The *first ionisation energy* is the energy needed to remove completely the first electron from an atom in the gaseous state.

Example

$$M(g) + \text{energy} \rightarrow M^+(g) + e^-$$

Bohr's atomic model explained the trends in ionisation energy for the Periodic Table elements.

The electrostatic force of attraction between the valence electron and the nucleus is reduced by any electrons in the inner closed shells.

(a) Comparison between the ionisation energies of hydrogen, lithium and sodium shows that the ionisation energy of hydrogen is the highest since it is more difficult to remove an electron from the first shell closest to the nucleus. The

Table 8.11 Periodic Table for the first 20 elements

I	II	III	IV	V	VI	VII	VIII
1 H $1s^1$							2 He $1s^2$
3 Li $1s^2$ $2s^1$	4 Be $1s^2$ $2s^2$	5 B $1s^2$ $2s^2\,2p^1$	6 C $1s^2$ $2s^2\,2p^2$	7 N $1s^2$ $2s^2\,2p^3$	8 O $1s^2$ $2s^2\,2p^4$	9 F $1s^2$ $2s^2\,2p^5$	10 Ne $1s^2$ $2s^2\,2p^6$
11 Na $1s^2$ $2s^2\ 2p^6$ $3s^1$	12 Mg $1s^2$ $2s^2\ 2p^6$ $3s^2$	13 Al $1s^2$ $2s^2\ 2p^6$ $3s^2\ 3p^1$	14 Si $1s^2$ $2s^2\ 2p^6$ $3s^2\ 3p^2$	15 P $1s^2$ $2s^2\ 2p^6$ $3s^2\ 3p^3$	16 S $1s^2$ $2s^2\ 2p^6$ $3s^2\ 3p^4$	17 Cl $1s^2$ $2s^2\ 2p^6$ $3s^2\ 3p^5$	18 Ar $1s^2$ $2s^2\ 2p^6$ $3s^2\ 3p^6$
19 K $1s^2$ $2s^2\ 2p^6$ $3s^2\ 3p^6$ $4s^1$	20 Ca $1s^2$ $2s^2\ 2p^6$ $3s^2\ 3p^6$ $4s^2$						

Table 8.12 Electron configurations of elements in the first four periods of the periodic table

Element	Atomic No.	K shell	L shell	M shell	N shell	Electronic structure
Hydrogen	1	1				$1s^1$
Helium	2	2				$1s^2$
Lithium	3	2	1			$1s^2\ 2s^1$
Beryllium	4	2	2			$1s^2\ 2s^2$
Boron	5	2	3			$1s^2\ 2s^2\ 2p^1$
Carbon	6	2	4			$1s^2\ 2s^2\ 2p^2$
Nitrogen	7	2	5			$1s^2\ 2s^2\ 2p^3$
Oxygen	8	2	6			$1s^2\ 2s^2\ 2p^4$
Fluorine	9	2	7			$1s^2\ 2s^2\ 2p^5$
Neon	10	2	8			$1s^2\ 2s^2\ 2p^6$
Sodium	11	2	8	1		$[Ne]\ 3s^1$
Magnesium	12	2	8	2		$[Ne]\ 3s^2$
Aluminium	13	2	8	3		$[Ne]\ 3s^2\ 3p^1$
Silicon	14	2	8	4		$[Ne]\ 3s^2\ 3p^2$
Phosphorus	15	2	8	5		$[Ne]\ 3s^2\ 3p^3$
Sulfur	16	2	8	6		$[Ne]\ 3s^2\ 3p^4$
Chlorine	17	2	8	7		$[Ne]\ 3s^2\ 3p^5$
Argon	18	2	8	8		$[Ne]\ 3s^2\ 3p^6$
Potassium	19	2	8	8	1	$[Ar]\ 4s^1$
Calcium	20	2	8	8	2	$[Ar]\ 4s^2$
Scandium	21	2	8	9	2	$[Ar]\ 3d^1\ 4s^2$
Titanium	22	2	8	10	2	$[Ar]\ 3d^2\ 4s^2$
Vanadium	23	2	8	11	2	$[Ar]\ 3d^3\ 4s^2$
Chromium	24	2	8	13	1	$[Ar]\ 3d^5\ 4s^1$
Manganese	25	2	8	13	2	$[Ar]\ 3d^5\ 4s^2$
Iron	26	2	8	14	2	$[Ar]\ 3d^6\ 4s^2$
Cobalt	27	2	8	15	2	$[Ar]\ 3d^7\ 4s^2$
Nickel	28	2	8	16	2	$[Ar]\ 3d^8\ 4s^2$
Copper	29	2	8	18	1	$[Ar]\ 3d^{10}\ 4s^1$
Zinc	30	2	8	18	2	$[Ar]\ 3d^{10}\ 4s^2$
Gallium	31	2	8	18	3	$[Ar]\ 3d^{10}\ 4s^2\ 4p^1$
Germanium	32	2	8	18	4	$[Ar]\ 3d^{10}\ 4s^2\ 4p^2$
Arsenic	33	2	8	18	5	$[Ar]\ 3d^{10}\ 4s^2\ 4p^3$
Selenium	34	2	8	18	6	$[Ar]\ 3d^{10}\ 4s^2\ 4p^4$
Bromine	35	2	8	18	7	$[Ar]\ 3d^{10}\ 4s^2\ 4p^5$
Krypton	36	2	8	18	8	$[Ar]\ 3d^{10}\ 4s^2\ 4p^6$

ionisation energy of sodium would be the lowest since the valence electron is removed from the third shell which is the furthest shell from the nucleus.

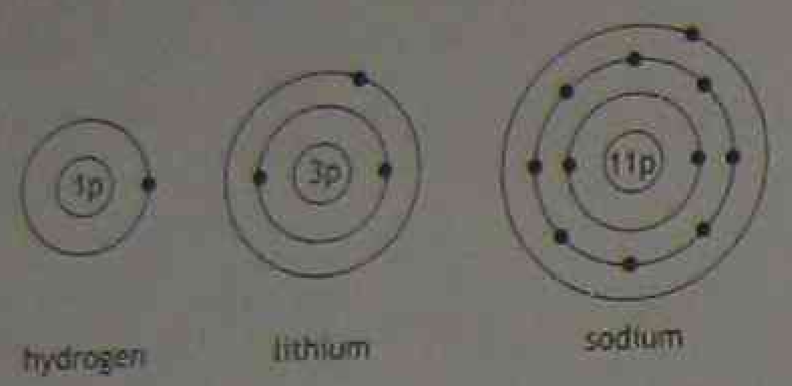


Figure 8.18 Shell diagrams of hydrogen, lithium and sodium

(b) Comparison between hydrogen and helium shows that helium has twice the effective charge and almost twice the ionisation of hydrogen.

Figure 8.19 Shell diagrams of hydrogen and helium

Note 1: The *first ionisation energy* (IE) *decreases down the groups* of the Period Table owing to the increasing atomic size as the valence electron moves further from the nucleus.

Note 2: The *first ionisation energy generally increases across the periods* of the Periodic Table owing to the increase in effective nuclear charge across the period.

Note 3: The *second ionisation energy* is always greater than the first since the electron is now being removed from a positive ion.

Example 1

$$M^{+}(g) + \text{energy} \rightarrow M^{2+}(g) + e^{-}$$

Table 8.13 Comparison of the ionisation energies of the first 20 elements

Group	Examples	No. of valence electrons	Ionisation energy
I (alkali metals)	Li, Na, K	1	lowest
VII (halogens)	F, Cl	7	high
VIII (noble gases)	He, Ne, Ar	8	highest

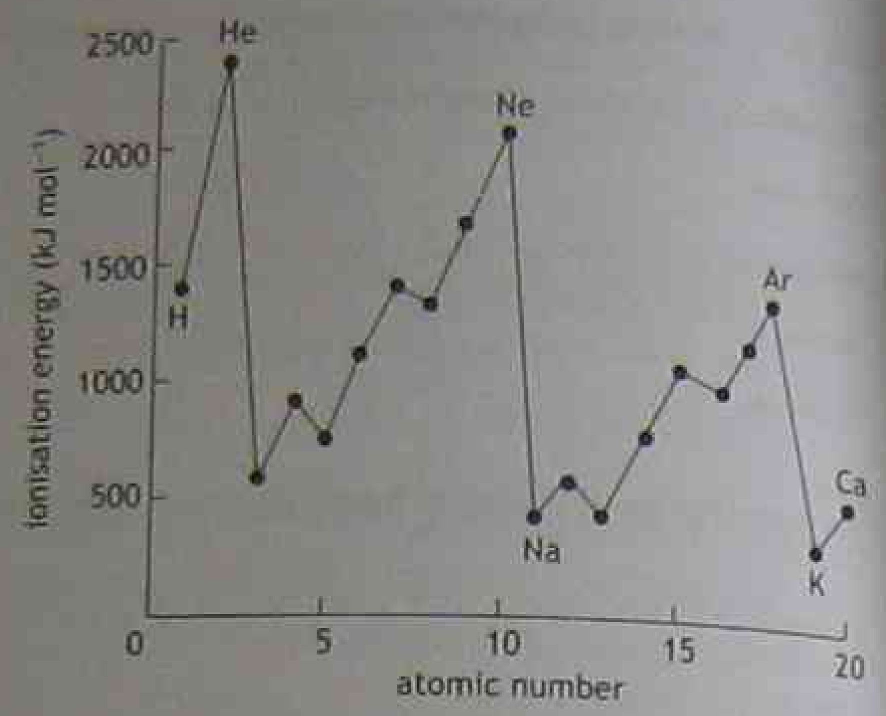


Figure 8.20 First ionisation energy for the first 20 elements

Example 2

For sodium: 1st IE 2nd IE

500 kJ mol^{-1} 4570 kJ mol^{-1}

Ionisation energy trends provide evidence that chemical bonding attempts to reach noble gas configuration.

8.21 Electronegativity of elements

Electronegativity is the ability of an atom in a covalent bond to attract the electron in the bond towards itself. The attraction between the electron (outside the bond) and the atomic nucleus is dependant on the effective nuclear charge between the external electron and the atomic nucleus. The effective nuclear charge and the electronegativity increase across the Periodic Table to a maximum at Group VIII. The greater the difference in electronegativity values, the greater is the ionic nature of the bond.

Table 8.14 Electronegativity values of the first 20 elements and some transition metals

Metals		Non-metals						Transition metals
Li 1.0	Be 1.5	H 2.1	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Fe, Co, Ni 1.8 Cu 1.9
Na 0.9	Mg 1.2		Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Zn 1.6

The *electron affinity* E_a of an element is the energy released in the gaseous state when an atom forms an ion by combining with an electron. Electron affinities (kJ mol^{-1}) would, as expected, be highest in the halogens (Group VII) and lowest in the noble gases (Group VIII).

Trend for the first 20 elements:

Group I → Group VII
low high

Exercise 8.1

1. Complete the table at the bottom of the page.
2. Use the table below in answering this question.

Species	Electron configuration
A	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$
B^{3-}	$1s^2\ 2s^2\ 2p^6$
C^{2+}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^2$
D	$1s^2\ 2s^2\ 2p^6$

(a) Name the transition element present as its ion.

(b) Name the two species that are isoelectronic.

(c) How many protons are there in the nucleus of element B?

(d) Name the most electronegative element.

3. The list below contains the electron configurations of atoms of 12 different elements. The elements are represented by the letters of the alphabet

A	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$
D	$1s^2\ 2s^2\ 2p^6\ 3s^2$
E	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$
G	$1s^2\ 2s^2\ 2p^2$
J	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$
L	$1s^2\ 2s^2\ 2p^3$
M	$1s^2$
Q	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$
R	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$
T	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$
X	$1s^2\ 2s^2\ 2p^5$
Z	$1s^2\ 2s^2\ 3s^1$

Use one of the letters above to identify

(a) the element which has 14 neutrons and 13 protons in each of its nuclei;

(b) the element which has the highest electronegativity among the 12 elements;

(c) the element which is classed as a transition metal;

(d) the element which forms a stable ion with 2^{+} charge;

(e) the element which can have multiple valencies;

(f) the element which is classed as a noble gas;

(g) the element which belongs to the same group as calcium; and

(h) the only element among the 12 having an atom which is in an excited state.

8.22 Colour in transition metals

When white light, consisting of all the wavelengths in the visible region of the electromagnetic spectrum, falls on an array of atoms (or molecules), energy is transferred to the atom only if the energy associated with a wavelength in the light corresponds exactly to the energy required to raise an electron to a higher energy level. The atom then absorbs the energy and raises the electron to a higher level. The corresponding wavelength is removed from the light leaving a coloured substance.

The energy required to raise d-electrons, especially unpaired d-electrons to higher energy levels is similar to the energy associated with wavelengths in the visible region. Compounds of transition metals (except Scandium (Sc) with one 3d electron and zinc (Zn) with no unpaired electrons in its full 3d shell) are usually coloured.

Table for Question 1

Element or ion	Atomic No.	Electron configuration	Period	Group
Ca				
Cu				
	26	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$		transition metal
	9	$1s^2\ 2s^2\ 2p^5$		
	16			
V	23			

Example 1

In many cobalt compounds, e.g. $[Co(NH_3)_4Cl_2]^+$ the energy required to raise the 3d electrons to higher levels is the same as that for red light. When light of this wavelength and energy is removed from the white light and the emitted light, colour of the compound is cyan (i.e. white – red = cyan).

The energy of the wavelength in the visible region is insufficient to excite s- or p-electrons, so light in the visible region is not absorbed by such compounds and they appear colourless (e.g. zinc compounds such as $ZnCl_2$).

Example 2

It is assumed that electrons in the lower d-levels may absorb photons and move to higher levels. The colour of the $Ti(H_2O)_6^{3+}$ ion is a result of the single d-electron which absorbs a photon of wavelength 500 nm and moves to one of the higher d-levels. The light transmitted by the solution will be white minus the green and yellow photons at wavelengths 490–590 nm. Such light is magenta to the eye (i.e. white – green = magenta).

8.23 Variable oxidation states

The maximum number of oxidation states occurs at manganese (7) and decreases on either side (see Table 8.16). The variety in the valency states is due to the small difference in energy between the 4s, 3d and 4p subshells. The electrons in these subshells are very versatile in forming chemical bonds. The unoccupied subshells of similar energy result in the atoms having good acceptor properties in the formation of coordination compounds. Except for scandium (which forms only Sc^{3+} ions) all the rest (Ti → Zn) have a stable +2 state as a result of losing the two 4s electrons. Other states result from the loss of some or all of the 3d electrons.

Example 1

To form the +7 compounds of manganese, e.g. the MnO_4^- ion, manganese uses two 4s electrons and five 3d electrons in forming the four bonds with oxygen to give a tetrahedral ion. The eighth electron comes from the negative charge, e.g. $KMnO_4$, potassium permanganate.

For a given element in the higher oxidation states, the oxides are acidic and the compounds are more covalent, often easily hydrolysed and readily reduced (electrons easily gained), so they are good oxidising agents.

The reverse is true for the lower oxidation states where the oxides are basic and ionic, and the compounds are often reducing agents.

Example 2

For chromium, the +6 state is acidic, e.g. complex anions are chromates and dichromates which are strong oxidising agents. The +6 state is reduced to the +3 state.

$$\underset{\text{(orange soln.)}}{Cr_2O_7^{2-}} \rightarrow \underset{\text{(green soln.)}}{2Cr^{3+}}$$

The chromous ion Cr^{2+} is spontaneously oxidised by air to Cr^{3+}, is basic and is a strong reducing agent. $Cr(OH)_3$ is amphoteric, producing chromic salts with acids and chromites with alkalis:

Alkaline reaction:

$$\underset{\text{chromium hydroxide}}{Cr(OH)_3(s)} + OH^-(aq) \rightarrow \underset{\text{chromite ions}}{Cr(OH)_4^-(aq)}$$

Acid reaction:

$$Cr(OH)_3(s) + 3HCl(aq) \rightarrow CrCl_3(aq) + 3H_2O(l)$$

The formation of complex ions by transition metal ions increases the variety of coloured compounds that can be produced, owing to d-orbital splitting.

Oxidation states of transition metals

In forming ions, the transition metals lose the valence shell s-electrons first and then as many d-electrons as are required to form an ion of particular charge (see Table 8.17).

Table 8.15 Colours of aquo or oxo ions of the first transition series

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Sc^{3+} colourless	Ti^{2+} violet Ti^{3+} violet	V^{2+} violet V^{3+} green	Cr^{2+} blue Cr^{3+} green CrO_4^{2-} yellow	Mn^{2+} pink Mn^{3+} brown MnO_4^- purple	Fe^{2+} green Fe^{3+} orange	Co^{2+} pink Co^{3+} blue	Ni^{2+} green	Cu^+ colourless Cu^{2+} blue

Property	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	*Zn
First ionisation energy (kJ mol⁻¹)	637	664	656	659	724	766	764	743	752	913
Electron structure of atom	[Ar] $3d^1 4s^2$	[Ar] $3d^2 4s^2$	[Ar] $3d^3 4s^2$	[Ar] $3d^5 4s^1$	[Ar] $3d^5 4s^2$	[Ar] $3d^6 4s^2$	[Ar] $3d^7 4s^2$	[Ar] $3d^8 4s^2$	[Ar] $3d^{10} 4s^1$	[Ar] $3d^{10} 4s^2$
Total number of 3d and 4s electrons	3	4	5	6	7	8	9	10	11	12
Stable oxides (showing colour)	Sc_2O_3 (w)	Ti_2O_3 (bk) TiO_2 (w)	V_2O_3 (bl) V_2O_5 (o)	Cr_2O_3 (g) CrO_3 (o)	MnO_2 (gy) MnO_2 (bk) Mn_2O_7 (r)	FeO (bk) Fe_2O_3 (r)	CoO (g) Co_2O_3 (gy)	NiO (gy)	Cu_2O (r) CuO (bl)	ZnO (w)
Stable chlorides (showing colour)	$ScCl_3$ (w)	$TiCl_3$ (v)	VCl_3 (v)	$CrCl_2$ (w) $CrCl_3$ (r)	$MnCl_2$ (p) $MnCl_3$ (b)	$FeCl_2$ (y) $FeCl_3$ (bn)	$CoCl_2$ (b)	$NiCl_2$ (y)	CuCl (w) $CuCl_2$ (y)	$ZnCl_2$ (w)
Oxidation states in compounds (main valences in bold type)	+3	+4 +3 +2 +1	+5 +4 +3 +2 +1	+6 +5 +4 +3 +2 +1	+7 +6 +5 +4 +3 +2 +1	+6 +5 +4 +3 +2 +1	+5 +4 +3 +2 +1	+3 +2 +1	+3 +2 +1	+2

* Note that zinc is a transition metal where the d-shell is full

Colour code: (b) blue (bk) black (bn) brown (g) green (gy) grey (o) orange (p) pink (r) red (v) violet (w) white or colourless (y) yellow

Example

Vanadium [Ar] $3d^34s^2$ shows oxidation states of V, IV, III and II using the 4s-electrons plus 3, 2, 1 or 0 d-electrons respectively. For Sc-Mn, the highest oxidation state is the sum of electrons in the 4s and 3d orbitals. Beyond Mn, the d-electrons become more tightly bound.

Reactions where metal atoms show different oxidation states (e.g. transition metals)

Oxidation number is very useful in dealing with elements with compounds that show a variety of oxidation states.

The oxidation number is the *formal charge* that an atom would have if it existed as an ion in a compound.

Iron is a typical transition metal showing more than one oxidation state. Another example is titanium which has oxidation of +2, +3 and +4.

Other metals which are not transition metals may exist in more than one oxidation state, for example, tin (+2 and +4).

Rules for assigning oxidation numbers (O.N.)

1. In uncombined elements, each atom has an oxidation number of zero, for example, Na, Cl_2 have an oxidation number of 0.
2. The oxidation number of a monatomic ion is equal to the charge on that ion, for example, Na^+ (O.N. = +1), Fe^{3+} (O.N. = +3), S^{2-} (O.N. = −2).
3. Oxygen has an oxidation number of −2 in compounds. [Peroxides and superoxides are the exceptions, for example, H_2O_2 (O.N. = −1) and KO_2 (containing O_2^- ion).]
4. Hydrogen has an oxidation number of +1 in compounds. [Ionic hydrides are the exception where the O.N. = −1, for example, NaH (O.N. = −1).]
5. The sum of the oxidation numbers of all atoms
   (a) in a neutral molecule is zero, and
   (b) in a polyatomic ion
   is equal to the charge on the ion.

Table 8.17 Transition metals

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Valency	3	2,3,4	2,3,4,5	2,3,6	2,3,4,6,7	2,3	2,3	2	1,2	2
Inner electrons	1	0,1,2	0,1,2,3	0,1,4	0,1,2,4,5	0,1	0,1	0	0,1	0

Example 1

In the compound $FeCl_3$, the O.N. for iron is +3.

