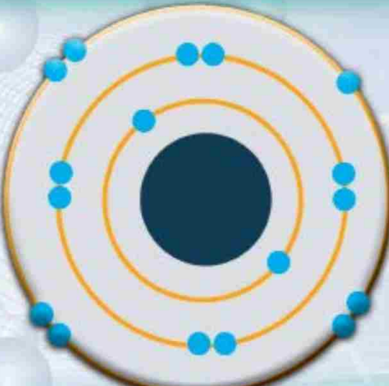
General Chemistry

for Advanced Level Secondary Schools

Student's Book
Form Five and Six



Tanzania Institute of Education

General Chemistry
for Advanced Level Secondary Schools
Student's Book
Form Five and Six

THE UNITED REPUBLIC OF TANZANIA
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Preface

This book, *General Chemistry for Advanced Level Secondary Schools*, is written specifically for Form Five and Six students in the United Republic of Tanzania. The book is prepared according to the 2009 Chemistry Syllabus for Advanced Secondary Education, Form V – VI, issued by the Ministry of Education and Vocational Training.

The book consists of five chapters, which are: The atom, Chemical bonding, Environmental chemistry, Soil chemistry, and Chemical analysis. Each chapter comprises illustrations, exercises, revision questions, and some of practical work. Answers to numerical questions are provided at the end of the book. Learners are encouraged to do all practical work and answer all questions. This will enhance their understanding, and promote the acquisition of the intended skills and competencies for this level.

Tanzania Institute of Education

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Table of contents

Chapter One

The atom

Introduction

All things are made up of matter, whose basic unit is the atom. An atom is the smallest particle of an element that can take part in a chemical reaction. An understanding of the atom paves the way for understanding substances, their nature, manipulations, and how they can be used. In this chapter, you will learn about the Dalton's Atomic Theory and its amendments, Bohr's Atomic Theory, atomic mass, and Quantum Theory.

1.1 Dalton's Atomic Theory

The history of discovery of the structure of an atom was fascinating but a complicated subject. A study about matter started in early 1800s when John Dalton postulated his theory, the *Dalton's Atomic Theory*. In this section, you will learn about the Dalton's Atomic Theory and its amendments, establish evidence for the electronic structure of the atom and the atomic model.

1.1.1 Postulates of the Dalton's Atomic Theory

Dalton's Atomic Theory is summerised into the following main postulates:

(a) Matter is made up of small indivisible particles called atoms.

(b) Atoms can neither be created nor destroyed.

(c) Atoms of the same element resemble one another in mass and properties but they differ from atoms of other elements.

(d) The atoms combine with each other in simple whole number ratios to form compounds.

1.1.2 Amendments of Dalton's Atomic Theory

Dalton's Atomic Theory was widely accepted up to the end of the 19th century. Thereafter, a series of experimental evidence showed that the Dalton's Atomic Theory has some limitations. Despite its limitations, the Dalton's Atomic Theory gave a major foundation on the study about the nature of an atom. The following amendments were made on the Dalton's Atomic Theory that led to the modern atomic theory which states as follows:

(a) Atoms are made up of sub-atomic particles called *electrons, protons, and neutrons.*

(b) Atoms can be created or destroyed by nuclear reactions (nuclear fission and fusion).

(c) Atoms of the same element may have different atomic masses and they are called isotopes. For example, protium (^1_1H), deuterium (^2_1H), and tritium (^3_1H). However some elements have no isotopes. In some few cases, atoms of different elements may have the same atomic mass. For example, argon (^{40}Ar) and calcium (^{40}Ca). Such elements are called *isobars*.

(d) Atoms do not necessarily combine in simple whole number ratios. For example, the discovery of large molecular compounds shows that atoms can combine with larger integers as it is in hydrocarbons such as heptane (C_7H_{16}) as well as in polymers.

Activity 1.1

Investigation of the fact that matter is made up of small particles

Requirements: Small amount of matter such as pieces of chalk, copper sulphate crystals, potassium permanganate crystals, and water.

Procedure

1. Grind each of the given solid samples into fine powder by using motor and pestle.
2. Put a small amount (for example, 2 g) of each of the ground sample into separate beakers.
3. Add a small amount of water into each beaker to get concentrated solutions.
4. Add more water until the solutions become more or less colourless.

Question

Explain the observation made based on the Dalton's Atomic Theory.

Activity 1.2

Investigation of the fact that matter is made up of small particles that can take part in chemical reactions

Requirements: Any sample of matter containing fibre, for example, dry palm fruit fibre or coconut fruit fibre, motor and pestle, knife, and a beaker of 500 mL.

Procedure

1. Take the fibres found inside the dry coconut fruit bunch and cut them into small pieces by using a knife then grind them using motor and pestle until you get fine fibres.
2. Take 5 g of the fine fibres and dissolve it into 100 mL of 0.5 M NaOH and stir for about 30 minutes. Observe the contents.
3. Filter the contents to remove the residue.
4. Add 150 mL of 1 M H_2SO_4 in the filtrate.
5. Heat to boiling.

Note: If dry palm oil fruits or coconut fruit are not available other sources of fibre can be used, for example, sesame hulls, groundnuts hulls, sunflower hulls, cashewnuts hulls, maize husks, rice husks, wheat husks, bare maize cobs, sugarcane bagasse, and pumpkin seeds hulls.

Question

What have you observed in steps 2 and 4? Discuss and make your conclusion based on the Modern Atomic Theory.

1.1.3 Discovery of the fundamental particles of an atom

The discussion on the amendments of the Dalton's Atomic Theory pointed out that atoms consist of sub-atomic particles which are protons, neutrons and electrons. This part discusses how these sub-atomic particles were discovered.

The discovery of electrons by Thomson

The existence of electrons in an atom was first suggested by Joseph John Thomson using a discharge tube under low pressure. The discharge tube consists of a glass tube with a metal electrode fused on the wall. A gas in a discharge tube at low pressure is a good conductor of electricity. When the electricity was allowed to pass through a gas in a discharge tube, it gave a bright luminous stream of cathode rays moving from cathode to anode of the discharge tube. The tube connects to the suction pump which is used to reduce the pressure inside the tube. When the tube is connected to the electrical source, the luminous rays, which are called *cathode rays,* are formed. When the pressure of the gas in the discharge tube is lowered to a certain level (e.g. 10^{-2} atm), the dark space fills the whole length of the tube and the wall starts to glow. The glow on the wall of the tube indicates that some invisible rays are coming from the cathode and move towards the anode at a right angle, with high velocity. These were called cathode rays since they originate from the cathode and are attracted to the anode.

According to Thomson, cathode rays are negatively charged because when they are allowed to pass through an electric field (Figure 1.1) they are deflected towards a positively charged plate. Cathode rays consist of moving particles with definite mass and velocity, produce heat when they strike a material surface, and cause chemical changes.

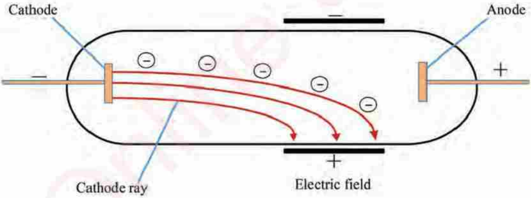


Figure 1.1 Cathode rays production using a discharge tube

Properties of cathode rays

The aim of the Thomson's experiment was to discover and understand the nature of the cathode rays. Thus, following his experiment and those of others, several properties of cathode rays were identified as follows:

(a) They cause a greenish fluorescence on the glass wall of the discharge tube.

(b) They travel in straight lines and therefore causing sharp shadows on the walls opposite to the cathode when a solid object is placed on its way.

(c) They cause a heating effect when allowed to strike a thin metal foil as the foil becomes hot.

(d) They have momentum because when a small paddle wheel is placed in their path, the wheel rotates.

(e) They are deflected by both electric and magnetic fields towards the positive plate away from the negative plate when put in their path.

Therefore, from J. J. Thomson's experiment, it was concluded that cathode rays are negatively charged particles emerging from the cathode. These negatively charged particles are called electrons.

The discovery of protons

The proton was the second sub-atomic particle to be discovered. Eugen Goldstein in 1886, while carrying out an experiment with a discharge tube containing a perforated cathode, discovered anode rays which were also called *canal rays* and later named as positive rays. In 1910, Geiger and Marsden (Mueller) bombarded a thin sheet of gold foil with a beam of alpha (α)-particle produced from radium salt. Some beams passed straight through the foil while others were deflected. The experiment provided the evidence that atoms consisted of a very small positively charged nucleus surrounded by a large space containing negatively charged electrons. Furthermore, Ernest Rutherford proposed the existence of the proton and showed that its mass was 1800 times that of the electron (Figure 1.2)

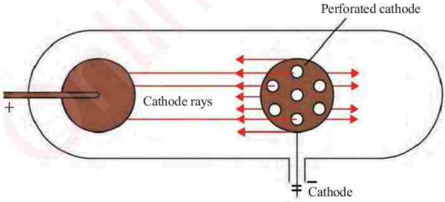


Figure 1.2 Positive rays production using a discharge tube

Properties of positive rays

The following are the properties of positive rays:

(a) When subjected to the electric or magnetic fields, they are deflected from their original path. The path of their deflection indicates that the rays are positively charged.

(b) They also cause mechanical motion in the mica wheel which indicates the particle nature of these rays.

(c) They also cause fluorescence when they strike on a certain material.

(d) The charge to mass (*e/m*) ratio of the positive particles is always less than that of *e/m* ratio of the electrons.

(e) When the charge on the positive particles of H_2 gas was measured, the charge on each particle was found to be $+1.6 \times 10^{-19}$ Coulombs with equal magnitude to that of an electron but opposite in sign.

Therefore, by using the charge of each positive particle of hydrogen gas and their *e/m* ratio, Rutherford concluded that the lightest positive particle can be obtained from hydrogen gas, and he called it a proton.

The discovery of neutrons

In 1932, an English Physicist James Chadwick (1891–1974) discovered neutrons by bombarding the beryllium atom with α–rays. The bombarded beryllium emitted penetrating particles which could neither be deflected by the electric nor magnetic fields. Since these particles were neutral, they were called neutrons. The equation for the bombardment of beryllium with α–particles is as follows:

$$^{10}_{4}\text{Be} + ^{4}_{2}\text{He} \rightarrow ^{13}_{6}\text{C} + ^{1}_{0}\text{n}$$

Properties of neutrons

The following are the properties of neutrons:

(a) They are deflected by neither electric nor magnetic fields and therefore they possess no charge.

(b) They have the same mass as protons.

(c) Neutrons are constituents of all atoms except that of protium.

1.1.4 Atomic models

Atomic models explain how electrons, protons and neutrons are arranged inside the atom. The discovery of the sub-atomic particles posed another challenge to earlier scientists in determining the actual structure of the atom. Among the earlier scientists to explore the atom's structure were J. J. Thomson, E. Rutherford and N. Bohr. These scientists attempted to understand the actual structure of the atom based on the Dalton's Atomic Theory. This approach led to the development of concepts of the atomic structure as described in the following atomic models.

J. J. Thomson's Atomic Model

J. J. Thomson (1856–1940) suggested the plum pudding model or raisin pudding model of an atom. Raisins are sweet dry grapes which can be spread on a bread cake as raisin pudding. The distribution of raisins on a cake (raisin pudding) and the distribution of seeds in some fruits such as watermelon (Figure 1.3) are related to the distribution of electrons in an atom as suggested by J. J. Thomson's Atomic Model.

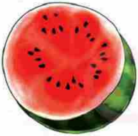


Figure 1.3 Cross-section of a watermelon showing distribution of the seeds

According to Thomson, the atom is a large positive sphere with electrons evenly enclosed in it. The relative massive distribution of positive charge in a sphere cancels that of electrons and the whole atom remains neutral as shown in Figure 1.4.

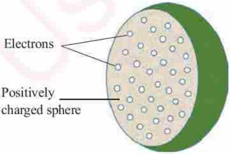


Figure 1.4 J. J. Thomson's Plum Pudding Atomic Model

The success and limitation of the J. J. Thomson's Atomic Model

J. J. Thamson's Atomic Model successfully explained the electrical neutrality of an atom. This neutrality comes from the fact that, an atom consists of equal number of positively and negatively charged sub-atomic particles. However, the model failed to explain how these sub-atomic particles were arranged in the atom.

Activity 1.3

Relation of the arrangement of particles in J. J. Thomson's Atomic Model with real life things

Requirements: Knife and fruits such as watermelon, oranges, pumpkins or tomatoes.

Procedure

1. Cut the fruit in cross-section area to get two equal halves.
2. Observe the arrangement of seeds from one of the halves.

Use the observed arrangement of seeds to explain the J. J. Thomson's Atomic Model.

Rutherford's Atomic Model

In 1909, Ernest Rutherford (1871–1937) performed an α-particle scattering experiment. The alpha particles are positively charged. In his experiment, a stream of α-particles was directed to a thin gold foil. A fluorescent detector was arranged surrounding the gold foil leaving only a small hole for the entry of the particles as shown in Figure 1.5.

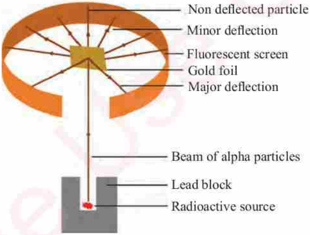


Figure 1.5 Rutherford's Gold Foil Experiment

The following are the observations which were made from Rutherford's experiment as shown in Figure 1.6.

(a) Most of the α-particles passed straight through the gold foil without any deflection from their original path.

(b) Few particles were deflected through small angles and few were deflected through large angles.

(c) Very few particles completely rebound on hitting the gold foil just as a ball rebounds on hitting a hard surface.

If the Thomson's Atomic Model was correct, the large positive sphere should have offered little resistance to the passage of α-particles even though they were also positively charged. This is because α- particles move at a high speed with high momentum. Even though there would have been some repulsion due to like charges, the momentum would have overcome the repulsive effect and the particles would have deflected slightly or gone straight through.

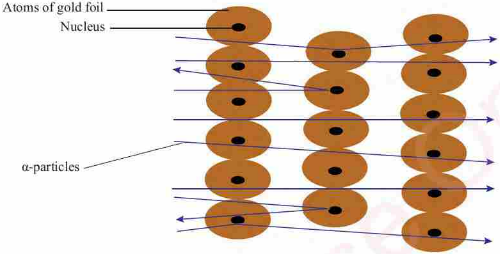


Figure 1.6 Observations from Rutherford's Experiment

Interpretations of Rutherford's observation

The fact that most of the α-particles passed straight through the gold foil without any deflection shows that there is a lot of empty spaces in an atom. The deflections of some of the particles indicate that there is a centre of positive charge in an atom. This centre repels the positively charged particles as well as deflecting them away from the original path. The rebound of α-particles on hitting the gold foil shows that there is a centre of mass which is very dense. The positively charged centre of mass in the atom is called nucleus. The positive charge of the nucleus is due to the positively charged particles, which Rutherford called them protons and are found within the nucleus. The interpretation of the Rutherford's observation is summarised in Figure 1.7.

Rutherford suggested that electrons revolve around the nucleus of an atom in a circular orbit just as planets revolve around the sun. It was also suggested that the number of electrons in an atom is equal to that of protons indicating that an atom is electrically neutral.

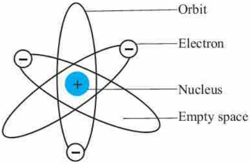


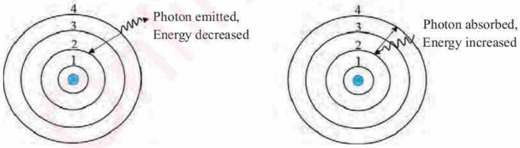
Figure 1.7 The distribution of positive and negative charges in an atom

Success and limitation of Rutherford's Atomic Model

Rutherford's Model of an atom successfully explained the charged nature of an atom, but it could not account for the whole mass of an atom. As suggested by Rutherford, if electrons were continuously revolving around the nucleus, then these electrons would have continuously lost their rotational energy and get attracted to the nucleus. Therefore, Rutherford's Atomic Model could not account for the stability of an atom as well as explaining the emission of line spectra which was later explained by Niels Bohr.

Bohr's Model of an atom

In 1913, Niels Bohr (1885–1962) expanded the Rutherford's Atomic Model by proposing that an atom possesses successive orbits of fixed size and energy where electrons travel through. Rutherford suggested that an atom consists of positively charged nucleus with negatively charged electrons revolving in an orbit around it. According to Bohr, the inner orbits hold fewer electrons than the outer orbits and the number of electrons in the outer orbit determines the atom's chemical properties. Upon studying the hydrogen atom, Bohr also discovered that when an electron moves from an outer orbit to an inner one, it emits light. Also, when an electron absorbs light in the form of photons it moves from the inner to the outer orbit. Figure 1.8 (a) and (b) shows the emission and absorption of photons by electrons with their corresponding transitions.



(a) Emission (b) Absorption

Figure 1.8 Electron move between energy levels due to emission and absorption of energy (photons)

Exercise 1.1

1. Differentiate between an atom and an element as applied in chemistry.
2. Explain the Dalton's Atomic Theory.

3. Which statements in Dalton's Atomic Theory are now considered to be incorrect and why?

4. Describe the characteristics of sub-atomic particles and how they were discovered.

5. (a) Describe the J. J. Thomson's Model of the atom.

   (b) Briefly explain how Thomson's Model differs from the Rutherford's Model of an atom.

6. Explain the reason for the α-particles to penetrate the positively charged gold foil in Rutherford's scattering experiment.

7. Using Dalton's Atomic Theory, explain the fact that potassium sulphate from Tanzania and that from other countries has the same mass percentages of potassium, sulphur and oxygen.

8. Describe the Rutherford's observation that:

   (a) the nucleus has a relatively small diameter compared with that of an atom.

   (b) most of the mass of an atom is concentrated in the nucleus.

9. State the reason(s) for the deflection of α-particles in the Rutherford's Gold Foil Experiment.

10. Explain the fact that Rutherford's observations challenged the Thomson's Model of the atom.

1.2 Bohr's Atomic Theory

After his exploration and proposition of the atomic model, Niels Bohr put forward a model for hydrogen atom which predicted the existence of line spectra. In this section, you will learn about the assumptions of Bohr's Atomic Theory, energy levels and the hydrogen spectrum, nature of electromagnetic radiation and the atomic spectra.

The assumptions of Bohr's Atomic Theory are:

(a) The hydrogen atom has only certain allowed energy levels, called stationary states. Each of these states is associated with a fixed circular orbit in which electrons move around the nucleus.

(b) The angular momentum of the electrons in stationary state is localised (Equation 1.1), that is,

$$mvr = \frac{nh}{2\pi} \tag{1.1}$$

where, n = Principal quantum number which can be 1, 2, 3,4, …,

m = mass of an electron,

v = velocity of an electron,

r = radius of an orbit, and

h = Planck's constant.

(c) The electron does not radiate energy while it is in its stationary states. That is, the atom does not change energy while the electron moves within an orbit.

(d) The electron moves to another stationary state (orbit) only by absorbing or emitting a photon of specific energy, where the change in energy is equal to the difference in energy between the two states. Mathematically, this is represented by Equation 1.2.

$$\Delta E = E_2 - E_1 = h\upsilon \tag{1.2}$$

where, υ = frequency of radiation,

E_1 = lower energy state, and

E_2 = higher energy state.

A photon of specific energy is emitted as the electron moves from a higher energy state to a lower one. Therefore, according to Bohr, an atomic spectrum is not continuous because the atom's energy has only discrete levels or states.

1.2.1 Shortcomings of Bohr's Atomic Theory

Although the Bohr's Atomic Theory was successful in accounting for the presence of spectral lines of the hydrogen atom, it has the following weaknesses:

(a) It could not explain the spectrum of atoms with more than one electron even that of helium, the next simplest element.

(b) It could not explain why energy is quantised.

(c) It could not explain the existence of sub-energy levels in the main quantum number.

(d) It did not explain why an atom did not collapse as the theory of electromagnetic radiations predicted.

(e) No justification was given for the quantisation of the momentum of the electron.

(f) The Bohr's idea of orbit assumed that the electron in an atom is located at definite distance from the nucleus and its velocity is definite. However, this idea was later proved wrong by Heisenberg's Uncertainty Principle.

(g) The theory could not account for the shapes of molecules.

1.2.2 Nature of electromagnetic radiation

An electromagnetic radiation is an array of wavelengths which result into the electromagnetic *spectrum*. A spectrum is the arrangement of radiations in order of increasing or decreasing wavelength and frequency. The idea of Max Planck (1858–1947), a German Physicist about quantisation of energy is the basis for the modern understanding of the atomic structure. The scholar expressed the relationship between energy and frequency of electromagnetic radiation. In this part, the nature of electromagnetic radiation is discussed focusing on the visible region.

Visible light is one of the types of electromagnetic radiation. Other types of electromagnetic radiation which are invisible include gamma rays, x-rays, ultraviolet, infrared, microwave, and radio waves. All electromagnetic radiations possess a certain amount of energy. Therefore, the light as a type of electromagnetic radiation also possesses energy and can be propagated in different ways. Light can be propagated as waves, characterised by frequency, wavelength, velocity and ww. A wave is a disturbance that travels and propagates energy. The disturbance creates crests and troughs as the wave travels. Frequency is a number of complete wavelengths a wave makes in one second. It is expressed in Hertz (Hz). Velocity of a wave is a distance travelled by a wave in one second. Wavelength is the distance between two successive crests (maxima) or troughs (minima) of a wave. It is denoted by Greek letter λ (lambda) and is expressed in different units such as picometre (pm), Angstrom (Å), nanometre (nm), centimetre (cm) or metre (m).

$$1\text{ pm} = 10^{-12}\text{ m}$$

$$1\text{ Å} = 10^{-10}\text{ m}$$

$$1\text{ nm} = 10^{-9}\text{ m}$$

$$1\text{ cm} = 10^{-2}\text{ m}$$

The shorter the wavelength the higher the frequency of the propagating wave. Mathematically, wavelength is inversely proportional to frequency.

$$\lambda \, \alpha \, \frac{1}{\upsilon}$$

$$\lambda = \frac{c}{\upsilon} \tag{1.3}$$

where c is a proportionality constant called the speed of light.

Thus, the speed of light,

$$c = \upsilon\lambda$$

All the types of electromagnetic radiation travel in the vacuum at the same speed of 2.99×10^8 m s^{-1}. Amplitude of a wave is the highest point of crest or depth of the trough of each wave. It is related to the intensity of radiation which accounts for brightness in visible light. The higher the amplitude the brighter the intensity of light and vice versa. An illustration of the wave properties of light is shown in Figure 1.9.

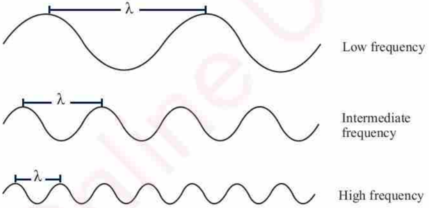


Figure 1.9 Variation of frequency with wavelengths of electromagnetic radiations

Other properties that account for the wave nature of light are refraction, reflection and diffraction. Refraction is the bending of the waves as they pass from one phase to another as a result of the change in speed. Reflection is the change in the direction of light waves as they hit an object such as a mirror. Diffraction is the phenomenon in which when a wave passes through a narrow slit as wide as its wavelength it forms a circular wave. An illustration of the refraction, reflection, and diffraction of waves is shown in Figure 1.10.

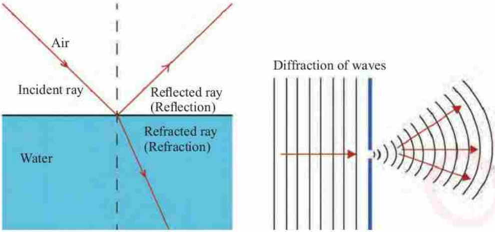


Figure 1.10 Refraction, reflection and diffraction of waves

It was generally accepted that light behaves as waves because of its observed wave properties. Later, three phenomena involving matter and light, led to the deduction of the particle nature of light and hence the development of Modern Atomic Theory. These phenomena are; emission of light by solid object when heated, photo electric effect and atomic spectra.

It was observed that when a solid object is heated it emits visible light of which its intensity and colour change with temperature. In 1900, Max Planck developed an equation that led to the explanation of the particle nature of light and quantisation of energy. He proposed that a heated object could emit or absorb only a certain quantity of energy which is directly proportional to the frequency (Equation 1.4).

$$E \propto \upsilon$$

$$E = h\upsilon \qquad (1.4)$$

where h is the proportionality constant called Planck's constant,

$= 6.626 \times 10^{-34}$ J s.

It was later proposed that the colour of a hot object is caused by the emission of radiation from atoms contained in the object. If an atom can emit only a certain quantity of energy, that means there is a specific quantity of energy that is present within the atom. Therefore, the energy of an atom is quantised (not continuous) in a discrete "packets" of energy called *quanta*.

The discovery led to the support of the particle nature of light as explained by a German-born Physicist Albert Einstein (1879–1955) in his photon theory (Photoelectric effect). Einstein's Photon Theory provided support to the particle model of light. Photoelectric effect is the ejection of electrons when light of a sufficient energy hits a metallic object (Figure 1.11). Einstein deduced that the photons of light beam have a characteristic energy, which is determined by the frequency of the light. If an electron absorbs enough energy than the minimum required threshhold level, it is ejected from the material.

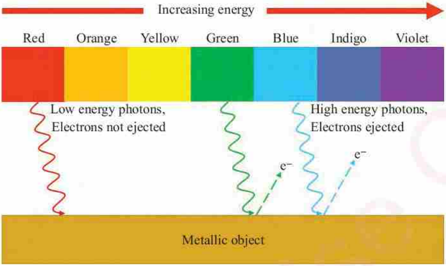


Figure 1.11 Ejection of electrons from a metallic object when hit by high energy photons

If the photon energy is too low, the electron is unable to escape the surface of the material. An increase in the intensity of the light beam leads to an increase of the number of photons in the light beam. This leads to an increase in the number of electrons emitted without an increase in the energy that each photon possesses. Thus, the energy in the emitted electrons does not depend on the intensity of the incoming light, but on the energy of individual photons. The effect suggests the particle nature of light, and such particles of light are called photons. By considering Planck's equation, the energy of an individual photon is given by Equation 1.5.

$$\Delta E_{atom} = h\upsilon \qquad (1.5)$$

where, h = planks constant, and

υ = frequency of the light.

Since ΔE_{atom} = the energy of photon, then,

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

Example 1.1

If the wavelength of a certain electromagnetic radiation is 1.20 cm, what is the energy of one photon of this radiation?

Solution

Convert the wavelength into metres.

$$\lambda = 1.20\ \text{cm} = \frac{1.20\ \text{cm} \times 10^{-2}\ \text{m}}{1\ \text{cm}} = 1.20 \times 10^{-2}\ \text{m}$$

Applying Planck's equation,

$$E_{\text{photon}} = h\upsilon = \frac{hc}{\lambda}$$

$$c = 3.00 \times 10^{8}\ \text{m s}^{-1},\ h = 6.626 \times 10^{-34}\ \text{J s}$$

Then,

$$E = \frac{(6.626 \times 10^{-34}\ \text{J s})(3.00 \times 10^{8}\ \text{m s}^{-1})}{1.2 \times 10^{-2}\ \text{m}} = 1.66 \times 10^{-23}\ \text{J}$$

Therefore, the energy of one photon of this radiation is 1.66×10^{-23} J.

1.2.3 Atomic spectra

Atomic spectra are the emitted light in the form of series of coloured lines with dark spaces in between, which occurs when atoms are excited. This light possesses wavelengths which correspond to different colours. Each element produces a unique set of spectral lines. These lines can therefore be used to identify elements. When an element in a vapour or gaseous state is heated in a flame or discharge tube, the atoms are excited (energised) and emit light radiations of a characteristic colour. For example, a Bunsen burner flame is coloured bright or golden yellow by sodium salts, red by strontium and violet by potassium. In a discharge tube, gaseous elements such as neon and helium glow orange-red and pink colours, respectively.

If the emitted light is examined with a spectroscope, the spectrum which is obtained on the photographic plate consists of bright lines. A spectroscope is a device that is used to produce and observe the spectrum of light or radiations from different sources. Such spectrum whose lines represent specific wavelengths of radiations which are emitted by the atoms is referred to as the *line spectrum* or *atomic emission spectrum* of an element, and an individual line is called a *spectral line*.

Types of spectra

There are two major types of spectra, namely, the absorption and the emission spectra. These types of spectra are described in detail in the following section.