Example 2

Find the O.N. for manganese in the following compounds:

(a) $\underline{Mn}Cl_2$ +2
(b) $\underline{Mn}Cl_3$ +3
(c) $K\underline{Mn}O_4$ +7 [1 + Mn + (−8)]

Example 3

Write half-equations for the reaction which takes place when iron (II) nitrate has bromine added to it. Write the balanced equation for the reaction and state the oxidant and the reductant.

(i) $Fe^{2+} \rightarrow Fe^{3+} + e^-$ (oxidation)
(ii) $Br_2 + 2e^- \rightarrow 2Br^-(aq)$ (reduction)
Multiple (i) by 2:
(iii) $2Fe^{2+} \rightarrow 2Fe^{3+} + 2e^-$
Add (ii) and (iii):

$$2Fe^{2+}(aq) + Br_2(l) \rightarrow 2Fe^{3+}(aq) + 2Br^-(aq)$$

Br_2 is the oxidant; Fe^{2+} is the reductant.

Exercise 8.2

Calculate the oxidation state of the underlined elements in each of the following:

(a) $K\underline{Mn}O_4$
(b) $K_2\underline{Cr}_2O_7$
(c) $[\underline{Cr}(H_2O)_4Cl_2]^{+1}$
(d) $\underline{Fe}\,(CN)_6^{4-}$
(e) $Na_2\underline{Cr}O_4$

Balancing redox equations

To obtain the overall equation, the half-equations, one for oxidation and one for reduction, must be combined. The species being oxidised and reduced must be known before these half-equations can be written. For this reason, tables of some common oxidising and reducing agents are given after the rules for balancing redox half-equations.

Rules for balancing redox half-equations in acid solutions

Step 1. Write down the reactant and product.

$$Cr_2O_7^{2-} \rightarrow Cr^{3+}$$

Step 2. Balance the number of atoms of the element being reduced or oxidised.

$$Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$$

Step 3. Balance the number of atoms of oxygen by adding water to the side with least oxygen.

$$Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$$

Step 4. Balance the number of atoms of hydrogen by adding H^+ ions to the side with least hydrogen.

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

Step 5. Balance the charge by adding electrons to the side with the highest total positive charge. Then write in the states for each substance present.

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

Balancing redox half-equations in alkaline solutions

Additional rules for balancing equations in alkaline solutions are as follows:

(a) Balance the half-equations as though they occur in acid solution.
(b) The H^+ ions are then removed to form H_2O by adding the same number of OH^- ions to each side of the equation.
(c) Collection of 'like' terms to simplify.

Example

$MnO_4^-(aq) \rightarrow MnO_2(s)$ (alkaline solution)

$MnO_2 + 2H_2O$

Step 1. $MnO_4^- \rightarrow MnO_2 + 2H_2O$

Step 2. $MnO_4^- + 4H^+ \rightarrow MnO_2 + 2H_2O$

Step 3. $MnO_4^- + 4H^+ + 4OH^- \rightarrow MnO_2 + 2H_2O + 4OH^-$

Step 4. $MnO_4^-(aq) + 2H_2O(l) + 3e^- \rightarrow MnO_2(s) + 4OH^-(aq)$

Balancing redox equations by combining half-reactions

Step 1. Write the two balanced half-reactions, one involving oxidation and one involving reduction.

Step 2. Multiply each equation by the factor needed in each case so that the number of electrons lost in one half-reaction equals the number of electrons gained in the other.

Step 3. Add the half-equations to give the overall balanced equation.

Example

Write a balanced equation for the reaction of iron (II) nitrate and acidified potassium dichromate solution.

Step 1. Half-reactions
(i) $Fe^{2+} \rightarrow Fe^{3+} + e^-$
(ii) $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

Step 2. Multiply (i) by 6
(iii) $6Fe^{2+} \rightarrow 6Fe^{3+} + 6e^-$

Step 3. Add (ii) and (iii)

$$6Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 6Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$$

Activity 8.2

Part A

Volumetric analysis using potassium permanganate

1. Dissolve a few crystals of iron (II) sulfate ($FeSO_4.7H_2O$) in about 5 mL of water in a test tube.

Table 8.18 Common oxidising agents (oxidants) in acid solutions

Name	Ion or molecule	Steps in balancing half-equations
Potassium permanganate (purple solution) ↓ Manganese (II) ion (colourless)	$\underline{Mn}O_4^-$ (O.N. +7) ↓ ↓ $\underline{Mn}^{2+}$ (O.N. +2)	1. $MnO_4^- \rightarrow Mn^{2+}$ 2. $MnO_4^- \rightarrow Mn^{2+} + 4H_2O$ 3. $MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$ 4. $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$
Potassium dichromate (orange solution) ↓ Chromium (III) ion (green solution)	$\underline{Cr}_2O_7^{2-}$ (O.N. +6) ↓ ↓ $2\underline{Cr}^{3+}$ (O.N. +3)	1. $Cr_2O_7^{2-} \rightarrow 2Cr^{3+}$ 2. $Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 7H_2O$ 3. $Cr_2O_7^{2-} + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$ 4. $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$

2. Add 2 mL of 2 M H_2SO_4 solution.
3. Use a dropper to add 0.02 M $KMnO_4$ and state why a reaction occurred.
4. (a) Balance the half-equation for the reaction involving the MnO_4^- ion.
   (b) Write the half-equation for the oxidation of Fe^{2+} to Fe^{3+}.
   (c) Combine the two half-equations to give the complete equation for the redox reaction.
   (d) Calculate the molar mass of $FeSO_4.7H_2O$.

Part B

Standardisation of potassium permanganate solution

1. Weigh three clean conical flasks (A, B, C) and record their mass.
2. To each flask carefully add 1–1.5 g of hydrated iron (II) sulfate. Reweigh the flask + iron salt and record the mass.
3. Add 10 mL of 2 M H_2SO_4 and about 10 mL of water. Carefully swirl each flask and wash down the inside of each flask using a wash bottle.
4. Rinse and fill your burette with the approximately 0.02 M $KMnO_4$ provided. Record the initial burette reading.
5. Titrate flask A as shown in Figure 8.21 until a persistent, very faint pink colour indicates the end point. Record the final volume reading on the burette.
6. Repeat for flasks B and C.

During titration, the burette tap is turned with the left hand and the flask is swirled with the right hand (Figure 8.21). When the end point is near, add the reagent dropwise. Carry out several titrations until they agree to within 0.1 mL.

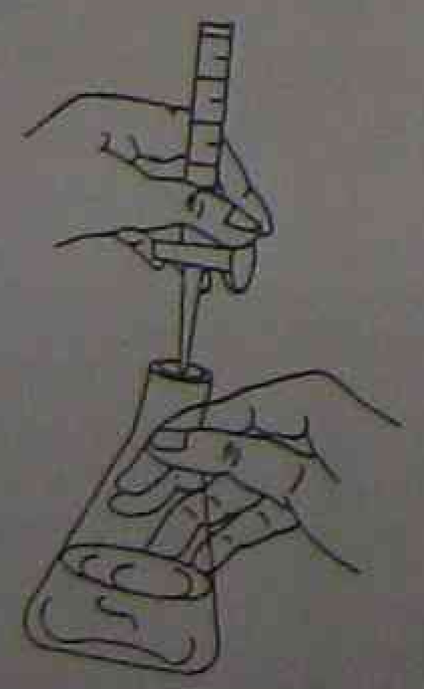


Figure 8.21 How to titrate

Results

Measurement	Flask A	Flask B	Flask C
Mass of empty flask (g)			
Mass of flask + iron salt (g)			
Initial burette reading (mL)			
Final burette reading (mL)			

Using the equation and molar mass of $FeSO_4.7H_2O$ calculate the number of moles for each flask.

Using the formula

$$c = \frac{n \times 1000}{V}$$

where c is the concentration (molarity), n is the number of moles, V is the volume in mL, find the average concentration of $KMnO_4$ from the measurements found in the table below.

Measurement	Flask A	Flask B	Flask C
Volume of $KMnO_4$ used (mL)			
Concentration of $KMnO_4$ (M)			

Average concentration of $KMnO_4$ = _______ M

Solving problems in volumetric analysis

Practical work

An example of volumetric analysis has been given in Activity 8.2. A variety of redox titrations should be carried out.

Example

20.0 mL of a solution of $KMnO_4$ oxidises a solution containing 0.150 g of oxalic acid $H_2C_2O_4.2H_2O$, in the presence of dilute sulfuric acid. Find the molarity of the $KMnO_4$ solution.

Step 1. Write the half-equations for oxidation and reduction.

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

(ii) $C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$

Step 2. Write a balanced ionic equation for the reaction.

$2 \times$ (i) + $5 \times$ (ii)

(iii) $2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq)$
$\rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$

Step 3. Work out mole ratio.

2 moles MnO_4^- oxidises 5 moles of $C_2O_4^{2-}$.

Step 4. Work out the number of moles of oxalic acid present.

Molar mass of $H_2C_2O_4.\ 2H_2O = 126$ g

No. of moles $= 0.15 \div 126$
$= 1.19 \times 10^{-3}$

Step 5. Use balanced equation to find the number of moles of MnO_4^-.

No. of moles $= {}^2/_5 \times 1.19 \times 10^{-3}$
$= 4.76 \times 10^{-4}$

Step 6. Calculate the molarity of $KMnO_4$.

$$\text{No. of moles} = \text{M} \times \frac{\text{V mL}}{1000}$$

$$\text{Molarity} = \frac{4.76 \times 10^{-4} \times 10^{3}}{20} = 0.024\ \text{M}$$

Some applications of redox reactions

(a) *Potassium permanganate* ($KMnO_4$) dissolves in water to form a purple solution. This makes it useful in volumetric titrations, since it can act as its own indicator.

(b) *Potassium dichromate* ($K_2Cr_2O_7$) dissolves in water to form an orange solution. It is also used in titrations and as an oxidant in organic reactions. Acidified solutions are stable for long periods of time. 'Breathalysers' used to depend on the fact that the orange $K_2Cr_2O_7$ crystals oxidised alcohol (ethanol) to ethanoic acid and were themselves reduced to green Cr^{3+} ions.

Example

A student decided to analyse one of the iron tablets she had to take for anaemia. From the label she found that iron was present as iron (II) sulfate. She found that the mass of the tablet was 0.390 g and then dissolved it in a conical flask using dilute H_2SO_4. She then titrated the sample with 0.010 M potassium dichromate, using a volume of 38.2 mL. Find the number of moles of Fe^{2+} present and the percentage by mass of the iron (II) sulfate ($FeSO_4$) present in the tablet.

Step 1. Write the half-equation for oxidation and reduction.

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

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

Step 2. (i) + (ii) $\times 6$

(iii) $6Fe^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq)$
$\rightarrow 6Fe^{3+}(aq) + 2Cr^{3+}(aq) + 7H_2O(l)$

Step 3. Work out mole ratio.

1 mole of $Cr_2O_7^{2-}$ oxidises 6 moles of Fe^{2+}.

Step 4. Work out the number of moles of potassium dichromate.

$$\begin{aligned}\text{No. of moles} &= \text{M} \times \frac{\text{V mL}}{1000}\\ &= 0.01 \times \frac{38.2}{1000}\\ &= 3.82 \times 10^{-4}\end{aligned}$$

Step 5. Use the balanced equation to find the moles of Fe^{2+}.

No. of moles $= 6 \times 3.82 \times 10^{-4}$
$= 2.29 \times 10^{-3}$

Step 6. Calculate the number of grams of $FeSO_4$ (molar mass) = 151.9 g mol^{-1}
$= 2.29 \times 10^{-3} \times 151.9 = 0.365$ g

Step 7. Calculate the percentage of $FeSO_4$ in the tablet.

$$\frac{0.348}{0.390} \times 100 = 89.2\%$$

Exercise 8.3

1. A length of pure iron wire of mass 0.560 g was dissolved in dilute H_2SO_4 and the resulting solution was titrated with 0.020 M potassium permanganate solution. (The molar mass of iron = 55.8 g mol^{-1}.)
   (a) Write half-equations for the oxidation and reduction reactions.
   (b) Write a balanced ionic equation for the reaction.
   (c) Find the volume of potassium permanganate required.
2. A student was asked to standardise a solution of approx. 0.02 M potassium permanganate using oxalic acid ($C_2H_2O_4.2H_2O$) as the standard ($C = 12$, $H = 1$, $O = 16$). He calculated that the molar mass of the standard was 90 g mol^{-1}.

   From the half-equations

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

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

he deduced that 2 mole of MnO_4^- would reduce 1 mole of $C_2O_4^{2-}$.

The procedure required him to weigh out enough oxalic acid to produce 250 mL of a 0.05M solution of $C_2H_2O_4.2H_2O$. The student weighed out 1.12 g of oxalic acid and transferred the sample to a 500 mL beaker. He then added 250 mL of hot water from a measuring cylinder and stirred it to dissolve the oxalic acid. He rinsed a 25 mL pipette with distilled water and then pipetted by mouth a 25 mL sample into a dry conical flask. He rinsed the burette with distilled water, then filled it with the $KMnO_4$ solution. He carried out the titration and recorded the result. He then calculated his results.

Carefully read through this procedure and list the errors the student made, giving the correct calculations or procedures in each case.

3. 25 mL of acidified iron (II) ammonium sulfate required 23 mL of 0.10 M potassium permanganate when titrated. From the following information

$$MnO_4^- \rightarrow Mn^{2+}$$
$$Fe^{2+} \rightarrow Fe^{3+}$$

   (a) write half-equations for the oxidation and reduction reactions and hence a balanced ionic equation; and
   (b) find the molarity of the iron (II) ammonium sulfate solution.

4. A solution of potassium permanganate was standardised by titrating it against a weighed amount of sodium oxalate in the presence of sulfuric acid. 0.120 g of sodium oxalate needed 21.5 mL of permanganate to reach the endpoint of the titration.
   (a) Write half-equations for oxidation and reduction.
   (b) Write the overall balanced ionic equation for the reaction.
   (c) Calculate the molarity of the potassium permanganate.

5. What volume of 0.03 M $KMnO_4$ will just oxidise 40 mL of 0.06 M H_2O_2 solution? Write a balanced ionic equation.

6. Calculate the number of grams of $FeSO_4.7H_2O$ which will be oxidised in an acidified solution by 24.0 mL of 0.05 M $KMnO_4$. Write a balanced ionic equation.

7. Oxalic acid ($H_2C_2O_4$) is found in the leaves of rhubarb. A student boiled down 100 g of chopped rhubarb leaves to extract the oxalic acid. Then drained off the liquid, which was found to measure 530 mL. She then titrated 100 mL of the original liquid with 0.020 M $KMnO_4$ and found that 12.6 mL of the permanganate solution was needed to oxidise the oxalic acid.
   (a) Write half-reactions and hence a balanced ionic reaction.
   (b) Find the number of grams of oxalic acid in the original sample.
   (c) Find the percentage by mass of oxalic acid in the rhubarb leaves.

8.24 Hydrated ions as examples of coordination complexes

Hydrated ion in solution

Water can cause molecules, e.g. HCl, to dissociate into ions such as H^+ and Cl^- ions.

$$Cl-H---:\underset{H}{O}-H \rightarrow Cl^- + [H-\underset{H}{O}-H]^+$$

Water is a polar liquid.

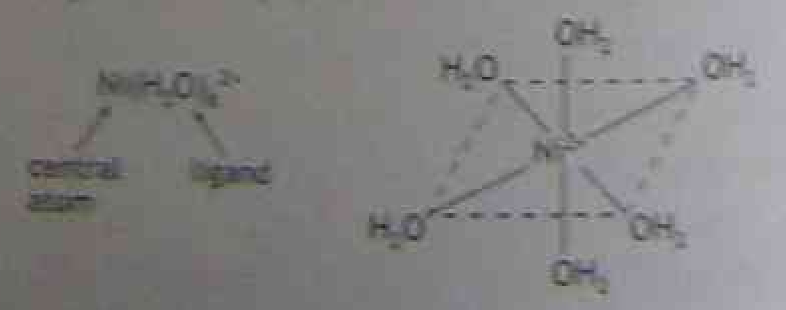
A proton from HCl transfers to the water molecule producing $[H_3O]^+$ the hydronium ion. Because water tends to hydrate ions readily, most ions in aqueous solution can be considered as complex ions. Complex ions can occur in both solid state and solution.

Complex ions

A simple bonding picture for complex ions involves electrostatic attraction between the central metal ion and the dipolar (and basic) ligands.

Example

Hexaaquonickel (II) ion

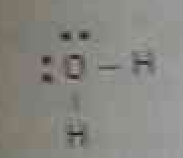
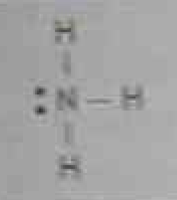
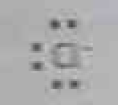


8.25 Naming of complex ions

In the example $Ni(H_2O)_6^{2+}$, there are six water molecules surrounding the metal ion. The name given to the ligand is aquo. The central atom nickel is in the II oxidation state.

The species which surround the central atoms are called *ligands*. Ligands donate electrons for the coordinate covalent bonds. The number of ligands which coordinate to the metal depends on how many unshared electrons they have.

Examples of common ligands are

Structure:				
Name:	aquo	ammine	chloro	cyano

Ligands may be neutral or anionic.

A metal complex is a distinct chemical species with its own characteristic chemical and physical properties. For example, complexes may have colours that differ markedly from their component metal ions and ligands.

A compound in which a metal atom is bonded to other species by coordinate covalent bonds is called a coordination compound.

Table 8.19 Names of some neutral and anionic ligands

Type	Name	Formula
Neutral ligands	aquo ammine carbonyl nitrosyl	H_2O NH_3 CO NO^+
Anionic ligands	fluoro chloro bromo iodo hydroxo cyano	F^- Cl^- Br^- I^- OH^- CN^-

Table 8.20 Names of some metal ions in polyatomic anions

Metal	Name in anion
Iron	ferrate
Copper	cuprate
Lead	plumbate
Silver	argentate
Gold	aurate
Platinum	platinate
Tin	stannate
Nickel	nickelate

Writing names and formulas for coordination compounds

1. The cation (positive ion) is written before the anion (negative ion).
2. The charges of cation(s) and anion(s) are balanced.
3. In the complex ion, ligands are written in alphabetical order, whether neutral or charged. The whole ion is bracketed. A complex ion may be an anion or a cation.

Naming complex ions

The general pattern is number and name of the ligand — name of metal — oxidation state of metal.

Case 1 — $[Ni(H_2O)_6]^{2+}$

Hexaaquonickel (II) ion. Here metal ion is part of a complex cation.

Case 2 — $Fe(CN)_6^{4-}$

Hexacyanoferrate (II). Here the metal ion was part of a complex anion. (Table 8.24)

Case 3 — $[Cu(NH_3)_4(H_2O)_2]^{2+}$

Tetraamminediaquocopper (II) ion. Within the complex ion, the ligands are named in alphabetical order before the metal ion.

Case 4 — $[Co(NH_3)_2Cl_4]^{2-}$

Diamminetetrachlorocobalt (II) ion. The neutral ligand is named before the anionic ligand.

Naming coordination compounds

The only space in the name is between the cation and anion.

Case 1 — $[Co(NH_3)_4Cl_2]$ Cl

tetraamminedichlorocobalt (III) chloride

Case 2 — $[Co(NH_3)_5Cl]$ Cl_2

Contains five NH_3 and one Cl^- ligand. The cation is named pentaamminechlorocobalt (III). The anion is called chloride. The compound is named *pentaamminechlorocobalt (III) chloride*, where metal forms part of the cation.

Case 3 — $K_2[Ni(CN)_4]$

The cation is called potassium. The anion contains the metal Ni which is called nickelate. The compound is named *potassium tetracyanonickelate (II)*.

Ligand exchange rates

Some complexes in solution exchange ligands at a very rapid rate.

Example

The addition of ammonia to an aqueous solution of $CuSO_4$ changes almost instantly as the pale blue

$Cu(H_2O)_4^{2+}$ is converted to the deep blue $Cu(NH_3)_4^{2+}$. When this deep blue solution is acidified the pale blue colour rapidly reappears.

$$Cu(NH_3)_4^{2+}(aq) + 4H_2O(l) + 4H^+(aq) \rightarrow Cu(H_2O)_4^{2+}(aq) + 4NH_4^+(aq)$$

- Complexes like those of $Cu(NH_3)_4^{2+}$ that undergo rapid ligand exchange are called labile.
- $Co(NH_3)_6^{3+}$ undergoes slow ligand change and is called inert.
- Chromium (III) and platinum (IV) also form inert complexes with ammonia.