Absorption spectrum

It is a type of spectrum formed when light of a particular wavelength is absorbed by passing through a substance such that black lines are formed in the spectrum corresponding to the wavelength of the light absorbed (Figure 1.12).

This method is particularly useful in determining the molecular structures of unknown substances.

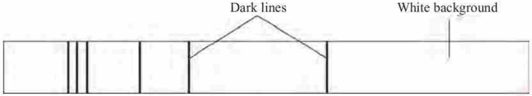


Figure 1.12 A typical absorption spectrum

Emission spectrum

It is a type of spectrum obtained when certain wavelengths are emitted or projected by an atom. It can be observed by a means of spectrograph. A spectrograph is a form of a spectroscope in which its telescope is replaced with a photographic film. By its nature, a spectroscope consists of a prism for dispersing light and a telescope for observing the spectra. The emission spectrum is further divided into continuous, band and line spectrum.

Continuous spectrum

It is the arrangement of all possible radiations of all frequencies over a wide range of frequencies. Most of the continuous spectra are from hot and dense objects like stars, planets or moons. A common example is a rainbow which is produced when sunrays are dispersed by the rain drops or moisture. Figure 1.13 shows a continuous spectrum of a visible light.

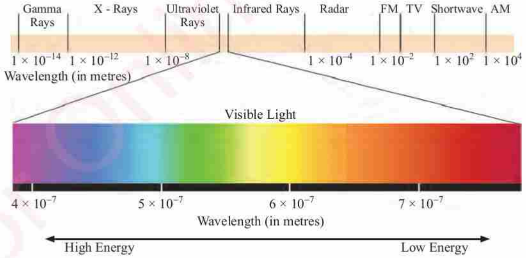


Figure 1.13 The continuous spectrum of the visible light

Band spectrum

This is a type of emission spectrum which consists of well-defined number of groups of closely packed lines usually emitted by molecules as shown in Figure 1.14.

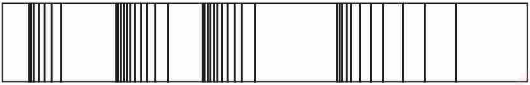


Figure 1.14 The band spectrum

Line spectrum

This is a type of spectrum which consists of separate lines with very little or no groupings at all. The lines which vary with intensity are emitted by an element if electricity is passed in a discharge tube containing the element. A good example of a line spectrum is a hydrogen spectrum obtained when electricity is passed through hydrogen in a discharge tube. Details of the hydrogen spectrum are discussed in the following section. Figure 1.15 represents a line spectrum.

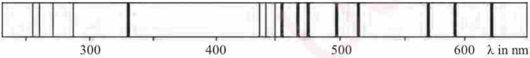


Figure 1.15 Line spectrum

1.2.4 Energy levels and the hydrogen spectrum

In Bohr's Hydrogen Model, the quantum numbers, n (1, 2, 3 ...) are associated with the radius of an orbit, which is directly related to the electrons' energy levels. The lower the value of n the smaller the radius of the orbit and the lower the energy level. When the electron is in the first orbit, that is the orbit closest to the nucleus ($n = 1$), the H atom is in the lowest (first) energy level called the *ground state*.

If the hydrogen atom absorbs a photon whose energy equals the difference between the first and the second energy levels, the electron moves to the second orbit ($n = 2$). When the electron is in the second or any higher orbit, the atom is said to be in an *excited state*. If the hydrogen atom is in the first excited state, it emits a photon of the same energy that was absorbed during excitation, and returns to the ground state.

According to the Bohr's Theory, hydrogen atoms absorb light when electrons are excited from a lower energy orbit (such as $n = 1$) into a higher energy orbit (such as $n = 2$). Atoms that have been excited by an electric discharge can give off light when an electron drops from a higher energy orbit (such as $n = 6$) to a lower energy orbit (such as $n = 1$).

Bohr deduced that, if E_2 was the energy of the electron in a higher level and E_1 is that of a lower level, $\frac{1}{\lambda}$ is directly proportional to $E_2 - E_1$ *i.e.* ΔE. Thus, a greater energy is associated with a shorter wavelength of radiation in the ultraviolet region, since the energy change is inversely proportional to the wavelength of radiation. This concept can lead to the relationship between Planck's Quantum Energy and wave number equation.

$$\Delta E \propto \frac{1}{\lambda}$$

$$\Delta E = h\upsilon \text{ but } \upsilon = \frac{c}{\lambda}$$

Therefore, the energy difference between two levels is given by Equation 1.6.

$$\Delta E = \frac{hc}{\lambda} \qquad (1.6)$$

where, ΔE is the energy difference between two levels,

h = Planck's constant,

λ = wavelength,

c = velocity of light,

υ = frequency, and

$\frac{1}{\lambda}$ is known as the wave number ($\bar{v}$).

Therefore, from the wave number equation Rydberg gives an Equation 1.7.

$$\frac{1}{\lambda} = \bar{v} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad (1.7)$$

where, R_H is the Rydberg's constant, ($= 1.09737 \times 10^7$ m^{-1} or 1.09737×10^5 cm^{-1}), n_1 and n_2 are principal quantum numbers of lower and higher energy levels, respectively.

The energy possessed by an electron moving in the orbit (or principal quantum number n_1 and n_2) is given by Equation 1.8.

$$E_1 = -hcR_H\left(\frac{1}{n_1^2}\right)\text{J} \text{ and } E_2 = -hcR_H\left(\frac{1}{n_2^2}\right)\text{J}$$

$$\Delta E = E_2 - E_1 = \frac{hc}{\lambda}$$

$$E_2 - E_1 = \left(-hcR_H\frac{1}{n_2^2}\right) - \left(-hcR_H\frac{1}{n_1^2}\right)$$

$$E_2 - E_1 = \left(-hcR_H \frac{1}{n_2^2}\right) + \left(hcR_H \frac{1}{n_1^2}\right)$$

$$\Delta E = E_2 - E_1 = \left(hcR_H \frac{1}{n_1^2}\right) - \left(hcR_H \frac{1}{n_2^2}\right)$$

$$\Delta E = hcR_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{ J} \qquad (1.8)$$

Substituting the values of the constants h, c and R_H in the expressions for E_1 and E_2 gives Equation 1.9.

$$E_1 = -2.178 \times 10^{-18} \left(\frac{1}{n_1^2}\right) \text{J} \quad \text{for } n = 1, \text{ and}$$

$$E_2 = -2.178 \times 10^{-18} \left(\frac{1}{n_2^2}\right) \text{J} \quad \text{for n} = 2.$$

Therefore, $\Delta E = 2.178 \times 10^{-18} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$ J

(1.9)

However, the energy possessed by an electron within the orbit is given by Equation 1. 10.

$$E = \frac{-13.6 \text{ eV}}{n^2} \qquad (1.10)$$

where, eV is an electron volt with a value of 1.6×10^{-19} J.

The negative sign indicates that the energy of an electron within the orbit will be lower than the energy possessed by the free electron, that is, the electron far away from the nucleus which is assumed to possess zero energy.

Example 1.2

If the wavelength of a yellow line in the atomic spectrum of sodium is 589 nm, the difference in energy between the two orbits concerned in this change, ΔE, is given by:

$$\Delta E = h\upsilon = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \text{ J s} \times 3.00 \times 10^{8} \text{ m s}^{-1}}{5.89 \times 10^{-7} \text{ m}} = 3.37 \times 10^{-19} \text{ J}$$

Therefore, the energy difference between the two orbits is 3.37×10^{-19} J.

1.2.5 Hydrogen spectrum

Hydrogen spectrum is one of the simplest emission lines spectrum observed for atomic hydrogen. It is obtained by passing electric charge through a hydrogen gas contained in a discharge tube at low pressure. This produces bright lines on the photographic plate, which constitutes the atomic spectrum of hydrogen.

In 1884, a Swiss Mathematician and Mathematical Physicist Johann J. Balmer (1825–1898) observed that there were four prominent coloured lines in the visible region of hydrogen spectrum. These spectral lines consisted of red line with a wavelength 6563 Å, blue-green line with a wavelength of 4861 Å, blue line with wavelength of 4340 Å and violet line with a wavelength of 4102 Å. The above series of four lines in the visible region of hydrogen spectrum was named as the Balmer series. The spectrogram of the visible lines in the Balmer series of hydrogen is shown in Figure 1.16.

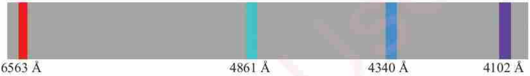


Figure 1.16 Spectrogram of the visible lines in the Balmer series of hydrogen

In 1885, J. J. Balmer discovered in an empirical way the formula for calculating the wavelengths of the lines present in the visible region of hydrogen spectrum which is given by Equation 1.11.

$$\bar{v} = \frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{n_2^2}\right) \tag{1.11}$$

where, R_H = Rydberg's constant (= $1.09677 \times 10^7\ m^{-1}$), and
$n_2 = 3, 4, 5.....$

In addition to Balmer series, four other spectral lines were discovered in the infrared and ultra violet regions of the hydrogen spectrum. All the series were given names of their discoverers and are shown in Table 1.1.

Table 1.1 Spectral line series in the regions of the hydrogen spectrum

Line series	n_1	n_2	Region
Lyman series	1	2, 3, 4......	Ultra violet
Balmer series	2	3, 4, 5…	Visible
Paschen series	3	4, 5, 6…	Infrared
Brackett series	4	5, 6, 7…..	Infrared
Pfund series	5	6, 7, 8…..	Infrared

From Table 1.1, for Lyman series n_1 equals to 1 and n_2 can be equal to 2, 3, 4, … and for Balmer series n_1 equals to 2 and n_2 can be equal to 3, 4, 5, … If n_1 is equal to 3, that line series corresponds to the Paschen series and n_2 can be equal to 4, 5, 6, … The values of n_1 which are equal to 4 and 5, correspond to the Brackett and Pfund series, respectively whereby the values of n_2 can be equal to 5, 6, 7,… for Brackett series and 6, 7, 8,… for Pfund series. The value of n can take any value up to infinity energy level ($n = \infty$) in the atom. When the value of n increases, these energy levels get closer and closer together and converge to a certain limit above which the electron will be free. Therefore, convergence limit corresponds to the ionisation energy of an atom and to the series limit in the spectrum. These line series are also illustrated in Figure 1.17 where the energy change associated with electron movement from outer to inner energy levels are also shown.

It should be noted that in the discharge tube there are very large numbers of hydrogen atoms, and electrons in these atoms are excited differently as they absorb different quanta of energy. If the electrons move back to the ground state, they may jump directly from the excited state to the ground state or they may move in steps hence different lines are produced.

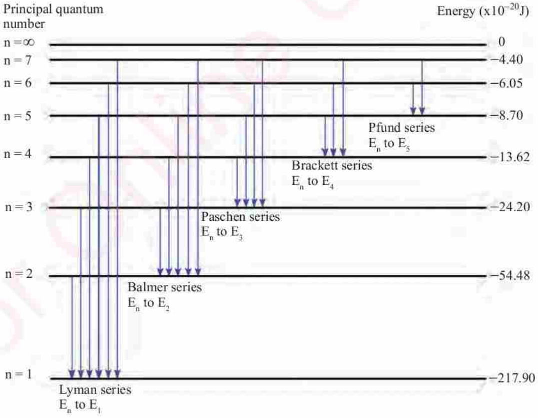


Figure 1.17 Energy level diagram for hydrogen atom

Exercise 1.2

1. (a) What is atomic spectrum?

   (b) Describe the three types of emission spectra.

2. Some of the new cell phones are said to operate at 900 MHz. Calculate the wavelength and energy of these waves.

3. List the seven colours of the visible light spectrum in the order of increasing energy.

4. The electron in a ground state of H atom absorbs a photon of wavelength 97.20 nm. What energy level does the electron move to?

5. Why does hydrogen spectrum have large number of lines despite the fact that hydrogen has only one electron?

6. Which of the following electron transitions correspond to the absorption or emission of energy?

   (a) $n = 2$ to $n = 5$

   (b) $n = 4$ to $n = 1$

   (c) $n = 5$ to $n = 2$

   (d) $n = 2$ to $n = 4$

7. Distinguish between absorption spectrum and emission spectrum. Which one did Bohr work on?

8. (a) Briefly discuss the Bohr's Atomic Theory.

   (b) Explain how Bohr's Atomic Theory successfully explained the spectra of a hydrogen atom.

9. Calculate the wavelength of light that corresponds to the transition of the electron from the $n = 4$ to the $n = 2$ state of the hydrogen atom. Is the light absorbed or emitted by the atom?

1.3 Atomic mass

The atomic mass is measured by determining the different isotopes in a given sample of an element. Isotopes are atoms of the same element with the same atomic number but different mass number. It is the different number of neutrons which bring about the differences in the mass number of the same element. The mass of an isotope is concentrated at the centre of the atom. However, the actual mass number of the atom is determined by using mass spectrometer. The average mass of the isotopes gives the relative atomic mass of the element. In this section, you will learn about the concept of atomic mass, sub-atomic particles, atomic number, mass number, mass spectroscopy and isotopes.

1.3.1 Fundamental particles of an atom

An atom is a neutral, spherical entity which is composed of a positively charged central nucleus surrounded by one or more negatively charged *electrons*. The electrons move around the nucleus and are held by the nuclear force of attraction. The nucleus is a dense central region of an atom. It consists of *protons* and *neutrons* except for the simplest hydrogen nucleus, which has a single proton.

The proton ($p+$) has a positive charge with +1unit charge and 1unit mass. The neutron (n°) has no charge but has 1unit mass. The positive charge of nucleus is due to combined charges of its protons. The magnitude of the charge carried by a proton is equal to that of an electron (e^-) but with opposite signs. Thus, electrons have a negative charge with −1 unit charge and $\frac{1}{1840}$ unit mass which is approximately equal to zero mass. An atom is neutral because the number of protons in its nucleus is equal to the number of electrons surrounding it. Table 1.2 summarises the properties of sub-atomic particles.

Table 1.2 Properties of sub-atomic particles

Particle	Mass (kg)	Atomic mass unit	Charge unit (relative)	Charge (C)
Electron	9.1×10^{-31}	0.00055	−1	-1.60218×10^{-19}
Protons	1.67262×10^{-27}	1.00727	+1	$+1.60218 \times 10^{-19}$
Neutrons	1.67493×10^{-27}	1.00866	0	0

Atomic number

The atomic number of an element is the number of protons in the nucleus of an atom. The atomic number of an element never changes because the number of protons in the nucleus of each atom is always the same. The atomic number of an element is denoted by a letter Z. Each element, which is identified by a unique atomic number is represented by a unique chemical symbol (with either one, two or three letters abbreviation listed directly below its atomic number in the periodic table). For example, all oxygen atoms have 8 protons ($Z = 8$) and all carbon atoms have 6 protons ($Z = 6$).

Mass number

The mass number of an atom is the sum of the number of protons and neutrons in the nucleus. It is denoted by capital letter A.

Mass number (A) = Number of protons (P) + number of neutrons (N)

Substituting the number of protons equals the atomic number (Z), Equation 1.12 is obtained.

$$A = Z + N \tag{1.12}$$

Atomic symbol

An atomic symbol is a notation or representation which consists of one to three letters abbreviation for the name of an element (which can be in English, Latin or Greek), and it is also known as element symbol. The atomic symbol of an element provides information about the atomic number (Z), mass number (A), and the name of that atom. In the atomic symbol, the atomic number (Z) is written as a left subscript and the mass number (A) is written as a left superscript. If the element is represented by letter X, then its full description would be ${}^{A}_{Z}X$. Every element has its own symbol based on English, Latin or Greek name. For example, C is for carbon, Ca is for calcium, O for oxygen (from English), Na for sodium (from *natrium* in Latin), Sn is for tin (from *stannum* in Latin) and Ar for argon (in Greek).

Example 1.3

How many protons, neutrons and electrons are in ${}^{23}_{11}\text{Na}$ atom?

Solution

For a neutral atom, atomic number equals the number of electrons and the number of electrons equals the number of protons. Thus, number of protons = 11.

From mass number (A) = Number of protons (P) + number of neutron (N).

Mass number = 23

Number of protons = 11

Number of Neutrons = mass number – number of protons

= 23 − 11

= 12

Thus, the number of protons, electrons and neutrons are 11, 11 and 12 respectively.

1.3.2 Isotopes

Isotopes are atoms of the same element that have the same atomic number but have different mass numbers. Isotopes arise due to different number of neutrons. The state of an element that exists into atoms with different number of neutrons is called *isotopy*. Figure 1.18 symbolizes isotopes. Examples of isotopes are: carbon which has three naturally occurring isotopes; carbon–12 (^{12}C), carbon–13 (^{13}C) and carbon–14 (^{14}C). All of these carbon isotopes have 6 protons and 6 electrons but the number of their neutrons is different. Carbon–12 (^{12}C) has 6 neutrons, ^{13}C has 7 neutrons and ^{14}C has 8 neutrons. Hydrogen has three naturally occurring isotopes namely, protium (^{1}H), deuterium (^{2}H) and tritium (^{3}H). The isotopes of hydrogen are illustrated in Figure 1.18. These isotopes have one proton but with varied number of neutrons; protium has no neutron, deuterium has 1 neutron, and tritium has 2 neutrons.

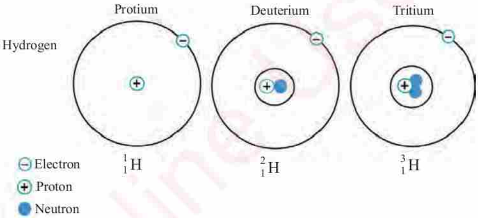


Figure 1.18 Isotopes of hydrogen

All isotopes of an element have nearly identical chemical behaviour, even though they have different masses. This is because the chemical properties of an element are primarily determined by the number of electrons. The mass of an atom is measured relative to the mass of a ^{12}C atom as an atomic standard. This mass is defined exactly as 12 atomic mass units (a.m.u). Thus, the atomic mass unit (a.m.u) is $\frac{1}{12^{th}}$ of the mass of a ^{12}C isotope. The hydrogen atom ^{1}H basing on this standard, has a mass of 1.008 a.m.u. In other words, a ^{12}C atom has almost 12 times the mass of ^{1}H atom. The isotopic make-up of an element is determined by mass spectrometry, a method for measuring the relative masses and abundances of atomic particles. For example, using a mass spectrometer, the mass ratio of ^{28}Si to ^{12}C is measured as

$$\frac{\text{Mass of } ^{28}\text{Si atom}}{\text{Mass of } ^{12}\text{C atom}} = 2.3333$$

From this mass ratio, the isotopic mass of ^{28}Si atom can easily be calculated which is the mass of the isotope relative to the mass of the standard ^{12}C isotope.

$$\begin{aligned}\text{Isotopic mass of } ^{28}\text{Si} &= \text{measured mass ratio} \times \text{mass of } ^{12}\text{C}\\ &= 2.3333 \times 12 \text{ a.m.u}\\ &= 27.9996 \text{ a.m.u}\end{aligned}$$

Along with the isotopic mass, the mass spectrometer gives the relative abundance (fraction) of each isotope in a sample of the element. This is a portion which an isotope contributes to the atomic mass of an element. The relative atomic mass of an element can be calculated using Equation 1.13.

$$\text{Relative Atomic Mass (R.A.M)} = \sum\left(\frac{\text{A} \times \text{percentage abundance of each isotope}}{100}\right)$$

or

$$\text{R.A.M} = \sum\left(\text{A} \times \text{Fraction abundance of each isotope}\right)$$

or

$$\text{R.A.M} = \sum\left(\frac{\text{A} \times \text{abundance of each isotope}}{\text{Total abundance}}\right) \tag{1.13}$$

where $\sum$ is the sigma notation representing the sum of terms and A is the atomic mass of each isotope.

Example 1.4

Silver has two naturally occurring isotopes, ^{107}Ag and ^{109}Ag. Given the following mass spectrometric data, calculate the relative atomic mass of Ag.

Isotope	Mass (a.m.u)	Abundance (%)
^{107}Ag	106.90509	51.84
^{109}Ag	108.90476	48.16

Solution

$$\text{R.A.M of Ag} = \sum\left(\frac{\text{A of Ag} \times \text{percentage abundance of each isotope of Ag}}{100}\right)$$

$$\text{R.A.M of Ag} = \frac{106.90509 \times 51.84}{100} + \frac{108.90476 \times 48.16}{100} = 107.87$$

Therefore, the relative atomic mass of silver is 107.87 a.m.u

Alternatively,

Find the portion of atomic mass from each isotope.

The portion of the atomic mass from ^{107}Ag = isotopic mass × fractional abundance

$= 106.90509 \text{ a.m.u} \times 0.5184$

$= 55.42 \text{ a.m.u}$

The portion of the atomic mass from ^{109}Ag = isotopic mass × fractional abundance

$= 108.90476 \text{ a.m.u} \times 0.4816$

$= 52.45 \text{ a.m.u}$

Finding the atomic mass of silver,

The atomic mass of Ag = atomic mass of ^{107}Ag + atomic mass of ^{109}Ag

$= 55.42 \text{ a.m.u} + 52.45 \text{ a.m.u}$

$= 107.87 \text{ a.m.u}$

Therefore, the relative atomic mass of silver is 107.87 a.m.u.

Significance of isotopes

The existence of isotopes has found to have significant application in various fields. Isotopic properties are applied in fields such as in medicine, age approximations (dating) of objects and in generation of nuclear energy.

Radioactive dating

Isotopes are vital in finding ages of substances through a process of radioactive dating. It is a process of finding the age of a certain matter by comparing its activity to that of a fresh sample of the same matter. However, the respective substance must contain some radioactive isotopes. Examples of such atoms are carbon and uranium.

In medicine

In hospitals, cancer can be treated using gamma (γ) rays. Cancer cells can be destroyed by employing the radiations from the isotope of ^{60}Co. Other isotopes such as ^{226}Ra or ^{137}Cs are planted in deep-lying tumours inside the body near the tumour as a means of treatment.

Generation of nuclear energy

The disintegration of uranium for example, is used as a source of heat in heating water to produce steam for driving turbines in the generation of electricity.

1.3.3 Mass spectrometry

Mass spectrometry is a technique used for measuring the relative masses of particles in a sample by creating charged particles and separating them according to their mass to charge ratio. This method is used to determine the isotopic masses of elements, which are used to calculate their atomic masses. The instrument used in this technique is called mass spectrometer. The structure of this instrument is illustrated in Figure 1.19.

Working mechanism of mass spectrometer

The sample is introduced into the vapourisation chamber and vaporised (if liquid or solid). The resulting vapour is bombarded by high energy electrons to form positively charged particles. These particles are attracted towards a series of negatively charged plates with slits in them and some particles are accelerated into an evacuated tube which is exposed to a magnetic field. As the particles pass through this region they are deflected according to their mass to charge ratio (*m/e* or *m/z*)

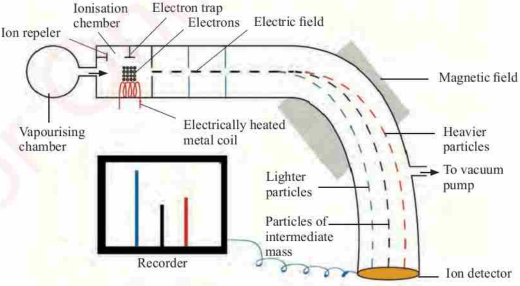


Figure 1.19 The sketch of a mass spectrometer

The lightest particles are the most deflected and the heaviest particles are the least deflected. At the end of the magnetic region, the particles strike a detector, which records their relative positions and abundances. In determining the isotopic masses and abundances, the substance of known amount and masses is used to calibrate the instrument. For example, when neon is introduced in the ionisation chamber, high energy electron bombards the ^{20}Ne atom and one electron is knocked away. The resulting particle has one positive charge, Ne^+ (Figure 1.20).

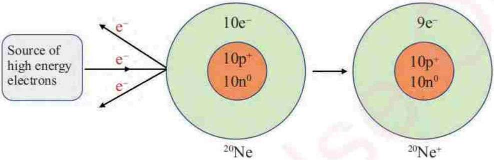


Figure 1.20 Ionisation of neon (Ne) by using high energy electron source

As shown in Figure 1.20, high energy electrons hit gaseous Ne atom. One electron is ejected from Ne. The number of electrons is reduced from $10e^-$ to $9e^-$. One positive charge is therefore formed on Ne. Thus, its mass to charge ratio (*m/e*) is equal to the mass divided by 1^+. The values of mass to charge ratio are used to identify the masses of different isotopes of an element. The mass spectrometry is also used to identify the mass of any atom, molecule, or a fragment of organic molecules such as drugs, petroleum and protein.

Isotopic peaks

The heights of the peaks are proportional to the relative abundance of the different ions. The mass spectrum shows the percentage abundance versus the mass to charge ratio of each species in a mass spectrometer. The isotopes present in the sample are shown as peaks and the size of the peak is proportional to the abundance of the mass. Each peak indicates one isotope with its percentage abundance and relative isotopic

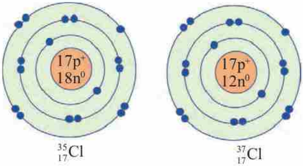


Figure 1.21 Isotopes of chlorine atom

mass or mass number. The number of peaks equals the number of isotopes. For example, chlorine has two naturally occurring isotopes; ^{35}Cl (75%) and ^{37}Cl (25%) as illustrated in Figure 1.21. When a sample of chlorine molecule is fragmented into different isotopes in the mass spectrometer, it gives two ions, ^{35}Cl and ^{37}Cl. The ^{35}Cl will give a mass reading at a mass to charge ratio of 35, and ^{37}Cl will give a mass reading at a mass to charge ratio of 37. The ratio between the heights of the two peaks and the abundance of the isotopes will be 3:1.

A pair of peaks like this indicates that two isotopes of chlorine are present in the compound as shown in Figure 1.22.

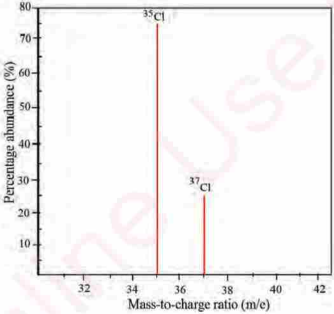


Figure 1.22 Percentage abundances in chlorine isotopes

Example 1.5

Use the data of chlorine element in the table below to:

(a) find the missing fractional abundance 'X' and mass number 'Y'.

(b) calculate the relative atomic mass of chlorine.

Isotope	Relative isotopic mass	Mass number	Fractional abundance
$^{35}_{17}Cl$	34.97	35	X
$^{37}_{17}Cl$	36.97	Y	0.2423

Solution

(a) Required: fractional abundance of ^{35}Cl, X

Given: fractional abundance of ^{37}Cl = 0.2423

The sum of fractional abundances is equal to 1

Therefore,

$$X + 0.2423 = 1$$

$$X = 1 - 0.2423$$

$$X = 0.7577$$

Required: mass number of ^{37}Cl, Y

From the atomic symbol, the mass number (A) is the superscript number.

Therefore, mass number Y = 37.

(b) Relative atomic mass of chlorine is given by:

$$\begin{aligned} \text{RAM} &= \sum(\text{Relative isotopic mass of each isotope} \times \text{Fractional abundance}) \\ &= (34.97 \times 0.7577) + (36.97 \times 0.2423) \\ &= 26.496769 + 8.957831 \\ &= 35.45 \approx 35.5 \end{aligned}$$

Therefore, the relative atomic mass of chlorine is 35.5 a.m.u

Example 1.6

Copper has two isotopes, ^{63}Cu and ^{65}Cu. The isotope ^{63}Cu has a relative isotopic mass of 62.9, and ^{65}Cu has a relative isotopic mass of 64.9. If the naturally occurring copper has a relative atomic mass of 63.55, what will be the percentage abundance of each isotope?

Solution

Data given;

Relative isotopic mass of ^{63}Cu = 62.9

Relative isotopic mass of ^{65}Cu = 64.9

Relative atomic mass of naturally occurring Cu = 63.55

Required: percentage abundance of each isotope.

The R.A.M of copper (Cu) = ∑(Relative isotopic mass of each isotope × Fractional abundance)

Let x be the fractional abundance of ^{63}Cu (isotope 1). Since, the sum of fractional abundances is equal to 1, therefore $1 - x$ is equal to the fractional abundance of ^{65}Cu (isotope 2).

$$63.55 = 62.9 \times x + 64.9\,(1 - x)$$

$$63.55 = 62.9x + 64.9 - 64.9x$$

$$63.55 - 64.9 = 62.9x - 64.9x$$

$$-1.35 = -2x$$

$$\frac{-1.35}{-2} = \frac{-2x}{-2}$$

$$x = 0.675$$

Therefore, fractional abundance of ^{63}Cu = 0.675

Then,

Fractional abundance of ^{65}Cu = $^{65}\text{Cu} = 1 - 0.675 = 0.325$

The percentage abundance is given by fractional abundance times 100%.