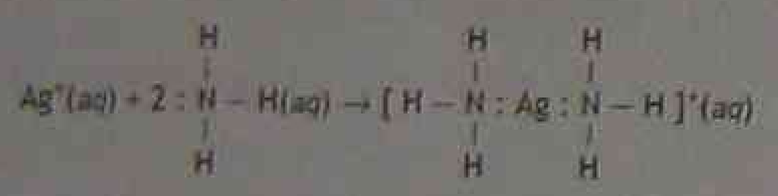
The effect of ligands on the properties of ions

(a) *Solubility*. AgCl is insoluble in water but is soluble in ammonia because of the formation of the $Ag(NH_3)_2^+$ ion.

(b) *Reactivity*. Iron (II) ions react with sulfide ions but iron (II) ions in an $Fe(CN)_6^{4-}$ complex do not. These examples show that the chemical properties of transition metal ions are markedly affected by the ligands present.

(c) *Metal-ligand bond*. The bond between the metal and ligand is the result of their sharing a pair of electrons that was originally on the ligand.

Example



$$Ag^+(aq) + 2 : \overset{H}{\underset{H}{N}} - H(aq) \rightarrow [H - \overset{H}{\underset{H}{N}} : Ag : \overset{H}{\underset{H}{N}} - H]^+(aq)$$

8.26 Crystal-field theory

This theory was first developed to explain the properties of crystalline substances such as ruby. The theory accounts for the colour and magnetic properties of transition metal complexes in terms of the splitting of the energies of the metal ion d-orbitals by the electrostatic interaction of ligands.

- The theory involves the modification of the energy levels around the central atom by the ligands donating into the hybridised orbitals of that atom.

Example

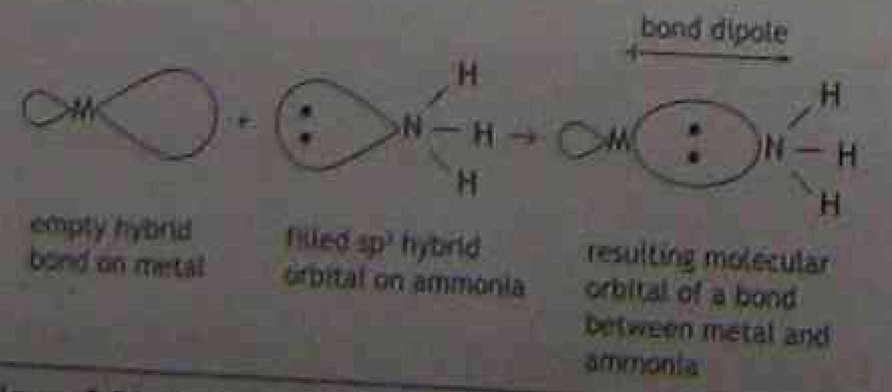


Figure 8.22 A metal-ligand bond in a complex

- The ligand donates charge to the metal via a metal hybrid orbital. The crystal-field model assumes that the metal-ligand interaction is electrostatic in character.
- Much of the attractive interaction between the metal ion and the surrounding ligands is due to the electrostatic forces between the positive charge on the metal and the negative charge on the ligands, e.g. SCN^-.
- If the ligand is neutral, e.g. H_2O or NH_3, the negative ends of these polar molecules containing an unshared electron are directed towards the metal (an ion-dipole type of attraction). At the same time the ligands repel one another.
- In any metal complex, there is a balance between the attractive force between metals and ligands and ligand-ligand repulsive interactions.
- The most stable complex results when the geometrical arrangement of the ligands around the metal maximises metal-ligand attractions and minimises ligand-ligand repulsions.
- In a six-coordination complex, the overall energy of the metal ion plus ligands will be lower (more stable) when the ligands are drawn towards the metal centre. There is, however, a repulsion between the outermost electrons on the metal and the negative charges on the ligand. This is called the *crystal field*.

Valence bond theory

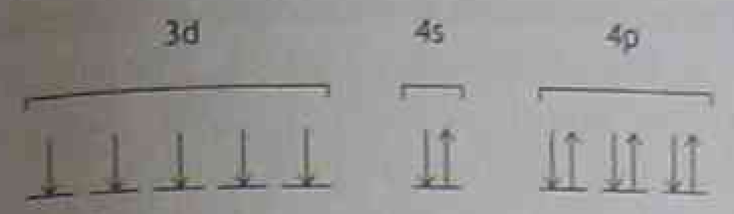
The formation of complex ions depends on the following:

- The orbitals available for coordinate covalent bond formation.
- The tendency for ions or groups to share a pair of electrons.
- The number of molecules or ions that can be placed around a central ion.
- The geometry assumed by the ligands and the metal ion.

According to the *valence bond theory*, metal ions can form bonds with ligands having a pair of electrons that can enter the unfilled 3d, 4s or 4p orbitals to form coordinate covalent type bonds. The reaction that occurs to form this bond is a Lewis acid-base type of reaction as shown in the following example

$$Mn^{2+} + 4Cl^- \rightarrow MnCl_4^{2-}$$

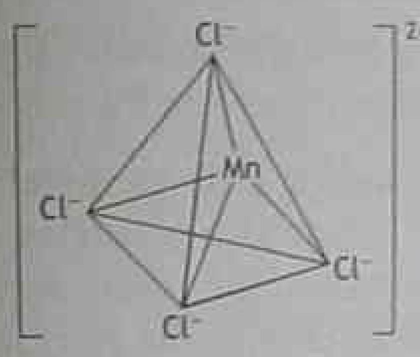
Mn^{2+} orbitals ($MnCl_4^{2-}$):



Example 1

One pair of electrons on each chloride ion can form a covalent bond with the 4s and each of the 4p orbitals on the manganese ion. The Mn^{2+} is surrounded by four Cl^- ions to form a tetrahedral structure.

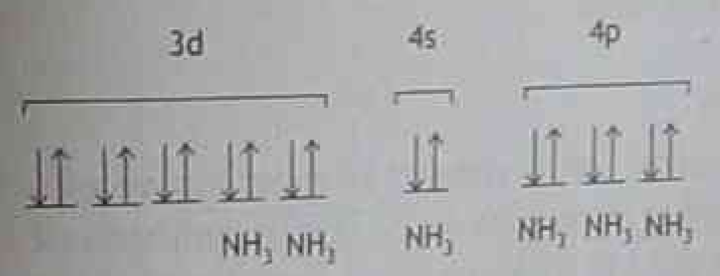
$[MnCl_4]^{2-}$



Example 2

$$Co^{3+} + 6NH_3 \rightarrow Co(NH_3)_6^{3+}$$

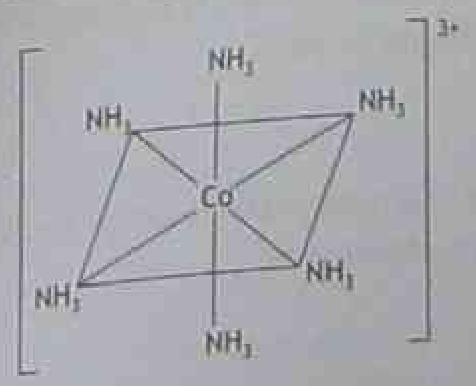
Co^{3+} orbitals [$Co(NH_3)_6^{3+}$]:



The extra pairs of electrons from the ammonia molecules are bonded in 2d, 1s and 3p-orbitals of the metal ion.

Example 3

The Co^{3+} is now surrounded by six ammonia molecules. The configuration is octahedral.



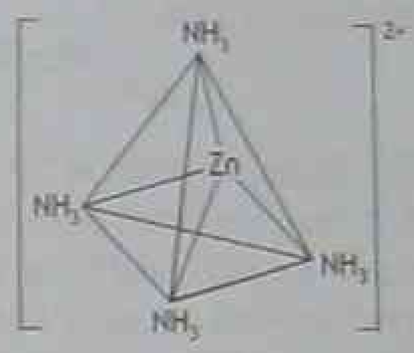
8.27 Coordination numbers and structures

(a) Where the metal in the complex has a co-ordination number of four.

(i) *Tetrahedral*

Example

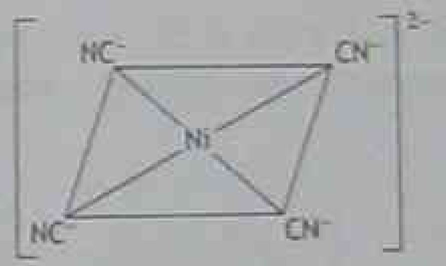
$[Zn(NH_3)_4]^{2+}$



(ii) *Square planar*

Example

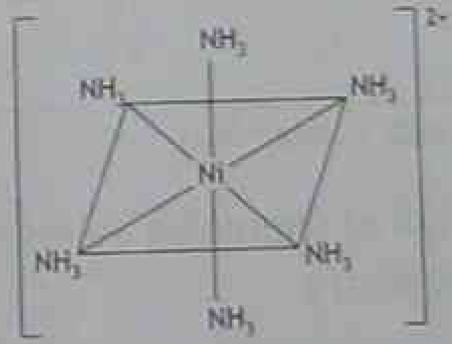
$Ni(CN)_4^{2-}$



(b) Where the metal in the complex has a co-ordination number of six.

Example

$[Ni(NH_3)]^{2+}$



Exercise 8.4

(a) Name the following complex ions:

(i) $Co(NH_3)_6^{2+}$
(ii) $Cr(H_2O)_4^{3+}$
(iii) $Fe(CN)_6^{4-}$
(iv) VCl_4^-
(v) $Cu(NH_3)_4^{2+}$

(b) Write the formula for the following complex ions:

(i) diammine-silver (I) ion
(ii) tetracyanonickelate (II) ion
(iii) tetrammine-zinc (II) ion
(iv) hexaaquocobalt (II) ion
(v) hexacyanoferrate (II) ion

8.28 Chelates

The previous ligands, e.g. NH_3, H_2O and Cl^-, are *monodentate ligands* and possess a single donor atom. Ligands that have two or more donor atoms which can simultaneously coordinate to a metal ion are called *polydentate ligands* or *chelating agents*, e.g. ethylenediamine.

This ligand, written as 'en', has two nitrogen atoms that have unshared pairs of electrons. These donor atoms are sufficiently far apart that the ligand can wrap around a metal ion with the two nitrogen atoms simultaneously complexing to the metal. The $Co(en)_3^{3+}$ ion contains three ethylenediamine ligands bound to the octahedral sphere of cobalt (III).

Note: In Figure 8.23, the ethylenediamine is represented as two nitrogen atoms connected by a line.

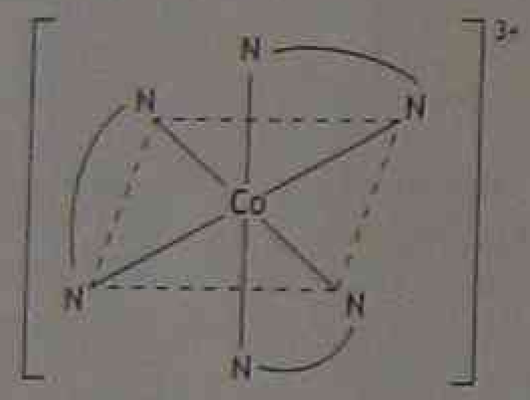


Figure 8.23 $Co(en)_3^{3+}$ ion

The role of transition elements in human biochemistry

Iron

Important chelating agents in nature are called porphyrins. Different porphyrins contain different metals, e.g. a haeme which contains iron (II). Haemoglobin contains four haeme sub-units.

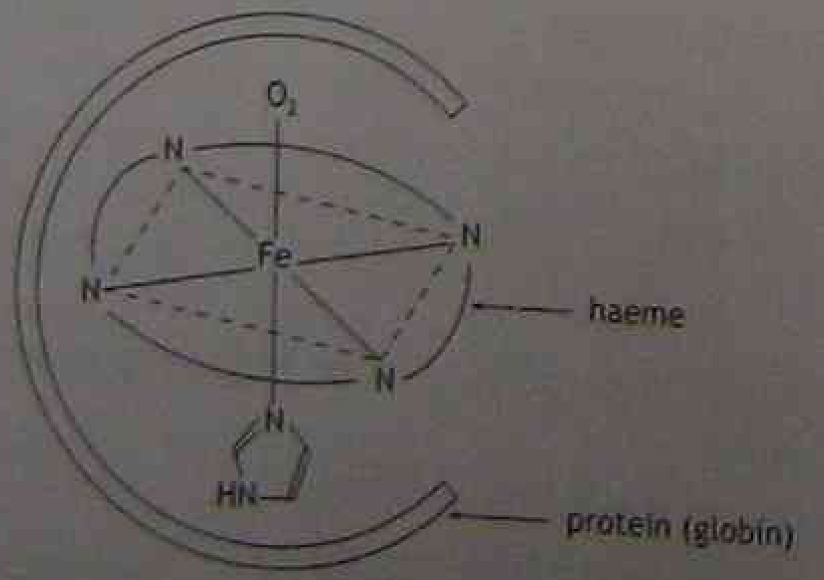


Figure 8.24 A schematic representation of oxyhaemoglobin showing one of the four haeme units in the molecule. The iron is bound to four nitrogen atoms of the porphyrin to one nitrogen atom from the surrounding protein and to an O_2

About four of every million atoms present in an adult are iron atoms. Insufficient iron in the diet leads to iron-deficient anaemia. The rest of the transition metals, cobalt, copper, manganese molybdenum and zinc are each present in amount of about 1 atom per million. Most of these ions mentioned have the following chemical properties needed to carry out biochemical processes:

- They form stable coordination complexes with proteins and other biologically active substances.
- They are versatile catalysts.
- They have several oxidation states that are readily formed and interconverted in the cell environment.

One important function of these metal ions is their role as co-factor in reactions involving enzymes. In this case, the metal ion may function as a coordinating group to bind the reactant species to the enzyme by forming a coordination complex. It may also act as a catalyst for the reaction. Since co-enzymes frequently contain structures not found in ordinary metabolites, these are recovered in their original form.

Cobalt

The cobalt ion is present in a derivative of vitamin B_{12} and is important in the *in vivo* synthesis of amino acids used to make proteins. Deficiency of cobalt can lead to pernicious anaemia.

Copper

The protein called ceruloplasmin serves as a reservoir for copper and supplies copper ions to certain enzyme systems in the tissues. The copper containing enzyme system, cytochrome oxidase, is responsible for the end steps of oxidation of food.

Zinc

The zinc ion is an essential co-factor in the hydrolysis of proteins to amino acid.

Manganese

Manganous ion complexes with ADP or ATP enable phosphate transfer in the energy utilisation cycle.

Chelating agents

These are often used as *sequestering agents*. They are complexing agents which can suppress the normal reactions of metal cations.

Examples

(a) *Used in the food industry as preservatives*. The metal ions such as copper and nickel which would otherwise catalyse the oxidation of food.

(b) *Used in 'water softening'*. EDTA is used as a sequestrant to prevent calcium and magnesium ions from interfering with the action of soaps and detergents.

(c) *Used in analytical chemistry*. EDTA is used in complexometric titrations.

(d) *Heavy metals* such as mercury, lead and cadmium often act by bonding to the ligand sites of enzymes and other proteins. One method of treating lead poisoning is to administer $Na_2[CaEDTA]$. The EDTA chelates the lead allowing its removal from the body in urine.

Note: $EDTA^{4-}$ is the abbreviated form of the ethylenediamminetetraacetate ion. It is a common polydentate ligand.

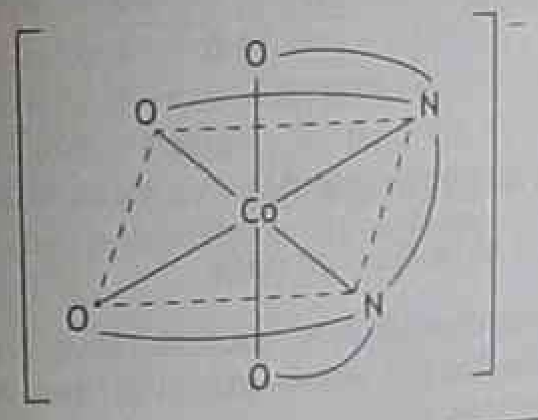


Figure 8.25 The $CoEDTA^-$ ion showing how the ethylenediaminetetraacetate ion is able to wrap around a metal ion occupying six places in the coordination sphere

Answers

Answers for Activity 8.1

Results for flame tests

Name of substance	Formula	Cation present	Colour of flame
Sodium chloride	$NaCl$	Na^+	yellow
Potassium nitrate	KNO_3	K^+	lilac
Lithium oxide	Li_2O	Li^+	crimson
Calcium nitrate	$Ca(NO_3)_2$	Ca^{2+}	black-red
Barium chloride	$Ba(NO_3)_2$	Ba^{2+}	apple-green
Strontium nitrate	$Sr(NO_3)_2$	Sr^{2+}	scarlet
Copper sulfate	$CuSO_4$	Cu^{2+}	green

Answers to questions

1. Yes
2. Sodium, potassium and lithium
3. Yes
4. Calcium, barium and strontium
5. Copper is an element present in the 1st transition series.
6. Carry out a series of experiments using the same cation with a selection of anion, e.g. using NaCl, Na_2SO_4, $NaNO_3$.

Conclusion

Na^+ ion was responsible for the yellow flame colour.

Answers for Activity 8.2

Part A

Volumetric analysis using potassium permanganate

3. The purple colour of the $KMnO_4$ faded.
4. (a) $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)$
   (b) $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$
   (c) $5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+$
   $\rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$
   (d) 278

Part B

Standardisation of potassium permanganate solution

Titration of Flask A:

Mass of iron salt = 1.00 g
Moles of iron salt = 1/278
= 3.60×10^{-3}
= moles of $Fe^{2+}(aq)$
Final burette reading = 34.8 mL

$$\text{Moles of } MnO_4 = \frac{3.60\times10^{-3}}{5} \text{ (from balanced equation)}$$
$$= 7.20\times10^{-4}$$

$$\text{Molarity for } KMnO_4 = \frac{7.20\times10^{-4}\times1000}{34.8} \quad \left(c=\frac{n\times100}{V}\right)$$
$$= 0.021\,M$$

Answers for Exercise 8.1

1. See table at bottom of page.
2. (a) Manganese (as Mn^{2+} ion). (C^{2+})
   (b) Oxide ion (O^{2-}) and neon. (B^{2-} and D)
   (c) 8 protons
   (d) Oxygen
3. (a) E (the element with 13 protons in its nucleus must have 13 electrons in each of its atoms).
   (b) X (element must be in group VIII); higher electronegativity than Q.
   (c) T (transition elements contain d-electrons); d shell is unfilled.
   (d) D (valence shell contains two s-electrons).
   (e) T (a transition metal).
   (f) M
   (g) D
   (h) Z (its ground state would be $1s^2\,2s^2\,2p^1$).