The percentage abundance of ^{63}Cu = 0.675 × 100% = 67.5%

The percentage abundance of ^{65}Cu = 0.325 × 100% = 32.5%

Thus, the percentage abundances of ^{63}Cu and ^{65}Cu are 67.5% and 32.5%, respectively.

Exercise 1.3

1. (a) Define the terms atomic number and mass number.

   (b) Which one between the atomic number and mass number can vary without affecting the nature of the element?

2. Explain the fact that several elements have more than one isotope, however their isotopes still exhibit similar chemical properties.

3. The nuclei of atoms M contain 7 neutrons and 7 protons, and N contains 14 neutrons and 12 protons. Write down:

   (a) the mass numbers of M and N.

   (b) the atomic numbers of M and N.

4. (a) State the number of protons, neutrons and electrons in the following atomic symbols:

   (i) $^{11}_{5}X$ (ii) $^{41}_{20}Y$ (iii) $^{131}_{53}Z$

   (b) Identify the elements represented by the symbols X, Y, and Z in 4(a).

5. Silicon (Si) has three naturally occurring isotopes; ^{28}Si, ^{29}Si, and ^{30}Si. Determine the number of protons, neutrons and electrons in each isotope.

6. Boron (B) has two naturally occurring isotopes which are ^{10}B and ^{11}B. Calculate the percentage abundances of each isotope from the following information. Atomic mass of B = 10.50 a.m.u; isotopic mass of ^{10}B = 10.0129 a.m.u; isotopic mass of ^{11}B = 11.0093 a.m.u.

7. Calculate the average atomic mass of gold with 50% gold–197 and 50% gold–198.

8. The following are three isotopes of an element:

   $^{12}_{6}E$, $^{13}_{6}E$, and $^{14}_{6}E$.

   (a) The element is _____

   (b) Number 6 refers to _____

   (c) Numbers 12, 13, and 14 refer to ___

   (d) How many protons and neutrons are in the first isotope?

   (e) How many protons and neutrons are in the second isotope?

   (f) How many protons and neutrons are in the third isotope?

9 Iodine has three isotopes; ^{127}I, ^{126}I, and ^{128}I with the abundances of 80%, 17%, and 3%, respectively. Calculate the average atomic mass of iodine.

1.4 Quantum Theory

Niels Bohr succeeded to give the first quantitative model of an atom. However, the quantum theory rejects the idea that electrons move in a fixed circular orbit as proposed by Bohr. According to quantum theory, electrons move in a complex nature described by its wave properties and probabilities. The wave mechanical theory of matter is the key to our modern atomic structure. The theory suggests that small particles such as electrons, protons and even atoms possess wave properties when they are in motion. Thus, in this section, you will learn about wave particle duality of electron, Heisenberg's uncertainty principle, quantum number, atomic orbitals and electronic configuration, Pauli's Exclusion Principle, Hund's Rule, and Aufbau Principle.

Wave particle duality of an electron

The Planck's idea on the particle nature and wave nature of light makes it difficult to distinguish the two properties of light. In 1924, a French Physicist Louis de Broglie (1892–1987) formulated that every sub-atomic particle such as an electron has both wave and particle properties. This hypothesis is referred to as the *wave-particle duality (the de Broglie's hypothesis)*. The hypothesis may be extended to any kind of matter and thus not confined to electrons alone. The Physicist formulated this hypothesis with the help of Planck's and Einstein's ideas. According to de Broglie, there is a relationship between the magnitude of the wavelength associated with mass (m) and velocity (v) of a moving body.

From Planck's idea, the energy of a photon is given by

$$E = h\upsilon \tag{1.14}$$

where, h = Planck's constant, and
υ = frequency of radiation.

The Einstein energy associated with a photon of mass "m" is given by Equation 1.14.

$$E = mc^2 \tag{1.15}$$

where, c is the velocity of radiation.

Combining the Planck's and Einstein's ideas gives;

$$mc^2 = h\upsilon = \frac{hc}{\lambda}$$

This results into Equation 1.15 which is known as the *de Broglie equation*:

$$mc = \frac{h}{\lambda} \qquad (1.16)$$

where, m = mass of a particle,

c = velocity of a particle,

h = Planck's constant, and

λ = de Broglie's wavelength.

But mass × velocity = momentum (p).

Therefore,

$$p = \frac{h}{\lambda} \qquad (1.17)$$

Equation 1.16 implies that $p \propto \frac{1}{\lambda}$

According to the de Broglie's equation, the momentum of a particle in motion is inversely proportional to the wavelength, Planck's constant, h, being the constant of proportionality. The wavelength, λ, is called the de Broglie's wavelength. However, the de Broglie's equation is limited to very small particles such as electrons with significant wave-like behaviour. Large moving particles possess wavelengths that are too small to be measured by any instrument hence not significant. Therefore, the equation works only to microscopic particles that their radii are smaller than their wavelengths.

Example 1.7

Calculate the wavelength of an alpha particle having a mass of 6.7×10^{-25} kg moving with a speed of 10^3 m s^{-1} given that the Planck's constant, $h = 6.626 \times 10^{-34}$ J s.

Solution

Data given;

Mass of alpha particle, $m = 6.7 \times 10^{-25}$ kg

Speed of alpha particle, $c = 10^3$ m s^{-1}

Planck's constant, $h = 6.626 \times 10^{-34}$ J s

From the de Broglie equation, $mc = \frac{h}{\lambda}$,

Then,

$$\lambda = \frac{h}{mc}$$

$$\lambda = \frac{6.626 \times 10^{-34}\,\text{kg m}^2\,\text{s}^{-1}}{6.7 \times 10^{-25}\,\text{kg} \times 10^3\,\text{m s}^{-1}}$$

$$= 9.89 \times 10^{-13}\ \text{m}$$

Therefore, the wavelength of the alpha particle is $9.88 \times 10^{-13}\,\text{m}$.

1.4.1 Heisenberg's Uncertainty Principle

A large moving particle has a definite location at any instant while waves are spread out in space. According to de Broglie, small particles such as electrons in motion possess both particle and wave properties. Because an electron is very small with wave like properties in motion and waves are spread out in space, it is therefore difficult to locate both its position and momentum in an atom. In 1927, a German Physicist Werner Heisenberg (1901–1976) anticipated how difficult it was to characterise the physical behavior of microscopic particles and postulated the principle for such difficulties. This principle is called the *Heisenberg Uncertainty Principle* and it states that it is impossible to determine simultaneously both the exact position and the momentum of a sub-atomic particle.

If the momentum is measured very accurately, the measurement of position of the particle becomes less precise. Similarly, if the position of the particle is measured accurately, the measurement of momentum becomes less accurate due to the wavelength of the energy applied to locate an electron in an atom being higher than the energy of the viewed electron. For example, the uncertainty associated with the measurement of the position, Δx, and the momentum, Δp or $m\Delta v$, are related by Heisenberg's equation as shown in Equation 1.18.

$$\Delta x \Delta p \geq \frac{h}{4\pi}$$

or

$$\Delta x m \Delta v \geq \frac{h}{4\pi} \qquad (1.18)$$

where, m is a mass of the moving particle,

Δx is the uncertainty in position,

Δv is the uncertainty in velocity,

Δp is the uncertainty in momentum, and

h is the Planck's constant.

The product of the uncertainty in position and momentum is negligible in the case of large objects. This agrees with the de Broglie equation in which the wavelength of large objects is too small to be measured, hence insignificant.

Example 1.8

Calculate the uncertainty in the velocity of a bullet whose mass is 10 g and its position is known with an accuracy of ± 0.1 nm.

Solution

Data given:
Mass of bullet (m) = 10 g
Position (Δx) = ± 0.1 nm
Planck's constant (h) = 6.626×10^{-34} kg m^2 s^{-1}
Velocity (Δv) =?

From Heisenberg's equation,

$$\Delta x \Delta p = \frac{h}{4\pi}, \text{ but } \Delta p \text{ (change in momentum)} = \Delta v \times m$$

$$\Delta x m \Delta v = \frac{h}{4\pi}$$

$$\Delta v = \frac{h}{4\pi \Delta x m}$$

$$= \frac{6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{4 \times 3.14 \times 10^{-3} \text{ kg} \times 1 \times 10^{-10} \text{ m}}$$

$$= 5.28 \times 10^{-22} \text{ m s}^{-1}$$

Therefore, the uncertainty in velocity of a bullet is = 5.28×10^{-22} m s^{-1}

Example 1.9

Calculate the uncertainty in momentum of an electron if the uncertainty in position is approximately 100 pm.

Solution

Data given;

Uncertainty in position (Δx) = 100 pm = 1×10^{-10} m
pi (π) = 3.14
Planck's constant (h) = 6.626×10^{-34} kg m^2 s^{-1}

From uncertainty equation, $\Delta x \Delta p = \dfrac{h}{4\pi}$

$$\Delta p = \frac{h}{4\pi\Delta x}$$

$$= \frac{6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{4 \times 3.14 \times 100 \times 10^{-12} \text{ m}}$$

$$= 5.28 \times 10^{-25} \text{ kg m s}^{-1}$$

Therefore, the uncertainty in momentum of an electron is = 5.28×10^{-25} kg m s^{-1}

Exercise 1.4

1. State the Heisenberg's Uncertainty Principle with respect to its determination of the position and momentum of an object.
2. How would the doubling of the frequency of a given photon affect the following values?

   (a) E (b) λ (c) c (d) h
3. Suppose the location of an electron is determined within 0.53 Å (the Bohr radius). Calculate the minimum uncertainty in its speed.
4. Explain the de Broglie's Wave Theory of wave particle duality and give the de Broglie's equation.
5. The alpha particles emitted from radium have the energy of 4.8 eV. What is the de Broglie's wavelength? Hint: 1 eV = 1.6×10^{-19} J.
6. Calculate the wavelength of an α particle having a mass of 6.6×10^{-27} kg moving with a speed of 105 cm s^{-1}.

7. The Heisenberg's Uncertainty Principle is one of the founding concepts for the quantum mechanical picture of the electrons in atoms.
   (a) As a result of the Heisenberg's Uncertainty Principle, what part of the Bohr's Theory of the atom is considered unrealistic?
   (b) Explain why the Heisenberg's Uncertainty Principle or the wave nature of particles is not a practical way of examining the behaviour of macroscopic objects, but, it is the most significant in describing the behaviour of electrons or systems on a very small scale.

1.4.2 Quantum numbers

The wave equations which are developed in quantum mechanics are used to describe the energy of an electron and the region where there is a high probability of finding that electron. This region of high probability of locating electrons in an atom is called *atomic orbital*. Each atomic orbital can be described by a set of quantum numbers. *Quantum numbers* are the numbers which are used to describe the properties of electrons in an atom. The movement and paths of each electron in an atom are described by a total of four quantum numbers. Each electron in an atom has a unique set of quantum numbers. Quantum numbers also determine other characteristics of atoms such as atomic radius and ionisation energy. There are four quantum numbers which designate specific shells, sub-shells, orbitals, and spins of electrons. These are the principal quantum number (n), the orbital angular momentum quantum number (l), the magnetic quantum number (m_l), and the electron spin quantum number (ms).

The principal quantum number

The principal quantum number (n) describes the energy of an electron and the most probable distance of the electron from the nucleus. Large value of n means the electron is far from the nucleus and therefore the size of the orbital is large; n has positive integer values from 1, 2, 3 to infinity and cannot be zero or negative because there are no atoms with zero or negative amount of energy levels. When the value of $n = 1$, it designates the first principal shell (the innermost shell). At this level, the electron possesses lower energy than when it occupies the $n = 2$ orbital.

The orbital angular momentum quantum number

The orbital angular momentum quantum number (l) is also known as *azimuthal or subsidiary quantum number*. It determines the shape of an orbital, and therefore the angular distribution. It has positive integer values from 0 to $n - 1$. For an orbital with $n = 1$, $l = 0$; for $n = 2$, l can have a value of 0 or 1; for $n = 3$, l can be 0, 1 or 2, for $n = 4$, l can be 0, 1, 2 or 3.

The magnetic quantum number

The magnetic quantum number (m_l) is an integer ranging from $-l$ to $+l$ through 0. It determines the number of orbitals and their orientation within a sub-shell. For example, for $l = 0$ the value of $m_l = 0$ only, which means that there is only one orientation. An orbital with $l = 1$ can have three possible values of m_l, which are -1, 0 and $+1$. This means that, this orbital can have three possible orientations. For an orbital with $l = 2$, there are five possible values of m_l, which are; -2, -1, 0, $+1$ and $+2$. This means that, this orbital can have five possible orientations. Generally, the possible values of magnetic quantum number (m_l) of the orbital is given by $2l + 1$, where l is the angular momentum quantum number.

The electron spin quantum number

The electron spin quantum number (ms) designates the direction of the electron spin and may have a spin of $+\frac{1}{2}$ which corresponds to spin up ($\upharpoonleft$) and $-\frac{1}{2}$ which corresponds to spin down ($\downharpoonright$). Unlike l and m_l, the electron spin quantum number does not depend on other quantum numbers. The electron spin helps to determine if an atom has the ability to generate a magnetic field or not. Table 1.3 summarises the relationship of the four quantum numbers.

Table 1.3 Relationship of the n, l, m_l and ms

n	l	m_l	ms	Number of electrons ($2n^2$)
1	0	0	$+\frac{1}{2}, -\frac{1}{2}$	2
2	0	0	$+\frac{1}{2}, -\frac{1}{2}$	8
	1	-1	$+\frac{1}{2}, -\frac{1}{2}$	
		0	$+\frac{1}{2}, -\frac{1}{2}$	
		+1	$+\frac{1}{2}, -\frac{1}{2}$	

The total number of orbitals for a given n value is n^2. For an orbital with $n = 1$, the total number of orbitals is 1, and for $n = 2$, the total number of orbitals is 4. The total number of electrons in a given principal quantum number (n) is $2n^2$.

1.4.3 Atomic orbitals and electronic configuration

The wave mechanical theory of the atom developed the concept of electron cloud in the atom. The concept of electron cloud simply describes the high probability region in an atom where electrons can be found. This region is called an *orbital*. The atomic orbital is a three dimensional region within an atom where there is a high probability of finding an electron within a certain energy level. The energy of an electron which is confined in an atomic orbital is always the same. In this region, the electron spends most of its time while in a constant motion in a certain energy level. There are various types of atomic orbitals, which include, *s, p, d,* and *f* orbitals. These orbitals differ in shape and orientation in space.

The *s*-orbital

This is an orbital with $l = 0$ and has a spherical shape with the nucleus at the centre. The *s-orbital* has no specific orientation in space and the corresponding magnetic quantum number $m_l = 0$. That means, the probability of finding an electron in the s-orbital is equal in all directions, thus, a spherical shape. The *s*-orbitals are numbered according to their energy levels; for example, 1*s*-orbital is the atomic orbital in the sub-energy level "*s*" of the first energy level. The 2*s*-orbital is the atomic orbital in the sub-energy level of the second energy level. The size of the *s*-orbital increases as the value of the principal quantum number (*n*) increases. The shape of an *s*-orbital is shown in Figure 1.23.

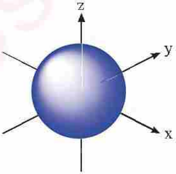


Figure 1.23 The shape of an s-orbital

The *p*-orbital

This is an orbital with $l = 1$ and has two regions of high probability of finding electrons, one on either side of the nucleus. The *p*-orbital has a dumb-bell shape and has three possible orientations p_x, p_y, and p_z derived from three m_l values which are −1, 0 and +1. The *p*-orbitals exist only in an orbital with $n = 2$ or higher and therefore the lowest energy *p*-orbital is the 2*p*. All *p*-orbitals are identical in shape, size and energy, and differ in their orientation in space. Like in *s*-orbital, the size of the *p*-orbital increases as the value of the principal quantum number increases. Orbitals with nearly the same energy, size and shape but different in their orientation in space are called *degenerate orbitals*. The three orientations of *p*-orbitals are shown in Figure 1.24.

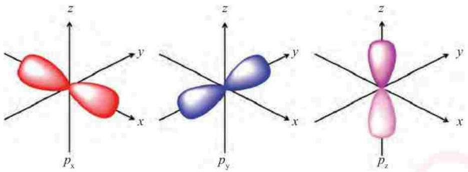


Figure 1.24 The shapes and orientations of p-orbitals

The *d*-orbital

This is an orbital with $l = 2$. There are five possible values of magnetic quantum number (m_l) which are –2, –1, 0, +1 and +2 which signify the presence of five different orientations leading to five *d*-orbitals. The *d*-orbital exists from the third energy level ($n = 3$) and higher so that the lowest energy *d*-orbital is the 3*d*. Three of the five *d*-orbitals (d_{xy}, d_{xz} and d_{yz}) have four lobes directed in the x-y plane (d_{xy}), x-z plane (d_{xz}), and y-z plane (d_{yz}).

Unlike the other three *d*-orbitals, the lobes of $d_{x^2-y^2}$ orbital are directed along the x and y axes. The fifth *d*-orbital (the d_{z^2}) consists of two lobes which lie along the z axis with a doughnut-shaped (torus) region of electron density at the centre. The probability of the *d*-orbital electrons to be located in any of the orbital lobes is the same. The shapes and orientations of the five 3*d*-orbitals are shown in Figure 1.25.

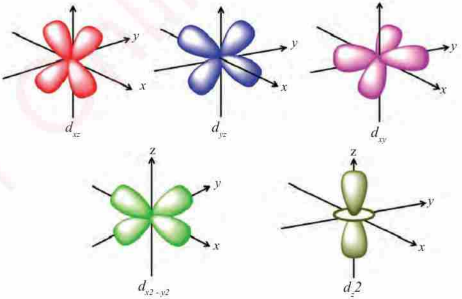


Figure 1.25 The shapes and orientations of *d*-orbitals

The *f*-orbital

This is an orbital with $l = 3$. There are seven possible values of magnetic quantum number (m_l) for this value of angular momentum quantum number (l) which are -3, -2, -1, 0, $+1$, $+2$, and $+3$. This implies the presence of seven degenerate *f*-orbitals which start from the fourth energy level ($n = 4$). Therefore, the lowest energy *f*-orbital is the 4*f*. Shapes and orientations of *f*-orbitals are beyond the scope of this book.

Electronic configuration of an atom

The electronic configuration of an atom is the representation of the arrangement of electrons in atomic orbitals. The electronic configuration can be used to describe the orbitals of an atom in its ground state, in excited state or ionised state. The unique electronic configuration of elements accounts for many of their physical and chemical properties, which are determined by the electrons in the outermost shell.

Presentation of electronic configuration

The electronic configuration of an element can be presented by *s, p, d, f*-form (short hand notation) or by orbital diagrams.

s, p, d, f- form or shorthand notation

In the *s, p, d, f-* form or shorthand notation, a number is used to represent energy level followed by a letter *s, p, d* or *f* which represents the value of *l*. The superscript number represents the number of electrons occupying a particular orbital. For example, $1s^2$ (pronounced as *one-ess-two,* which means, two electrons occupying the *s*-orbital of the first energy level); $2p^2$ (pronounced as *two-p-two*) means that two electrons occupy *p*-orbitals of the second energy level.

Orbital diagrams

An orbital diagram consists of a box or a line for the energy level grouped by sub levels in each orbital. Each box or a line can contain a maximum of two electrons which are represented by arrows. In the orbital diagram, an electron spinning in the clockwise direction is indicated by an upward arrow (↿) and the one spinning in the counter clockwise direction is indicated by a downward arrow (⇂) as shown in Figure 1.26.

(a) A box method

(b) A line diagram method

Figure 1.26 Methods of representing orbitals

However, the number of boxes or lines involved depend on the number of orbitals of a particular atom.

1.4.4 Rules for assigning electrons into various orbitals

Electrons fill orbitals in a way that minimises the total energy of the atom. Therefore, filling of electrons into orbitals is done in the order of increasing energy. There are three rules that govern the way in which electrons are filled in the atomic orbitals namely; Pauli's Exclusion Principle, Hund's Rule and Aufbau Principle.

The Pauli's Exclusion Principle

Pauli's Exclusion Principle was named after the Austrian-born Swiss physicist Wolfgang Pauli (1900 – 1958), who is one of the pioneers of quantum physics. The principle states that *no two electrons in an atom can have the same set of all the four quantum numbers.* The first three quantum numbers (n, l, and m_l) may be the same, but the fourth (ms) must be different. Therefore, an atomic orbital can hold a maximum of two electrons which must have opposite spins. This principle describes two electrons in the same orbital, but not the order of filling electrons in the presence of other orbitals. The principle is illustrated by the orbital diagrams in Figure 1.27.

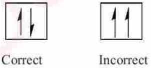
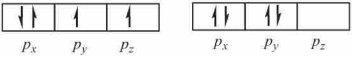


Figure 1.27 Pairing of electrons as per Pauli Exclusion Principle

The Hund's Rule

The Hund's Rule was named after the German physicist Friedrich Hund (1896 – 1997). The rule guides us on how electrons should be filled in the degenerate orbitals. The *Hund's Rule* states that, the most stable arrangement of electrons in degenerate orbitals is the one with the maximum number of parallel spins. This means that electron pairing in the degenerate orbitals is not allowed until each orbital is singly occupied. Therefore, when assigning electrons in the orbitals of the same energy, each orbital is first filled with one electron to make a half-filled orbital before pairing with another electron. Atoms at the lower energy (ground state) tend to have a maximum number of unpaired electrons before pairing. For example, in the degenerate orbitals such as $2p_x$, $2p_y$, and $2p_z$ electrons do not pair up until each orbital is singly occupied by an electron. The Hund's Rule is illustrated by the orbital diagrams in Figure 1.28.



Correct Incorrect

Figure 1.28 Filling of electrons in degenerate p-orbitals as per Hund's rule

The Aufbau Principle

The word Aufbau originates from a German word "aufbauen" which means to build up. The *Aufbau Principle* states that, electrons in an atom are arranged in the order of increasing orbital energies. This principle is called the building up principle because orbitals with the lowest energy are filled first before the orbitals with the higher energy levels. That means, the electrons fill the orbitals in which their values of $n + l$ is minimum. When the rule is followed, the Aufbau process for filling the electrons in the orbitals can easily be predicted such that the increase in energy for those orbitals follows the trend 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, 4*d*, 5*p*, 6*s*, 4*f*, 5*d*, 6*p*,7*s*, 5*f*, 6*d*, and 7*p*. The easy way of studying this order is illustrated in Figure 1.29. Start at 1*s* and move along the arrow.

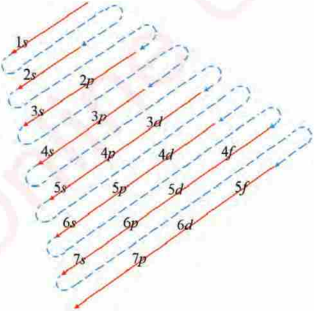


Figure 1.29 The order of filling electrons in atomic orbitals

Figure 1.29 shows the order of filling electrons in atomic orbitals according to Aufbau Principle. The trend in electronic configuration is $1s^22s^22p^63s^23p^64s^23d^{10}$ and so forth. Electrons cannot be filled in the 2*s*-orbital unless the 1*s*-orbital is fully filled. Similarly, the orbitals in the third energy level; 3*s*, 3*p* and 3*d* cannot be filled with electrons until all the orbitals in the second energy level are fully filled. Filling of electrons according to Aufbau Principle is shown in Figure 1.30.

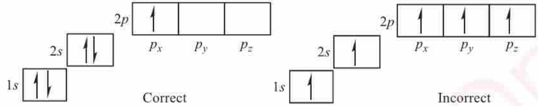
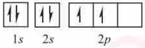
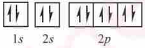
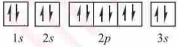
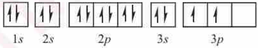
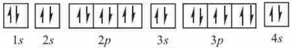
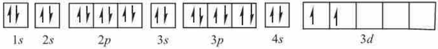
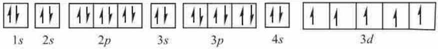
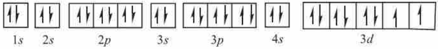


Figure 1.30 Filling of electrons in orbitals of different energy levels as per Aufbau principle

Table 1.4 shows the electronic configuration of few elements written following the Aufbau Principle under *s, p, d, f* notation and orbital diagrams.

Table 1.4 Electronic configurations of various elements

$_{2}$He	$1s^2$	
$_{6}$C	$1s^22s^22p^2$	
$_{10}$Ne	$1s^22s^22p^6$	
$_{12}$Mg	$1s^22s^22p^6$ $3s^2$	
$_{14}$Si	$1s^22s^22p^6$ $3s^23p^2$	
$_{20}$Ca	$1s^22s^22p^6$ $3s^23p^64s^2$	
$_{22}$Ti	$1s^22s^22p^6$ $3s^23p^64s^2$ $3d^2$	
$_{25}$Mn	$1s^22s^22p^6$ $3s^23p^64s^2$ $3d^5$	
$_{28}$Ni	$1s^22s^22p^6$ $3s^23p^64s^2$ $3d^8$	

Note that the 4*s*-orbital has a slightly lower energy than 3*d*-orbitals hence the 4*s*-orbital is filled first followed by all 3*d*-orbitals. In case of ionisation, the electrons are first lost from 4*s*-orbital which is the outermost shell then from 3d which is the inner shell.

Electronic configuration

Electronic configuration is the representation of the arrangement of electrons in atomic orbitals. You have seen that three rules govern the way in which electrons are filled in the atomic orbitals namely; Pauli's Exclusion Principle, Hund's Rule and Aufbau Principle. However, some configurations may seem too long and thus condensation is done to shorten. Besides, some elements have pecurliar behaviour, and therefore they need a special way of assigning electronic configurations.

The condensed electronic configuration

The condensed electronic configuration is used to shorten the electronic configuration of other atoms by using noble gas configurations. In this method, the electronic configuration of an immediate noble gas with less atomic number than a given element is written in square brackets to represent electrons in the inner orbitals of a particular element.

The noble gas core is then followed by the outer electronic configuration of the element. For example, the condensed electronic configuration of boron ${}_5B$ is $[He]2s^22p^1$ in which [He] represents $1s^2$. The condensed electronic configuration of chlorine is $[Ne]3s^23p^5$ in which [Ne] represents $1s^22s^22p^6$. Similarly, the condensed electronic configuration of vanadium (${}_{23}V$) is $[Ar]4s^23d^3$ in which [Ar] represents $1s^22s^22p^63s^23p^6$.

The unique electronic configuration of some elements

The electronic configuration of some elements such as chromium and copper is slightly different from that of other elements. The expected electronic configurations of copper (${}_{29}Cu$) and chromium (${}_{24}Cr$) are $[Ar]4s^23d^9$ and $[Ar]4s^23d^4$, respectively. However, the actual electronic configurations of these elements are $[Ar]4s^13d^{10}$ and $[Ar]4s^13d^5$ for copper (${}_{29}Cu$) and chromium (${}_{24}Cr$), respectively. This uniqueness of the electronic configuration of Cu and Cr is attributed by *full and half-full filled rule* which states that for *d* and *f*-orbitals, full and half-full-filled configurations are very stable with minimum energy content. Thus, to acquire the increased stability, one of the 4*s* electrons goes into the nearby 3*d*-orbitals so that it gets half-filled in Cr and full-filled in Cu. This peculiarity in the configuration is also applicable in elements with f^7 and f^{14} half-filled and full-filled configurations, respectively.

Exercise 1.5

1. Write the electronic configurations of the following elements:

   (a) Sodium (b) Iron (c) Bromine (d) Barium.

2. Write the names of the elements represented by each of the following electronic configurations:

   (a) $1s^2 2s^2 2p^5$ (b) $[Ar]4s^2$

   (c) $[Kr]5s^2 4d^{10} 5p^4$ (d) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$

3. Determine which of the following electronic configurations are not correct:

   (a) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$ (b) $1s^2 2s^2 2p^6 3s^3 3d^5$

   (c) $[Kr]7s^2 5f^8$ (d) $[Kr]\ 5s^2 4d^{10} 5p^5$ (e) [Xe]

4. Identify the element that:

   (a) contains a full 3rd energy level.

   (b) contains one electron in the first *p*-orbital.

   (c) contains 3 electrons in the 2*p* level.

   (d) has $4s^2$ outer energy level

   (e) contains one electron in the first *d*-orbital.

   (f) contains 4 electrons in the 4*d* level.

5. Which pair of quantum numbers determines the energy of an electron in an orbital? Give reasons to your answer.

   (a) n and l (b) n and m_l (c) n and ms

   (d) l and m_l (e) l and ms (f) m_l and ms

6. Which of the following combinations of quantum numbers are allowed for an electron in a one-electron atom and which are not?

   (a) $n = 2, l = 2, m_l = 1, ms = ½$

   (b) $n = 3, l = 1, m_l = 0, ms = -½$

(c) $n = 5, l = 1, m_l = 2, ms = ½$

(d) $n = 4, l = -1, m_l = 0, ms = ½$

7. What orbital is described by the following set of quantum numbers?

   (a) $n = 1, l = 0, m_l = 0$ ________

   (b) $n = 2, l = 0, m_l = 0$ ________

   (c) $n = 4, l = 1, m_l = -1$ ________

   (d) $n = 4, l = 2, m_l = 2$ ________

   (e) $n = 3, l = 1, m_l = -1$ ________

8. (a) What is an atomic orbital?

   (b) How does *s*-orbital differ from *p*-orbitals?

9. Describe the difference between an orbit in Bohr's Atomic Theory and an orbital in the quantum theory.

10. With the aid of diagrams, describe the shapes and orientations of *p*-orbitals.

Revision exercise 1

1. According to Dalton's Atomic Theory, an element is made up of tiny indivisible particles called atoms. Provide a description by either supporting or rejecting the statement.

2. 1.008 g of hydrogen combines with 35.453 g of chlorine to form 36.463 g of a pure hydrogen chloride. State the Dalton's explanation for this experimental fact.

3. Calculate the average atomic mass of lithium, which occurs as two isotopes that have the following atomic masses and abundances in nature: 6.017 a.m.u, 7.30% and 7.018 a.m.u, 92.70%.

4. What is the atomic mass of hafnium, if out of every 100 atoms, 5 have a mass of 176, 19 have a mass of 177, 27 have a mass of 178, 14 have a mass of 179, and 35 have a mass of 180.0?

5. Hydrogen is 99% ^{1}H, 0.8% ^{2}H and 0.2% ^{3}H. Calculate its average atomic mass.

6. Explain how Rutherford's results overturned the Thomson's Model of the atom.

7. Summarise the evidence used by J. J. Thomson to argue that cathode rays consist of negatively charged particles.

8. Excited sodium atoms may emit radiation with the frequency of 5.09×10^{14} s^{-1}. Calculate the energy of photons in this radiation.

9. Explain how Bohr rectified the drawbacks of Rutherford's Model.

10. What equation describes the Heisenberg's Uncertainty Principle?

11. Calculate the de Broglie wavelength of an electron moving with the velocity of 1.0×10^6 m s^{-1} given that its mass is 9.11×10^{-31} kg.

12. Calculate the de Broglie's wavelength of a baseball of mass 0.17 kg that is thrown with a velocity of 30 m s^{-1}. Compare your answer with that obtained for the de Broglie's wavelength of electron in question 11, and comment on the difference.

13. Name the orbitals described by each of the following sets of quantum numbers:

    (a) $n = 4, l = 1$ (b) $n = 2, l = 0$ (c) $n = 6, l = 3$

14. Complete the following table:

n	l	Name	Number of orbitals
2	1	…..	…..
…...	….	3*d*	…..
4	….	…..	7

15. Specify the values for the quantum numbers that describe the following orbitals:

    (a) 5*s* $n =$ ___, $l =$ ___, $m_l =$ ___

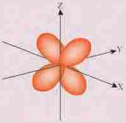
    (b) 4*f* $n =$ ___, $l =$ ___ $m_l =$ ___

    (c) 3*p* $n =$ ___, $l =$ ___, $m_l =$ ___

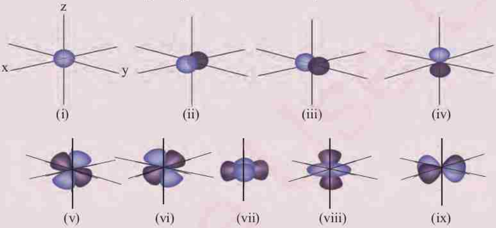
    (d) 3*d* $n =$ ___, $l =$ ___, $m_l =$ ___

16. Explain the phenomenon of electron cloudy as applied in atomic orbitals.

17. Identify the pictured orbital as *s*, *p* or *d*. Can this type of orbital be found in the *n* = 2 energy level? Explain.



18. Observe the following images and answer the questions that follow:



(a) Use the axes in (i) as a reference to name the orbitals labeled (i) − (ix).

(b) If all the above orbitals belong to the same energy level, name the minimum energy level possible for the orbitals.

19. Explain how the Aufbau Principle, Pauli's Exclusion Principle, and Hund's Rule are applied in determining the electronic configurations.

20. Identify the elements from each of the following given electronic configurations:

(a) [Ne]$3s^2 3p^2$ (b) [Ar]$4s^2 3d^7$ (c) [Xe]$6s^2$

21. Identify the element that is composed of atoms whose last electron:

(a) enters and fills the 4s sub-shell.

(b) enters but does not fill the 4*s* sub-shell.

(c) is the first to enter the 2*p* sub-shell.

Chapter Two

Chemical bonding

Introduction

Chemical bonding is an interaction process that results into the association of atoms to form molecules, ions, crystals, and any other stable substances. In this chapter, you will learn about different types of chemical bonds, the strengths of ionic and covalent bonds, intermolecular forces, and hybridisation of atomic orbitals.

2.1 Types of chemical bonds

There are three types of chemical bonds which are ionic (electrovalent), covalent and metallic bonds. In this section, you will learn about the characteristics of the electrovalent bond, covalent (including the dative bond) and the metallic bonds. Also, you will learn about the types of intermolecular forces and hybridisation of atomic orbitals.

2.1.1 Ionic (electrovalent) bonds

An ionic bond is the chemical bond which is formed by the electrostatic force of attraction between two opposite charged ions, namely, cations and anions that are formed as a result of transfer of one or more electrons from one atom to another. A cation is a positively charged ion which is formed by the loss of electrons; and an anion is a negatively charged ion which is formed by the gain of electrons. An ionic bond occurs between metal and non-metal atoms which have large differences in their electronegativity. Electronegativity is the relative ability of an atom to attract the bonding electrons towards itself. For an ionic bond to occur, the bonding atoms need to be ionised. The metal atoms which have low ionisation energy (group IA and IIA) lose their one or two valence electrons and form metal ions. The following are some examples of metal atoms which form ionic bond by the loss of electrons at certain ionisation energies (IEs).

$$Na(g) \longrightarrow Na^+(g) + e^- \qquad IE = +496\ kJmol^{-1}$$

$$Mg(g) \longrightarrow Mg^{+}(g) + e^{-} \qquad IE = +736 \text{ kJ mol}^{-1}$$
$$Mg^{+}(g) \longrightarrow Mg^{2+}(g) + e^{-} \qquad IE = +1448 \text{ kJ mol}^{-1}$$

Ionisation energy (IE) is the energy required to completely remove one mole of electrons from one mole of gaseous atoms or ions. Atoms with relatively lower IE easily lose electrons to form cations.

Non-metal atoms which have high electron affinity gain electrons to form negatively charged ions.

$$Cl(g) + e^{-} \longrightarrow Cl^{-}(g)$$
$$O(g) + 2e^{-} \longrightarrow O^{2-}(g)$$

Electron affinity (EA) is the energy change that is associated with the addition of one mole of electrons to one mole of gaseous atoms or ions. Atoms with relatively higher EA (more negative EA) attract electrons more easily to form anions as shown in the following gaseous atoms:

$$Cl(g) + e^{-} \longrightarrow Cl^{-}(g) \qquad EA = -364 \text{ kJ mol}^{-1}$$
$$Br(g) + e^{-} \longrightarrow Br^{-}(g) \qquad EA = -342 \text{ kJ mol}^{-1}$$
$$I(g) + e^{-} \longrightarrow I^{-}(g) \qquad EA = -295 \text{ kJ mol}^{-1}$$

Thus, Cl^{-} is more stable than Br^{-} and I^{-} hence attracts electrons more easily. The cations and anions then attract each other to form ionic compounds. The energy which is required to form one mole of an ionic compound is called *lattice energy* (LE). For example,

$$Na^{+}(g) + Cl^{-}(g) \longrightarrow NaCl(s) \qquad LE = -781 \text{ kJ mol}^{-1}$$

The negative sign indicates that the energy is given out to the surroundings (exothermic). The transfer of electrons in ionic bonds, such as the formation of NaCl, can be represented by a dot and cross model.

$$\dot{Na} + Cl \longrightarrow Na^{+}\left[Cl\right]^{-}$$

Characteristics of ionic compounds

Compounds formed by ionic bonds are called ionic compounds. These have several characteristics.

(a) They are crystalline solids at room temperatures.

(b) In solution or molten states, they are electrolytes and hence they conduct electricity.

(c) They have generally high melting and boiling points as compared to covalent compounds.

(d) They are generally insoluble in non-polar solvents such as toluene but soluble in polar solvents such as water.

2.1.2 Covalent bonds

A covalent bond is a chemical bond formed by sharing of electrons between two bonding atoms of non-metals. A covalent bond occurs between two atoms of the same or small differences in electronegativity. Each of the bonding atoms have high IE, and therefore holds its electrons tightly and tends to attract other electrons due to high negative EA. Atoms are drawn together by the attraction of each nucleus for the valence electrons of other atoms. The shared electrons between the two bonding atoms are said to be localised because they spend most of their time in between the atoms, linking them together. A neutral particle which is formed when atoms share electrons is called a molecule. This is the basic unit of a molecular compound.

Factors affecting the degree of covalency according to Fajan's Rule

Fajan's Rule states that, the atomic ions with low positive charges, large cations, and small anions form ionic bonds, whereas those with high positive charges, small cations and large anions are covalently bonded.

Fajan's Rule is used to predict whether a chemical bond will be covalent or ionic depending on the charge and the relative size of cations and anions. The following are the factors that influence the bond polarisation and hence the degree of *covalency*:

Ionic charge

High charge of the ions, for instance, C^{4+}, favours the covalent character while low charge of the ions, for instance Na+, favours the ionic character.

Size of the cation

Small cations favour the covalent character while large cations favour the ionic character. For example, C^{4+} with the ionic radius of 0.015 nm favours the covalent character while a larger cation, Na^+ with the ionic radius of 0.095 nm favours the ionic character.

The size of anion

Large anions favour covalent character while small anions favour ionic character. For example, iodide (I^-) ion with ionic radius of 0.216 nm favours covalent character relative to the smaller fluoride (F^-) ion with ionic radius of 0.136 nm, that favours ionic character.

In general, small anion, large cation and low positive charge favour ionic character while large anion, small cation and high positive charge favour covalent character. Compounds formed by the covalent bonds are called *covalent compounds* and have different characteristics compared to the ionic bonds. The characteristics inlude the fact that they:

(a) have generally low melting and boiling points.

(b) are soluble in non-polar solvents such as benzene and toluene and are generally insoluble in polar solvents like water.

(c) are usually gases and liquids at room temperatures.

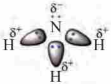
(d) do not conduct electricity.

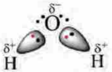
Types of covalent bonds

There are three types of covalent bonds which are polar covalent, non-polar covalent (normal covalent), and dative (coordinate) covalent bonds. The formation of these types of bonds is based on the electronegativity of the bonding atoms.

Polar covalent bond

Polar covalent bond is the covalent bond which is formed between atoms of different electronegativity, due to the unequal sharing of electrons. The molecule formed by the unequal sharing of electrons is called a *polar molecule*. In a polar covalent bond, the electrons which are shared by the atoms spend a greater amount of time closer to the more electronegative atoms than the other creating opposite partial charges. These opposite partial charges existing between two different atoms which are bonded together in a covalent molecule are known as *dipole*. For example, in a water molecule, the shared electrons spend a greater amount of time closer to oxygen nucleus than to the hydrogen nucleus because oxygen is more electronegative than hydrogen. The oxygen atom acquires a partial negative charge (δ^-) because it attracts the bonding electrons towards itself. The hydrogen atom acquires a partial positive charge (δ^+) because the electrons are withdrawn away from its nucleus. Other examples, of polar covalent compounds include hydrogen chloride (HCl), ammonia (NH_3), and water (H_2O).

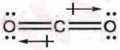




The geometry of water molecule is bent because of the repulsive effect of lone pair of electrons on the oxygen atom.

Non-polar covalent bond

Non-polar covalent bond is the type of covalent bond formed between identical atoms, which have the same electronegativity. In this type of bond, there is equal sharing of bonding pair of electrons. The resulting compound is said to be non-polar covalent compound. Examples of molecules or compounds that consist of non-polar covalent bonds include hydrogen (H–H), fluorine (F–F) and chlorine (Cl–Cl). However, some of non-polar covalent compounds can be formed through polar covalent bonding, since not every molecule with dipole forms polar molecule. Therefore, the presence of polarity is not a satisfactory factor for a molecule to be polar but also the geometrical shape of the molecule can be considered. An example of non-polar compound, which is formed by polar covalent bonding is carbon dioxide (CO_2). In this compound there are two polar bonds between carbon and oxygen atoms. The dipole moments existing within CO_2 cancel out and there is no net molecular dipole moment because the bonds point 180º away from each other making the molecule non-polar as shown in structure (a). Sharing of electrons in covalent bonding can be represented using Lewis structure (b).



Carbon dioxide

(a)

Chlorine

(b)

Dative (coordinate) covalent bond

Dative or coordinate covalent bond is the type of covalent bond in which the shared electron pair is donated by only one atom. The atom which provides the shared electrons is known as electron donor, and the atom which gains a pair of electrons is known as electron acceptor. The electron donor has unused pair of electrons called *lone pair*. The lone pair of electrons is the outer pair of electrons of an atom which do not take part in the normal covalent bond formation. The acceptor atom possesses an empty orbital in its outermost shell. For instance, the reaction between aluminium chloride and ammonia to form ammonium aluminium chloride involves dative bond formation. In the formation of aluminium chloride ($AlCl_3$), aluminium has only six electrons in its outer most shell, that is, two electrons are missing to attain the noble gas structure of argon. This can be shown by the electronic configuration of aluminium and covalent bond formation between aluminium and three chlorine atoms as illustrated in Figure 2.1

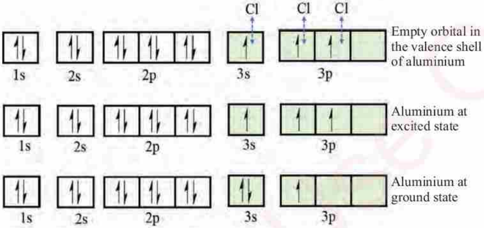
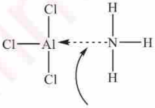


Figure 2.1 Formation of covalent bond between aluminium and three chlorine atoms

To be stable, aluminium chloride coordinates with electron donor molecule (ammonia) that consists of lone pair of electrons and forms dative covalent bond using its empty orbital.



Dative covalent bond

In the previous example, $AlCl_3$ acts as an electron acceptor and NH_3 acts as an electron donor (Figure 2.2). The resulting bond between aluminium and nitrogen (Al-N) is called dative or coordinate covalent bond.

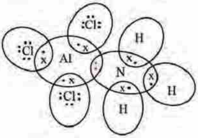
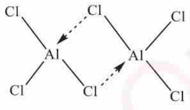


Figure 2.2 The dative covalent bond between aluminium and nitrogen in $AlCl_3$

Other examples of molecules formed by dative bonding are the dimers of aluminium chloride (Al_2Cl_6), ammonium ion (NH_4^+), and ammonium chloride (NH_4Cl) and the hydroxonium ion (H_3O^+) described as follows:

Formation of Al_2Cl_6

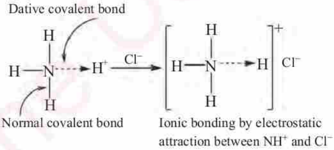
When anhydrous aluminium chloride ($AlCl_3$) is cooled, the molecule dimerises to form molecules of Al_2Cl_6. The two monomers of $AlCl_3$ are held together in Al_2Cl_6 dimers by dative bonding.



Al_2Cl_6

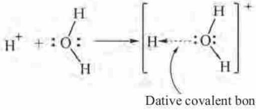
Ammonium ion (NH_4^+) and ammonium chloride (NH_4Cl)

If ammonia comes into contact with an acid, for example, hydrochloric acid in ionised form (H^+Cl^-) the proton accepts a lone pair of electrons from ammonia ($:NH_3$) and produces ammonium ion (NH_4^+). The ammonium ions are associated by electrovalent bond with chloride ions to form ammonium chloride. Ammonium chloride therefore shows all three common bonds (electrovalent or ionic, dative and normal covalent bond).



The hydroxonium ion (H_3O^+)

When an acid dissolves in water, the resulting hydrated hydrogen ion is known as *hydroxonium ion*. The formation of hydroxonium ion is the result of the coordination of water (H_2O) with hydrogen ion from the acid by using the lone pair of electrons present in the oxygen atom. The electrovalent character accounts for the properties of a salt as crystalline solid, soluble in water, and electrolyte in solution.



2.1.3 Metallic bonds

Metallic bonds are the electrostatic forces of attraction between positive metal ions and the negative delocalised electrons (sea of electrons). Metals do not have enough electrons in their valence shells to form a stable octet. Even though they do not form covalent bonds, they do share their electrons. In metallic bonding, atoms release their electrons in a shared sea of electrons (Figure 2.3). A metallic object is considered as a non-rigid arrangement of metal ions in a sea of free electrons, and the force that holds the metal atoms together is called *metallic bond.* The valence electrons form a mobile sea of electrons which occupy the space between the metal ions and are free to move throughout the metal.

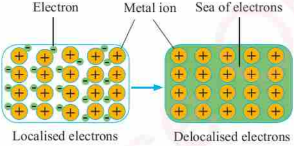


Figure 2.3 Localised and delocalised electrons in a metals

The strength of metallic bond system increases with an increase in the number of electrons in the delocalised system. The strength also increases with a decrease in the size of the atomic core which forms a structural unit. For example, sodium as an alkali metal has only one electron in each atom available to enter the delocalised system. Therefore, alkali metals are soft and have low melting points due to their weak metallic bonds. Metals that can release large number of electrons such as transition elements are hard with high tensile strengths and have high melting points corresponding to a strong metallic bond system.

The existence of the metallic bond accounts for some other physical properties of metals such as malleability, ductility and good conductivity of heat and electricity. *Malleable* means, the substance can be shaped in different forms. *Ductile* means the substance can be stretched into thin wires such as the wires used in installation. Examples of metallic objects are shown in Figure 2.4.

Figure 2.4 Example of objects in which atoms are linked together by metallic bonding

Exercise 2.1

1. Give four differences between ionic and covalent compounds.
2. Describe the concept of dative covalent bonding.
3. Draw the Lewis structures of the following substances:
   (a) Nitrogen
   (b) Hydrogen sulphide
   (c) Sodium fluoride
4. Which of the following compounds would you expect to be polar or non-polar? Give reasons.
   (a) Cl_2
   (b) BeF_2
   (c) CO
   (d) SO_2
5. Differentiate a coordinate covalent bond from a non-polar covalent bond.
6. Explain the nature of covalent bond, using carbon tetrachloride as an example.
7. (a) State the nature of bonding in the following:
      (i) Sodium chloride
      (ii) Nitrogen
      (iii) Hydrogen chloride gas
   (b) How does the nature of the bonding affect the properties of the substances in 7(a)?
8. Draw the electronic formulae of hydrogen chloride and ammonium chloride.

2.2 Strengths and lengths of ionic and covalent bonds

2.2.1 Ionic bond strength

An ionic compound is stable because of the electrostatic attraction between its positive and negative ions. The lattice energy of a compound is a measure of the strength of this attraction. The *lattice energy* of an ionic compound is defined as the energy required to separate one mole of the solid into its component gaseous ions. Note that the convention is used where the ionic solid is separated into ions, so the lattice energies will be *endothermic* (positive values). A larger magnitude for lattice energy indicates a more stable ionic compound. The lattice energy for sodium chloride is 786 kJ; thus, it requires 786 kJ to separate one mole of solid NaCl into gaseous Na^+ and Cl^- ions. When one mole of each of the gaseous Na^+ and Cl^- ions form solid NaCl, 786 kJ of heat is released. The lattice energy of an ionic crystal increases rapidly as the charges of the ions increase and the sizes of the ions decrease. Different inter-atomic distances produce different lattice energies.

2.2.2 Covalent bond strength

Bond strength describes how strongly each atom is joined to another atom, and therefore how much energy is required to break the bond between the two atoms. Stable molecules exist because covalent bonds hold the atoms together. The strength of a covalent bond is measured by the energy required to break it, that is, the energy necessary to separate the bonded atoms. Separating any pair of bonded atoms requires energy. The stronger the bond, the higher the energy required to break it. The energy required to break a specific covalent bond in one mole of gaseous molecules is called the *bond energy* or the *bond dissociation energy*. Therefore, the strength of a covalent bond is measured by its bond dissociation energy, that is, the amount of energy required to break that particular bond in a mole of molecules. A molecule with three or more atoms has two or more bonds. The sum of all bond energies in such a molecule is equal to the standard enthalpy change for the endothermic reaction that breaks all the bonds in the molecule.

The strength of a bond between two atoms increases as the number of electron pairs in the bond increases. Generally, as the bond strength increases, the bond length decreases. Multiple bonds are stronger than single bonds between the same atoms. Thus, it is found that triple bonds are stronger and shorter than double bonds between the same two atoms. Likewise, double bonds are stronger and shorter than single bonds between the same two atoms. Average bond energies for some common bonds and a comparison of bond lengths and bond strengths for some common bonds are shown in Table 2.1. When one atom bonds to various atoms in a group, the bond strength typically decreases down the group of the periodic table. For example, the bond energies of C–F, C–Cl and C–Br are 439 kJ/mol, 330 kJ/mol and 275 kJ/mol, respectively.

Table 2.1 Average bond lengths and bond energies for some common bonds

Bond	Bond length (nm)	Bond energy (kJ/mol)
C—C	0.154	347
C═C	0.134	611
C≡C	0.120	837
C—N	0.147	305
C═N	0.128	615
C≡N	0.116	891
C—O	0.143	360
C═O	0.123	745
C—Cl	0.177	339
F—F	0.143	159
Cl—Cl	0.199	243
Br—Br	0.228	193
I—I	0.266	151
H—H	0.074	436
H—C	0.110	414
H—N	0.100	389
H—O	0.097	431
H—F	0.092	565
H—Cl	0.127	431
H—Br	0.141	364
H—I	0.161	297
N—N	0.145	160
N═N	0.123	418
N≡N	0.109	946

Exercise 2.2

1. Explain the concept of hybridisation of an atomic orbital.
2. Explain why the bond angle in ammonia (107.3º) and methane (109.5º) differ, although they both have tetrahedral structure.
3. Differentiate between atomic orbital and molecular orbital.
4. Using the concept of hybridisation of atomic orbitals, describe the shape of carbon tetrachloride (CCl_4).
5. Explain the type of hybridisation of the central atom and geometry in each of the following compounds:

   (a) H_2S (b) CS_2 (c) Cl_2O (d) NH_3 (e) SO_2
6. Which is the strongest bond in each of the following pairs?

   (a) C – C or C = C (b) C – N or C ≡ N

   (c) C ≡ O or C = O (d) H – F or H – Cl

   (e) C – H or O – H (f) C – N or C – O

2.3 Intermolecular forces

Intermolecular forces are forces which facilitate the interaction between molecules. In this section, you will learn about two types of intermolecular forces which are hydrogen bonding and van der Waals forces.

2.3.1 Hydrogen bonding

Hydrogen bonding is a special type of bonding formed by *dipole-dipole* forces between hydrogen atom of one molecule and a more electronegative atom of a neighbouring molecule.

Conditions for the formation of a hydrogen bond

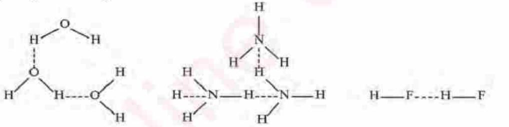
Apart from forming a normal covalent bond, under certain conditions hydrogen can form a hydrogen bond with other elements within the same or different molecules. The following are the necessary conditions for the formation of a hydrogen bond:

(a) Hydrogen atom must be bonded to a highly electronegative atom such as fluorine, oxygen and nitrogen.

(b) The electronegative atom to which the hydrogen is bonded must possess at least one lone pair.

(c) The electronegative atom should have small size.

Generally, hydrogen bond is a special type of dipole-dipole force between a hydrogen atom covalently bonded to a more electronegative atom with another highly electronegative atom that possess lone pair(s) of electrons. It is important to note that, a covalent bond that exists between hydrogen and a small highly electronegative atom is not a hydrogen bond, but a polar covalent bond. The most important elements whose molecules form hydrogen bonds are nitrogen (N), oxygen (O), and fluorine (F) because they are small in size and have large electronegativity values. Examples of molecules that exhibit hydrogen bonds include water (H_2O), ammonia (NH_3), and hydrogen fluoride (HF) as shown in Figure 2.5. The dished line (-----) in the molecules in Figure 2.5 indicates hydrogen bonding.



hydrogen bonding in H_2O, hydrogen bonding in NH_3 hydrogen bonding in HF

Figure 2.5 Hydrogen bonding in H_2O, NH_3, and HF

Types of hydrogen bond

There are two types of hydrogen bonds, namely the *intermolecular* and the *intramolecular* hydrogen bonds. An intermolecular hydrogen bond is the type of hydrogen bond that exists between a hydrogen atom of one molecule and a small highly electronegative atom of another molecule. Examples of molecules that exhibit intermolecular hydrogen bonds are water, ammonia and hydrogen fluoride as shown in Figure 2.5. An intramolecular hydrogen bond is the type of hydrogen bond that exists between hydrogen atom and a small highly electronegative atom within the same molecule. This type of hydrogen bond occurs mostly in organic compounds and is possible in organic structures with five or six membered ring structures. Examples of molecules that exhibit intramolecular hydrogen bonding are ortho-nitrophenol and salicylaldehyde as illustrated in Figure 2.6. The dashed line (----) indicates hydrogen bonds.

Intramolecular hydrogen bonding decreases the boiling point of the compound as well as its solubility in water, because it cannot form hydrogen bond with water and thus causes decrease in intermolecular forces of attraction.

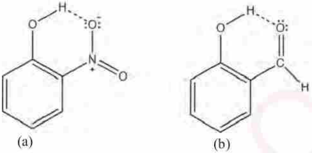


Figure 2.6 Intramolecular hydrogen bonds in (a) *ortho* nitrophenol and (b) salicylaldehyde

Properties of a hydrogen bond

Hydrogen bond is a form of covalent bond. However, due to its nature it has characteristics which differentiate it from a normal covalent bond. The following are the properties of a hydrogen bond:

(a) Hydrogen bond (3-10 kcal/mol) is a weaker bond than a covalent bond (50 -100 kcal/mol) but it is stronger than van der Waal's forces (1 kcal/mol).

(b) In the formation of hydrogen bond, the electron pair is not shared, hence different from covalent bond.

(c) The strength of a hydrogen bond depends on the electronegativity of the atom to which a hydrogen atom is attached with a covalent bond. As the electronegativity of the atom increases, the strength of the hydrogen bond increases.

(d) A typical hydrogen bond is linear, but angular in solids such as ice.

Effects of hydrogen bonds

The formation of hydrogen bonds has significant effects on some chemical and physical properties of molecules in which it occurs. The following are some of its effects:

Abnormally high melting and boiling point point

Under normal circumstances, the melting point (*mp*) and boiling point (*bp*) of compounds in a group of the periodic table increase with increase in molecular weights. But in the case of group VA, VIA, and VIIA, the *mp* and *bp* of H_2O, NH_3, and HF are exceptionally higher than the hydrides of other members of the group. This is because these molecules form hydrogen bonds which need extra energy to be broken. The trend in boiling points of hydrides of groups IVA, VA, VIA, VIIA is shown in Figure 2.7.

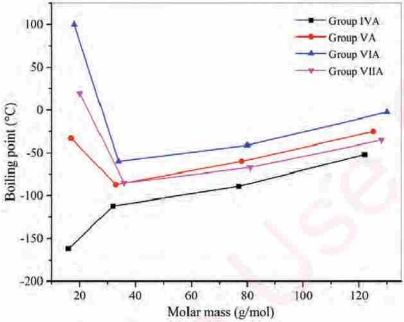


Figure 2.7 A plot of boiling point of hydrides of group IVA, VA, VIA, and VIIA against molar mass

Solubility

Hydrogen bond also influences the solubility of one substance in another. Covalent compounds do not generally dissolve in water, but those forming a hydrogen bond, readily dissolve in water. For example, alcohols (ethanol), ammonia, amines, lower aldehydes, and ketones are soluble in water due to the formation of hydrogen bonds with water molecules.