Answers for Exercise 8.2

(a) +7 (b) +6 (c) +3 (d) +2 (e) +6

Element or ion	Atomic No.	Electronic configuration	Period	Group
Ca	20	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2$	4	II
Cu	29	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^1$	4	transition metal
Fe^{3+}	26	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5$	4	transition metal
F^-	9	$1s^2\,2s^2\,2p^6$	2	VII
S^{2-}	16	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6$	3	VI
V	23	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^3\,4s^2$	4	transition metal

Answers for Exercise 8.3

1. (a) (i) $Fe^{2+} \rightarrow Fe^{3+} + e^-$
   (ii) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
   (b) 5 × (i) + (ii):
   (iii) $5Fe^{2+}(aq) + MnO_4(aq) + 8H^+(aq)$
   $\rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$
   (c) No. of moles of Fe^{2+} = 0.56 ÷ 55.8 = 0.010
   From equation,
   No. of moles of MnO_4^- = 0.010 ÷ 5 = 2.00×10^{-3}
   No. of moles = M × V mL ÷ 1000
   V = $2.00 \times 10^{-3} \times 10^3$ ÷ 0.020 = 100 mL
2. (a) The molar mass of standard is 126 g mol^{-1}, not 90 g mol^{-1}. The student did not add in the water of crystallisation.
   (b) Balanced equation is:
   $2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq)$
   $\rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$
   2 moles of MnO_4^- oxidises 5 moles of $C_2O_4^{2-}(aq)$
   (c) The student should have weighed about 1.58–1.60 g accurately.
   (d) Standard solutions are made up in volumetric flasks, not measuring cylinders, because of accuracy of measurement. If hot water is used to dilute a sample, it must be cooled to room temperature before being made up to volume in the volumetric flask. These flasks are calibrated for 20°C.
   (e) The pipette should be rinsed with the solution that will fill it. This avoids dilution of the oxalic acid. Oxalic acid is poisonous and should not be pipetted by mouth. A pipette filler should be used.
   (f) The burette should be rinsed with the $KMnO_4$ solution so that the molarity is not altered.
   (g) More than one sample should be titrated until results are less than 0.2 mL apart.
3. (a) (i) $MnO_4^-(aq) + 8H^+(aq) + 5e^-$
   $\rightarrow Mn^{2+}(aq) + 4H_2O(l)$
   (ii) $5Fe^{2+}(aq) \rightarrow 5Fe^{3+}(aq) + 5e^-$
   (iii) $MnO_4(aq) + 8H^+(aq) + 5Fe^{2+}(aq)$
   $\rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$
   (b) Moles of $KMnO_4$ = $0.10 \times 23/1000$
   Moles of Fe^{2+} = $x \times 25/1000$
   Moles ratio MnO_4/Fe^{2+} = 1/5
   = $(0.10 \times 23) \div (x \times 25)$.
   $x = 0.10 \times 23 \times 5/25$
   = 0.46 M
4. (a) (i) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
   (ii) $C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$
   (b) 2 × (i) + 5 × (ii):
   (iii) $2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq)$
   $\rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$
   (c) 2 moles of MnO_4^- oxidises 5 moles of $C_2O_4^{2-}$.
   No. of moles $C_2O_4^{2-}$ = 0.12 ÷ 134
   = 8.96×10^{-4}
   No. of moles of MnO_4^- = $2 \times 8.96 \times 10^{-4} \div 5$
   = 3.58×10^{-4}
   No. of moles = M × V ÷ 1000
   3.58×10^{-4} = M × 21.5 ÷ 1000
   Molarity = 0.017 M
5. (a) (i) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
   (ii) $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$
   (b) 2 × (i) + 5 × (ii)
   (iii) $2MnO_4^-(aq) + 5H_2O_2(aq) + 6H^+(aq)$
   $\rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5O_2(g)$
   (c) 2 moles of MnO_4^- oxidises 5 moles of H_2O_2.
   No. of moles of H_2O_2 = 0.08 × 40 ÷ 1000
   = 3.2×10^{-3}
   No. of moles of MnO_4^- = $2 \times 3.2 \times 10^{-3} \div 5$
   1.28×10^{-3} = 0.03 × V ÷ 1000
   V = 42.7 mL
6. (i) $Fe^{2+} \rightarrow Fe^{3+} + e^-$
   (ii) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
   (i) × 5 + (ii)
   (iii) $5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq)$
   $\rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$
   1 mole of MnO_4^- oxidises 5 moles of Fe^{2+}.
   No. of moles of MnO_4^- = 0.05 × 24/1000
   = 1.2×10^{-3}
   No. of moles of Fe^{2+} = $5 \times 1.2 \times 10^{-3}$
   = 6.0×10^{-3}
   Molar mass of $FeSO_4.7H_2O$ = 278 g mol^{-1}
   No. of grams of $FeSO_4.7H_2O$
   = $6 \times 10^{-3} \times 278$ = 1.668 g
7. (a) (i) $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
   (ii) $C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$
   (b) 2 × (i) × 5 × (ii):
   (iii) $2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq)$
   $\rightarrow 10CO_2(aq) + 2Mn^{2+}(aq) + 8H_2O(l)$
   (c) No. of moles of MnO_4^- = 0.02 × 12.6 ÷ 1000
   = 2.52×10^{-4}
   No. of moles of $C_2O_4^{2-}$ = $5 \div 2 \times 2.52 \times 10^{-4}$
   = 6.3×10^{-4}
   No. of grams of oxalic acid = $6.3 \times 10^{-4} \times 90$
   = 0.0567 g
   No. of grams of oxalic acid in original sample
   = 530 ÷ 100 × 0.0567 = 0.301 g
   % by mass of oxalic acid in leaves
   = 0.301 ÷ 100 × 100 = 0.301%

Answers for Exercise 8.4

(a) Naming:
   (i) hexaamminecobalt (II) ion
   (ii) tetraaquochromium (III) ion
   (iii) hexacyanoferrate (II) ion
   (iv) tetrachlorovanadate (III) ion
   (v) tetraamminecopper (II) ion

(b) Writing formula:
   (i) $Ag(NH_3)_2^+$
   (ii) $Ni(CN)_4^{2-}$
   (iii) $Zn(NH_3)_4^{2+}$
   (iv) $Co(H_2O)_6^{2+}$
   (v) $Fe(CN)_6^{4-}$

Test on Chapter 8 – (option 5) The Chemistry of Art

1. [9 marks]
Chemicals can be used in many ways to attract people's attention by providing bright colours. Two examples of this are the following:
   - Illuminated signs, where electricity is passed through neon gas in a sealed low pressure tube to provide a red glow.
   - The painting of the kerbing on roadsides with bright yellow lines to indicate areas of no parking for cars. The yellow colour is due to the pigment zinc chromate ($ZnCrO_4$) in the paint.

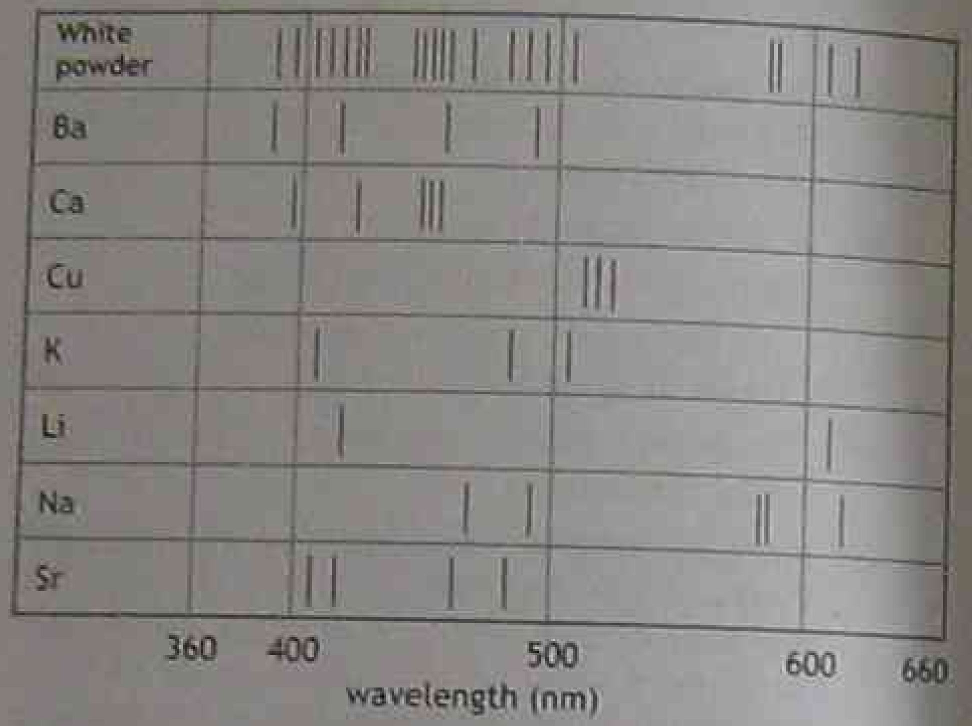
   (a) Which of the chemicals, neon gas or zinc chromate, produce their visual effect by generating
      (i) an emission spectrum?
      (ii) an absorption spectrum?

   (b) Use the two examples to explain the difference between an emission spectrum and an absorption spectrum.

   (c) The transition metal chromium can occur in several oxidation states.
      (i) Write down the oxidation states of chromium in each of the following ions:
      CrO_4^{2-} chromate ion
      $Cr_2O_7^{2-}$ dichromate ion
      Cr^{3+} chromium ion
      (ii) Which of the above ion(s) would act as oxidising agent(s)?
      (iii) Write down electronic configurations in terms of subshells for the metals chromium and calcium.
      (iv) Use these electronic configurations to explain the green colour of $CrCl_3$ when $CaCl_2$ is colourless (white, and the ability of chromium to show several oxidation states whereas calcium has a valency of +2 only.

2. [4 marks]
   (a) Draw the electron configuration for the element iron (atomic no. 26).
   (b) To which group of the Periodic Table does iron belong?
   (c) Write the names and chemical formulae for two ionic chlorides of iron.

3. [8 marks]
After a fireworks display at Darling Harbour in Sydney, a quantity of white powder was left over and known to contain some of the chlorides of the elements used. In the diagram below, spectroscopic lines of all the elements used in the fireworks are shown. The emission spectrum of the white powder is also shown.
   (a) Identify which salts were present in the white powder residue.
   (b) State the colours which those salts would produce.
   (c) Explain a simple laboratory experiment which you could have carried out to determine the colours of the chlorides of single elements.
   (d) Explain why each element has its own unique set of spectroscopic emission lines.
   (e) Outline the contribution which Bohr made to the understanding of the significance of these lines.



4. [4 marks]
From prehistoric times humans have been fascinated by colour.
   (a) Name a coloured mineral used by the Australian Aborigines in ceremonial art.
   (b) State the colour of the mineral, its chemical composition and explain the chemical basis for the colour.
   (c) Many cosmetics used in Egyptian and Roman times are no longer used. Name two such compounds and explain why their use was discontinued.

Answers for Test on Chapter 8 – (option 5) The Chemistry of Art

1. [9 marks]
   (a) (i) Neon gas (ii) Zinc chromate
   (b) An emission spectrum is the result of electrons returning from an excited state to a ground state following an input of energy. In this case, electricity is exciting electrons in neon atoms and, on their return to the ground state, energy equivalent to red light is emitted.
   An absorption spectrum is the result of absorption of energy by the electrons in atoms allowing them to become excited.
   In this case some of the energy of white light (in the violet region of the spectrum) is absorbed by the zinc chromate and the remainder is reflected where it appears as yellow to the human eye.
   (c) (i) Chromate ion (+6), dichromate ion (+6), chromium ion (+3).
      (ii) Chromate and dichromate ions.
      (iii) Cr – $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
      Ca – $1s^2 2s^2 2p^6 3s^2 3p^5 4s^2$
      (iv) Many transition elements, e.g. Cr, show several oxidation states because some or all of the electrons in the 3d orbital may be used with the valence state 4s electrons in compound formation. The transition metals form a variety of coloured ions because the electronic energy levels lie close enough together for electrons to move to higher energy levels by absorbing visible light. The colour of the compound is the complement of the colour absorbed, e.g. $CrCl_3$
      In the case of calcium, which is not a transition element and has no 3d electrons, only the two 4s electrons which are lost in the formation of the Ca^{2+} ion. The compounds of calcium are white, since the wavelength in the visible region is insufficient to excite the electrons to higher energy levels.

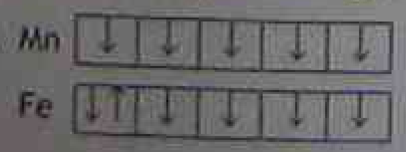
2. [4 marks]
   (a) $1s^2 2s^2 sp^6 3s^2 3p^6 4s^2$
   (b) The first group – transition series.
   (c) Iron II chloride $FeCl_2$
   Iron III choride $FeCl_3$

3. [8 marks]
   (a) By matching the line spectra for the elements with that of the white powder, the salts present are $BaCl_2$, $CaCl_2$, KCl, LiCl, NaCl and $SrCl_2$.
   (b) $BaCl_2$ – apple green; $CaCl_2$ – brick red; KCl – lilac; LiCl – crimson; NaCl – yellow; $SrCl_2$ – scarlet
   (c) See Activity 8.1. Use a loop of platinum wire, cleaned by dipping it in conc. HCl and then in the non-luminous Bunsen flame until no colour shows. Each salt is then tested for colour in the flame. The wire is cleaned between samples.
   (d) Each element has its own unique electronic configuration. The emission spectrum of each element occurs as a result of electrons moving between the element's electronic levels. Each line corresponds to light of a particular wavelength. When the electrons fall back to their normal energies, they emit the excess energy as light photons of a particular frequency.
   (e) Bohr suggested that electrons in atoms can only exist in stable orbits. Light is emitted when an electron in an allowed high energy (excited) orbital falls back to a low energy (ground state) orbital. Light is emitted as single quantum or photon of light.

4. [4 marks]
   (a) Red ochre powder.
   (b) Colour is red. $Fe_2O_3H_2O$: red iron oxidehaematite. The colour is due to the presence of the transition metal iron in the compound. The abridged electronic structure of iron is $[Ar]3d^6 4s^2$. In the unfilled 3d shell, the electrons can move to higher energy levels by absorbing visible light. The energy needed to raise the 3d electrons to higher energy levels it he same as that of green light. This is absorbed from the white light and the emitted light appears red to the human eye.
   (c) Many cosmetics used in earlier times were extremely toxic. Examples are as follows:
   Cinnabar (HgS) – This red-coloured compound of mercury was used to brighten the lips.
   Orpiment (As_2S_3) – This yellow-coloured pigment was used by Egyptians as eye make-up and contained arsenic.
   White lead [$2PbCO_3.Pb(OH)_2$] – was used for face make-up until the 19th century. Lead is extremely toxic if ingested.

Total 25 marks

Glossary

Absorption spectrum	The line spectrum of an element which is complementary to the emission spectra. It results from the selective absorption of characteristic wavelengths by an element when white light is passed through the vapour of the element at a temperature too low to excite the electrons.
Atomic orbital	A region in space where a pair of electrons is most likely to be found.
Aufbau order	A means of illustrating the order in which orbitals are filled.
Canopic jars	Jars in which viscera are placed during mummification.
Chelating agents or polydentate ligands	They have two or more donor atoms which can simultaneously coordinate to a metal ion, e.g. ethylenediamine.
Complex ion	A charged species where ligands are bound to a central metal ion (or atom), e.g. $Cu(NH_3)_4^{2+}$.
Coordination compound	A compound in which a metal atom is bonded to other species by coordinate covalent bonds.
Egg tempera paint	The wet pigment bound in the medium of a whole egg or egg yolk. As protein in the egg hardens, a tough skin is formed and the colours are given sheen.
Electromagnetic spectrum	The range of wavelengths of energy radiated by electromagnetic waves and extending from gamma rays to radio waves.
Electronegativity	The relative power of an atom in a covalent bond to attract electrons to itself.
Emission spectra	The result of electrons returning from an excited state to the ground state following a spectrum of radiation emitted by a substance.
Excited state	The state of an atom that has some electrons in a state of higher energy than the ground state owing to the absorption of energy.
Face blanche	A cosmetic used to lighten face colour.
FIRS	Frustrated internal reflectance spectroscopy.
Fresco	Painting done on layers of plaster, which are built up on a dry wall. As the lime dries and the water evaporates, a hard crystalline surface is formed in which the colour is bound.
Ground state	The arrangement of electrons in an atom in its lowest energy condition, e.g. Na $1s^2 2s^2 2p^6 3s^1$
Hund's rule	When filling a subshell, the electrons occupy orbitals of equal energy one at a time before there is any pairing, e.g. 3d shell of Mn. 

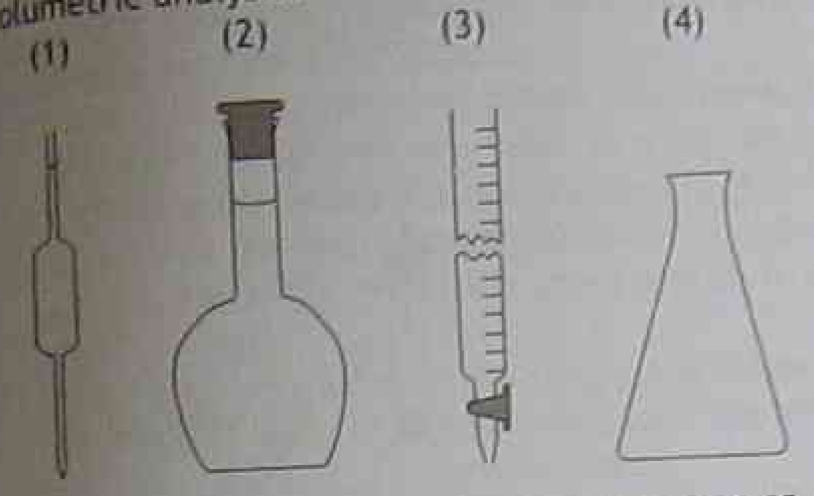
Infrared (IR) spectroscopy	Atoms in molecules are constantly vibrating. Their vibrational energy is quantised. Quanta of vibrational energy correspond to infrared radiation.
Ionisation energy	The first ionisation energy is the energy needed to remove completely the first electron from an atom in the gaseous state, e.g. $M(g) + \text{energy} \rightarrow M^+(g) + e^-$.
Isoelectronic ions	These ions have the same number and arrangement of electrons, e.g. O^{2-}, F^-, Na^+, Mg^{2+} and Al^{3+}.
Paramagnetism	A paramagnetic material which is attracted by a magnetic field. It is due to unpaired electrons in the atomic orbitals of the central ion (or atom) in a coordination species.
Pauli's exclusion principle	A rule that states that there can be no more than two electrons in any given orbital and that these must have opposite spins.
Photon	Emitted when an electron in an atom loses energy. When absorbed by the atom, the electron is excited.
Pigment	Solid material composed of fused particles which are insoluble in the vehicle.
Principle quantum number (n)	In the arrangement of electrons in atoms, the energy levels can be grouped in energy shells, each of which has a principle quantum number, n.
Reflective spectra	Radiation reflected from the surface of a sample such as a solid pigment in paint may be measured and compared with the radiation reflected from a non-absorbing sample. If the reflectance intensity is plotted as a function of wavelength, it gives a reflectance spectrum.
Sarcophagus	An outer stone coffin bearing sculpture or inscriptions.
Size	A glue used to seal wood prior to it being used for a painting.
Spectroscopy	A study of the way light interacts with matter.
Transition metals	Elements in which the d shell is being filled.
Ultraviolet (UV) spectroscopy	Ultraviolet light is passed through the sample. The near ultraviolet region ranges from 200–400 nm. A UV spectrum is a plot of absorption versus wavelength. Usually only the position of the absorbance maximum is reported. The UV radiation is absorbed by outer electrons of atoms in the substance being analysed which become excited to higher energy levels. It is therefore possible to obtain UV spectra of chemical substances.
Vehicle	Liquid part of a paint which carries the pigment.

9 — Sample HSC Examination Paper

Part A

Multiple choice questions [worth 1 mark each]

1. The following are sketches of glassware used for volumetric analysis:



A student prepared a standard solution of 0.05 M anhydrous sodium carbonate and used it to standardise an approximate 0.1 M solution of hydrochloric acid.
Which numbered pieces of equipment should be used after rinsing with distilled water without further rinsing with an appropriate solution?
(A) 1 and 3
(B) 2 and 4
(C) 1 only
(D) 3 only

2. Which of the following is the conjugate base of $H_2BO_3^-$?
(A) H_2BO_3
(B) H_3BO_3
(C) BO_3^{3-}
(D) HBO_3^{2-}

3. Several drops of bromine solution are added to separate test tubes containing samples of two different hydrocarbons marked P and Q. Solution P becomes colourless immediately on shaking the test tube. Test tube Q decolourises slowly on shaking. Intense UV light on solution Q is found to speed up the reaction.
Which of the following statements is correct?
(A) Hydrocarbon P is saturated and undergoes an addition reaction with bromine.
(B) Hydrocarbon Q is unsaturated and undergoes a substitution reaction.
(C) Moist blue litmus paper held over the mouth of test tube Q turns pink as hydrogen bromide is evolved.
(D) Moist blue litmus paper held over test tube P will turn pink as a gas is evolved.