Increase in molecular mass

Some compounds exist as dimers because of the formation of hydrogen bond. The molecular masses of such compounds are found to be double those calculated from their simple formula. For example, the molecular mass of acetic acid is found to be 120 instead of 60. The molecular structure of the dimer of acetic acid is shown as in Figure 2.8

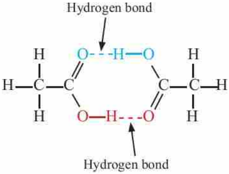


Figure 2.8 The molecular structure of acetic acid dimer

Hydrogen bond in ice

Oxygen atom in water consists of two lone pairs of electrons that can participate in hydrogen bond formation. Therefore, each water molecule can have four hydrogen bonds. The formation of hydrogen bond in water is illustrated in Figure 2.9.

The structure (Figure 2.9) shows that hydrogen bonds are directional. The directional effect of hydrogen bond makes each oxygen atom in ice (frozen water) tetrahedral surrounded by four hydrogen atoms. This arrangement of atoms causes the formation of vacant spaces in ice and hence the abnormal behaviour of water. Due to the vacant spaces in ice, their density is lower than that of liquid water, making it to float on water (Activity 2.1). As temperature of ice water increases, some hydrogen bonds break and ice melts causing the water molecules to be closely packed, hence the volume decreases.

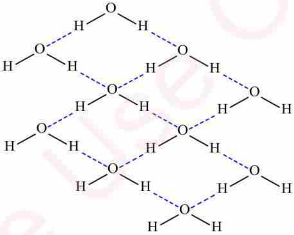


Figure 2.9 The hydrogen bonding in ice

Activity 2.1

To investigate the effect of hydrogen bonding in water

Requirements: 2000 mL of water, deep-freezer or refrigerator, one beaker of 1000 mL, two plastic beakers of 50 mL and measuring cylinder of 500 mL

Procedure

1. Fill the two 50 mL plastic beakers with water.
2. Measure 500 mL of water and pour it into a 1000 mL beaker.
3. Put the two plastic beakers filled with water into the deep-freezer or refrigerator and allow the water in it to freeze.
4. Remove the frozen ice blocks and pour them into a 1000 mL beaker containing 500 mL of water and note the observation.

Question

What have you observed in the experiment based on the concept of hydrogen bonding?

2.3.2 The van der Waals forces

The van der Waals forces were named after Dutch Scientist Johannes Diderik van der Waals (1837−1923) who discovered the force of attraction between molecules or atoms. The van der Waals forces are weak attractive forces between uncharged molecules arising from the interaction of permanent or transient electric dipoles. They are only significant when the molecules or atoms are very close to one another and hence they are said to be short-range forces. The van der Waals forces include the dipole−dipole interactions, the induced dipole interactions and the dispersion or London forces.

Dipole–dipole interactions

These are electrostatic interaction between molecules which have permanent dipole. Example of dipole–dipole interactions can be seen in HCl and $CHCl_3$ as illustrated in Figure 2.10. The positive end of one polar molecule will attract the negative end of another molecule.

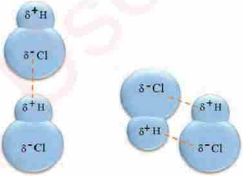


Figure 2.10 Dipole–dipole interactions

Induced dipole interactions

Induced dipole interactions are attractive forces which exist between polar molecules and non-polar molecules or atoms, when they are so close to one another. When a molecule with a dipole gets closer to another molecule which has no dipole, after some time it tends to induce the dipole by polarising it as shown in Figure 2.11.

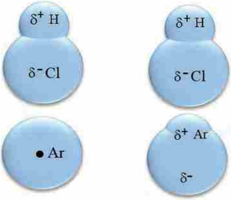


Figure 2.11 Induced dipole attraction

Dispersion (London) forces

Dispersion forces are temporary attractive forces existing between non-polar molecules as a result of electrons in two adjacent atoms occupying positions that make the atoms form temporary dipole. Consider two non-polar molecules which are very close to each other. Since they are non-polar, the arrangements of their electrons are on the average symmetrical.

Yet at any given instant the electron distribution in one molecule may be unsymmetrical due to constant motion of electrons which may cause a molecule to develop temporary dipole. The illustration in Figure 2.12 shows how temporary dipole in molecule A can attract the electron cloud of a neighbouring molecule B. This means that both molecules will have dipoles and they will attract one another. Generally, van der Waals forces between small molecules are weak and strong between large linear molecules.

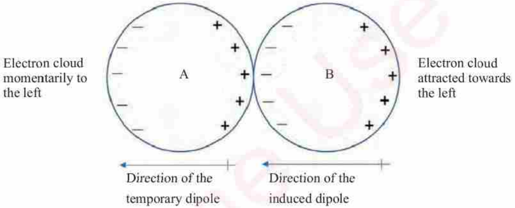


Figure 2.12 Dispersion forces

Exercise 2.3

1. (a) What is a hydrogen bonding?

   (b) What are the necessary conditions for the formation of hydrogen bonding?

2. Why does ice float on water? Explain.

3. Can hydrogen bonding occur in the following compounds in their liquid state? Give reasons.

   (a) NH_3 (b) CaF_2 (c) HBr

   (d) CH_3OH (e) NaH (f) H_2O

   (g) C_3H_8 (h) HCO(OH)

4. Arrange the compounds HF, H_2O and HBr in order of the increasing strength of the hydrogen bonding.
5. Describe the effects of hydrogen bonding in some of the molecules in which it exists.

2.4 Hybridisation of atomic orbitals

In chapter one, you learned about the quantum numbers and how they describe the characteristics of electrons in orbitals. In this section, you will learn about the concept of hybridisation of atomic orbitals, types of hybridisation of atomic orbitals, and overlapping of hybrid orbitals to form molecular orbitals.

2.4.1 Concept of hybridisation of atomic orbitals

The Lewis' Theory is used to determine the structure of molecules in a simple and rapid way using dot structures. However, the theory does not account for odd electron species and resonance structures. The valence shell electron pair repulsion (VSEPR) model successfully predicted the shapes of molecules.

Valence Shell Electron Pair Repulsion (VSEPR) Theory

The VSEPR theory is based on the repulsion between the electron pair in the valence shell of atoms of the molecule. It is also useful to predict correctly the molecular geometries of many substances. The theory states that the electron pairs tend to remain as far apart from each other as possible to minimise repulsion. This theory explains that the shape of the molecule is determined by bonding and non-bonding (lone pair) electrons around the central atom of a molecule. These electrons tend to be far apart from each other so as to minimise the repulsion force between them. Lone pairs are closer to the nucleus than bonding pairs and hence exert a greater repulsive force. For example, lone pair-lone pair has greater repulsion than lone pair-bonding pair.

Molecules with two bonds electron pairs around the central atom form a linear shape at an angle of 180 °C. Examples of there molecules are $BeCl_2$, C_2H_2 and CO_2. Molecules with three bonds electron pairs or two bonds electrons and one electron pair form trigonal planar shape. An example of such molecule is BCl_3. Boron has three bonds electron while tin has two bonds electron and one lone pair.

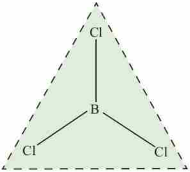
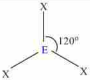
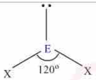
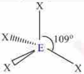
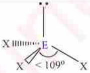
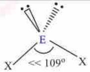
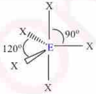
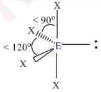
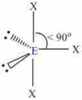
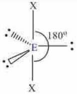
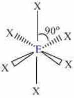
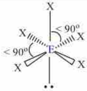
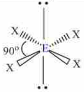
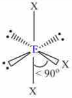
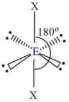


Figure 2.13 Molecular geometry of BCl_3

Molecules having four pairs of electrons around the central atom, for example, HCl, NH_3, NH_4^+, and H_2O experience mutual repulsion of the bonding and the lone pairs of electrons. Hence, geometrical distribution of electron pair (arrangement of valence electron pair) is tetrahedral. The arrangement of atoms in methane and ammonium ion forms a tetrahedral geometry with the bond angle of 109.5°, in ammonia trigonal pyramid (107.5°) and in water angular or bent shape (104.5°). The decrease in the bond angle is due to increasing number of lone pairs. Neither the Lewis nor the VSEPR theory accounted for the quantitative information about the bond length or the energies of molecules. Table 2.2 shows the geometries of various compounds based on VSEPR theory.

Table 2.2 Geometries of various compounds based on VSEPR Theory

Steric No.	Basic geometry No lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
1	 Linear				
2	 Trigonal planar	 Bent or angular			
3	 Tetrahedral	 Trigonal pyramid	 Bent or angular		
4	 Trigonal bipyramid	 Sawhorse or seesaw	 T-shape	 Linear	
5	 Octahedral	 Square pyramid	 Square planar	 T-shape	 Linear

The valence bond theory treats a covalent bond in terms of the overlap of pure or hybrid orbitals. This theory explains what a covalent bond is, and gives a relationship between molecular shapes and interactions of atomic orbitals. According to the valence bond theory, a covalent bond forms when half-filled orbitals of two atoms overlap. When a molecule of H_2 forms, for instance, the two 1*s* electrons of the two H atoms overlap. The electrons occupying the overlapping 1*s*-orbitals have opposite spins as illustrated in Figure 2.14.

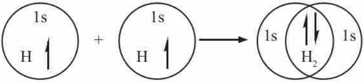


Figure 2.14 Orbital overlap in hydrogen molecule

The stability of the bond depends maily on the attraction of the nuclei for the shared electrons. The greater the orbital overlap, the stronger the bond. Since the extent of overlap depends on the shape and direction of the orbitals involved, the lobes of *p* or *d*-orbitals are oriented in the directions that maximises the overlap due to having more electron density in one direction. The combinations of different atomic orbitals to maximise the overlap forms new atomic orbitals because the valence atomic orbitals in the molecule are different from those in the isolated atoms. The spatial orientation of these newly formed orbitals leads to more stable bonds which are consistent with the observed shapes of molecules. The process of mixing orbitals to form stable bonds is called *hybridisation* and the newly formed atomic orbitals are called *hybrid* orbital*s*. The types of hybrid orbitals vary with the type of atomic orbitals mixed, but their number equals to the number of mixed orbitals.

Rules of hybridisation

Hybridisation follows some rules including the following:

1. Only the orbitals of a central atom undergo hybridisation.
2. Orbitals of nearly the same energy level combine to form hybrid orbitals.
3. The numbers of the hybridising atomic orbitals are always equal to the number of hybrid orbitals.
4. The hybrid orbitals tend to be scattered in space and farthest apart.
5. Hybrid orbitals are stronger than non-hybrid orbitals.
6. During hybridisation the number of combined orbitals is as per requirement of the bonding atoms.

2.4.2 Types of hybridisation of atomic orbitals

There are different types of hybridisation of atomic orbitals which include *sp*, sp^2, sp^3, sp^3d^1 and sp^3d^2 hybridisation. In this section, the discussion is based on *sp*, sp^2, sp^3, and sp^3d^1 hybridisation.

sp hybridisation

The *sp* hybridisation involves the mixing of two non-equivalent orbitals of a central atom each one from *s* and *p*-orbitals to form two equivalent *sp* hybrid orbitals. For example, the *sp* hybridisation in beryllium ($_4$Be) atom can be used to explain the formation of beryllium chloride as illustrated in Figure 2.15

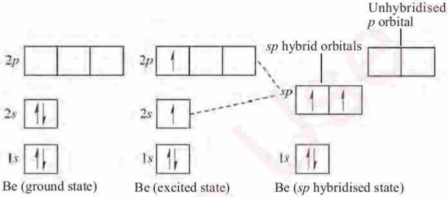


Figure 2.15 *sp* hybridisation of beryllium

One electron from 2*s* is promoted to 2*p* to form two unequal orbitals; hybridising them produces two new and equal hybridised orbitals. The hybridised state of beryllium consists of two *sp* equivalent hybrid orbitals with two unpaired electrons. These unpaired electrons can form covalent bond with unpaired electrons from chlorine atoms to form $BeCl_2$. The other two 2*p*-orbitals remain unhybridised. Examples of other molecules with sp hybridisation are carbon dioxide (CO_2) and ethyne (C_2H_2) as shown in figure 2.16.

Figure 2.16 Molecular geometries of carbon dioxide and ethyne

sp² hybridisation

The sp^2 hybridisation involves the mixing of one *s* and two *p*-orbitals of the central atom to give three hybrid orbitals that point towards the vertices of an equilateral triangle. The axes of these hybrid orbitals are 120° apart. The orbitals formed are called sp^2 hybrid orbitals. Molecules with sp^2 hybridised orbitals include boron trifluoride (BF_3), aluminium chloride ($AlCl_3$), iron (III) chloride ($FeCl_3$), and tin chloride ($SnCl_2$). Such molecules have a trigonal planar shape as shown in Figure 2.17.

Figure 2.18 shows sp^2 hybridisation in boron ($_5B$) which can be used to explain the formation of boron trifluoride (BF_3).

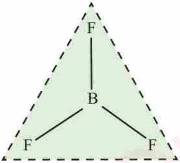


Figure 2.17 Trigonal planar shape of boron trifluoride

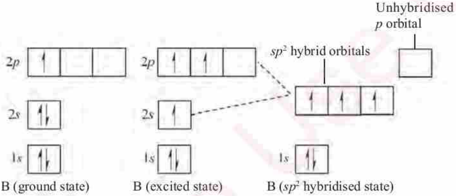


Figure 2.18 sp^2 hybridisation of boron atom

The 2*s* and two of the three 2*p*-orbitals of the B atom mix to make three sp^2 hybrid orbitals. The third 2*p*-orbital remains empty and unhybridised. The overlap of 2*p*-orbitals on the three F atoms with the sp^2 hybrids form BF_3, where each of the three sp^2 orbitals become fully filled by sharing electrons with F atom. The three sp^2 hybrid orbital of B lie at 120° apart and the unhybridised 2*p*-orbitals is perpendicular to the trigonal planar.

sp^3 hybridisation

The sp^3 hybridisation involves mixing of one *s* and three *p*-orbitals of the central atom to form four equivalent sp^3 hybrid orbitals as shown in Figure 2.19. These hybrid orbitals point towards the vertices of the tetrahedral. The four hybrid orbitals (of carbon for example), consist of unpaired electrons which can combine covalently with hydrogen to form methane (CH_4). The axes of these hybrid orbitals are 109.5° apart.

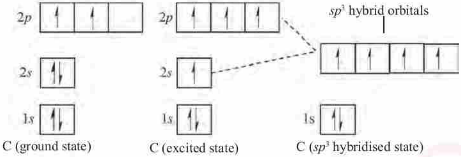


Figure 2.19 sp^3 hybridisation of carbon atom

Some compounds in sp^3 hybridisation involve lone pairs. Examples of such compounds are water and ammonia. Their hybridisation involves 2*s* (lone pair) and three 2*p*-orbitals. Figure 2.20 shows the hybridisation of oxygen.

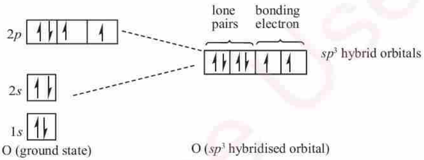


Figure 2.20 sp^3 hybridisation of oxygen

Normally, pure hybrid orbitals which include bonding hybrid orbitals have more *p*-characters than those involving a lone pair of electron. The later, has more *s*-character. Hence the electron cloud of a lone pair spreads out more laterally resulting to the observed H-N-H angle of 107.3° in NH_3 and H-O-H angle to be 104.3° in water. Molecules or compounds formed by sp^3 hybridisation have the tetrahedral shapes as shown in Figure 2.21.

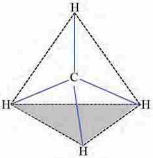


Figure 2.21 Tetrahedral shape of methane

sp^3d^1 hybridisation

The sp^3d^1 hybridisation involves the mixing of one *s*, three *p* and one *d*-orbitals of the central atom. Molecules with this type of hybridisation have a central atom from period three to higher periods. Mixing of one of the 3*s*-orbital, three of 3*p*-orbitals and one of 3*d*-orbital form five sp^3d^1 hybrid orbitals. Examples of molecules that their central atoms form sp^3d^1 hybridisation are PCl_5, SF_4, ClF_3, and XeF_2. Figure 2.22 shows the hybridisation of phosphorous ($_{15}P$) atom which can be used in the formation of phosphorous pentachloride.

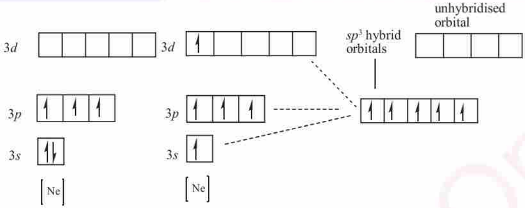


Figure 2.22 sp^3d^1 hybridisation phosphorous

The molecular shape in sp^3d^1 are trigonal bipyramid with respect to the arrangement of valence electrons. On the other hand, the shape of molecules with respect to atoms in sp^3d^1 molecules change slightly. For example, the shapes of PCl_5, SF_4, ClF_3, and XeF_2 are trigonal bipyramid, irregular tetrahedral, T-shaped, and linear respectively.

2.4.3 Overlapping of hybrid orbitals

The overlap of atomic orbitals in carbon (C) atom can also result into the formation of sp^3, sp^2 and sp hybrid orbitals as described in this section. However, before discussing the overlapping of orbitals, it is worth to understand the types of overlaps based on the orientation of the orbitals and their influence on the strength of the bonds. Depending on the nature of the overlap, there are basically two types of bonds formed which are *sigma (σ)* and *pi (π)* bonds.

Sigma (σ) bond

The sigma bond is formed by a head to head overlapping of atomic orbitals along the nuclear axis. There are three types of overlaps that result into sigma bond. These are *s-s*, *s-p* and *p-p* as shown in Figure 2.23.

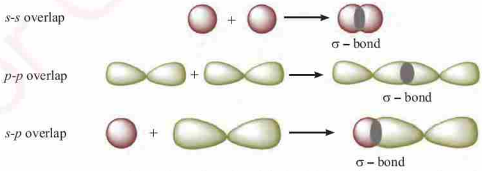


Figure 2.23 Types of overlaps of atomic orbitals which results into bond formation

The *pi* (π) bond

This type of bond is formed by the side by side overlap which occurs perpendicular to the internuclear axis. The sideways orientation result into the formation of a weak bond as opposed to that of the sigma bond which is formed by head to head overlap. Figure 2.24 summarises the *pi* bond formation.

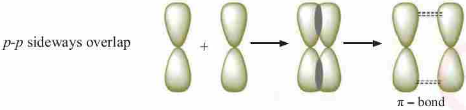


Figure 2.24 The *pi* bond formation by side by side overlap

Strengths of the molecular bonds

According to Pauling and Slater, the strength of the chemical bond is proportional to the extent of overlapping between the atomic orbitals. Overlapping takes place only between the outermost atomic orbitals containing the valence electrons. The *p*-orbitals are more directionally concentrated than *s*-orbital. Thus, the orbital overlapping which is more directionally concentrated will form a strong bond of the order $s-s < s-p < p-p$ for sigma bond. The *pi* (π) bonds are generally weaker since the extent of overlapping is less than the overlapping which occurs during sigma bond formation. Table 2.3 summarises the differences between σ and π onds.

Table 2.3 Differences between *σ* and π-bonds

Sigma (σ) bond	***pi* (π) bond**
It is formed by head to head overlapping of atomic orbitals.	It is formed by side to side overlapping of p_y or p_z atomic orbitals.
The overlap is along internuclear axis.	The overlap is perpendicular to internuclear axis.
It results into strong bond formation.	It results into weak bond formation.
The orbital is symmetrical to the rotation through the line joining two nuclei.	The orbital is asymmetrical to the rotation through the line joining two nuclei.
Its region of overlap is large.	Its region of overlap is small.

The overlap of atomic orbitals in carbon compounds

Carbon atom is among the elements which exhibit both types of hybridisation of atomic orbitals. In this section, taking carbon compounds as examples, the hybridisations of *sp* in ethyne, sp^2 in ethene, and sp^3 in methane will be discussed.

sp hybridisation

In this type of hybridisation, the 2*s* and only one of 2*p* ($2p_x$) orbitals hybridise to form two *sp*-orbitals or diagonal orbitals. The remaining two 2*p*-orbitals ($2p_y$ and $2p_z$) are left unhybridised. The two *sp*-orbitals lie along a straight line and thus make an angle of 180° with each other. The *sp* hybridisation of carbon is shown in Figure 2.25.

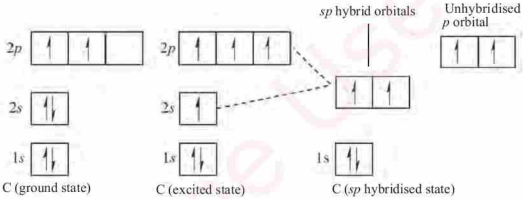


Figure 2.25 The *sp* hybridisation of carbon atom

The unhybridised 2*p*-orbitals, lie in different planes at right angles to each other as well as to the *sp*-orbitals.

Formation of sigma and pi bonds in acetylene

The C-C sigma bond in acetylene is formed when one *sp* hybrid orbital of one carbon atom overlaps axially with the *sp* hybrid orbital of the other carbon atom. The hybridised orbital of each carbon atom overlaps axially with the half-filled hydrogen orbital to form a sigma bond. Each of the two unhybridised orbitals of one carbon atom overlaps sideways with the similar orbitals of the carbon atom to form two π bonds. This overlapping results into the formation of a carbon-carbon triple bond (C≡C), which consists of one σ bond and two π bonds. The formation of sigma and pi bonds in acetylene is illustrated in Figure 2.26.

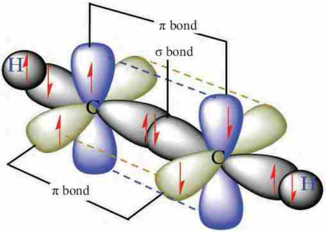


Figure 2.26 The formation of sigma and *pi* bonds in acetylene

sp^2 hybridisation

In this type of hybridisation, one 2*s* and two of the 2*p*-orbitals ($2p_x$ and $2p_y$) are hybridised to form three equivalent orbitals called sp^2 hybrid orbitals as shown in Figure 2.27.

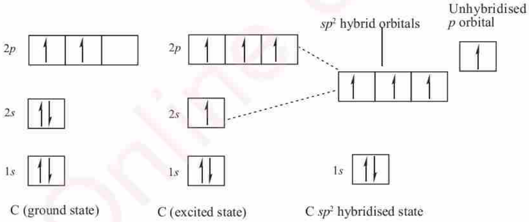


Figure 2.27 sp^2 hybridisation of carbon atom

Each hybrid orbital has one third of the '*s*' character and two third of '*p*' character. The bond angle between the two hybridised orbitals is 120°: and the shape of orbitals is called trigonal planar. The unhybridised orbital ($2p_z$) of carbon is oriented in a plane perpendicular to the plane containing sp^2 orbitals (Figure 2.28).

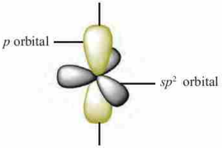


Figure 2.28 The unhybridised $2p_z$ orbital

Formation of sigma and pi bond in ethene

In ethene (C_2H_4) molecule, the three sp^2 hybrid orbitals of each carbon atom share the electron pair on an area centred on a line running between the atoms. This type of overlap forms a covalent bond known as sigma (σ) bond. Two of the three sp^2 hybrid orbitals on each carbon form σ bonds with 1*s*-orbital on each hydrogen atom. One sp^2 hybrid orbital on one carbon atom overlaps with one sp^2 hybrid orbital of another carbon atom to form σ bond, which is strong. The two unhybridised orbitals ($2p_z$) from two carbon atoms undergo sideway overlap to form pi (π) bond, which is weak. This bond has two regions of electron density, one above and one below the σ bond axis. The π bond holds two electrons that move through both regions of the bond. Therefore, one σ bond and one π bond constitute the double bond of ethene (Figure 2.29).

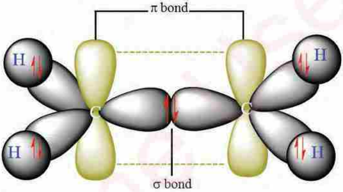


Figure 2.29 Formation of π and σ bond in ethene

sp^3 hybridisation

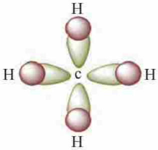


Figure 2.30 sp^3 hybrid orbitals overlap in methane

The one "*s*" orbital from hydrogen atom and three *p*-orbitals from the carbon atom hybridise to form four sp^3 hybrid orbitals as in Figure 2.18.

The sp^3 hybridised orbitals overlap with the "*s*" orbitals of hydrogen to form a methane molecule as shown in Figure 2.30.

Revision exercise 2

1. Discuss the necessary conditions for the formation of ionic and covalent bonds.

2. Explain at least three properties of ionic compounds.

3. (a) What is meant by hydrogen bonding?
   (b) Describe the conditions necessary for the formation of hydrogen bond and how this bond differs from other intermolecular forces.

4. Describe the difference between sigma and *pi* bonds. What types of orbitals are involved in each?

5. Using examples, explain the differences between intramolecular and intermolecular hydrogen bonding.

6. Complete the table below by filling in the missing information.

Compound	Type(s) of bonds	Number of lone pair(s)	Type of hybridisation	Geometrical shape
PCl_3				
NH_3				
CF_4				
H_2O				
$AlCl_3$				

7. Why do NH_3, H_2O and HF have higher boiling point than those of PH_3, H_2S and HBr?

8. Account for the following observation; although CO_2 and SO_2 have the same empirical formulae, CO_2 is non-polar while SO_2 is a polar compound.

9. Explain the types of intermolecular forces existing in the following molecules:

   (a) HBr(*g*) (b) Cl_2(*g*) (c) HF(*l*)

10. Give the molecular geometry of the following molecules using VSEPR theory.

    (a) SF_4 (b) ClF_4 (c) BrF_5 (d) SO_4^{2-} (e) PCl_5

Chapter Three

Environmental chemistry

Introduction

All living creatures are surrounded by an environment that comprises the biotic, abiotic, and climatic factors which support life. It is important to study the environment so as to understand how it can be conserved and manipulated for sustainable life. In this chapter, you will learn about the general concept of environmental chemistry, environmental conservation, environmental pollution, the ozone layer depletion, as well as the greenhouse effect and global warming.

3.1 The general concept of environmental chemistry

Environmental chemistry is a branch of chemistry that deals with the study of various chemical processes that take place in the environment. It is concerned with the sources, reactions, transport, effects and fate of the chemical species in the environment. Various activities such as industrial, agricultural, infrastructure, mining and housing development, and the pressure of the growing population have significantly contributed to contamination of the environment with solid, liquid and gaseous harmful materials.

Nature has a self-regulatory property to withstand the adverse effect caused by human activities or natural disasters if they are within its tolerance limit. Excessive drought and rainfall, temperature rise, depletion of ozone layer, and storms are some of the results of failure of the environment to assimilate the contaminants and effects produced by human activities and natural phenomena. Effort to address these problems are supplemented by knowledge of environmental chemistry.

3.2 Environmental conservation

Environment comprises the water, land, atmospheric sub-systems and meteorological factors such as sunlight, temperature and rainfall affecting them. When a disturbance is introduced in any of the sub-systems, the system (environment) regulates itself to offset the effects of the disturbance if it is within the tolerance limits of the system. Human activities being undertaken in various segments of the environment, should be managed to reduce the production of contaminants or effects which exceed threshold line of tolerance of the environment. Violation of this law of nature can be disastrous to life. Intervention measures taken by the governments, non-governmental organisations and individuals to protect environment from destructive human activities is called *environmental conservation*. Intervention measures include treatment of industrial emissions and effluents, and ban of overgrasing and uncontrolled harvesting of trees. In adition, there are rules, regulations and guidelines that are set to manage the environmental activities.