4. A substance HIn which is a very weak acid acts as an acid-base indicator because of the equilibrium

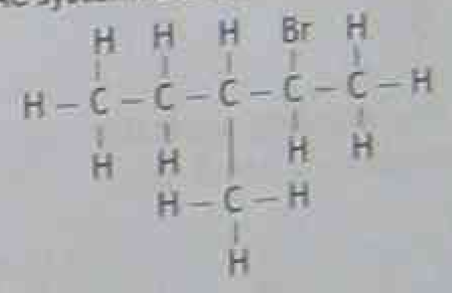
$$\underset{\text{red}}{HIn(aq)} \rightleftharpoons \underset{\text{colourless}}{H^+(aq)} + \underset{\text{blue}}{In^-(aq)}$$

The indicator would definitely be red in a 0.1 M solution of
(A) HCl
(B) NH_3
(C) NaCl
(D) NaOH

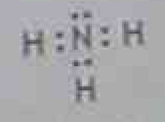
5. Which of the following structures is NOT an isomer of the other three?
(A) 2,2-dimethyl-1-butene
(B) 2,4-dimethyl-1-pentene
(C) 2-hexene
(D) 2-methyl-2-pentene

6. Consider these reactions involving a metal *M*:
(i) *M* reacts with a solution of silver nitrate causing a deposit of metallic silver to occur.
(ii) *M* does not react with a solution of zinc sulfate.
The correct way to list the metals M, Ag and Zn in order of decreasing strength as reducing agents is
(A) M, Ag, Zn
(B) Zn, M, Ag
(C) Ag, M, Zn
(D) Ag, Zn, M

7. The IUPAC systematic name for the structure below is



(A) 2-bromo-3-methyl-pentane
(B) 2-bromo-3-ethyl-butane
(C) 3-methyl-4-bromo-pentane
(D) 4-bromo-3-ethyl-butane

8. Which of the following chemical species contains a coordinate covalent bond?
(A) oxygen 
(B) ammonia 
(C) oxide ion 
(D) ozone 

9. The identity of X in the following nuclear reaction is

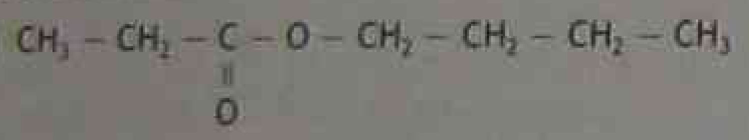
$$^{232}_{90}Th \rightarrow\ ^{228}_{88}Ra + X$$

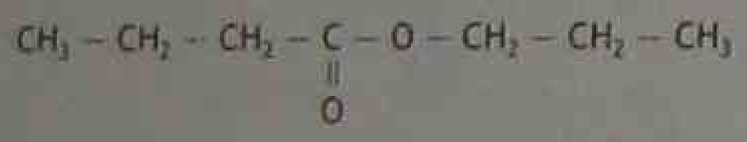
(A) $^{0}_{-1}e$
(B) $^{0}_{+1}e$
(C) $^{4}_{2}He$
(D) Radiation

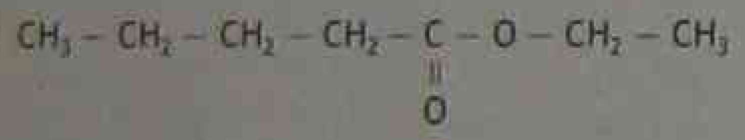
10. Which one of the following oxygen-containing species would you expect to be acidic?
(A) Aluminium oxide
(B) Ozone
(C) Magnesium oxide
(D) Phosphorus pentoxide

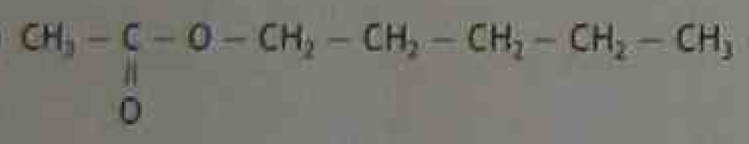
11. 10.0 mL of a 0.001 M solution of hydrochloric acid was added to a 1.00 L volumetric flask and the volume was made up to 1.00 L. The pH of the resultant solution would be
(A) 3
(B) 10^{-3}
(C) 5
(D) 10^{-5}

12. Which of the following is the structural formula for propyl butanoate?

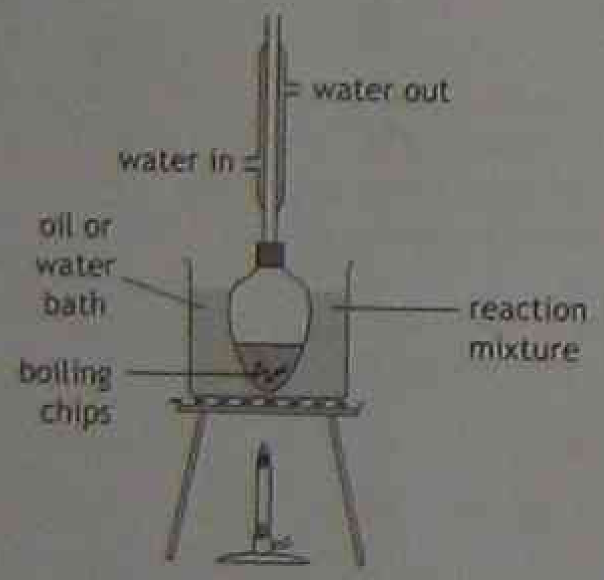
(A)

$CH_3-CH_2-\underset{\overset{\|}{O}}{C}-O-CH_2-CH_2-CH_2-CH_3$

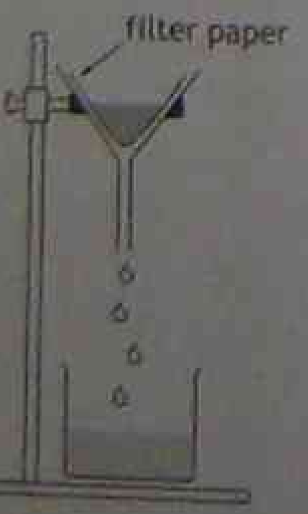
(B)

$CH_3-CH_2-CH_2-\underset{\overset{\|}{O}}{C}-O-CH_2-CH_2-CH_3$

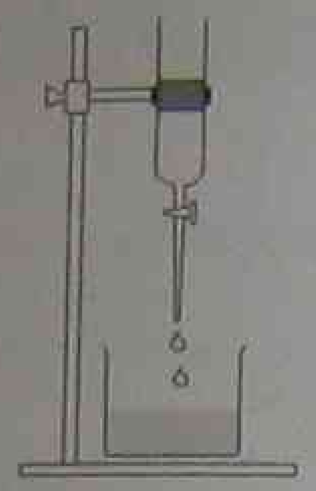
(C)

$CH_3-CH_2-CH_2-CH_2-\underset{\overset{\|}{O}}{C}-O-CH_2-CH_3$

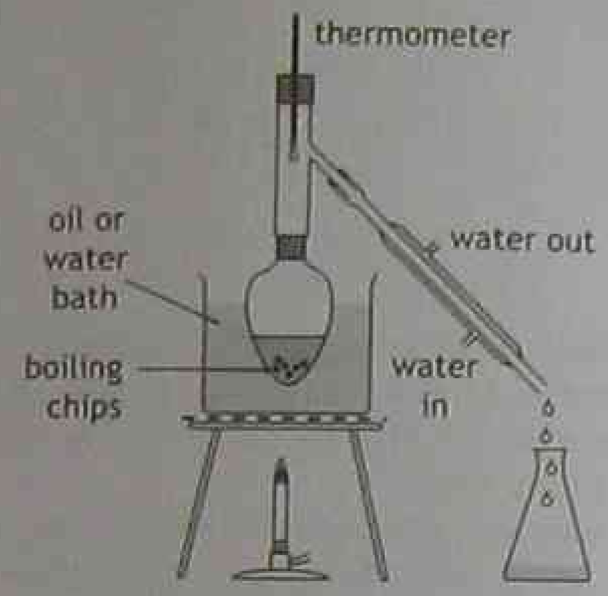
(D)

$CH_3-\underset{\overset{\|}{O}}{C}-O-CH_2-CH_2-CH_2-CH_2-CH_3$

13. Which of the following apparatus could be used to extract ethanol from wine?

(P)


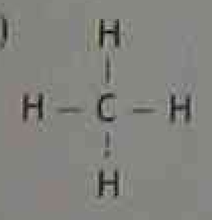
(Q)


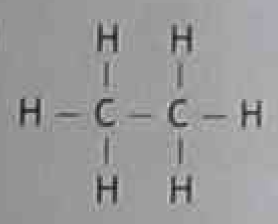
(R)


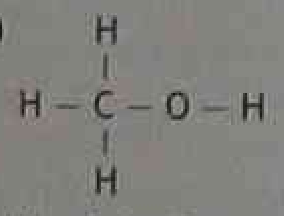
(S)


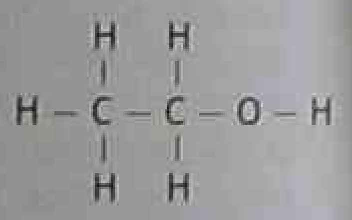
(A) P
(B) Q
(C) R
(D) S

14. Consider the polarities and intermolecular forces of the four compounds drawn below:

(M)

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

(N)

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

(O)

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

(P)

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

Which of the four compounds has the highest boiling point?
(A) M
(B) N
(C) O
(D) P

15. A radioactive 'cocktail' of iodine-131 taken in water is concentrated in the thyroid gland of the patient where it destroys cancerous tissue in the gland. The most likely reaction of this isotope is
(A) ${}^{131}_{53}I \rightarrow {}^{131}_{54}Xe + \beta$ particle
(B) ${}^{131}_{53}I \rightarrow {}^{127}_{52}Te + \alpha$ particle
(C) ${}^{131}_{53}I \rightarrow {}^{131}_{55}Cs + \gamma$ rays
(D) ${}^{131}_{53}I \rightarrow {}^{84}_{35}Br + {}^{40}_{18}Ar + 7$ neutrons

Part B

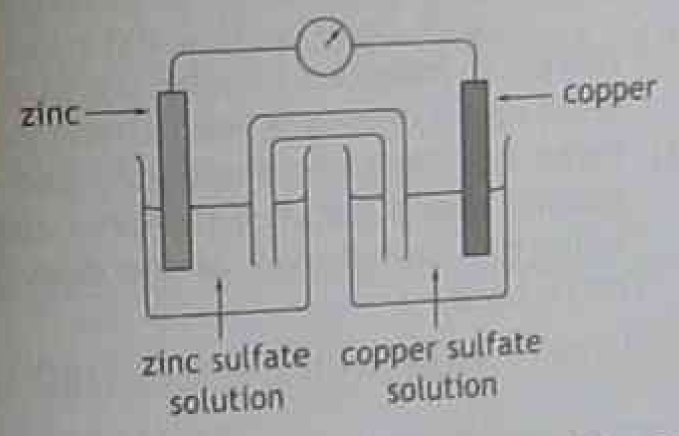
Extended Questions

16. [7 marks]
The instant cold packs used to treat sporting injuries often contain ammonium nitrate crystals and a sealed plastic water bag. When the bag is broken

$$NH_4NO_3(s) + \text{water} \rightarrow NH_4NO_3(aq)$$

(a) Is this reaction exothermic or endothermic? Briefly explain.
(b) When 0.86 g of ammonium nitrate was completely dissolved in 100 mL of water in a styrofoam container, the temperature dropped by 0.6°C. Given that the heat capacity for water is 4.18 kJ g^{-1} K^{-1}, calculate ΔH for the above process in kJ mol^{-1}.
(c) Draw and fully label an energy profile diagram for the dissolving of ammonium nitrate in water.

17. [7 marks]
The Daniell cell was one of the first galvanic cells to be developed. Use the diagram of the Daniell cell shown below to



(a) Write a schematic representation of the cell.
(b) State two changes that might be observed if a large current flowed for several hours.
(c) On the diagram show the direction of the flow of electrons in the external circuit.
(d) Give balanced half-equations for the reactions occurring at
  (i) the anode, and
  (ii) the cathode.
(e) If the salt bridge contained $KNO_3(aq)$, show the direction of flow of the positive ions on the diagram.

18. [5 marks]
(a) Explain briefly how gamma rays are produced in industrial gamma radiography.
(b) How are the tests carried out?
(c) State the benefits involved with its use in the detection of flaws in casts or welds.

19. [6 marks]
As part of a practical exam, a student was given four bottles labelled A, B, C and D and told that they contained hexane, hexene, hexanol and hexanoic acid. The student's test results are given in the following column:

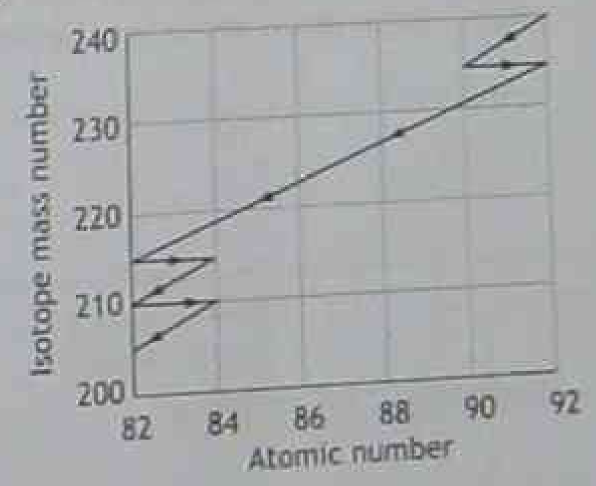
Sample	Boiling point (°C)	Na_2CO_3 (gas evolved)	$K_2Cr_2O_7$ (colour change)	Br_2 (stayed same?)
A	68.7	no	no	yes
B	157.1	no	orange → green	yes
C	63.5	no	orange → green	decolourised
D	164	yes	no	yes

(a) Use the result table to identify the substances, A, B, C and D. Briefly explain your reasoning.
(b) Explain the boiling point variations between the four substances.

20. [5 marks]
In a nuclear fission reactor, one possible reaction is:

$${}^{235}_{92}U + {}^{1}_{0}n \rightarrow {}^{137}_{56}X + {}^{95}Y + 3\,{}^{1}_{0}n$$

(a) Identify element X and and element Y.
(b) If there was a leak of nuclear material into the environment, which element – X or Y – would accumulate in the bones? Explain your answer.
(c) Give a brief account of two hazards in the nuclear industry and ways of overcoming these hazards.
(d) The decay of ${}^{238}U$ is shown below.



  (i) Name the final product.
  (ii) Write the equation for the production of radon-222.
  (iii) Give a reason why radon-222 is a health hazard.

21. [12 marks]
(a) In 1913, Haber was able to produce ammonia for Germany's World War I machine by using a viable economic process to obtain a 20% yield of ammonia from nitrogen and hydrogen gases. The equilibrium reaction was

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \Delta H = -92\text{ kJ}$$

The industrial process was not done under equilibrium conditions. Explain the modifications Haber used to obtain a 20% yield of ammonia.
(b) Draw a Lewis formula structure for
  (i) ammonia, and
  (ii) the ammonium ion
using the structures to illustrate the formation of a coordinate-covalent bond.

22. [6 marks]
Families of radioisotopes can be described as neutron-rich or neutron-deficient.
(a) How can the neutron-rich families be produced? State two methods.
(b) How can neutron-deficient families be produced? State two methods.
(c) Name the two types of equipment which can be used and state which equipment is used to produce which family.
(d) In nuclear medicine, a radioisotope can be administered to a patient for use as a diagnostic agent or for therapeutic purposes. In each case a different set of selection criteria will apply.
    (i) For which case should the radioisotope emit gamma and beta radiation?
    (ii) When, and for what reason, should gamma rays be emitted?
    (iii) Give an example of a radioisotope commonly used as a diagnostic agent.
    (iv) Give an example of a radioisotope commonly used as for therapeutic purposes.

23. [12 marks]
In analysing a water sample, it is necessary to measure temperature and pH when the sample is being collected, to measure the dissolved oxygen and the biological oxygen demand to determine water quality.
(a) How does temperature influence further test results?
(b) On warm sunny days, photosynthesis by algae can lead to higher than normal pH values in streams and rivers. This is due to a change in the equilibrium given in the equation below:

$$OH^- + CO_2 \xrightleftharpoons{H_2O} HCO_3^- \xrightleftharpoons{H_2O} H^+ + CO_3^{2-}$$

Explain the higher pH value in terms of equilibrium shift.
(c) Why is it important to carry out dissolved oxygen (DO) and biological oxygen demand (BOD) tests on water samples?
(d) The Winkler tritation method is often used in laboratories to determine the dissolved oxygen. One mole of O_2 is equivalent to 2 moles of I_2. The I_2 is then titrated using a standard sodium thiosulfate solution with a few drops of starch solution as the indicator (deep blue to colourless).

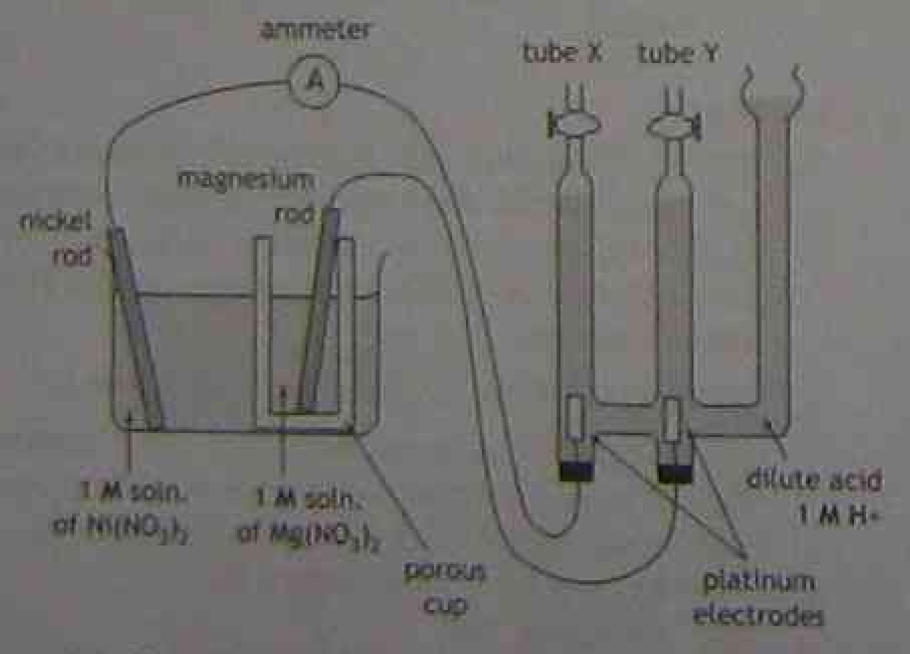
$$I_2 + 2\,Na_2S_2O_3 \rightarrow 2\,NaI + Na_2S_4O_6$$

A 500 mL sample of river water needed 9.6 mL of 0.100 M $Na_2S_2O_3$ to titrate the iodine which was formed.
Calculate:
    (i) the number of moles of I_2 formed, and
    (ii) the concentration of the oxygen in the river water in moles per litre and in mg L^{-1} (ppm).
(e) Why is it so important for plant life that the 'hole' in the ozone layer is at least contained?
(f) Name the class of compounds and give one specific example stating its name and formula which has caused most of the damage to the ozone layer.

Total 75 marks

Option 1 – Industrial Chemistry

1. [10 marks]
An electrochemical cell and an electrolytic cell were constructed and connected as shown in the following diagram:



(a) Reactions which occur in the electrochemical cell cause a voltage difference between the copper and magnesium rods.
    (i) Write equations for the half-reactions in the electrochemical cell.
    (ii) Identify the oxidation half-reaction in the electrochemical cell.
(b) Write equations for the half-reactions which occur in the electrolytic cell.
(c) Calculate the voltage of the electrochemical cell and show that this is sufficient to cause reaction in the electrolytic cell.
(d) Which gas will collect in tube X of the electrolytic cell?

Three electrolysis methods are currently used to extract sodium hydroxide:
- the mercury process, where titanium is used as the anode and mercury flowing along the bottom of the cell is the cathode;
- the diaphragm process, where the products of electrolysis are kept apart by an asbestos diaphragm; and
- the membrane process which has a titanium anode and a nickel cathode. The anode and cathode compartments are separated by an ion exchange membrane.

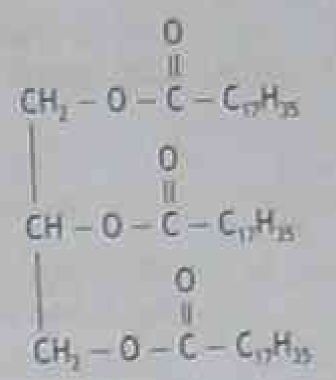
(e) Explain how the ion exchange membrane works.
(f) Why (on safety grounds) is the membrane method likely to replace the other two?

2. [7 marks]
The following equation describes the conversion of sulfur dioxide to sulfur trioxide, an important reaction in the commercial preparation of sulfuric acid by the contact process.

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g) \quad \Delta H = -197\ kJ$$

(a) Is this an exothermic or an endothermic reaction? Give a reason for your choice.
(b) If the above reaction was considered to be an equilibrium system, how would the position of the equilibrium system be affected by an increase in temperature?
(c) Why is the process run commercially at a temperature of 450° C?
(d) Would an increase in pressure raise or lower the rate of formation of sulfur trioxide? Give a reason for your answer.
(e) Give one method (other than temperature or pressure changes) that could be used to increase the rate of production of sulfur trioxide.