In Tanzania, environmental issues are controlled by an environment division under the responsible ministry. The environment division has the role of formulating policies, planning, co-ordinating and monitoring all environmental issues in the country through its institutions. One of the institution is the National Environmental Management Council (NEMC) which is a technical advisory agency with the role of regulating environmental practices and protection as well as ensuring sustainable use of natural resources in the country. Another division is Tanzania Forest Research Institute (TAFORI) which is responsible in performing researches on forest plantation, forest genetics and protection, agroforestry and forest ecology. The Ministry may use research results from its institutions in policy and decision making related to environmental issues. It is through this relationship the environmental conservation, protection and utilisation can successfully and sustainably be implemented.

3.2.1 Resource protection and utilisation

Natural resources are there to support life, but they are always scarce and most of them are non-renewable. Due to this, their utilisation must balance with their protection. However, the world is currently experiencing over-utilisation of natural resources such as fossil fuels (petroleum, coal and natural gas), forests, soil, water, and mineral ores. These natural resources are the raw materials for production of products such as food, shelter, transportation facilities, medicine and many other products. Increasing demand for natural resources are prompted by massive production of different life supporting products to meet the increased market demands. The extent to which each natural resource is exploited and the impacts of that exploitation to the environment are discussed in the next section.

Fossil fuels

Fossil fuels are formed from gradual decay of animal or plant remains over millions of years. They provide most of the energy that powers modern industrial societies. The gasoline (petroleum) that fuels our cars, the coal that powers many electrical plants and the natural gas that heats our homes are all fossil fuels.

These fuels are extracted from the earth's crust and processed into suitable fuel products such as petrol, diesel and kerosene. Some of these products are further processed into basic chemicals and products such as plastics, lubricants, paints, solvents and drugs. World reserve of petroleum, coal and natural gas is available in limited quantities and therefore, they are going to be exhausted as a result of continuous use. A proper use and management of fossil fuels is needed to avoid future scarcity which can cause crises and cripple human development. On the other hand, burning of fossil fuels to generate energy produces environmental contaminants such as acidic gaseous oxides (CO_2, SO_2 and NO_2) which are the sources of acid rain and greenhouse effect. Acid rain is formed as a result of excessive dissolution of SO_2 and NO_2 in the atmosphere to produce acids with pH less than 5. The dissolution of acidic gaseous oxides in rain water to form acid rain is given by the chemical equations below.

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons 2H^+(aq) + CO_3^{2-}(aq)$$

(normal rain water)

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

$$2SO_2(g) + 2H_2O(l) + O_2(g) \rightleftharpoons 2H_2SO_4(aq)$$

$$2NO_2(g) + H_2O(l) \rightleftharpoons HNO_2(aq) + HNO_3(aq)$$

These acids are washed down to the earth through rain water, snow and dew. The rain water, snow or dew containing these acids is called *acid rain*. Acid rain with the pH below 5 has damaging effects to the plant leaves and buildings by causing corrosion of the roofing materials, destruction of structures made of marble, cement or lime. In addition, acid rain causes loss of soil fertility and death of the aquatic life such as fish.

Beside the formation of acid rain, burning of fossil fuels releases CO_2 into the atmosphere. Carbon dioxide can also be released to the air by volcanic eruptions, respiration and decay of living organisms. The natural production of carbon dioxide is balanced with its consumption by the green plants and oceans, to maintain a natural equilibrium concentration of the gas in the atmosphere. The excessive production of carbon dioxide as a result of burning fossil fuels causes the increase in the concentration of the gas in the atmosphere. Carbon dioxide is a known greenhouse gas which is capable of absorbing infrared radiation and warming the atmosphere. This in turn causes the rise in the global temperature, a phenomenon known as *global warming*. This layer of carbon dioxide does not permit the escape of the infrared radiation from the warm earth through it. As a result, the infrared radiation emitted by the earth gets trapped in the lower part of the earth's atmosphere, thereby increasing the atmospheric temperature. Such heating effect resulting from the trapping of infrared radiation of longer wavelengths by carbon dioxide in the atmosphere is called the *greenhouse effect.*

To reduce and control the current trend of environmental problems, the use of fossil fuel has to be well managed. The solution to this problem is to use alternative energy sources such as biogas, biofuels, solar, hydro, wind, tidal, nuclear, hydrogen and geothermal energies. The use of such non-conversional energy sources will solve the problem by reducing the consumption of the fossil fuels which in turn will reduce their exploitation and unwanted gases that are emitted due to their burning.

Forests

Forests are very important in maintaining ecological balance and provision of environmental benefits such as habitats for wildlife, control of flooding and soil erosion, provision of clean air, water and shelter for various biodiversity. Forests are also important in defending the globe against climate change. They produce oxygen and consume carbon dioxide. They also provide raw materials for papers, timber and chemical industries. However, the rate at which trees are harvested does not balance with the rate at which new trees are planted. This imbalance causes deforestation which in turn may lead to desertification. Figures 3.1 and 3.2 show the over-exploitation and burning of forests, respectively which may lead to desertification.

Figure 3.1 A photograph of deforestation caused by over-exploitation of forests (Source: TAFORI)

Figure 3.2 Buning of forest that may cause deforestation (Source: TAFORI)

In order to maintain the ecological balance for supporting life, preserving different kinds of species, and ensuring the survival of human race, it is necessary to conserve forests. Among the measures to be taken include planting of new trees to replace the harvested ones (re-afforestation), invention of paperless technology for printing industry, encouraging recycling, reduction of wastage in timber and paper industries, and improving harvesting practice and forest protection. Figure 3.3 shows a well reserved forest.

Figure 3.3 The conserved Mazumbai forest, in Tanga region (Source: TAFORI)

Soil

Soil is the uppermost layer of the earth's crust which supports growth of plants and other living organisms. It is a complex mixture of mineral particles, humus, mineral salts, water, air and living organisms. Soil is both a *renewable* and *non-renewable* resource. It is renewable because its productivity can be maintained with fertilisers and manure. Erosion transforms the soil into a non-renewable resource because once the top layers are removed, the formation of new layers may take hundreds and thousands of years. Soil is needed for food production, for growing plants which provide raw materials for different industries and also provides surface for shelter, transport, and industrial activities. Intensive construction and farming may result into deforestation which exposes the land to falling rains and consequently causing the top soil to be washed away into the rivers and oceans. About 29% of the global land is affected by deforestation. Improper tillage and failure to replace humus after successive harvesting of crops and burning of the stubble, reduce the water-holding capacity of the soil. The soil becomes dry and can be blown away as dust. Poor farming has caused 28% of the global land to be exposed to erosion factors.

Over-grazing is another contributing factor to soil erosion and is responsible for 34% of the global land affected by human activities. In order to sustain the biodiversity, soil needs to be conserved. This can be done by preventing soil erosion and improving soil fertility by adopting various methods such as adding manure and fertilisers regularly as well as practising crop rotation. Animal grazing should be done only in specified areas and not on agricultural land. Planting of trees and vegetables to reduce soil erosion should be a continuous exercise, and banning of uncontrolled harvesting of trees should also be implemented.

Water

Clean fresh water resources are essential for domestic use, irrigation, processing industries, and for plant and animal survival. Due to the over-use, pollution and ecosystem degradation, most sources of fresh water such as groundwater (water located below the soil surface), reservoirs and rivers are under severe and increasing environmental stress. Figure 3.4 is an example of a polluted river.

Over 95% of untreated urban sewage in developing countries is discharged into water bodies such as rivers, lakes and oceans. About 65% of the global fresh water supply is used in agriculture and 25% is used in industry. Fresh water conservation, therefore, requires reforms in agriculture and industry, and strict pollution controls and reduction of wasteful practices like inefficient irrigation.

Figure 3.4 A photography of a polluted water body

Mineral ores

The demand for metallic and non-metallic elements which are obtained from different mineral ores has been increasing with development of science and technology. Deposits of mineral ores like those of other natural resources are limited but their exploitation is accelerating at an alarming rate without considering its fate for future generations. Over-exploitation of mineral wealth depletes mineral deposits. Each step in mining and processing operations produces large quantities of waste materials sometimes including other minerals such as sulphur, heavy metals like mercury, cadmium, nickel, arsenic and zinc. To avoid massive production of solid wastes, mine water, and gaseous materials as a result of mining processes, a suitable technology is advised to be employed to extract valuable minerals without contaminating the environment. In order to reduce the depletion of mineral resources, the following measures need to be taken:

Identifying and evaluating mineral resources

Identifying and evaluating mineral resources can be done by exploring geological mapping of areas with high mineral potential and investigating into the mineral deposits. The geological mapping and investigations may include bedrock and quaternary surveys, integration of geophysical and geochemical surveys, and management of archival earth materials such as rock, till, and core samples.

Supporting the development of technology

Technical and financial support has to be provided for research and demonstration of technologies for the development of known ore reserves and for recycling of mineral products and wastes. By so doing, proper utilisation of deposits such as gold, iron ore, nickel, copper, cobalt, silver, diamond, tanzanite, ruby, limestone, soda ash, gypsum, common salt, phosphate, gravel, sand, graphite, coal and uranium through advancement in processing and recovery will be pursued.

Providing expertise

Provision of technical assistance by the experts in the field to the target group will enhance and maintain the scientific exploration of minerals by private sectors. Specialised geological expertise is critical in gathering, interpreting, and modelling geological information, advising exploration interests, and attracting investment in mineral exploration. Environmental experts should also be involved to safe guard the environmental issues during mineral exploitation and extraction.

3.2.2 Environmental destruction

Excessive accumulation of harmful substances as a result of human activities produces unbalanced situation in the ecological system which cannot be assimilated by the environment. When this happens, the environment is said to be destroyed. Thus, the practice of accumulating harmful materials in the ecosystem to the extent that the environment fails to assimilate them is called *environmental destruction*. Environmental destruction is mostly caused by human activities. Among the major human activities contributing to environmental destruction include uncontrolled damping of waste materials, farming, industrial production, mining, energy production and transport. The description on how each of the mentioned human activities contributes to environmental destruction is given below:

Poor management of waste materials

Uncontrolled dumping of solid and liquid wastes from domestic, industrial or agricultural sources causes harm to the surface land and underground water. Chemicals and chemical products, waste packaging materials, containers, plastic substances such as carrier bags and bottles, and many other household goods are the common materials which are damped on the land. These can have direct harmful effects or they can be harmful when burnt. For example, burning of plastic wastes dumped on the surface can produce greenhouse gases such as SO_2, NO_2, CO_2 and dioxins which are harmful to human beings, plants and animals. In addition, the improper treatment of sewage can contaminate the environment causing harm to aquatic organisms.

Farming

Commercial farming involves excessive use of chemicals such as fertilisers, pesticides, insecticides, herbicides and fungicides. All these chemicals can be carried away by rain water to rivers and underground water streams. This affects aquatic life by promoting rapid growth of aquatic weeds and causes death to fish and other aquatic organisms. This phenomenon is called eutrophication.

Industrial production

Processing industries produce gaseous and liquid effluents which are often discharged into the air and urban sewage systems. The energy used to run machines and equipment in processing industries is obtained from burning fossil fuels. This process produces gases such as SO_2, NO_2, CO, and CO_2. On the other hand, solid or liquid waste materials which are produced in the course of the production processes can cause direct harm or become harmful when burnt or exposed to sunlight for a long time. In this way, industries contribute to environmental destruction.

Mining

In most cases, mining involves surface excavation method starting with clearing of the land which lies over the mineral deposits. This method is not environmental friendly as it involves cutting of trees and other vegetation on the land. Operations involved in the processing of mines produce large quantities of waste materials which are harmful to the environment. Heavy machinery used in the mining process consume fossil fuel hence produce greenhouse gases. All these processes together contribute to environmental destruction. Energy producing plants and transport industry are the areas where there is much consumption of fossil fuels, hence contributing to generation of CO, CO_2, NO_2, and SO_2 which are environmental pollutants.

Energy production and transport

Energy production is accompanied with the production of wastes that are harmful to the environment. These wastes can be due to fossil fuel usage, animal methane, and effluent waste. Environmental destruction under this category can also be due to excessive water and land consumption. Transportation on the on one hand, conveys substantial socio-economic benefits, but at the same time it impacts environmental systems. Transportation is a major user of energy and burns most of the world's petroleum. This leads to air pollution, and is a significant cause for global warming.

3.2.3 Environmental management and intervention

Environmental management is a global issue which needs participation of all nations. Effective management of the environment and intervention to reduce the current environmental problems reassures that the governments, urban authorities, environmental experts, and other stakeholders actively engage in an integrated waste management and control. The common and affordable measures currently employed in many countries includes proper handling of wastes, minimising the production of wastes by using modern technology and renewable energy, treatment of wastes before disposal and raising of public awareness about environmental conservation. The adoption of the methods for safe handling and disposal of wastes depends on the nature and type of wastes produced. Below is the summary of some of the suggested methods for effective management of the environment.

Recycling of waste materials

Gaseous effluents emitted from factories contain heat, gases and solid particles. Heat can be absorbed for heating purposes or steam generations. Gases can be absorbed in scrubbers to produce acidic solutions which can be useful in other production lines. The recovery of useful materials from the wastes minimises waste production, reduces toxic gases and other materials from the effluents, and ensures safe disposal of the industrial wastes. If the waste is a solid, it can be burnt in incinerators to generate electricity or if the solid wastes are biodegradable (e.g. domestic wastes), they can be allowed to decompose in a controlled environment to get organic fertiliser which can be used for planting various vegetation to make the surroundings attractive. If the wastes are plastic, they can be recycled into other forms of useful materials and reused.

Treatment of domestic and industrial westewater

Sewage systems discharge wastes in liquid form from domestic and industrial sources to rivers, lake or oceans causing pollution. A typical sewage contains many different kinds of pollutants both organic and inorganic chemicals. To keep these water bodies clean and safe, sewage wastes must be treated before being discharged into any water body.

Wastewater treatment

Domestic wastewater contains dissolved chemicals originating from things such as soap, detergents, cosmetics and disinfectants which are not good for aquatic life. Therefore, urban water needs to be treated before disposal. Converting used water into environmentally acceptable water or even portable water is referred to as *wastewater treatment*. Wastewater treatments involve the removal of solids, bacteria, algae, plants, inorganic and organic compounds. The removal of solids is usually done by filtration and sedimentation. One of the most fundamental chemical principles in wastewater treatment is solubility. It is imperative to know the contaminants if they are soluble (forming solutions) or insoluble (forming suspensions) in order to determine how they can effectively be removed. On one hand, insoluble contaminants can usually be removed by physical separation processes which include screening, sedimentation and filtration. These physical processes may be aided by chemical processes such as coagulation that help to entrap the suspended particles. Soluble contaminants, on the other hand, can be removed by chemical methods that render them insoluble so that they can be removed by physical means such as sedimentation and filtration. Furthermore, an understanding of solubility is essential in choosing reactants that will generate insoluble precipitates with the dissolved contaminants.

Another chemical parameter to be considered in wastewater treatment is concentration. The concentrations of contaminants in the wastewater supply must be carefully measured in order to determine whether they fall within acceptable values. An understanding of concentrations is also necessary to calculate the proper amount of treatment reagents that must be added to attain the desired effect in treating wastewater. Many of the ions in solutions can be removed by precipitation, by reacting the ions (to be removed) with other ions to produce insoluble solids that can be removed by sedimentation. A typical precipitation reaction used to remove ions in wastewater follows the reaction shown in the equation below:

$$\underset{\text{An ion to be removed}}{\mathrm{A}(aq)} + \underset{\text{Added ion}}{\mathrm{B}(aq)} \longrightarrow \underset{\text{Precipitate}}{\mathrm{AB}(s)}$$

This reaction is similar to the precipitation reaction that take place in the laboratory when ions from two aqueous solutions react to produce a solid precipitate. Typical ions which are usually removed from water by precipitation method include Ca^{2+}, Mg^{2+}, Fe^{2+}, and Mn^{2+}. The removal of bacteria and algae may involve treatment of the wastewater with disinfectants like chlorine.

Drinking water treatment

Water supplies to towns is often taken from rivers, lakes and underground sources, which in most cases are polluted. Therefore, a thorough treatment of water is needed to ensure that it is safe for consumption. Water treatment for domestic use occurs in several stages. First, the water is filtered by sand and gravel off shore before it enters in a filtration well. This removes coarse particles and part of the organic pollutants. Then, it is allowed to stand in large settling tanks in which fine sand, suspended clay and mud settle out. To coagulate colloidal dissolved substances, cacium oxide (CaO) and hydrated aluminium sulphate ($Al_2(SO_4)_3 \cdot 16H_2O$) or alums are often added. When alum is used, it undergoes hydrolysis forming $Al(OH)_3$ which precipitates as a gelatinous sticky substance. The precipitates carry along with them most of the suspended materials, colloids and most bacteria. It also absorbs emulsified oils and chemically binds cyanide, arsenic compounds and thiols. The water is then filtered through a fine sand filter and may be sprayed into the air (aeration) in order to dissolve more oxygen in it. This accelerates the destruction of dissolved organic substances by oxidation. Finally, a small amount (1-3 ppm) of chlorine is usually added to kill any remaining bacteria and viruses. The sterilising effect is due to the chloric(I) acid formed when chlorine reacts with water.

$$Cl_2(g) + H_2O(l) \longrightarrow \underset{\text{Chloric(I) acid}}{HOCl(aq)} + HCl(g)$$

The dissolved cations of Ca^{2+} and Mg^{2+} are removed through precipitation, leading to water softening. In this process, two minerals, lime ($Ca(OH)_2$) and soda ash (Na_2CO_3) are used to soften public water supplies. When lime is added to water, it dissolves to give three aqueous (solvated) ions: one Ca^{2+} ion and two OH^- ions for each unit of $Ca(OH)_2$. Likewise, soda ash dissolves to give two Na^+ ions and one CO_3^{2-} ion for each unit of Na_2CO_3 that dissolves. A number of reactions occur to generate the insoluble precipitates, $CaCO_3$ and $Mg(OH)_2$ from Ca^{2+} and Mg^{2+} ions respectively. The most important reaction for the removal of Mg^{2+} ions is:

$$Mg^{2+}(aq) + 2OH^-(aq) \longrightarrow Mg(OH)_2(s)$$

Ca^{2+} ions are removed from water by reacting with CO_3^{2-} furnished by Na_2CO_3 and the reaction takes place as follows:

$$\underset{\substack{\uparrow \\ \text{From water}}}{Ca^{2+}(aq)} + \underset{\substack{\uparrow \\ \text{From lime}}}{Ca^{2+}(aq)} + \underset{\substack{\uparrow \\ \text{From soda ash}}}{2CO_3^{2-}(aq)} \longrightarrow 2CaCO_3(s)$$

The solids (precipitates) generated by the water-softening precipitation reaction are then removed by sedimentation or filtration. If excess lime is used to precipitate magnesium ions in water, some unused hydroxide (OH^-) ions will remain in the water, resulting into high pH (basic). If necessary, the pH can be lowered by bubbling carbon dioxide gas through the water. This chemical reaction lowers the pH of the water.

$$CO_2(g) + H_2O(l) \longrightarrow H_2CO_3(aq)$$

$$H_2CO_3(aq) + OH^-(aq) \longrightarrow H_2O(l) + HCO_3^-(aq)$$

Hydrogen carbonate (HCO_3^-) remaining in the water is non-toxic and has no effect on the flavour of the water. Household water softeners can be used to soften water at family level by removing Ca^{2+} and Mg^{2+} from water. This can be done by allowing water to pass through the ion exchange equipment consisting of a bed of plastic beads covalently bound to anion groups such as $-COO^-$. The negative charge of these anions is balanced by Na^+ cations attached to them as shown in Figure 3.5.

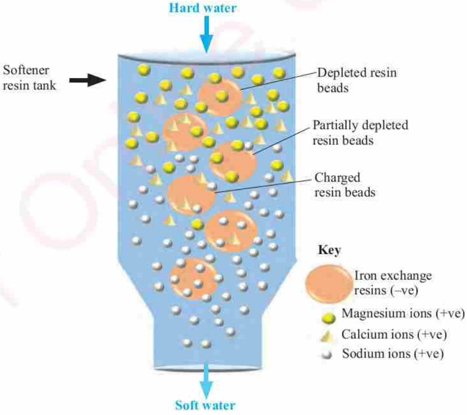


Figure 3.5 Ionic exchange resins equipment used for water softening

Other cations dissolved in water such as Fe^{2+} and Mn^{2+} can also be removed by using precipitation method. A suitable precipitating agent is added to the water and the formed precipitate is filtered off.

Exercise 3.1

1. Briefly explain how conservation of natural resources is related to environmental protection.
2. Why is it necessary that environmental conservation should be a sustainable practice?
3. Evaluate the effects of rapid population growth on resource use and management.
4. Describe three human activities which can contribute to environmental destruction.
5. Suggest the environmental management interventions used for solving waste disposal problems.

3.3 Environmental pollution

Contamination of the environment with harmful substances by certain natural phenomena and human activities is called *environmental pollution.* A substance or energy that pollutes the environment is called a *pollutant*. Some pollutants cause damage to the environment at the place of generations while others take time before their effects are observed. When the concentration of the pollutant exceeds a certain permissible limit in the environment, it starts to affect the environment. Thus, emission of SO_2, CO, NO_2, CO_2, and other materials like metals becomes dangerous when the environment fails to assimilate them.

3.3.1 Types of environmental pollution

Depending upon the compartment of the environment being polluted, environmental pollution can be classified as water, land, and air.

Water pollution

Harmful materials in solid, liquid or gaseous form can be produced by human activities or natural phenomena such as volcanic eruption. When they contaminate the surface or underground water, water is said to be polluted. Such type of pollution is called *water pollution or aquatic pollution.* That means contaminating water with harmful substances or energy which make it unfit for use. The major causes of water pollution are listed in Table 3.1.

Table 3.1 Major water pollutants and their sources

Pollutants	Sources
1. Oxygen consuming materials (a) Microorganisms	Bacteria and viruses in domestic sewage and animal wastes.
(b) Excess plant nutrients	Nitrates and phosphates from fertilisers and industrial wastes.
(c) Organic matter	Detergents, pesticides, sewage, animal wastes, decaying animals, plants and wastes from food-processing industries.
2. Other pollutants (a) Minerals and chemicals	Acids, bases, salts and heavy metals from chemical industries and other activities.
(b) Sediments	Silt from soil erosions and strip mining.
(c) Radioactive substances	Radioactive mineral mining and processing of radioactive materials such as uranium and radioactive wastes from hospitals or nuclear factories.
(d) Excess heat	Waste heat in the form of hot water from cooling towers.

Land pollution

Contaminating land or soil with solid or liquid waste materials to the extent that exceeds permissible levels is called *land or terrestrial pollution.* Land pollution is caused by the solid or liquid wastes discarded from domestic, agricultural, mining and industrial activities. People in urban areas produce thousands of tons of solid waste per day which create acute shortage of space for disposal. Burning method which is commonly used causes the formation of toxic gases that are harmful to organisms. Excessive use of fertilisers and pesticides causes land pollution. Land is also polluted by industrial emissions such as gases which dissolve in rain water and contaminate the land through rainfall. In addition, the discharge from mining sites results into land pollution if not well treated.

Air pollution

A layer of gases that surrounds the earth is called the *earth's atmosphere or atmosphere*. The atmosphere extends from the earth's surface to about 1000 km above the earth. However, 99% of the atmospheric air is found within 40 km from the earth's surface. It is therefore, within the reach of industrial emissions and other gaseous and solid particles which are produced as a result of human activities. The atmosphere is often used as a sink to dump all sorts of wastes in the form of gas and suspended solid particles in air. The World Health Organisation (WHO) estimates that about 6 million of premature deaths were recorded in 2012 due to air pollution. With the growing pressure of industrial development, the air is at risk of acting as a sink for all solid and gaseous wastes. Gaseous pollutants include oxides of sulphur, nitrogen and carbon, unburnt hydrocarbons (C_xH_y), hydrogen sulphide (H_2S), and chlorofluorocarbons (CFCs). Air pollutants also include particulate matter emitted by industries and other sources such as dust, fumes, mist, smoke, and metal particles. Table 3.2 presents the WHO's recommendations for permissible limits of the air pollutants that one can be exposed to at any time and in a 24 hours' range without having serious impact.

Table 3.2 Maximum permissible concentration of common air pollutants

Air Pollutant	**Permissible concentration (mg/m^3)**	
	Maximum average	**Minimum average**
Nitrogen dioxide	0.15	0.1
Carbon monoxide	6.0	1.0
Ozone	5.0	0.1
Sulphur dioxide	0.5	0.15
Carbon dioxide	6.0	2.0
Lead	-	0.0007
Particulate matter (PM)	0.23	0.15
Dust	0.5	0.15
Soot	0.15	0.05
Mercury	-	0.0003
Chlorine	0.1	0.03
Phenol	0.3	0.1

The major sources of air pollutants are human activities such as domestic activities for example, burning of firewood and charcoal, transport activities for example, vehicles and industrial activities which burn fossil fuels including power plants. The air near the earth's surface is expected to contain gases such as oxygen, nitrogen, carbon dioxide and water vapour. Carbon dioxide is not taken as an air pollutant because it is part of the ecosystem. However, if its concentration exceeds the threshold value, it affects climatic conditions on the earth. Due to human activities, the atmosphere contains other particles. Some common particulates which are present in the atmosphere are dust, smoke, fumes, mist, fly-ash, pesticides, insecticides and dust from cement and asbestos. The major sources of particulates are power plants and transport industry. Emissions from power plants contain particles such as smoke, ash and water vapour whereas transport facilities produce smoke and mist which contribute to air pollution. Pesticides like insecticides, herbicides and fungicides are also pollutants as they can be blown away from the surface to the atmosphere by wind. Cement industries also produce particles which pollute the air.

Effects of environmental pollution

Generally, polluted environment (air, water and land) is hazardous to plants, animals and microorganisms, and can bring adverse effects to the entire ecosystem. Pollution, also brings adverse effects to the climate as explained below.

Effects of air pollution

Some gaseous pollutants (e.g. carbon dioxide, methane, CFCs) can cause global warming. The global warming cause flooding due to rise in water sea level caused by melting of ice at the earth poles. The gaseous pollutants such as oxides of S, C, and N can cause chronic respiratory diseases as well as cancer. Table 3.3 summarises the possible effects of some major air pollutants on the human health and on the environment.

Table 3.3 Effects of some air pollutants on human health and on the environment

Air pollutants	Effects on human health	Effects on the environment
Carbon monoxide (CO)	disrupt the transport of oxygen by the blood, leading to health problems such as headache, reduced mental alertness, heart attack, cardiovascular diseases, impaired foetal development, death	enhances the abundance of greenhouse gases such as carbon dioxide and methane, indirectly causing global warming
Carbon dioxide (CO_2)	difficulties in breathing	global warming
Sulphur dioxide (SO_2)	eye irritation, breathing problems, cardiovascular diseases	formation of acid rain, visibility reduction, plant damages
Nitrogen dioxide (NO_2)	irritation of the lung, respiratory symptoms, susceptibility to respiratory infections	formation of photochemical smog, formation of acid rain, visibility reduction, water quality deterioration
Ozone (O_3)	respiratory symptoms, eye irritation, asthma	plant and ecosystem damage, decreased productivity, reduced crop yield, global warming
Particulate matter (PM)	asthma, cardiovascular effects, lung damage, allergic diseases	visibility impairment, impacts on trace gas cycles, cloud and fog formation, absorption and scattering radiation

Effects of water pollution

Water pollution produces significant effects to the environment, and eventually to living organisms including man. Biological water contaminants (e.g. bacteria, virus and protozoans) can cause waterborne diseases like typhoid, cholera, and disentry, affecting people who consume or come into contact with such contaminated water. Excessive release of nutrients into water bodies may cause rapid growth of aquatic plants and increase the turbidity of water. Excessive growth of water weeds blocks sunlight needed by sea plants and makes it hard for aquatic organisms to find food but also the decomposition of water weeds takes a lot of oxygen leading to death of some aquatic organisms. Excessive nutrients from fertilisers may stimulate the growth of toxic algae leading to eutrophication of the water body, making it unfit for aquatic life. Oil spills in the water body prevent the penetration of oxygen and thus affect the aquatic life.

Effects of land pollution

Land pollution has many effects. Decaying of waste from land attracts household pests such as rats and cockroaches which make homes and other places unhealthy. Land pollution also reduces the amount of land available for agriculture and settlement. In addition, land pollution leads to loss of biodiversity due to anthropogenic activities. Apart from health effects, it also makes environments look ugly because most of the solid waste matters are not easily biodegradable and tend to accummulate on land. Toxic chemicals on the land especially radiation from nuclear waste can cause human health problems such as cancer.