3. [5 marks]
The molecule A represented below is an example of a saturated triglyceride molecule, glyceryl tristearate.



$$\begin{array}{l} CH_2-O-\overset{\overset{O}{\|}}{C}-C_{17}H_{35}\\ |\\ CH-O-\overset{\overset{O}{\|}}{C}-C_{17}H_{35}\\ |\\ CH_2-O-\overset{\overset{O}{\|}}{C}-C_{17}H_{35} \end{array}$$

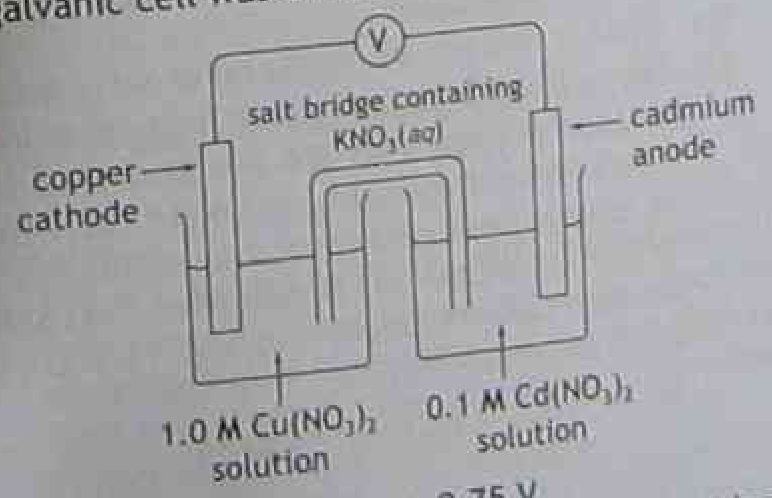
(a) How would you expect the formula of an unsaturated triglyceride to differ from A?
(b) What difference does this make to the physical properties of the compound?
(c) Write an equation for the alkaline hydrolysis of A using hot, concentrated sodium hydroxide. Include in the equation the structural formulae and names of any molecules formed.
(d) Explain briefly why soaps form a scum with hard water but synthetic detergents do not.

4. [3 marks]
(a) What chemical compound is produced by the Solvay process?
(b) State the substances used in this continuous process.
(c) Why should there be continual monitoring of air quality during the Solvay process?

Total 25 marks

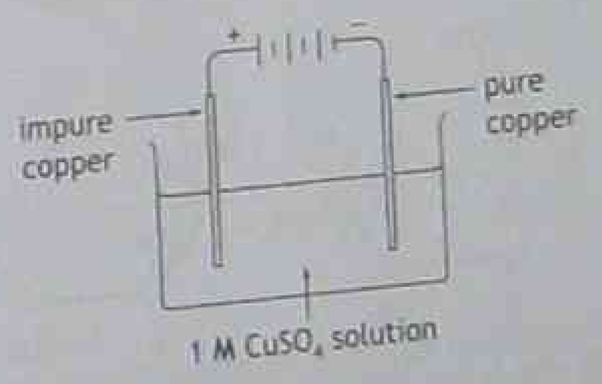
Test on Option 2 – Shipwrecks, Corrosion and Conservation

1. [10 marks]
A galvanic cell was constructed as shown below:



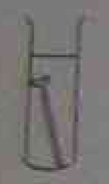
The voltmeter reading was 0.75 V.
(a) Briefly explain the purpose of the salt bridge.
(b) Write a net ionic equation to represent the reaction which occurs in the cell when the voltmeter is replaced by a conductor.
(c) What do you understand by the term 'standard reduction potential'?
(d) Calculate the standard reduction potential (E°) for the anode half cell.

For the electrolysis cell shown in the following diagram a voltage is applied across the wires in the direction shown.



(e) Name the anode and cathode.
(f) Write the anode and cathode equations.

2. [12 marks]
The first stage in the rusting of iron is the formation of iron (II) hydroxide. To investigate this process a student placed a clean iron nail in each of four test tubes (A, B, C and D) as shown in the diagram. The nails in test tubes A and D were the only ones to show rust after three days.
(a) The oxidation process in test tube A is $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$. Write an ion-electron half-equation to show the reduction process in A.
(b) Briefly explain why the nail in test tube B did not rust.
(c) Briefly explain why the nail in test tube C did not rust.
(d) Briefly explain why the nail in test tube D did rust.



A Nail immersed in tap water.
Tube open to the air.

B Nail immersed in boiled water.
Tube sealed off from the air.

C Zinc wire around nail.
Nail immersed in tap water.
Tube open to the air.

D Copper wire around nail.
Nail immersed in tap water.
Tube open to the air.

(e) What do you understand by the term 'corrosion'?

(f) Why is the active metal aluminium more resistant to corrosion than iron, which is lower in the activity series?

(g) Steel is an alloy. Explain the term 'alloy'. Give an example of a copper-based alloy.

(h) Stainless steels are alloys which contain about 18% of chromium. Why do they resist corrosion so much better than mild steels?

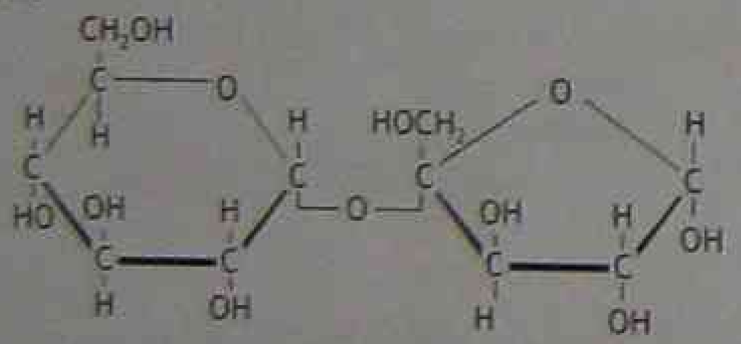
(i) At great depths, such as in the hull of the *Titanic*, reactions other than electrochemical reactions cause more rapid decomposition than expected. Briefly state how this is brought about.

3. [3 marks]
Artefacts from long-submerged wrecks will be saturated with dissolved chlorides and sulfates. To achieve long-term stabilisation of metals, it is necessary to remove salts, especially chlorides. This can rarely be done by simply washing with water. Briefly describe two processes that are used when stabilising metals.

Total 25 marks

Test on Option 3 – The Biochemistry of Movement

1. [8 marks]
The structure of the disaccharide sucrose is shown below:



(a) In the body, sucrose is broken down into two monosaccharides, glucose and fructose. Sketch the monosaccharide glucose and name this type of reaction.

(b) Monosaccharides may be broken down further by respiration in body cells. What are the products of respiration?

(c) In the event of the body's energy needs having been met, what happens to excess monosaccharides in the body?

(d) Describe a simple chemical test which you could carry out to show that a glucose solution was present.

(e) Write a balanced equation for the combustion of glucose.

(f) The oxidation of glucose yields 2800 kJ mol^{-1}. How is the body able to control the release of energy so that the whole oxidation process takes place at a satisfactory rate at normal body temperature?

(g) An Olympic marathon runner uses energy at the rate of 70 kJ per minute. Calculate the mass of glucose needed to supply the energy for him to run for four hours.

(h) Explain the role of ATP in cellular respiration.

2. [5 marks]

(a) Write a balanced equation for the formation of glyceryl tristearate.

(b) The decomposition of fatty acids occurs by oxidative removal of 2-carbon fragments. Identify the 2-C fragments.

(c) What is the site of oxidation of fatty acids?

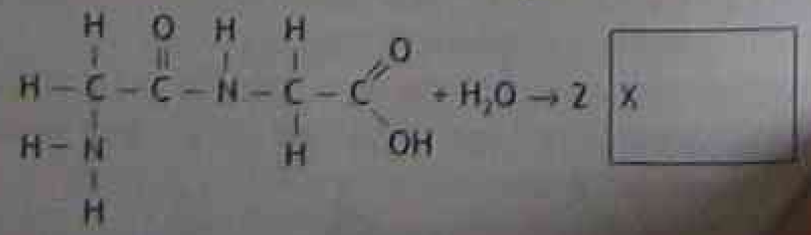
(d) Fats and carbohydrates can both be oxidised to release energy. Fats are the preferred fuel for heart and kidney cells. Calculate the difference in energy produced from the oxidation of 100 g of the fat tripalmitin (molar mass 807) and 100 g of the carbohydrate glucose ($C_6H_{12}O_6$). The relevant equations are:

$$\underset{\text{tripalmitin}}{(C_{15}H_{31}COO)_3C_3H_5(s)} + {}^{145}/{}_{2}O_2(g) \rightarrow 51CO_2(g) + 49H_2O(l) \qquad \Delta H = -31400\ \text{kJ mol}^{-1}$$

$$\underset{\text{glucose}}{C_6H_{12}O_6(s)} + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l) \qquad \Delta H = -2800\ \text{kJ mol}^{-1}$$

3. [7 marks]

(a) Draw a graphic constitutional formula and name the product in box X in the equation below.

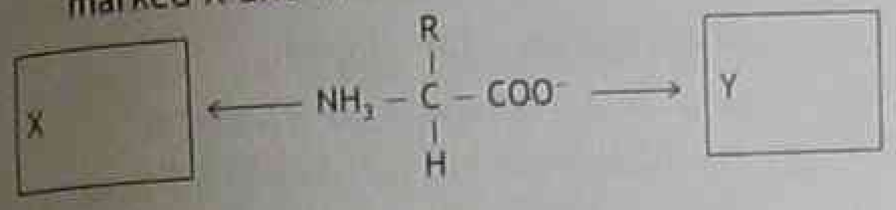


$$H_2N\text{–}CH_2\text{–}C(=O)\text{–}NH\text{–}CH_2\text{–}COOH + H_2O \rightarrow 2\ \boxed{X}$$

(b) What is the name given to this type of reaction?

(c) Proteins consist of various combinations of amino acids. Briefly explain three types of linkages found in proteins of relatively low molecular mass.

(d) The amphoteric character of amino acids leads to their ionic behaviour. Draw the appropriate structures which illustrate this in the boxes marked X and Y.



$$\boxed{X} \longleftarrow NH_2\text{–}\underset{H}{\overset{R}{C}}\text{–}COO^- \longrightarrow \boxed{Y}$$

(e) (i) What are enzymes?
(ii) To what large group of substances do they belong?
(iii) The diagrams below represent a model for enzyme action. What would be a suitable heading for these diagrams?

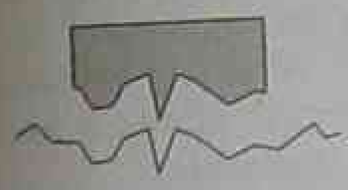


figure 1

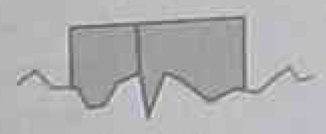


figure 2

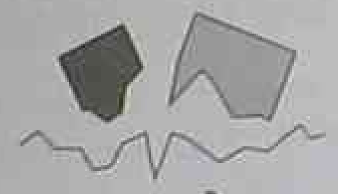


figure 3

(f) Label the substrate and the enzyme active site on the diagrams and write a short comment underneath each of the diagrams which will explain what is happening during the process.

4. [5 marks]

(a) Look at the reaction sequences I and II shown below:

(I)
glucose
↓
pyruvate
↓
carbon dioxide and water

(II)
glucose
↓
pyruvate
↓
lactic acid

State the type of respiration occurring in
(i) sequence I, and
(ii) sequence II.
(iii) for a runner competing in a half-marathon, what would be one disadvantage and one advantage during respiration as shown in sequence II?
(iv) Name the specific substances which are needed for both reaction sequences I and II.

(b) The following equation is a summary of 10 individual steps that occur in all organisms which utilise glucose as a source of energy:

$$C_6H_{12}O_6 + 2ADP + 2NAD \rightarrow 2CH_3COCOOH + 2ATP + 2NADH_2$$

(i) What name is given to this process?
(ii) In what part of the cell does it occur?
(iii) Name the 3-carbon compound formed in the reaction above.
(iv) Under what conditions will $NADH_2$ act as a source of energy?

Total 25 marks

Test on Option 4 – Forensic Chemistry

1. [6 marks]

(a) Specific experiments usually involve observing how something reacts under different conditions. In designing an experiment, it is best that only ONE factor is allowed to vary, whereas other factors are kept constant.
After hard exercise, traces of hydrogen peroxide (H_2O_2) can be found in liver tissue of athletes. The body contains a substance called catalase which hastens the decomposition of these traces of hydrogen peroxide into substances which are harmless to the body (water and oxygen).
(i) Write a balanced chemical equation for the reaction that would occur.
(ii) Describe how you would carry out an experiment in the laboratory that would determine the optimum temperature conditions for catalase activity using H_2O_2 (3 volume).

2. [6 marks]
Paper chromatography and high performance liquid chromatography (HPLC) have many things in common as analytical techniques.

(a) What is the major purpose of any form of chromatography?

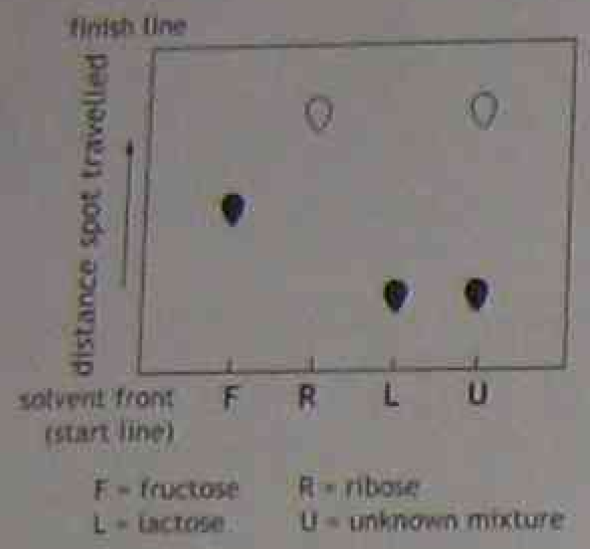
(b) Explain the chemical processes that allow this major purposes to be achieved in
(i) paper chromatography and
(ii) HPLC.

(c) How is qualitative information acquired in
(i) paper chromatography
(ii) HPLC?

(d) Explain how quantitative information can be obtained using an HPLC.

3. [5 marks]

(a) A student carried out a chromatography experiment using three solutions of fructose, ribose and lactose as standards. The student was then given an unknown solution mixture to identify. After the solvent movement and treatment with the developing solutions, the following results were obtained.



(i) What sugars were present in the unknown solution?
(ii) Which sugar moved the fastest?
(b) To which group of carbohydrates do cellulose, glycogen and starch belong?
(c) A student carried out the tests listed in the table below. Complete the table by adding the results you would expect.

Test	Cellulose	Glycogen	Starch
Solubility in cold water			
Solubility in hot water			
Addition of Benedict's solution			
Addition of iodine solution			

4. [8 marks]
Glycine is an amino acid which dissolves readily in water. In aqueous solution at a pH of 7, glycine is in the form $^+NH_3CH_2COO^-$.
(a) In a solution of high pH, draw the form of glycine.
(b) In a solution of low pH, draw the form of glycine.
(c) Give the structure of a possible product (other than water) of the condensation reaction between a molecule of glycine and a molecule of alanine

$NH_2 - \underset{\underset{CH_3}{|}}{CH} - COOH$.

(d) Electrophoresis can be used in the separation of protein molecules.
(i) Briefly state how the molecules are separated.
(ii) Define the term 'isoelectric point'.
(iii) At a low pH what will be the net charge on the protein? Will the molecule move towards the positive electrode (anode) or towards the negative electrode (cathode)?
(iv) At a pH of 8.6, what will be the charge on the serum protein albumin and to what electrode will it migrate?
(v) What do the letters 'DNA' stand for?
(vi) State two major uses for DNA testing.

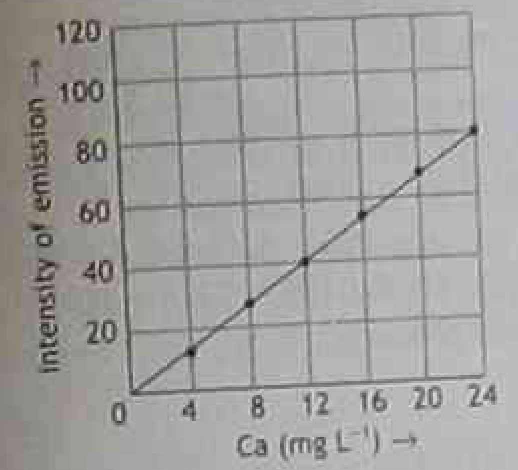
Total 25 marks

Test on Option 5 – The Chemistry of Art

1. [7 marks]
Potassium and cobalt are elements in period IV of the Periodic Table.
(a) Write out the ground state electronic configurations for (i) potassium and (ii) cobalt.
(b) Explain why the melting temperature of cobalt (1495°C) is much higher than that of potassium (64°C).
(c) Transition elements form many coordination compounds. Cobalt forms dichlorotetraamminecobalt (III) chloride $CoCl_2(NH_3)_4Cl$.
(i) Write the formula for the complex ion in the above compound.
(ii) What is the oxidation state of cobalt in the complex ion?
(iii) Draw a diagram representing the structure of the complex ion.
(iv) Use the diagram to explain the term 'ligand'.
(v) What type of bonding exists between the cobalt ion and the ammonia molecules?

2. [11 marks]
Yellow is a bright colour which readily attracts people's attention. Examples include:
- yellow sodium vapour street lights,
- yellow lines daubed on roads with paint containing yellow zinc chromate ($ZnCrO_4$), and
- yellow ochre used by Aborigines for ceremonial body painting.

(a) Which example(s) produce their visual effect by generating:
(i) an emission spectra, and
(ii) absorption spectrum?
(iii) Use the examples to explain how emission spectra and absorption spectra differ.
(iv) What is the valency of chromium in zinc chromate?
(v) Write out the ground state electronic configuration for chromium.
(vi) Name a white pigment containing a transition metal which is not discoloured as earlier lead-based paints were.
(b) One method of determining cations in water is to spray water into a flame and to measure the intensity of light from a certain wavelength emitted from the flame (Ca^{2+} at 422.4 nm) using a flame photometer.
(i) What colour would be emitted from a calcium flame?
(ii) On the graph plotted below, show the intensity of emission at 52 against concentration of calcium in mg L^{-1}. Calculate the molarity of the calcium solution.



(iii) What is the cause of emission lines in the flame?
(iv) Why do different elements (ions) have different line spectra at different wavelengths?

3. [7 marks]
1.50 g of $Fe_2SO_4.7H_2O$ was dissolved in 50.0 mL of an acidic solution. This sample was titrated using a 0.02 M solution of potassium permanganate and required a 50.0 mL for complete oxidation.
(a) (i) Write a balanced half-equation for the oxidation of Fe^{2+}.
(ii) Write a balanced half-equation for the reduction of MnO_4^-.
(iii) Write a balanced ionic equation for the reaction.
(iv) Determine the percentage purity of the sample of $FeSO_4.7H_2O$.
(b) G.N. Lewis proposed that an acid be defined as an electron-pair acceptor and a base as an electron pair donor. Consider the Lewis acid-base reaction:

$$BF_3(g) + F^-(aq) \rightarrow BF_4^-(aq)$$

(i) Name the Lewis acid present.
(ii) Everything that is a base in the Brønsted-Lowry sense (proton acceptor) is also a base in the Lewis sense (an electron pair donor). How does the Brønsted-Lowry definition of an acid restrict the number of acids compared with the Lewis theory?

Total 25 marks

Answers to Sample HSC Examination Paper

Part A

Multiple choice questions (each worth 1 mark)

1. B	2. D	3. C	4. A	5. B
6. B	7. A	8. D	9. C	10. D
11. C	12.B	13.D	14.D	15.A

Explanations for Multiple Choice Questions

1. Figure 2 is a volumetric flask and Figure 4 is a conical flask. Both are 'receiving' vessels and contain a certain number of moles. They can be rinsed with distilled water before use. Figure 1 is a pipette and Figure 3 is a burette. Both are 'transfer' vessels and must be rinsed with the solution which will fill them. Answer is (B).

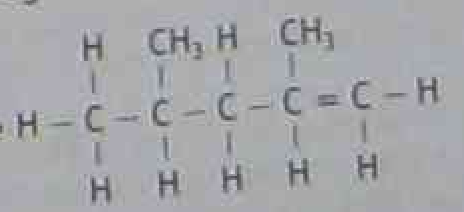
2. $\underset{\text{acid}}{H_2BO_3^-} \rightarrow H^+ + \underset{\text{conjugate base}}{HBO_3^{2-}}$ Answer is (D).

3. Unsaturated hydrocarbons undergo addition reactions so (A) is not correct.
Saturated hydrocarbons undergo substitution reactions, so (B) is not correct.
Q is saturated and undergoes a substitution reaction,
e.g. $CH_3CH_3 + Br_2 \rightarrow CH_3CH_2Br + HBr$
Correct answer is (C).
P is unsaturated so no gas is evolved,
e.g. $H_2C{=}CH_2 + Br_2 \rightarrow CH_2Br\ CH_2Br$
Incorrect answer is (D).

4. If the indicator is red, substance must be acid. HCl (A) is correct.

5. Isomers in this question must have the same number of carbon and hydrogen atoms.

(B) has a structure



$$\begin{array}{ccccccccccccc} & & H & & CH_3 & & H & & CH_3 & & & & \\ & & | & & | & & | & & | & & & & \\ H & - & C & - & C & - & C & - & C & = & C & - & H \\ & & | & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & H & & \end{array}$$

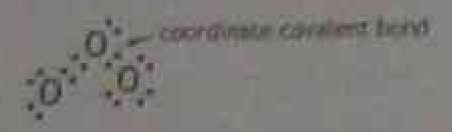
7 carbon and 14 hydrogen atoms.
(A), (C) and (D) each have 6 carbon and 12 hydrogen atoms.

6. M replaces silver from a solution of its salt so is above Ag in the activity series of metals.
M does not replace Zn from a solution of its salt so is

below Zn in the activity series.
By referring to the Table of Standard Potentials supplied with the test information, it can be seen that Zn is higher in the activity series than Ag, so in order of decreasing strength and reduction, the order is Zn, M, Ag.
(B) is the correct answer.

7. Five carbons in a chain indicate that the surname is pentane. Br is on the second and the $-CH_3$ group is on the third carbon atom so name is 2-bromo-3-methyl-pentane.
Correct answer is (A).

8. For a coordinate covalent bond to form, one pair of electrons is donated by one atom to complete the octet.
(D) is the correct answer.



9. Correct answer is (C).
232 − 228 = 4 (mass no. for X)
90 − 88 = 2 (atomic no. for X)
${}^{4}_{2}X = {}^{4}_{2}He$

10. Correct answer is (D). Phosphorous pentoxide is the oxide of a non-metal.

11.
$$M_1V_1 = M_2V_2$$
$$\frac{10}{1000} \times 0.001 = M_2 \times 1$$
$$\text{so } M_2 = 0.00001 = 10^{-5}$$
$$pH = -\log_{10}[H^+]$$
$$[H^+] = 10^{-5}, \text{ therefore } pH = 5$$

Answer is (C).

12. $\underset{\text{butanoic acid}}{CH_3CH_2CH_2COOH} + \underset{\text{1-propanol}}{CH_3CH_2CH_2OH} \rightarrow$
propyl butanoate + H_2O
So ester must be $CH_3CH_2CH_2COOCH_2CH_2CH_3$.
Correct answer is (B).

13. Distillation apparatus is 5, so correct answer is (D).

14. Alkanols will have higher boiling points than corresponding alkanes due to hydrogen bonding. As we ascend the series, the boiling points increase so P will have the highest boiling point.
Correct answer is (D).

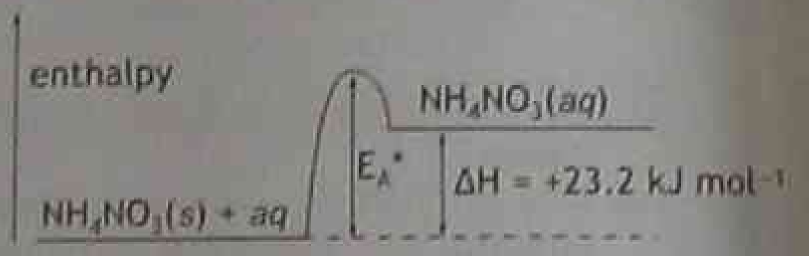
15. The correct answer is (A) which will emit beta radiation to destroy the cancerous tumour.

(B) is incorrect since an alpha particle is ${}^{4}_{2}He$, so element would be ${}^{127}_{51}Sb$.
(C) is incorrect since gamma rays easily escape the body and are used for diagnostic purposes.
(D) is incorrect since it is the 'splitting' of ${}^{131}_{53}I$.

Part B

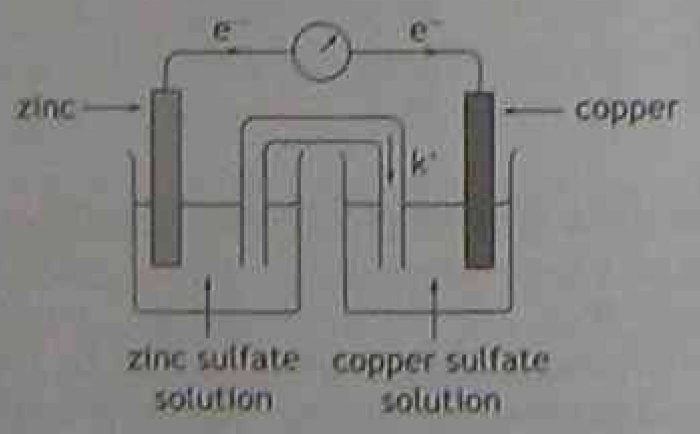
Extended questions

16. [7 marks]
   (a) Endothermic; the temperature of the surroundings decreases.
   (b) Molar mass of $NH_4NO_3 = (2 \times 14) + 4 + (3 \times 16)$
   $= 80.0 \text{ g mol}^{-1}$
   Moles of $NH_4NO_3 = 0.86 \div 80 = 0.0108$ mole
   Energy lost $= \text{mass}_{H_2O} \times SH_{H_2O} \times \Delta T$
   $= 100 \times 4.18 \times 0.6 = 250.8 \text{ J}$
   $\Delta H = 250.8 \div 0.0108 = 23.2 \times 10^3 \text{ J}$
   $\Delta H = +23.2 \text{ kJ mol}^{-1}$
   (c)



E_A^* = activation energy

17. [7 marks]
   (a) $Zn/Zn^{2+} // Cu^{2+}/Cu$
   (b) (i) The zinc anode would become pitted as it partly dissolved.
   (ii) The blue colour of the copper sulfate solution would fade.
   (c) See diagram in (e).
   (d) (i) $Zn \rightarrow Zn^{2+} + 2e^-$
   (ii) $Cu^{2+} + 2e^- \rightarrow Cu$
   (e) see next page



18. [5 marks]
   (a) The gamma rays are produced by a small pellet of radioactive material, e.g. iridium-192 or cobalt-60.
   (b) The pellet is placed in a sealed titanium capsule to prevent leakage of dangerous gamma rays. The capsule is placed on one side of the object being screened and photographic film is placed on the other side.
   (c) Gamma rays, like X-rays, show flaws in metal castings or welded joints. The main benefit is the easiness of transportation and that no power supply is needed. This makes gamma radiography especially useful in remote areas, e.g. to check welds in natural gas or oil pipelines.

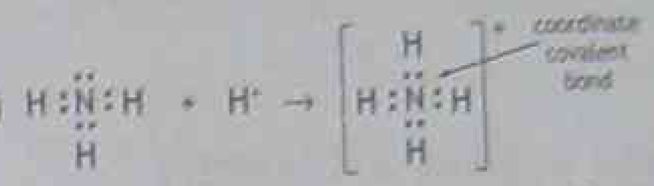
19. [6 marks]
   (a) D – hexanoic acid, since a gas (CO_2) is evolved with Na_2CO_3 solution.
   C – hexene, since both $K_2Cr_2O_7$ and Br_2 water were decolourised due to the presence of a double bond.
   B – hexanol, since acidified $K_2Cr_2O_7$ was reduced (orange–green) as hexanol was oxidised to hexanoic acid.
   A – must be an alkane which was unreactive.
   (b) Alkanols and alkanoic acids have higher boiling points than expected due to hydrogen bonding occurring. Alkanes and alkenes are non-polar molecules with only weak dispersion forces between molecules so boiling points are lower.

20. [5 marks]
   (a) Element X is barium. element Y has atomic number 36 and is krypton.
   (b) Element X, barium, should accumulate in the bones as it is in the same group as calcium in the Periodic Table.
   (c) Answers could include any two of:
   - Regulation of neutrons produced. Control rods are used to absorb neutrons.
   - Emission of radiation. Shielding is required.
   - Escape of radioisotopes. Operate at lower temperatures and with efficient practices.
   - Failure of cooling systems. Continuous monitoring should prevent this.
   - Radioactive wastes produced. Adequate storage facilities required.

   (d) (i) Lead ${}^{206}Pb$
   (ii) ${}^{222}_{88}Ra \rightarrow {}^{227}_{86}Rn + {}^{4}_{2}He$
   (iii) Radon is a radioactive gas which, if inhaled, can cause damage to chromosomes.

21. [12 marks]
   (a) The equilibrium reaction involved gases. Although the forward reaction was exothermic, under normal atmospheric conditions the reaction would be extremely slow. According to Le Chatelier's Principle, an increase in pressure would favour NH_3 formation.
   A catalyst would be used to lower the activation energy and aid the breaking of N_2 and H_2 bonds.
   The Haber industrial process was not done under equilibrium conditions.
   - The temperature used was 400–500°C (moderately high) since all reactions proceed more rapidly when the molecules have more energy.
   - Optimum gas ratios were used and gases entered the reactor in an N_2:H_2 ratio of 1:3.
   - The pressure was increased to 250 atmospheres. Higher pressure would produce a higher yield but would not be economically viable.
   - Many catalysts were tried out and a porous iron oxide catalyst was selected over more expensive, though better, catalysts such as osmium.
   - To promote the forward reaction, the product liquefied ammonia was drawn off before the system reached equilibrium.

   (b)



   For a coordinate covalent bond to form, both electrons are donated by the same atom, in this case, the nitrogen atom.

22. [6 marks]
   (a) (i) By adding a neutron to the nucleus.
   (ii) By removing a proton from the nucleus.
   (b) (i) By removing a neutron from the nucleus.
   (ii) By adding a proton to the nucleus.
   (c) Almost always a nuclear reactor is used to produce neutron-rich families and a cyclotron is used to produce neutron-deficient families.
   (d) (i) In the case of therapeutic nuclear medicine where the radioisotope emits particulate (α, β^-) radiation of sufficient energy to penetrate to all parts of the lesion.
   (ii) In both treatments so that assessment can occur.
   (iii) Reactor-produced technetium-99*m* (${}^{99m}_{43}Tc$).
   (iv) Iodine-131 (${}^{131}_{53}I$)

23. [12 marks]
   (a) Temperature influences the amount of dissolved oxygen in the water. At higher temperatures, the dissolved oxygen level drops.
   (b) As CO_2 is used in photosynthesis, the equilibrium moves to the left since, according to Le Châtelier's Principle, it tries to replenish the CO_2. In this process, OH^- ions are also formed so the pH increases.
   (c) DO values determine the current oxygen status of the water and the BOD (5 days) measures the rate of consumption of the oxygen by organisms present in the water over the 5-day period.
   (d) (i) Moles $\frac{I_2}{Na_2S_2O_3} = \frac{1}{2}$,
   $$\text{so moles of } I_2 = \frac{1}{2} \times \frac{9.6}{1000} \times 0.100 \text{ mol}^{-1}$$
   $$= 4.8 \times 10^{-4} \text{ mol}$$

(ii) 1 mole of O_2 = 2 moles of I_2

$= 2.4 \times 10^{-4}$ mol/500 mL

$= 4.8 \times 10^{-4}$ mol L^{-1}

Molar mass of O_2 = 32 g

$= 32 \times 10^3$ mg

$= 4.8 \times 10^{-4} \times 32 \times 10^3$ mg L^{-1}

$= 15.36$ mg L^{-1}

or 15.36 ppm

(e) The ozone layer absorbs high energy UV radiation which would be damaging to life if it reached the Earth's surface. A large 'hole' in the ozone layer could damage the ability of plant life to carry out photosynthesis correctly.

(f) Chlorofluorocarbons, commonly called CFCs. For example CFC-11, trichlorofluoromethane [$CCl_3F(g)$].

Option 1 – Industrial Chemistry

1. [10 marks]

(a) (i) $Ni^{2+} + 2e^- \rightarrow Ni(s)$ −0.23 V
$Mg(g) \rightarrow Mg^{2+} + 2e^-$ +2.36 V
(ii) $Mg(s) \rightarrow Mg^{2+} + 2e^-$

(b) $2H^+ + 2e^- \rightarrow H_2(g)$ 0.00 V
$2OH^- \rightarrow {}^1/{}_2O_2(g) + H_2O + 2e^-$ −0.40 V

(c) Voltage produced by the electrochemical cell
= 2.36 V − 0.23 V = 2.16 V
Voltage required for electrolysis = 0.4 V; so that 2.16 V is sufficient for electrolysis to occur.

(d) Oxygen.

(e) The ion exchange membrane is a selective membrane which allows Na^+ ions and water to flow through, but no other ions. The Na^+ ions can flow freely to the cathode while the other products are kept separate. The Na^+ and OH^- ions collect in the cathode compartment and are removed as sodium hydroxide solution.

(f) There is no mercury leakage as can happen in the case of the mercury cathode cell. Unlike the diaphragm cell there is no asbestos present which could be a health risk to plant operators.

2. [7 marks]

(a) An exothermic reaction since ΔH is negative, showing that heat is evolved from the reaction.

(b) The equilibrium reaction would move to the left so less SO_3 would be formed.

(c) The rate of kinetic reaction is increased so that a practical rate of reaction occurs.

(d) Increase in pressure results in an increase in the rate of SO_3 produced, because an increase in [SO_2] and [O_2] would result from an increase in pressure and this must increase the rate of the forward process.

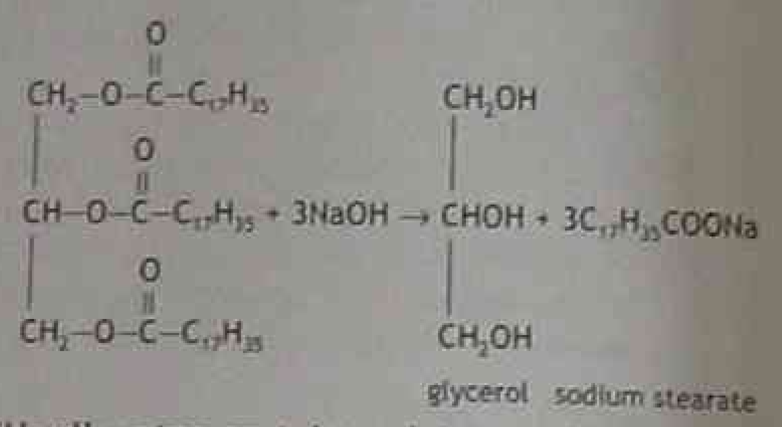
(e) Use a suitable catalyst such as V_2O_5.

3. [5 marks]

(a) Molecule A has a single C–C bond. An unsaturated triglyceride will have C=C double bonds or even C≡C triple bonds.

(b) The presence of double and even triple bonds in a triglyceride lowers the melting and boiling points of the compound so that instead of being a hard solid, e.g. A, it will be a soft solid or an oil at room temperature.

(c)



$$\begin{array}{l} CH_2-O-\overset{\overset{O}{\|}}{C}-C_{17}H_{35} \\ | \\ CH-O-\overset{\overset{O}{\|}}{C}-C_{17}H_{35} + 3NaOH \rightarrow CHOH + 3C_{17}H_{35}COONa \\ | \\ CH_2-O-\overset{\overset{O}{\|}}{C}-C_{17}H_{35} \end{array}$$

glycerol sodium stearate

(d) 'Hard' water contains calcium and magnesium ions in solution. When sodium stearate (soap) is added to hard water, calcium stearate and magnesium stearate are precipitated as an insoluble scum. Synthetic detergents do not form a scum with hard water. They have similar long hydrocarbon chains to soap molecules but the ionic group at the hydrophilic head is different, so the calcium and magnesium salts of these molecules are water soluble.

4. [3 marks]

(a) Sodium carbonate.

(b) The continuous process uses carbon dioxide (by heating limestone) and ammonia (dissolved in brine).

(c) The escape of ammonia gas could be hazardous.

Option 2– Shipwrecks, Corrosion and Conservation

1. [10 marks]

(a) To allow cations and anions to move across the salt-bridge to maintain charge neutrality.

(b) $Cd(s) \rightarrow Cd^{2+} + 2e^-$
$Cu^{2+} + 2e^- \rightarrow Cu(s)$
$Cd(s) + Cu^{2+}(aq) \rightarrow Cd^{2+}(aq) + Cu(s)$

(c) The standard reduction potential gives a measure of a species' ability to accept electrons, compared to the H^+ ion at 1 M concentration and 25°C.

(d) E° (cell) = E° (cathode) − E° (anode)
0.75 V = 0.35 V − E° (anode)
E° (anode) = −0.4 V

(e) Impure copper is the anode. Pure copper is the cathode.

(f) Anode: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$
Cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

2. [12 marks]

(a) $O_2 + H_2O + 4e^- \rightarrow 4OH^-$

(b) For rusting to occur both oxygen and water must be present with the nail.

(c) Zinc is a more active metal than iron and will form the anode.
$Zn \rightarrow Zn^{2+} + 2e^-$
Zinc, therefore provides 'sacrificial protection' for the iron nail.

(d) Copper is a less active metal than iron, so it will form the cathode. This means that the iron anode will oxidise and provide electrons for
$O_2(aq) + H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$.

(e) Corrosion is the oxidation of metals by substances (water and oxygen) in the environment.

(f) Aluminium is an example of a 'passivating' metal, that is a reactive metal which forms an active coating with oxygen or water. The oxide film formed by aluminium metal is inert and tenacious.

(g) An alloy is a material that contains more than one element and has the characteristic properties of metals such as lustre and electrical conductivity. An example of a copper-based alloy is bronze or brass.

(h) Stainless steel contains the passivating metal chromium which forms a protective oxide layer.

(i) An anaerobic sulfur-reducing species of bacteria produces wastes which result in an acidic environment that accelerates corrosion in non-passivating metals.

3. [3 marks]

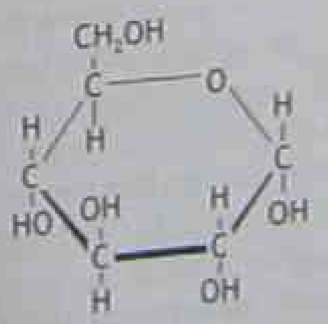
(a) Electrochemical and/or electrolytic treatments are commonly used. These involve some type of reduction process which will facilitate the release of chloride ions.

(b) Chemical corrosion inhibitors are also widely used during treatment. Protective surface coatings may be needed after treatment.

Option 3 – The Biochemistry of Movement

1. [8 marks]

(a) Glucose



The reaction is hydrolysis.

(b) Carbon dioxide and water.

(c) Monosaccharides such as glucose are synthesised into a complex energy storage molecule glycogen, granules of which are stored in the muscles and liver.

(d) Glucose is a reducing sugar and can be tested with Benedict's solution (a complex copper (II) basic salt). The sample is heated in a water bath with Benedict's solution. Copper (II) ions (blue) (Cu^{2+}) are reduced to copper (I) ions which form red copper (I) oxide (Cu_2O) as a precipitate in alkaline solution.

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

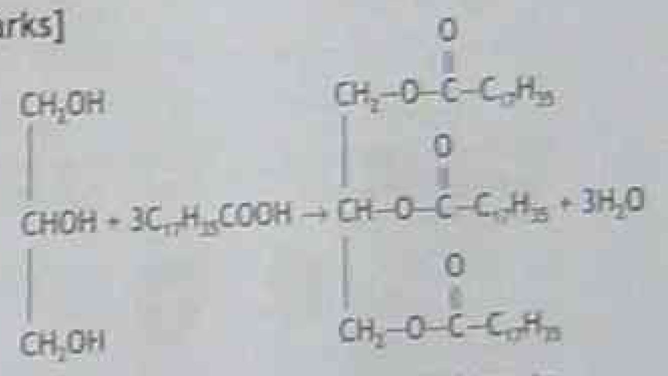
(f) Living cells contain specific enzymes which catalyse each step in the oxidation process so that the whole process occurs at the required rate at normal body temperature.

(g) Total energy needed = 70 × 60 × 4
= 16 800 kJ
Moles $C_6H_{12}O_6$ = 16 800 kJ ÷ 2800 kJ mol^{-1}
= 6 moles
Molar mass of $C_6H_{12}O_6$ = 180
Mass of $C_6H_{12}O_6$ needed = 6 × 180
= 1080 g or 1.080 kg

(h) Each ATP molecule produced during cellular respiration carries energy which is stored in the bond between ADP and P.
ATP ⇋ ADP + P + energy
The breakdown of ATP to ADP releases this energy to be used in metabolic reactions needing an energy input.

2. [5 marks]

(a)



$$\begin{array}{l} CH_2OH \qquad\qquad\qquad\qquad\qquad\;\; CH_2-O-\overset{\overset{O}{\|}}{C}-C_{17}H_{35} \\ | \qquad\qquad\qquad\qquad\qquad\qquad\; | \\ CHOH + 3C_{17}H_{35}COOH \rightarrow CH-O-\overset{\overset{O}{\|}}{C}-C_{17}H_{35} + 3H_2O \\ | \qquad\qquad\qquad\qquad\qquad\qquad\; | \\ CH_2OH \qquad\qquad\qquad\qquad\qquad\;\; CH_2-O-\overset{\overset{O}{\|}}{C}-C_{17}H_{35} \end{array}$$

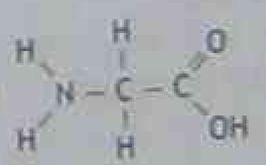
glycerol stearic acid glyceryl tristearate

(b) Acetyl Co-A.

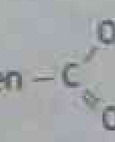
(c) The mitochondrial matrix.