Intervention measures for environmental protection

Major causes of environmental pollution are industrial production of wastes, including gaseous emission, liquid effluents, scraps and other unwanted materials. Other causes include improper disposal of wastes, and improper use of chemicals such as fertilisers and pesticides. Intervention measures should focus mainly on preventing pollution rather than treating wastes after being produced. To achieve this, the following measures can be taken:

(a) As energy production and transport industries are the major contributors to the environmental pollutions, the use of renewable energy must be emphasised as well as increasing investment in renewable energy production.

(b) Whenever practical, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

(c) Emphasise the use of renewable resources as feed-stock/raw materials for manufacturing industries.

(d) Conducting thorough Environmental Impact Assessment (EIA) before any major development activity and /or project is implemented.

(e) All industrial effluents should be treated before their disposal to reduce the level of contaminants for easy assimilation by the environment.

(f) Alternative domestic energy sources such as wind, solar and biogas may be used in place of fossil fuels, charcoal, coal and firewood.

(g) Car exhausts should be installed with catalytic converters. A catalytic converter is a vital part of the vehicle's emissions control system. Its function is to reduce toxic air by converting harmful pollutants into less harmful emissions such as water, carbon dioxide and nitrogen.

(h) Encourage the use of biological control of pests in place of pesticides.

(i) Encourage the use of public transport to minimise emissions caused by a large number of private vehicles.

3.3.2 Ozone layer depletion

A belt of naturally occurring ozone gas that sits 15 to 30 kilometres above the earth's surface is called *ozone layer*. Ozone is a highly reactive molecule made up of three oxygen atoms (O_3). When it is in the lower atmosphere (troposphere) it possesses harmful effects, while at the upper atmosphere (stratosphere) it is essential for the protection of life on earth. The ozone in the stratosphere is produced through photochemical reactions involving O_2 (Figure 3.6). When O_2 in the stratosphere absorbs ultra-violet (UV) radiations with wavelength less than 240 nm, it dissociates into two oxygen atoms.

$$O_2(g) \xrightarrow{\text{UV radiations}} 2O(g)$$

The resulting oxygen atoms combine with oxygen molecule to form ozone.

$$2O_2(g) + 2O(g) \longrightarrow 2O_3(g)$$

The overall reaction is obtained by adding up the two reactions given above.

$$3O_2(g) \longrightarrow 2O_3(g)$$

In the upper atmosphere, ozone filters (absorbs) harmful ultraviolet radiations from the sun. These ultraviolet radiations are highly energetic and will damage both plants and animals exposed to them on the earth's surface. Normally, diatomic oxygen (O_2) absorbs most of the ultraviolet radiations with the wavelength shorter than 240 nm from the sun. However, the oxygen molecule does not efficiently absorb ultra-violet radiations between 240 nm and 290 nm. These are absorbed by ozone (O_3) and cause the ozone to dissociate into diatomic molecules and oxygen atoms.

$$O_3(g) \xrightarrow{\text{harmful UV radiations}} O_2(g) + O(g)$$

The dissociated O_2 molecules and oxygen atoms recombine to form O_3.

$$O_2(g) + O(g) \longrightarrow O_3(g)$$

Therefore, in the presence of UV radiations in the upper atmosphere, ozone is constantly being formed and broken down. This explains how the ozone layer serves as a shield to protect the earth from harmful ultraviolet radiations emitted by the sun.

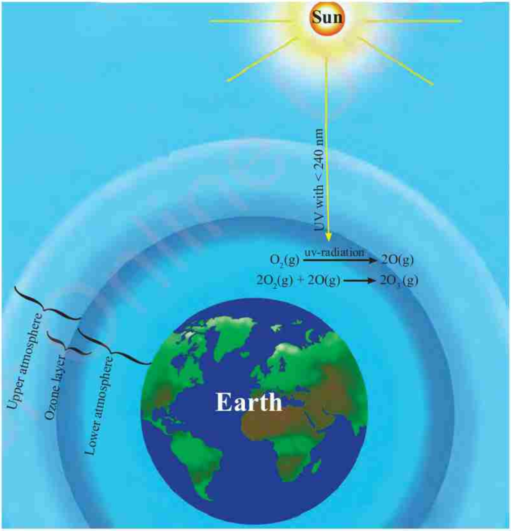


Figure 3.6 Natural ozone formation

To date, there is a global concern that the ozone layer is getting depleted due to accumulation of pollutants (e.g. chloro-fluorocarbons (CFCs), methane and nitrogen monoxide) in the atmosphere. *Ozone layer depletion* is the reduction in the amount of ozone in the stratosphere. CFCs are the primary causes of the ozone layer destruction. CFCs (e.g. CF_2Cl_2 or $CFCl_3$) are industrial chamicals widely used as solvents, aerosols, propellants, refrigerant fluids and blowing agents for plastic foams. In the presence of ultraviolet rays, CFCs in the upper atmosphere break down into highly reactive free radicals of chlorine.

$$CF_2Cl_2(g) \xrightarrow{UV} \dot{C}l(g) + C\dot{C}lF_2(g)$$

The highly reactive chlorine free radical reacts with ozone to form chlorine monoxide radical as per reaction.

$$\dot{C}l(g) + O_3(g) \longrightarrow \dot{C}lO(g) + O_2(g)$$

In the presence of chlorine monoxide free radical, some atomic oxygen (that would have reacted with O_2 to produce ozone) will react with the ClO free radical to form oxygen molecule and regenerate free radical chlorine.

$$\dot{C}lO(g) + O(g) \longrightarrow \dot{C}l(g) + O_2(g)$$

The regenerated chlorine radicals re-enter the chain reactions to destroy more ozone molecules (Figure 3.7). Other pollutants like the oxides of nitrogen produce the same effect.

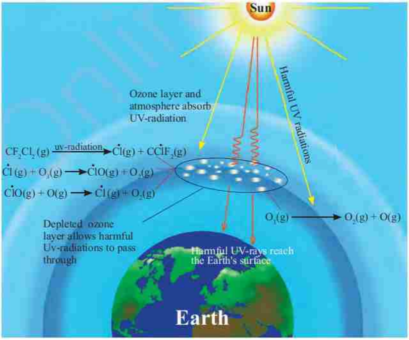


Figure 3.7 Ozone layer depletion

CFCs replacement

Following the Montreal Protocol (1987) – A protocol to the Vienna Convention and subsequent amendments (1990, 1992) for the protection of the ozone layer, the production of CFCs has been phased out. One of the success of this convention of ozone protection has been the development of alternative chemicals called hydrochlofluorocarbons (HCFCs) which have low ozone-depleting potentials compared to CFCs. This is due to the fact that HCFCs are less stable in the lower atmosphere, enabling them to break down before reaching the ozone layer. Nevertheless, a significant fraction of the HCFCs do diffuse to the stratosphere and break, contributing to more chlorine build-up there than originally predicted. Later alternatives lacking the chlorine, the hydrofluorocarbons (HFCs) have an even shorter lifetime in the lower atmosphere. One of these compounds, HFC-134a, is now used in place of CFC-12 in automobile air conditioners. Hydrocarbon refrigerants (a propane/isobutane blend) are also used extensively in mobile air conditioning systems in countries such as Australia, USA and many other countries in Europe as they have excellent thermodynamic properties and perform particularly well in high ambient temperatures.

Effect of ozone layer depletion

The depletion of ozone layer exposes the earth (environment) to ultraviolet B (UVB) radiations which are known to cause human skin cancer as well as other genetic deformities (for example, eye cataracts and weakening of immune system). Ozone layer depletion also causes damage to crops and reduction in primary producers (plankton) in the ocean. Ozone layer depletion may even affect the global climate. Therefore, it is imperative to reduce the production and use of these pollutants to avoid any possibility for them to reach the upper layers of the atmosphere that may cause ozone layer destruction.

3.3.3 Greenhouse effect and global warming

About 75% of the solar energy reaching the earth is absorbed by the earth's surface, which increases its temperature. The rest of the heat radiates back to the atmosphere. Some of the heat is trapped by gases such as carbon dioxide, methane, ozone, chlorofluorocarbon compounds (CFCs) and water vapour in the atmosphere. Thus, they add to the heating of the atmosphere. This causes global warming.

A greenhouse is a structure, primarily of glass or sheets of clear plastic, in which temperature and humidity can be controlled for the cultivation or protection of plants. Do you know that humans also live in a greenhouse? Of course, we are not surrounded by glass or plastic housing but a blanket of air called the atmosphere, which has kept the temperature on earth constant for centuries. However, it is now undergoing a change in temperature, though slowly. Just as the glass in a greenhouse holds the sun's warmth inside, the atmosphere traps the sun's heat near the earth's surface and keeps it warm. This is called a natural greenhouse effect because it maintains the temperature and makes the earth perfect for life.

In a greenhouse, solar radiations pass through the transparent glass and heat up the soil and the plants. The warm soil and plants emit infrared radiations. Since the glass is opaque to infrared radiations (thermal region), it partly reflects and partly absorbs these radiations. This mechanism keeps the energy of the sun trapped in the greenhouse. Similarly, carbon dioxide molecules in the atmosphere also trap heat as they are transparent to sunlight but not to the heat radiation. If the amount of carbon dioxide crosses the delicate proportion of 0.03%, the natural greenhouse balance may get disturbed. Carbon dioxide is the major contributor to global warming. Besides carbon dioxide, other greenhouse gases are methane (CH_4), water vapour (H_2O), nitrous oxide (N_2O), CFCs and ozone (O_3). Methane is produced naturally when the vegetation is burnt, digested or rotten in the absence of oxygen. Large amounts of methane are released in paddy fields, coal mines, from rotting garbage dumps and by fossil fuels. Chlorofluorocarbons (CFCs) are man-made industrial chemicals used in air conditioning. In recent years, their quantities have increased significantly due to the use of chemical fertilisers and the burning of fossil fuels. If these trends continue, the average global temperature will increase to a level which may lead to melting of polar ice caps and flooding of low lying areas all over the earth. Increase in the global temperature favours the growth of disease vectors such as mosquito and tsetsefly which in turn increase the incidence of infectious diseases like dengue, malaria, yellow fever, and sleeping sickness. In addition, most of the currently experienced natural disasters such as floods are the outcomes of global warming.

The chemical reactions involved in the production of greenhouse gases from anthropogenic activities include:

(a) Burning of coal to produce energy.

$$C(s) + O_2(g) \xrightarrow{\text{heat}} CO_2(g) + \text{heat}$$

(b) Burning of natural gas to produce energy.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g) + \text{heat}$$

(c) Burning of gasoline (petrol and diesel) which gives CO_2 and water vapour.

$$2C_8H_{18}(l) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(g) + \text{heat}$$

(d) Unburnt hydrocarbons such as CH_4 that are also emitted and get their way to the atmosphere.

All these activities increase the concentration of CO_2 and other greenhouse gases in the atmosphere.

Exercise 3.2

1. Explain the causes of air pollution and its effects on the environment.
2. Why should regulations be enforced with regard to pollution and harmful chemicals?
3. (a) In which layer of the atmosphere does the ozone layer occur?
   (b) Explain the role of ozone layer in the stratosphere.
4. Using chemical equations, show how ozone is formed.
5. With the aid of chemical equations, describe the ozone layer destruction.
6. What atom in the CFC molecule is the most destructive to the ozone? Explain.

Revision exercise 3

1. Explain the concept of pollution.
2. Describe water, land, and air pollution, and their intervention measures.
3. Describe the causes of environmental destruction.
4. Briefly explain the environmental conservation and it significance.
5. Suggest the proper utilisation of natural resources.
6. Describe the possible intervention measures of environmental management.
7. Explain how water can be conserved for future generation.
8. What is air pollution? Name any two pollutants produced by each of the following:
   (a) A cement factory (b) Vehicles
   (c) Households (d) Mining site
9. With the aid of chemical equations, explain how ozone in the atmosphere is destroyed and what measures can be taken to reduce the ozone layer depletion?
10. Describe the greenhouse effect.
11. Define the term acid rain.
12. With the aid of chemical equation(s), show how acid rain is formed and explain how it can be prevented.
13. With reasons, explain what would have happened if the greenhouse gases were totally missing in the earth's atmosphere.

Chapter Four

Soil chemistry

Introduction

Soil is a thin uppermost layer of the earth's crust on which plants grow. It is a dynamic matrix which anchors the biological, chemical, and physical interactions within its components. The soil components determine its quality, which is defined by its ability to support the ecosystem to sustain biological productivity, maintain environmental quality, and promote plant and animal health. In this chapter, you will learn about the concept of soil chemistry, soil colloids, ion exchange, and soil reaction. Besides, you will learn about liming and liming materials, chemical fertilisers, and organic manure.

4.1 The concept of soil chemistry

Several chemical and physical processes take place in the soil which include pH balancing, soil weathering and mineral composition that form the fundamental aspects of soil chemistry. Soil chemistry offers an understanding of soil colloidal particles in relation to soluble compounds of silica, aluminium and calcium with the water phase. Soil fertility, which is an important factor for the suitability of soil in farming, is also determined by the soil chemistry. Soil chemistry also offers knowledge to understand the differences in fertility among different soils and their response to fertilisation. The understanding of chemical processes in the soil is imperative as it provides an insight for proper use and management of soil. Therefore, soil chemistry deals with studies of the composition, properties, processes and chemical interactions of soil.

4.2 Soil colloids

4.2.1 Meaning and significance of soil colloid

A suspension of tiny particles in a medium of the soil solution is called a *colloidal dispersion* or *colloids*. The size of these particles range from 1.0 nanometre to 1000 nanometres. Soil colloids are responsible for promoting soil structure hence improving soil fertility. They aid in the adsorption of cations and also prevent nutrients from leaching out from soil. Chemical processes in the soil take place on the colloidal surface. Soil colloids can be classified as inorganic or organic depending on their sources. If they belong to the clay fraction of the soil are regarded as inorganic colloids. Colloids of this type are either aluminosilicate

(Al_2SiO_5) or hydrous oxides of aluminium and iron ($Al_2O_3.xH_2O$ or $Fe_2O_3.xH_2O$). Organic colloids are usually humus particles. *Humus* is an organic component of the soil formed by the decomposition of plants and animals by soil microorganisms.

4.2.2 Properties of soil colloids

Soil colloids have numerous properties. Only the properties which are related to soil chemistry are discussed in this chapter. These include the colloid size, surface charge, and adsorption of cations (ion exchange).

Size of colloids

Colloids are very small in size, therefore, they have large surface area per volume which is an important factor for chemical reactions and water retention. Colloid size however, depends on the type of the soil. For example, the surface area of one gram of colloidal clay is approximately a thousand times that of one gram of granular sand.

Surface (electric) charge

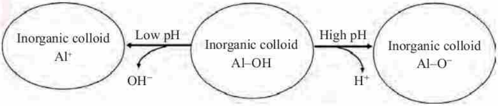
Soil colloidal surfaces are characterised by negative and positive charges. For most soil colloids positive charges are predominated by negative charges. However, some soils containing weathered kaolin minerals consist of colloids with net positive charges. When suspended in water, both organic and inorganic soil colloids carry a net negative charge. The negative charge on the soil colloidal surface is due to the isomorphic substitution of the central cations, the formation of H^+, OH^- and broken bonds. These reasons can be explained as follows:

Broken bonds

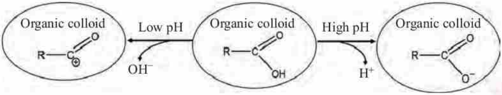
This involve breaking of the crystal lattice which leads to exposure of valences (positive or negative) at the broken edges of silica and alumina sheets.

Dissociation of $H+$ or OH^- ions from exposed surface

The broken edges and flat external surface of mineral colloids have some exposed oxygen and hydroxyl group attached to the silicon or aluminium atom within their respective sheets. Depending upon the soil pH, the H^+ or OH^- dissociate away leaving a positive or negative charge on the colloidal particle.



Similar, dissociation takes place from the functional groups such as carboxylic (−COOH) and phenol (phenyl-OH) of the organic soil colloids.



Isomorphic substitution

This is a process in which nearly equal sized ions replace one another. In a crystal lattice, for example, Si^{4+} in a tetrahedron is substituted by Al^{3+}. Similarly, Al^{3+} in an octahedron is substituted by Fe^{2+} or Mg^{2+}. Each substitution leaves the lattice with a negative charge.

Ion exchange

Since soil colloids carry a net negative charge, they attract cations and adsorb them on their surface. The attraction of cations such as H^+, K^+ Mg^{2+} or Ca^{2+} on the colloidal surface leads to the formation of electric double layer as shown in Figure 4.1.

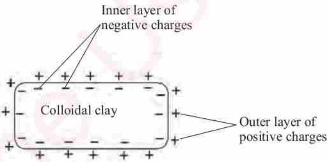


Figure 4.1 Diagrammatic representation of electric double layer of colloidal clay

Other properties

Other properties of soil colloids include water adsorption, cohesion and adhesion, swelling and shrinkage, dispersion and flocculation, non-permeability, and Brownian movement.

4.3 Ion exchange

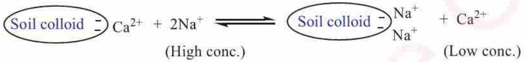
An ion in the vicinity of the colloidal particle may replace another one on its surface through ion exchange. *Ion exchange* is a reversible process which occurs between surfaces of closely lying particles. The exchange can take part between inorganic colloids and organic colloids or between colloids and soil solution or between colloids and plant roots. Depending on the charge of the ion involved in the exchange process, ion exchange can involve cations or anions.

Properties of cation exchange reactions

Cation exchange reactions exhibit some properties which can be used to account for the reversible exchange of cations between soil colloids and the surrounding medium.

Reversible cation exchange

Cation exchange reactions are reversible and because of this, they allow the forward or backward of the reactions, thus, facilitating the exchange of cations. The equation below demonstrates the exchange of Ca^{2+} by $2Na^+$.

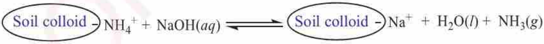


$$\text{Soil colloid}^{2-}\,Ca^{2+} + \underset{\text{(High conc.)}}{2Na^+} \rightleftharpoons \text{Soil colloid}^{2-}\begin{matrix}Na^+\\Na^+\end{matrix} + \underset{\text{(Low conc.)}}{Ca^{2+}}$$

If the concentration of Na^+ in this system is raised, the equilibrium will be driven to the right where it favours the replacement of Ca^{2+} ions by Na^+ ions in accordance with the Le Chàrtelier's Principle. Replacement (cation exchange) is much more favoured if the exchange results into the formation of a precipitate or a gas.

$$\text{Soil colloid}^{2-}\,Ca^{2+} + Na_2CO_3(aq) \rightleftharpoons \text{Soil colloid}^{2-}\begin{matrix}Na^+\\Na^+\end{matrix} + CaCO_3(s)$$

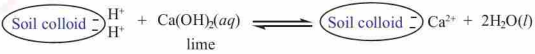
The equilibrium is driven more to the right to form $CaCO_3$. As a result, exchangeable Ca^{2+} ions are replaced by Na^+ ions. If the cation exchange reactions are accompanied by the formation of a volatile gas such as ammonia, the equilibrium is driven to the right to favour the replacement of the cation responsible for the formation of the evolved gas.



$$\text{Soil colloid}^{-}\,NH_4^+ + NaOH(aq) \rightleftharpoons \text{Soil colloid}^{-}\,Na^+ + H_2O(l) + NH_3(g)$$

Effect of anions

Cation exchange reaction is affected by the anions associated with an exchanging cation. This effect can be demonstrated by the liming reaction.



$$\text{Soil colloid}^{2-}\begin{matrix}H^+\\H^+\end{matrix} + \underset{\text{lime}}{Ca(OH)_2(aq)} \rightleftharpoons \text{Soil colloid}^{2-}\,Ca^{2+} + 2H_2O(l)$$

Since H_2O is a weakly dissociating molecule, this reaction is driven more to the right, whereby H^+ ions are exchanged by Ca^{2+} ions. Thus, the OH^- ions which are the anions associated with the exchanging cations Ca^{2+} influence the exchange of H^+ ions by Ca^{2+} ions.

Effects of colloidal surface charge density

The magnitude of the surface charge density of the colloids affects the cation exchange reactions. Soil colloids with high surface charge density favour the retention of polyvalent cations. Thus, Ca^{2+} ions are preferred to Na^+ ions, and therefore, the exchange of Na^+ ions by Ca^{2+} ions will take place. This can also be explained precisely by the Coulomb's Law of Electrical Attraction. Quantitatively, the attraction of cation by the negatively charged colloidal surfaces can be expressed by the Equation 4.1.

$$F_a = k\frac{q_1 q_2}{d^2} \qquad (4.1)$$

where, k = proportionality constant,

q_1 and q_2 = charges of the soil colloids and cation, respectively,

d = separation distance between the soil colloid and the cation, and

F_a = force of attraction between the charges.

From Equation 4.1, it can be deduced that the attraction force between soil colloids and cations is proportional to the magnitude of charge and inversely proportional to the square of the distance between the soil colloids and cations. This implies that cations with bigger charges are attracted more by soil colloids (less displaced from the soil colloids) than the cations with smaller charges. Thus, if Ca^{2+} and K^+ ions are present in the soil solution, Ca^{2+} will be attracted by the soil colloids in preference to K^+ ions. Similarly, if it happens that K^+ ions are adsorbed on the soil colloids and Ca^{2+} ions are in the solution, the later will displace the former from the surface of the colloid since they are attracted more by the soil colloids.

Coulomb's Law explains the cation exchange reactions successfully for cations of different charges. However, it fails to predict the selectivity or preference of one cation over another with the same valence. Such a preference can be explained using cation size. In soil solution, cations do not exist freely. They exist as positively charged ions surrounded by water molecules (hydrated molecules). A cation with a smaller radius has higher charge density per unit volume. Therefore, it attracts more water and its hydrated radius is much larger than that of the cation of the same valence but larger radius. Cations with smaller hydrated radius can get closer to the colloid surface, and their coulombic attraction by the surface is much stronger.

4.3.1 Mechanism of ion exchange

Positively or negatively charged atoms or group of atoms are called *ions*. Different ions which are found in soils are essential for plant growth and maintenance of soil fertility. Ions in soils are found adsorbed on the surface of soil colloids or suspended in soil solution. Negatively charged soil colloids adsorb positively charged ions and positively charged soil colloids adsorb negatively charged ions (Figure 4.2). As ions are needed by plants for nutrition, their movement from soil to plant roots is necessary. However, every plant type needs specific amount and type of ions for different metabolic activities. At the same time depending on the nature and the magnitude of the charge, the ions adsorbed in soil colloids, plant roots, and those in the solution can be interchanged. Thus, the ions in the soil colloids can be replaced by the ions from soil solution, at the same time the ions from soil colloids moving into the soil solution. Similarly, ions in the plant roots can be replaced by ions from the soil solution and the replaced ions from the plant roots move into the soil solution. The movement of ions from the surface of the soil colloids or plant roots to the soil solutions and vice versa is called *ion exchange.*

Soil colloids are predominantly negatively charged because of the isomorphic exchange of central cations. However, electric charges on the soil particles (colloids) is not equally distributed. Unequal distribution of charges on the surface of the soil colloids results into their polarisation, hence giving them power to hold both cations and anions. The amphoteric nature of soil colloids enables the exchange of both cations and anions (Figure 4.2).

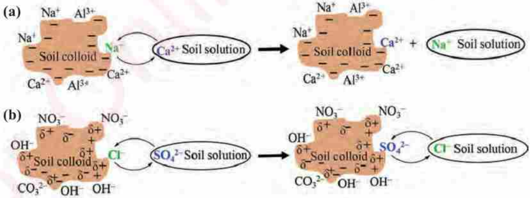


Figure 4.2 **(a)** Cation exchange between colloid and soil solution **(b)** anion exchange between colloid and soil solution

As seen from Figure 4.2 (a), if the net electric charge of colloidal particles initially holding Na^+ is negative, when the ion comes into contact with a soil solution containing Ca^{2+}, the exchange of cations takes place. Similarly, a soil colloid with a net positive charge initially holding Cl^- ions when it comes into contact with SO_4^{2-} ions in soil solution, an exchange of the ions takes place (Figure 4.2 (b)).

The exchange of ions can also take place between soil colloids as shown in Figures 4.3 (a) and (b).

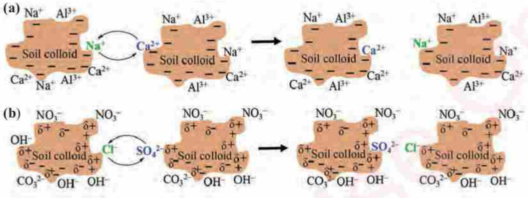


Figure 4.3 **(a)** Cation exchange between colloids **(b)** Anion exchange between colloids

4.3.2 Cation exchange capacity

The cations which are adsorbed on the surface of soil colloids may be replaced by other cations from the soil solution or from another colloid when the two surfaces in contact have different concentrations. The capacity of the soil to exchange cations is very important for storage of plant nutrients and hence for the potential fertility of soil. The amount of cations held by the soil is expressed in terms of *cation exchange capacity* (CEC), which is the sum of exchangeable cations held in 100 g of oven-dry soil. It is expressed in milliequivalent (*meq*) per 100 g of the oven-dry soil. One milliequivalent is equivalent to 1000 millimoles of H^+ ions or the amount of any other ion that will combine with or displace 1000 millimoles of H^+ ions.

The ability of a cation to be adsorbed on the surface of a colloid is characterised by its charge and size. The charge and size of the ion determine the number of water molecules that can interact with the surface charge to form a hydrated radius. The smaller the hydrated radius, the greater the affinity of the cation by the sorbent surface. Also, the higher the valence, the greater the exchange preference of the cation. Due to this reason, the CEC is dominated by calcium, aluminium, potassium, sodium, magnesium and protons. The arrangement of the cations in the order of their exchange preference is called the *cation affinity scale* (CAS). The CAS has the following order:

$$Al^{3+} > H^{+} > Ca^{2+} > Mg^{2+} > (NH_4^{+} = K^{+}) > Na^{+}$$

The dominating cations mentioned before fall into two groups; the basic cations (Ca^{2+}, Mg^{2+}, NH_4^+, K^+ and Na^+) and acidic cations (Al^{3+} and H^+). The acidity of Al^{3+} is accounted by its ability to hydrolyse in water to give an acidic solution as shown in the equation:

$$Al^{3+}(aq) + 3H_2O\,(l) \rightleftharpoons Al(OH)_3\,(s) + 3H^+\,(aq)$$

The CEC is usually experimentally determined by leaching a soil sample with enough ammonium acetate solution to cause ammonia to replace all the exchangeable cations. The amount of ammonium ions held in the sample is a measure of the CEC. The CEC depends on the type of the soil and nature of the clay minerals. The soil with 1:1 composition of silica:alumina has lower cation exchange capacity (5 – 20 meq/100 g of the oven-dry soil) than the soil with 2:1 composition of alumina:silica (40 – 100 meq/100 g of the oven-dry soil). Genarally, the CEC of the soil increases when the percentage of the clay is increased. Organic colloids have the highest cation exchange capacity (100 – 200 meq/100 g of the oven-dry soil). Thus, adding organic matter may increase the CEC of a soil considerably. In addition, CEC is affected by the soil pH. As the pH of the soil raise, the hydrogen held by organic colloids and silicates clay (kaolinite) becomes ionised and replaceable leading to increase in CEC.

4.3.3 Base saturation of soil

A soil sample is capable of holding only basic exchangeable cations as plant nutrients out of the available exchangeable cations. This fraction is expressed in percentage and it is called percentage base saturation (PBS). *Percentage base saturation* (PBS) is defined as the percentage of cation exchange sites occupied by basic cations. It signifies the availability of basic cations for plant nutrition. The greater the value of PBS, the more the availability of basic cations. It will be seen later that the PBS has a definite relationship with the pH of the soil and soil fertility. Like the CEC, percentage base saturation is controlled by the nature of the soil and both can be used as an index for soil fertility. The numerical value of PBS can be calculated using Equation 4.2.

$$\text{PBS} = \frac{\Sigma \text{EB}}{\text{CEC}} \times 100\% \tag{4.2}$$

where, PBS is percentage base saturation,
EB is exchangeable base, and
CEC is cation exchange capacity.

Both EB and CEC are measured in meq per 100 g of oven-dry soil where, 1 meq $= 10^{-3}$ eq and 1 eq ≡ 1 mol of H^+ or the amount of any ions that will combine with or displace 1 mol of H^+ ions.

Example 4.1

A certain soil contains the following cations where all the values are given in meq per 100 g of oven-dry soil. $Mg^{2+} = 20.0$, $Ca^{2+} = 38.0$, $Na^+ = 4.0$, $K^+ = 6.0$, $Mn^{2+} = 2.0$, $H^+ = 24.0$ and $Al^{3+} = 8.0$. If the PBS of the soil is 68.63%, calculate the:

(a) CEC of this soil.