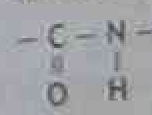
(d) Moles of tripalmitin in 100 g
= 100 ÷ 807 = 0.124 mole
Moles of glucose in 100 g
= 100 ÷ 180 = 0.555 mole
Energy from 100 g of tripalmitin
= 0.124 × 31 400 kJ = 3894 kJ
Energy from 100 g of glucose
= 0.555 × 2800 kJ = 1554 kJ
Energy difference = 3894 − 1554 = 2340 kJ

3. [7 marks]

(a) X = glycine 

(b) Hydrolysis reaction (involving water).

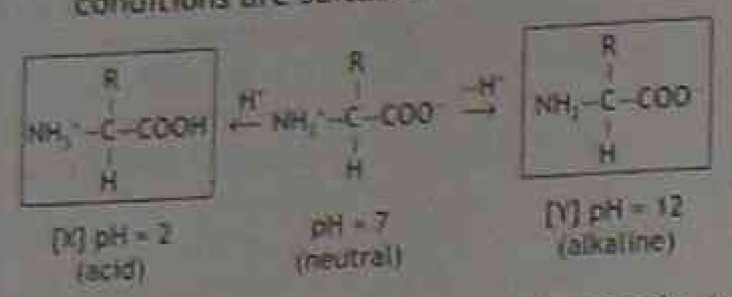
(c) Peptide bonds or amide links. This involves a condensation reaction between  $-C\overset{O^-}{\underset{O}{\Large\lessgtr}}$ ion of one amino acid and the $-NH_3^+$ group of another.



$-\underset{\underset{O}{\|}}{C}-\underset{\underset{H}{|}}{N}-$ link forms.

- The disulfide linkage. If the group forming the side chain contains sulfur atoms, a disulfide bridge may be formed (—C—S···S—C—) where S···S is a covalent bond.
- Hydrogen bonding. A special form of dipole-dipole attraction can occur.
- Electrostatic links can also occur if pH conditions are suitable.

(d)



(e) (i) Enzymes are complex organic catalysts produced by living cells.
(ii) Proteins.
(iii) The lock and key model for enzyme – substrate complex formation.

(f) E is the enzyme active site, S is the substrate, P is the products.

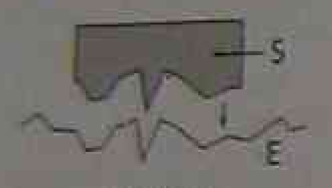


figure 1
Substrate approaches enzyme active site.

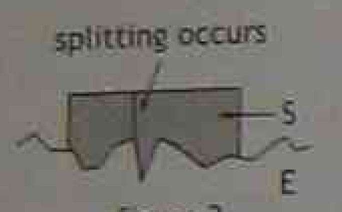


figure 2
Substrate joins enzyme active site.

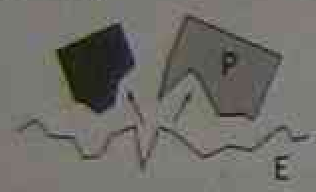


figure 3
Substrate leaves enzyme active site after splitting.

4. [5 marks]
(a) (i) Aerobic respiration.
(ii) Anaerobic respiration.
(iii) Low yield of ATP (1 molecule of oxygen produces 2 molecules of ATP) would be one disadvantage. A rapid release of energy to the muscle cells would be an advantage.
(iv) Enzymes. These act as biological catalysts.
(b) (i) Glycolysis.
(ii) Cytoplasm.
(iii) Pyruvic acid.
(iv) $NADH_2$ will only convert to ATP in the presence of oxygen.

Option 4 – Forensic Chemistry

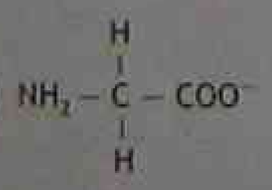
1. [6 marks]
(a) (i) $H_2O_2(aq) \rightarrow H_2O(l) + {}^1/{}_2O_2(g)$
(ii) • Chop up finely some fresh calves' liver which will contain the enzyme catalase.
• Set up four water baths at temperatures of 30°C, 35°C, 40°C and 45°C.
• Place 10 mL of H_2O_2 (3 volumes) in eight test tubes and place pairs of these in the four water baths.
• Add the same mass of chopped liver to one test tube in each water bath and measure the maximum height reached by the bubbling. The optimum activity could then be determined.
• The other tube containing no liver is used as the control.

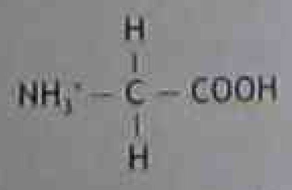
2. [6 marks]
(a) The separation of components in a mixture is usually done to provide qualitative or quantitative information about the components in the mixture.
(b) (i) Paper chromatography uses a water stationary phase (the water bound to the paper fibres) and an aqueous mobile phase.
(ii) HPLC uses a solid stationary phase and an aqueous mobile phase. Separation is achieved as a result of the different attraction that each component in the mixture has for the two phases.
(c) (i) Components in paper chromatography may be identified by comparison of their R_f values with known R_f values obtained under the same conditions.
(ii) Components in HPLC may be identified by comparing their retention times with the retention times of known standards obtained under the same conditions.
(d) Quantitative information may be obtained from an HPLC from the area under the peak on the chromatogram which is dependent on the amount of component present and may be determined by comparison with the areas of standards of known amounts.

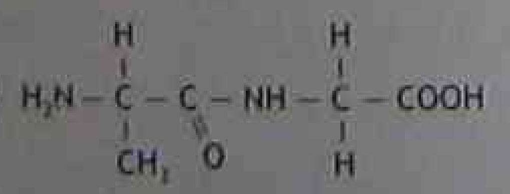
3. [5 marks]
(a) (i) Ribose and lactose.
(ii) Ribose.
(b) Polysaccharides.
(c)

Test	Cellulose	Glycogen	Starch
Solubility in cold water	insoluble	soluble	insoluble
Solubility in hot water	insoluble	soluble	soluble (colloid)
Addition of Benedict's solution	no reaction	no reaction	no reaction
Addition of iodine solution	no reaction	red-brown colour	blue-black colour

4. [8 marks]

(a)

$NH_2-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-COO^-$

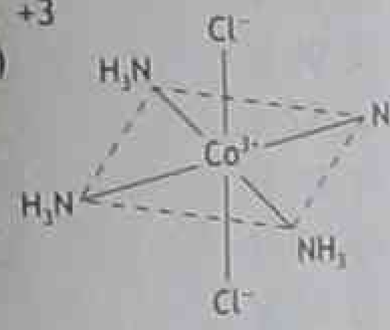
(b)

$NH_3^+-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-COOH$

(c)

$H_2N-\overset{\overset{H}{|}}{\underset{\underset{CH_3}{|}}{C}}-\underset{\underset{O}{\|}}{C}-NH-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-COOH$

(d) (i) By the migration of charged protein molecules in an electric field.
(ii) The isoelectric point is the pH at which there is no electric charge on the molecule.
(iii) Positive charge. Molecule will move towards the cathode.
(iv) Negatively charge. Molecule will move towards the anode.
(v) Deoxyribonucleic acid.
(vi) Identification of individuals. Identification of relationships, e.g. in determining paternity.

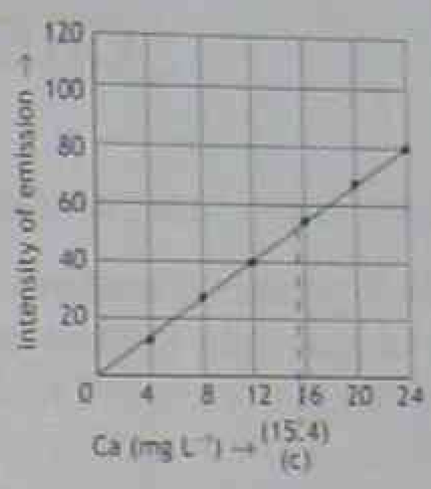
Option 5 – The Chemistry of Art

1. [17 marks]
(a) (i) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
(ii) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$
(b) The bonding within the metallic lattice of cobalt (a transition element with 3d electrons) is stronger than the bonding within the metallic lattice of potassium (a Group I metal with no 3d electrons).
(c) (i) $[CoCl_2(NH_3)_4]^+$
(ii) +3
(iii)



(iv) Ligands are polar molecules (e.g. NH_3), able to form ion-dipole bonds with the central ion (d-shell hybrid coordinate covalent bonds) or anions (e.g. Cl^-) able to form ion-ion bonds with the central ion.
(v) Ion-dipole bonding (d-shell hybrid coordinate covalent bonds).

2. [11 marks]
(a) (i) Sodium vapour lamps.
(ii) Zinc chromate and yellow ochre.
(iii) An emission spectrum is the result of electrons returning from an excited state to a ground state following an energy input. Electricity excites electrons in sodium atoms and on their return to the ground state yellow light is emitted. An absorption spectrum is the result of absorption of energy by the electrons in atoms so that they become excited. In the case of yellow objects, some of the energy from the white light (in the blue region of the spectrum) is absorbed and the remainder is reflected, where it appears yellow to the human eye.
(iv) +6
(v) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4 2s^2$
(vi) Titanium oxide (TiO_2).
(b) (i) Brick red.
(ii)



From the graph, intensity of 52 gives a calcium reading of 15.4 mg L^{-1}; molar mass of calcium is 40.08,

so molarity = $(15.4 \times 10^{-3}) \div 40.08$
$= 3.84 \times 10^{-4}$ M

(iii) Electrons are raised to higher energy levels by the flame. Line spectra occur from energy emitted when these electrons fall from high to low energy levels.
(iv) Different elements have different energy levels.

3. [7 marks]
(a) (i) $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$
(ii) $MnO_4^-(aq) + 8H^+(aq) + 5e^-$
$\rightarrow Mn^{2+}(aq) + 4H_2O(l)$
(iii) $5Fe^{2+}(aq) + MnO_4^-(aq) + 8H^+(aq)$
$\rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$
(iv) Mole ratio $Fe^{2+}/MnO_4^- = 5/1$
Number of moles of MnO_4^-
$= (0.02 \times 50.0) \div 1000 = 1 \times 10^{-3}$
From the equation,
molar mass of $FeSO_4.7H_2O = 5 \times 10^{-3} \times 278$
$= 1.39$
(mass of 1 mole of $FeSO_4.7H_2O$ = 278)
% purity = 1.39 ÷ 1.50 = 92.67%
(b) (i) Boron trifluoride.
(ii) In the Lewis theory, a base can donate its electron pair to something other than H^+. The Lewis definition greatly increases the number of species that can be considered as acids.

CHEMISTRY DATA SHEET

Values of some numerical constants

Avogadro's number (Constant) N_A	6.022×10^{23} mol^{-1}
Volume of one mole of ideal gas:	
at 101.3 kPa and 273 K (0°C)	22.41 L
at 101.3 kPa and 298 K (25°C)	24.47 L
Ionization constant for water at 298 K (25°C)	1.0×10^{-14}
Specific Heat Capacity of water	4.18×10^{3} J kg^{-1} K^{-1}

Some useful formulas

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

$\Delta H = -mC\Delta T$

Values of some Standard Potentials

$K^+ + e^- \rightleftharpoons K(s)$	-2.92 V
$Ba^{2+} + 2e^- \rightleftharpoons Ba(s)$	-2.90 V
$Ca^{2+} + 2e^- \rightleftharpoons Ca(s)$	-2.87 V
$Na^+ + e^- \rightleftharpoons Na(s)$	-2.71 V
$Mg^{2+} + 2e^- \rightleftharpoons Mg(s)$	-2.37 V
$Al^{3+} + 3e^- \rightleftharpoons Al(s)$	-1.66 V
$H_2O(l) + e^- \rightleftharpoons {}^1/_2H_2(g) + OH^-$	-0.83 V
$Zn^{2+} + 2e^- \rightleftharpoons Zn(s)$	-0.76 V
$Fe^{2+} + 2e^- \rightleftharpoons Fe(s)$	-0.44 V
$Ni^{2+} + 2e^- \rightleftharpoons Ni(s)$	-0.24 V
$Pb^{2+} + 2e^- \rightleftharpoons Pb(s)$	-0.13 V
$H^+ + e^- \rightleftharpoons {}^1/_2H_2(g)$	0.00 V
$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$	+0.34 V
${}^1/_2O_2(g) + H_2O(l) + 2e^- \rightleftharpoons 2OH^-$	+0.40 V
${}^1/_2I_2(s) + e^- \rightleftharpoons I^-$	+0.54 V
${}^1/_2I_2(aq) + e^- \rightleftharpoons I^-$	+0.62 V
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	+0.77 V
$Ag^+ + e^- \rightleftharpoons Ag(s)$	+0.80 V
$NO_3^- + 4H^+ + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	+0.96 V
${}^1/_2Br_2(l) + e^- \rightleftharpoons Br^-$	+1.07 V
${}^1/_2Br_2(aq) + e^- \rightleftharpoons Br^-$	+1.09 V
${}^1/_2O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O(l)$	+1.23 V
${}^1/_2Cl_2(g) + e^- \rightleftharpoons Cl^-$	+1.36 V
${}^1/_2Cl_2(aq) + e^- \rightleftharpoons Cl^-$	+1.40 V
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O(l)$	+1.51 V
${}^1/_2F_2(g) + e^- \rightleftharpoons F^-$	+2.87 V

PERIODIC TABLE OF THE ELEMENTS

KEY

Atomic Number	79	
	Au	Symbol of element
Atomic Weight	197.0	
	Gold	Name of element

1 H 1.008 Hydrogen																	2 He 4.003 Helium
3 Li 6.941 Lithium	4 Be 9.012 Beryllium											5 B 10.81 Boron	6 C 12.01 Carbon	7 N 14.01 Nitrogen	8 O 16.00 Oxygen	9 F 19.00 Fluorine	10 Ne 20.18 Neon
11 Na 22.99 Sodium	12 Mg 24.31 Magnesium											13 Al 26.98 Aluminium	14 Si 28.09 Silicon	15 P 30.97 Phosphorus	16 S 32.07 Sulfur	17 Cl 35.45 Chlorine	18 Ar 39.95 Argon
19 K 39.10 Potassium	20 Ca 40.08 Calcium	21 Sc 44.96 Scandium	22 Ti 47.87 Titanium	23 V 50.94 Vanadium	24 Cr 52.00 Chromium	25 Mn 54.94 Manganese	26 Fe 55.85 Iron	27 Co 58.93 Cobalt	28 Ni 58.69 Nickel	29 Cu 63.55 Copper	30 Zn 65.39 Zinc	31 Ga 69.72 Gallium	32 Ge 72.61 Germanium	33 As 74.92 Arsenic	34 Se 78.96 Selenium	35 Br 79.90 Bromine	36 Kr 83.80 Krypton
37 Rb 85.47 Rubidium	38 Sr 87.62 Strontium	39 Y 88.91 Yttrium	40 Zr 91.22 Zirconium	41 Nb 92.91 Niobium	42 Mo 95.94 Molybdenum	43 Tc [98.91] Technetium	44 Ru 101.1 Ruthenium	45 Rh 102.9 Rhodium	46 Pd 106.4 Palladium	47 Ag 107.9 Silver	48 Cd 112.4 Cadmium	49 In 114.8 Indium	50 Sn 118.7 Tin	51 Sb 121.8 Antimony	52 Te 127.6 Tellurium	53 I 126.9 Iodine	54 Xe 131.3 Xenon
55 Cs 132.9 Caesium	56 Ba 137.3 Barium	57–71 Lanthanides	72 Hf 178.5 Hafnium	73 Ta 180.9 Tantalum	74 W 183.8 Tungsten	75 Re 186.2 Rhenium	76 Os 190.2 Osmium	77 Ir 192.2 Iridium	78 Pt 195.1 Platinum	79 Au 197.0 Gold	80 Hg 200.6 Mercury	81 Tl 204.4 Thallium	82 Pb 207.2 Lead	83 Bi 209.0 Bismuth	84 Po [210.0] Polonium	85 At [210.0] Astatine	86 Rn [222.0] Radon
87 Fr [223.0] Francium	88 Ra [226.0] Radium	89–103 Actinides	104 Rf [261.1] Rutherfordium	105 Db [262.1] Dubnium	106 Sg [263.1] Seaborgium	107 Bh [264.1] Bohrium	108 Hs [265.1] Hassium	109 Mt [268] Meitnerium	110 Uun — Ununnilium	111 Uuu — Unununium	112 Uub — Ununbium	113	114 Uuq — Ununquadium	115	116 Uuh — Ununhexium	117	118 Uuo — Ununoctium

Lanthanides

57 La 138.9 Lanthanum	58 Ce 140.1 Cerium	59 Pr 140.9 Praseodymium	60 Nd 144.2 Neodymium	61 Pm [146.9] Promethium	62 Sm 150.4 Samarium	63 Eu 152.0 Europium	64 Gd 157.3 Gadolinium	65 Tb 158.9 Terbium	66 Dy 162.5 Dysprosium	67 Ho 164.9 Holmium	68 Er 167.3 Erbium	69 Tm 168.9 Thulium	70 Yb 173.0 Ytterbium	71 Lu 175.0 Lutetium

Actinides

89 Ac [227.0] Actinium	90 Th 232.0 Thorium	91 Pa 231.0 Protactinium	92 U 238.0 Uranium	93 Np [237.0] Neptunium	94 Pu [239.1] Plutonium	95 Am [241.1] Americium	96 Cm [244.1] Curium	97 Bk [249.1] Berkelium	98 Cf [252.1] Californium	99 Es [252.1] Einsteinium	100 Fm [257.1] Fermium	101 Md [258.1] Mendelevium	102 No [259.1] Nobelium	103 Lr [262.1] Lawrencium

Where the atomic weight is not known, the relative atomic mass of the most common radioactive isotope is shown in brackets.
The atomic weights of Np and Tc are given for the isotopes ^{237}Np and ^{99}Tc.

Useful Chemistry Websites

Useful Chemistry Websites

NSW HSC Online – Chemistry
hsc.csu.edu.au/chemistry

University of NSW, School of Chemistry, High School Resources
www.chem.unsw.edu.au/highschool

Virtual Chemistry
www.chem.ox.ac.uk/vrchemistry

The Chem Team
dbhs.wvusd.k12.ca.us/ChemTeamIndex.html

Weblinks (compiled by University of Sheffield)
www.chemdex.org

Web Elements Periodic Table
www.webelements.com

Paul's Chemistry Lab
www.geocities.com/CapeCanaveral/Lab/5875/

Online Chemistry Textbook
library.thinkquest.org

Department of Minerals and Energy, WA
www.dme.wa.gov.au

Department of Industry Science and Resources
www.dist.gov.au/resources/index.html

Australian Geological Survey Organisation
www.agso.gov.au

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C. M. Roebuck, BSc DipEd, has 10 years experience as an industrial chemist and over 20 years teaching experience in senior high school Chemistry, including 8 years as head teacher of Science at Barrenjoey High School. She is the author of a large number of textbooks and study guides for high-school Science students, including the successful ***Excel*** Preliminary Chemistry study guide.

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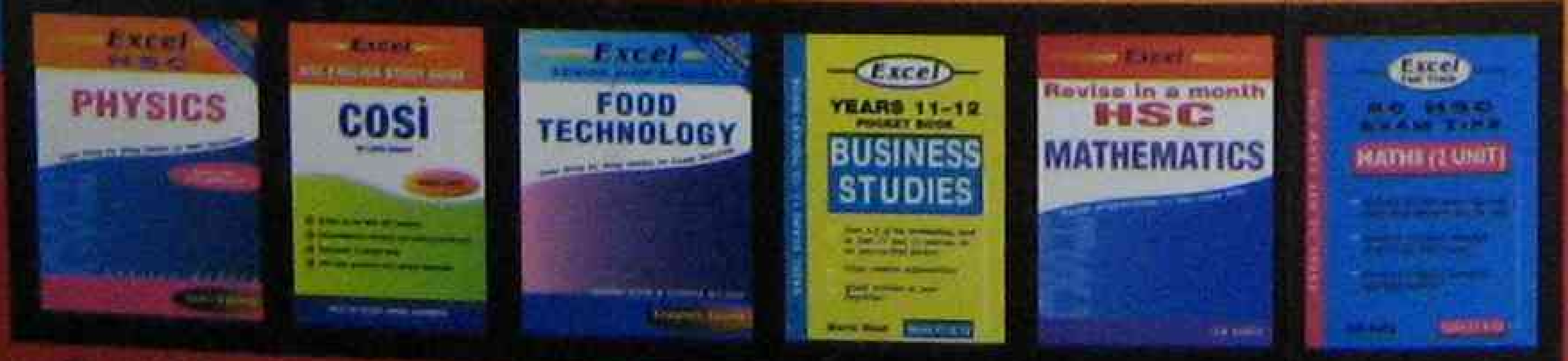

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