(b) quantity of Ca^{2+} ions in grams present in 100 g of oven-dry soil.

Solution

(a) $\Sigma EB = (Mg^{2+} + Ca^{2+} + K^+ + Mn^{2+} + Na^+)$ meq /100 g

$\Sigma EB = (20 + 38 + 6 + 4 + 2)$ meq /100 g

$\Sigma EB = 70.0$ meq /100 g

PBS = 68.63%

From Equation 4.2,

$$PBS = \frac{\Sigma EB}{PBS} \times 100\%$$

Thus,

$$CEC = \frac{\Sigma EB}{PBS} \times 100\% = \frac{70.0 \text{ meq/100 g}}{68.63\%} \times 100\%$$

$$= 102 \text{ meq/100 g}$$

Therefore, the CEC of the soil is 102 meq/100 g.

(b) From the definition, 1 eq of Ca^{2+} is the number of moles of Ca^{2+} which can combine with 1 mol of H^+

Therefore,

$$1 \text{ eq of } Ca^{2+} = \frac{\text{Atomic mass of Ca}}{\text{valence}} = \frac{40 \text{ g}}{2} = 20 \text{ g}$$

1 eq $= 10^3$ meq or 1 meq = 1/1000 eq $= 10^{-3}$ eq.

$$\text{Thus, 1 meq of } Ca^{2+} \equiv \frac{20}{1000} \text{g of } Ca^{2+} \equiv 0.02 \text{ g of } Ca^{2+}$$

If 1 meq of $Ca^{2+} \equiv 0.02$ g of Ca^{2+}, then 38 meq of $Ca^{2+} \equiv x$ g of Ca^{2+}

Solving for x, you will get;

$$x = \frac{38\ \text{meq} \times 0.02\ \text{g}}{1\ \text{meq}} = 0.76\ \text{g}$$

Therefore, the quantity of Ca^{2+} in 100 g of oven-dry soil is 0.76 g.

Example 4.2

A 10 mL of 0.1 mol dm^{-3} sodium hydroxide was used to neutralise the exchangeable hydrogen ions in a 5.0 g sample of oven-dry soil. If the total cation exchange capacity of the soil is 25 meq per 100 g of oven dried soil, calculate the:

(a) PBS of the soil sample.

(b) concentration of H^+ (in milliequivalent) in 75 g of the oven-dry soil.

Solution

(a) Given,

CEC = 25 meq per 100 g of oven-dry soil Weight of dry soil = 5.0 g

Concentration of NaOH solution = 0.1 mol dm^{-3}

Volume of NaOH used = 10 mL

The volume of NaOH used in $dm^3 = \frac{10\ \text{cm}^3}{1000\ \text{cm}^3\ \text{dm}^{-3}} = 0.01\ \text{dm}^3$

Moles of NaOH = Concentration of NaOH (mol dm^{-3}) × Volume of NaOH (dm^{-3})

$$= 0.1\ \text{mol dm}^{-3} \times 0.01\ \text{dm}^3 = 1 \times 10^{-3}\ \text{mol}$$

But from the chemical reaction,

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$

1 mol of OH^- neutralises 1 mol of H^+. Therefore, 1×10^{-3} mol of OH^- neutralises 1×10^{-3} mol of H^+.

If 1 mole of $H^+ \equiv 1 \times 10^{-3}$ meq, then, 1×10^{-3} mol of $H^+ \equiv x$

Solving for x gives

$$x = \frac{1 \times 10^{-3}\ \text{mol} \times 1 \ \times 10^{3}\ \text{meq}}{1\ \text{mol}} = 1\ \text{meq}$$

If 5 g of oven-dry soil contain 1 meq of H^+ ions, then 100 g of oven-dry soil will contain z meq. Solving for z gives:

$$z = \frac{100\ \text{g} \times 1\ \text{meq}}{5\ \text{g}} = 20\ \text{meq of oven-dry soil.}$$

Assuming that this is equal to the amount of all acidic cations present in 100 g of the oven-dry soil sample then,

$$\Sigma\text{EB} = \Sigma\text{CEC} - (\Sigma \text{ Exchangeable acidic cations})$$

$$= \Sigma\ \text{CEC} - \Sigma\ (H^+(aq) + Al^{3+}(aq))$$

$$\Sigma\text{EB} = 25\ \text{meq} - 20\ \text{meq} = 5\ \text{meq}$$

But the percentage base saturation (PBS) is given by Equation 4.2 as:

$$\text{PBS} = \frac{\Sigma\text{EB}}{\text{CEC}} \times 100\% = \frac{5\ \text{meq}}{25\ \text{meq}} \times 100\% = 20\%$$

Therefore, the percentage base saturation of the soil sample is 20%.

(b) From the solution in (a) above 5 g of oven-dry soil contains 1 meq of H^+, then in 75 g of the soil sample will contain x meq of H^+

$$x = \frac{75\ \text{g} \times 1\ \text{meq}}{5\ \text{g}} = 15\ \text{meq}$$

Therefore, the concentration of H^+ is 15 meq per 75 g of oven-dry soil sample.

Example 4.3

A 20 g soil sample was shaken with 40 mL of 0.1 mol dm^{-3} HCl solution. After filtering and washing the soil, the filtrate and the washings were titrated against sodium hydroxide solution. If 24 mL of 0.1 mol dm^{-3} NaOH were used for complete neutralisation, calculate the PBS of the soil sample, given that CEC of the soil sample is 25 meq per 100 g of oven-dry soil.

Solution

From the neutralisation reaction,

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l)$$

1 mol of H^+ neutralises 1 mol of OH^-, 24 mL of 0.1 mol dm^{-3} HCl neutralises 24 mL of 0.1 mol dm^{-3} NaOH. Since 24 mL of 0.1 mol dm^{-3} NaOH were required for the complete neutralisation, then out of 40 mL of 0.1 mol dm^{-3} HCl, 24 mL

remained unreacted in the soil. The amount of HCl reacted in the soil solution is (40 mL – 24 mL) = 16 mL of 0.1 mol dm^{-3} HCl.

If 0.1 mol of HCl are in 1000 mL, then the amount (mol) of HCl in 16 mL is;

$$x = \frac{16\ cm^3 \times 0.1\ mol}{1000\ cm^3} = 1.6 \times 10^{-3}\ mol$$

If 1 mol of $H^+ \equiv 1 \times 10^3$ meq,

1.6×10^{-3} mol of $H^+ \equiv x$ meq

$$x = \frac{1.6 \times 10^{-3}\ mol \times 1 \times 10^3\ meq}{1\ mol} = 1.6\ meq$$

If 20 g of the oven-dry soil sample contains 1.6 meq then, 100 g of the oven-dry soil sample contains *n* meq, hence,

$$n = \frac{100\ g \times 1.6\ meq}{20 g} = 8\ meq\ per\ 100\ g\ of\ oven-dry\ soil$$

Thus, $\Sigma EB = 8$ meq

From,

$$PBS = \frac{\Sigma EB}{CEC} \times 100\%$$

Substituting the values of ΣEB and ΣCEC in the above equation gives;

$$PBS = \frac{8\ meq\ /100\ g}{25\ meq\ /100\ g} \times 100\% = 32\%$$

Therefore, the percentage base saturation is 32%.

4.4 Soil reaction

4.4.1 The concept of soil reaction

Soil chemical environment can be acidic, basic or neutral. Soil reaction is defined as the condition of the soil solution which may be acidic, basic or neutral in reaction and is measured in terms of pH. Acidity of soil is due to the presence of acidic ions such as H^+ or Al^{3+} while the basicity is caused by the presence of basic ions like Ca^{2+}, K^+, and Na^+ in the soil solution. The pH is a measure of the concentration of hydrogen ions in the soil solution on a logarithmic scale that ranges from 1 (extremely acidic) to 14 (extremely alkaline). In a neutral soil, the concentration of hydrogen ions (H^+) equals the concentration of hydroxide (OH^-) ions.

The soil reaction depends on the response of the soil solution to the pH metre or indicator. Nearly, all soils have pH values between 4 and 7.5 (Figure 4.4). Soils with pH < 4 generally contain H_2SO_4 and are acidic while those with pH > 8 contain high percentages of Na^+, and thus they are alkaline soils.

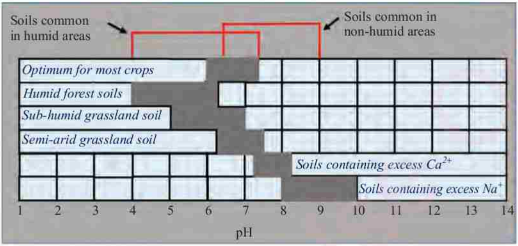


Figure 4.4 Typical pH range for various types of soils

4.4.2 Significance of soil pH

pH is a numerical measure expressed as a negative logarithm of molar concentration of hydrogen ions, pH = $-\log [H^+]$. The pH of a soil can be measured by using a pH metre or by titrating a suitable water suspension of the respective soil sample against a standard solution of alkali or acid (Figure 4.5).

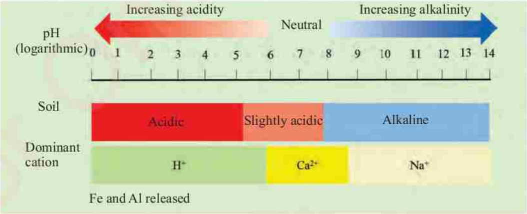


Figure 4.5 The pH scale showing soil acidity and alkalinity

Soil reaction is important because it affects nutrients availability, microbial activity and plant growth. Favourable conditions for growth of most crop plants lie between pH 5.5 and 7.5 that is in slightly acidic up to slightly alkaline soils. However, some plants commonly found in the tropics tolerate more acidic soils.

The availability of nutrients to plants greatly depends on soil pH. Most plant nutrients are reasonably available between pH 6 and pH 7.5 which is optimum. The availability of N, P, K, S, Ca, Mg and Mo decreases with the increase in soil acidity. Thus, acidic soils are often deficient in these nutrients. For example, at pH less than 5 phosphorus which is found as PO_4^{3-} in the soil reacts with the soluble iron, aluminium and manganese ions to form insoluble complexes of their respective ions such as $AlPO_4$ and $Mn_3(PO_4)_2$. As a result, the deposition of organic matter is slowed down, thus fixing the nutrients and make them unavailable to plants. Similarly, Fe, Mn, Cu, and Zn precipitate as hydroxides at high pH and become unavailable to plants. The deficiency of these nutrients often limits the growth of plants in limed or alkaline soils.

At a pH below 5.5, the activity of bacteria and other organisms drops sharply. Consequently, nitrification and nitrogen fixation are severely reduced. However, fungi are not affected even in strong acidic soils; they continue with the mineralisation of organic matter delivering at least some ammoniacal nitrogen to higher plants. Thus, the determination of pH of agricultural soils is very important because it helps to select suitable crops for a particular soil and also enables people to make decisions about the modification of the soil.

4.4.3 Soil acidity

Soil contains positively charged hydrogen ions. The measure of the degree of concentration of hydrogen ions in the soil solution is called *soil acidity*. Soil acidity depends on a balance between the hydrogen ions and hydroxide ions present in the soil. The acidity increases with the increase in the concentration of hydrogen ions in the soil whereas the alkalinity of soil increases with an increase in hydroxide ion concentration in the soil. When the concentration of hydrogen ions equals that of the hydroxide ions, the soil is said to be neutral (pH = 7). Soil acidity is caused by organic and inorganic sources.

The organic causes of soil acidity

The organic causes of the soil acidity are due to microbial activity in the soil which includes:

(a) Microorganisms and root respiration which produce carbon dioxide that forms carbonic acid with the soil solution as shown in the next equation.

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq) \rightleftharpoons 2H^+(aq) + CO_3^{2-}(aq)$$

However, the contribution of this process to the soil acidity is very low since H_2CO_3 is a weak acid.

(b) The nitrification of ammonium ions by bacteria produces H^+. Nitrification refers to the conversion of ammonia into nitrates that results in the production of hydrogen ions in the soil solution. The presence of H^+ ions in the soil solution influences the release of Al^{3+} and replacement of Na^+, K^+ and Ca^{2+}. The release of H^+ ions under the influence of bacteria is shown in the equation below:

$$NH_4^+(aq) + 2O_2(g) \xrightarrow{\text{bacteria}} 2H^+(aq) + NO_3^-(aq) + H_2O(l)$$

The decomposition of organic matter produces organic acids which ionise to give H^+ ions in the soil solution.

The inorganic causes of soil acidity

Soil acidity under this category is associated mainly with human activities and natural disasters such as:

(a) Heavy rains or over-irrigation which leach basic metals like Ca^{2+}, Mg^{2+}, Na^+ and K^+ ions, leaving excess of H^+ ions in the soil.

(b) Industrial emissions of gases such as NO_2 and SO_2 which dissolve in rain water to form acidic solution.

$$2NO_2(g) + H_2O(l) \rightleftharpoons HNO_3(aq) + HNO_2(aq)$$

$$SO_2(g) + H_2O(l) \rightleftharpoons H_2SO_3(aq) \rightleftharpoons 2H^+(aq) + SO_3^{2-}(aq)$$

(c) Acidic fertilisers like ammonium sulphate(VI) and ammonium chloride make the soil solution acidic due to hydrolysis.

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

Similarly, Al^{3+} and Fe^{3+} ions may undergo hydrolysis to produce H^+ ions.

$$Al^{3+}(aq) + 3H_2O(l) \rightleftharpoons Al(OH)_3(s) + 3H^+(aq)$$

$$Fe^{3+}(aq) + 3H_2O(l) \rightleftharpoons Fe(OH)_3(s) + 3H^+(aq)$$

Classification of soil acidity

Soil acidity can be classified as active or potential. *Active soil acidity* is determined by the free H^+ ions in the soil solution. *Potential soil acidity* or exchangeable acidity is determined by H^+ ions released from the soil surface, hydrolysed ions or decomposed organic matter. It is referred to as the soil's buffer capacity or the resistance towards change in the pH. Usually, the higher the clay or organic matter content the greater its buffer capacity. In this case, more liming materials are required to change the pH of the soil with high buffer capacity than a soil with low buffer capacity. The active soil acidity is always in equilibrium with the potential acidity.

When the concentration of H^+ ions in the soil solution is decreased by either rain or liming, further H^+ ions will move from the exchange sites into the soil solution according to Le Châtelier's Principle.

$$\{H^+(aq) \text{ and } Al^{3+}(aq)\} \rightleftharpoons \{H^+(aq) \text{ and } Al^{3+}(aq)\}$$

Potential soil acidity (adsorbed on exchange sites of soil colloids)	Active soil acidity (in soil solution)

Exercise 4.1

1. With the aid of chemical equations, explain how the interactions between water and both organic and inorganic colloidal particles in the soil affect the soil acidity.
2. Explain the significance of soil pH.
3. Explain the major causes of soil acidity.
4. The PBS of a certain soil sample was found to be 70% and its exchangeable basic cation was 35 meq. Calculate the CEC of this soil?
5. A 20 g soil sample was analysed and found to contain 0.0015 g of calcium. What is the concentration of calcium in the soil sample in mill-equivalent per 100 g soil?
6. Water was added to 100 g of soil to make a 200 mL soil solution. If this solution required 0.0074 g calcium hydroxide for neutralisation, calculate its pH.

4.5 Liming and liming material

The availability of soil nutrients is determined by the soil pH. The pH of soil is an important factor in determining which plants will grow because it controls the nutrients available for the plants. Plants have a recommended pH at which they grow best. Some flourish well in slightly acidic pH while others prefer slightly basic pH. The soil pH can be controlled by regulating the hydrogen ion concentration $[H^+]$ of the soil. In order to raise the pH of such soil, basic compounds of calcium and magnesium are added and mixed well with the top soil. The oxides, hydroxides, carbonates and silicates of calcium and magnesium, which are contained in limestone, dolomite, slaked lime, oyster shells and blast furnace slag are called *liming materials* or *agricultural limes*. The practice of adding agricultural limes to acidic soils with the purpose of neutralising acidity and creating favourable soil conditions for plant growth and microbial activity is called *liming*. In some cases, wood ash and press mud (waste product of sugar and paper industries) are used as liming materials.

When liming materials are applied to the acidic soil, they usually react with the water and/or with the carbonic acid in the soil as shown in the following reactions:

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s)$$

$$Ca(OH)_2(s) + 2H_2CO_3(aq) \longrightarrow Ca(HCO_3)_2(aq) + 2H_2O(l)$$

$$CaCO_3(s) + H_2CO_3(aq) \longrightarrow Ca(HCO_3)_2(aq)$$

The liming materials also react with hydrogen ions adsorbed on the soil colloids as follows:

$$\boxed{\text{Soil colloids}}\begin{matrix}H^+\\H^+\end{matrix} + CaCO_3(s) \rightleftharpoons \boxed{\text{Soil colloids}}Ca^{2+} + H_2O(l) + CO_2(g)$$

$$\boxed{\text{Soil colloids}}\begin{matrix}H^+\\H^+\end{matrix} + Ca(OH)_2(s) \rightleftharpoons \boxed{\text{Soil colloids}}Ca^{2+} + 2H_2O(l)$$

$$\boxed{\text{Soil colloids}}\begin{matrix}H^+\\H^+\end{matrix} + Ca(HCO_3)_2(aq) \rightleftharpoons \boxed{\text{Soil colloids}}Ca^{2+} + 2H_2O(l) + 2CO_2(g)$$

Thus, liming raises the pH and percentage base saturation of the soil. Besides neutralising the acidity, liming is beneficial to plant growth as it:

(a) supplies calcium and magnesium which are needed for plant growth.

(b) improves physical properties of the soil by providing conducive environment for microorganisms to decompose organic matters and forms humus which binds soil particles together.

(c) increases the availability of phosphorus and molybdenum in the soil since the soil becomes basic.

(d) stimulates the symbiotic and non-symbiotic fixing bacteria in the soil by providing good environment for their activities.

(e) prevents the accumulation of toxic iron, aluminium and manganese by precipitating them in the form of hydroxides thus making them unavailable.

(f) increases water infiltration capacity of the soil due to improved soil structure and thus indirectly controls soil erosion.

(g) reduces stem and root rotting resulting in a good straw/grain ratio.

These benefits raise the agricultural productivity and hence increasing the income of the society.

Efficiency of liming material

The quality of the liming material depends on purity (chemical composition) of the lime and fineness of individual soil particles. Presence of impurities in the lime will reduce its ability to neutralise soil acidity. On the other hand, large particles (small surface area) react more slowly and less completely than fine particles.

Neutralising value of the liming material

Organic acids are produced during the decomposition of organic matter. Due to such reasons, most soils in humid/tropical regions are acidic, such that they need to be neutralised to suit some requirement. In order to do so, determination of neutralisation value of liming materials is paramount.

Neutralising value (NV) or *calcium carbonate equivalent* (CCE) is defined as the capacity of liming material to neutralise the acidity expressed as percentage by mass of pure calcium carbonate. The $CaCO_3$ saves as a standard with neutralising value of 100%. NV is an index which determines the purity of the liming material and it is an important measurement in determining the amount of lime that should be applied to the soil. The higher the NV the more effective the product in neutralising acidity. That is, a lime with high NV indicates that a small amount of lime should be applied and vice versa. Mathematically, NV is given by;

$$\text{NV} = \frac{\text{grams of pure CaCO}_3 \text{ equivalent to 100 g of a given lime}}{\text{100 g of CaCO}_3} \times 100\%$$

Determination of the neutralising value of pure common liming materials

Determination of neutralising values of liming materials is done by comparing with the neutralising value of $CaCO_3$ which is 100%.

Example 4.4

Determine the neutralising value of quick lime (calcium oxide) to be used as a soil liming material if the neutralising value of lime ($CaCO_3$) is 100%.

Given

Molar mass of CaO = 56 g mol^{-1}

Molar mass of $CaCO_3$ = 100 g mol^{-1}

Grams of $CaCO_3$ equivalent to 100 g of a given liming material (x) = ?

Solution

Since 1 mole of CaO is equivalent to 1 mole of $CaCO_3$, then,

1 mole of CaO ≡ 1 mole of $CaCO_3$

If 56 g mol^{-1} of CaO ≡ 100 g of $CaCO_3$

100 g mol^{-1} of CaO ≡ x g of $CaCO_3$

$$x = \frac{100\text{ g mol}^{-1} \times 100\text{ g}}{56\text{ g mol}^{-1}}$$

$$= 178.57\text{ g}$$

The mass of $CaCO_3$ equivalent to 100 g of CaO is 178.57 g.

From the formula for calculating the neutralising value (NV),

$$\text{NV} = \frac{\text{grams of pure CaCO}_3\text{ equivalent to 100 g of a given lime}}{\text{100 g of CaCO}_3} \times 100\%$$

It follows that,

$$\text{NV} = \frac{178.57\text{ g}}{100\text{ g}} \times 100\%$$

$$= 178.57\%$$

Therefore, the neutralising value of CaO is 178.57%

Example 4.5

You are a specialist who wants to determine the quality of limes so that you can advise farmers and other stakeholders on the best liming material. Show how you can go about in calculating the neutralising value of calcium hydroxide($Ca(OH)_2$).

Given

Molar mass of $Ca(OH)_2$ = 74 g mol^{-1}

Molar mass of $CaCO_3$ = 100 g mol^{-1}

Grams of $CaCO_3$ equivalent to 100 g of a given liming material (x) =?

Solution

Since 1 mole of $Ca(OH)_2$ is equivalent to 1 mole of $CaCO_3$, then,

1 mole of $Ca(OH)_2 \equiv$ 1 mole of $CaCO_3$

If 74 g mol^{-1} of $Ca(OH)_2 \equiv$ 100 g of $CaCO_3$

100 g mol^{-1} of $Ca(OH)_2 \equiv x$ g of $CaCO_3$

$$x = \frac{100 \text{ g mol}^{-1} \times 100 \text{ g}}{74 \text{ g mol}^{-1}}$$

$$= 135 \text{ g}$$

The grams of $CaCO_3$ equivalent to 100 g of $Ca(OH)_2$ are 135 g.

From the formula for calculating the neutralising value (NV),

$$\text{NV} = \frac{\text{grams of pure } CaCO_3 \text{ equivalent to 100 g of a given liming material}}{\text{100 g of } CaCO_3} \times 100\%$$

It follows that,

$$\text{NV} = \frac{135 \text{ g}}{100 \text{ g}} \times 100\%$$

$$= 135\%$$

Therefore, the neutralising value of $Ca(OH)_2$ is 135%

Factors affecting the neutralising value of liming material

The neutralising value of liming materials is affected by the following factors:

(a) Amount of impurity present in the liming material

Pure liming materials have high neutralising values than impure limes. For example, if you have 56 g of pure lime, CaO and 60 g of impure CaO out of which the amount of impurity is 4 g, this means 56 g of pure lime will raise the pH of the same amount of the soil by the same amount as 60 g of impure and hence, pure CaO is said to have higher neutralising value than impure CaO.

(b) Molar mass of pure liming material

One mole of each common liming material will have the same effect of raising the soil pH. Smaller amount of pure liming material with lower molar mass will have the same effect as larger amount of pure lime with higher molar mass, and hence pure lime with lower molar mass is said to have high neutralising value. For example, 56 g (1 mole) pure CaO has the same effect as 100 g (1 mole) pure $CaCO_3$. Therefore, CaO has higher neutralising value than $CaCO_3$.

Over-liming

Over-liming is the application of too much lime leading to pH raise beyond the intended change to the levels that adversely affects plant growth. It is most likely to occur on soil with low CEC such as sand, which is deficient in buffering agents such as organic matter and clay. Generally, overliming turns the soil alkaline which results into making some plant nutrients like phosphorus, boron, zinc and cobalt unavailable for plant growth. In addition, overliming causes drying out of the soil.

Acidification of the soil

When the soil is too alkaline it can be neutralised by the addition of either ammonium fertilisers, elemental sulphur, aluminium sulphate or organic matter.

Addition of ammonium fertiliser

Acidification of soil is explained by nitrification and cationic hydrolysis of ammonium ion. Thus, the use of ammonium fertilisers e.g. urea results in the formation of H^+ as shown in the equation below.

$$NH_4^+(aq) + 2O_2(g) \xrightarrow{\text{action of bacteria}} 2H^+(aq) + H_2O(l) + NO_3^-(aq)$$

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

Addition of elemental sulphur

In rare cases the basic characteristics of the soil can be lowered by addition of elemental sulphur, which is converted to sulphuric acid by soil bacteria.

$$2S(s) + 2H_2O(l) + 3O_2(g) \xrightarrow{\text{action of bacteria}} 2H_2SO_4(aq)$$

For efficient conversion of elemental sulphur to sulphuric acid, the following conditions must be met:

(a) Sulphur must be properly mixed with the soil.

(b) The soil has to be moist and aerated.

(c) The soil has to be warm to facilitate the rapid growth of bacteria.

(d) Ample time is required for the reaction to go to completion.

Addition of aluminium sulphate

Unlike the acidification of the soil by ammonium fertilisers and elemental sulphur, the acidification using aluminium sulphate involves a chemical process. The acid formation is explained by cationic hydrolysis of aluminium sulphate.

$$Al_2(SO_4)_3(s) + 6H_2O(l) \longrightarrow 2Al(OH)_3(aq) + 3H_2SO_4(aq)$$

Exercise 4.2

1. (a) Define the following terms:
   - (i) Liming
   - (ii) Liming materials
   - (iii) Overliming

   (b) Briefly describe how repeated irrigation is related to liming.

2. Calculate the neutralising value of the following liming materials:
   - (a) $MgCO_3$
   - (b) $CaMgCO_3$
   - (c) $CaSiO_3$

3. (a) In measuring the soil pH, what is actually measured is the active acidity and not the potential acidity. Explain.
   (b) Explain how liming is related to percentage base saturation.
   (c) Liming has indirect effects to the potential soil acidity. Explain.
4. (a) What accounts for the fact that humid forest soil has a pH range between 4 and 6.5?
   (b) Briefly explain how liming
      (i) increases water infiltration.
      (ii) enhances microbial activities.
   (c) With the aid of chemical equations, show the mechanism of soil liming.
5. The application of manure increases CEC of the soil. Explain.

4.6 Fertiliser

4.6.1 Soil nutrients

A continuous use of a piece of land leads to the decrease in soil nutrients particularly the K, N and P, which in turn leads to the loss of soil fertility. In order to maintain a constant production of crops on the same piece of land, nutrient management must be taken into consideration. The lost nutrients must be replaced by using fertilisers or manures. Eighteen chemical elements have so far been recognised as essential for plant growth and production. Undersupply or oversupply of any of these elements may lead to severe problems such as low yields and plant death. Thus, they are essential plant nutrients. Three of these elements; namely carbon, hydrogen and oxygen are supplied by water and air (including carbon dioxide). Essential elements can further be grouped into macronutrients and micronutrients.

Macronutrients are elements needed in large amounts by the plant for its growth and survival. These include carbon, hydrogen, oxygen, calcium, magnesium, phosphorus, nitrogen, potassium, and sulphur. The functions of macronutrients are shown in Table 4.1.

Table 4.1 Functions of some plant macronutrients

Element	Function
C	Important in the formation of carbohydrates, proteins, and nucleic acids. It is the most abundant element in plant cells.
N	A component of proteins and the nucleic acids, used to synthesise vitamins
H	Used with oxygen in the formation of water.
O	Used for cellular respiration; required to store energy in the form of ATP.
P	Important in the synthesis of nucleic acids and phospholipids; enables the conversion of food energy into chemical energy.
K	Important in the stomata opening and closing, which maintains water balance
S	It is part of amino acids such as cysteine and methionine.
Ca	Supports the functioning of enzymes and regulates nutrient transport.
Mg	Important in the photosynthetic process.

Micronutrients are required in small quantities by the plant. They include boron, chlorine, copper, silicon, manganese, iron, molybdenum, cobalt, zinc and sodium. Since these elements are required in small amounts, they are also referred to as the *trace elements*. The term micronutrients should not be taken that the elements are of little or no significance for the plant growth. They are as important as the macronutrients and their deficiency is as severe as for macronutrients. All essential plant nutrients perform specific functions to aid plant growth and production. None of them can be replaced by another. They must all be available in the right proportions to facilitate optimum plant growth. Table 4.2 shows the functions of some of the micronutrients in plants.

Table 4.2 Functions of some plants micronutrients

Element	Function
Zn	Component of several enzymes, promotes growth, component of hormones, enhances starch formation, promotes seed formation and growth.
Fe	Component of several enzymes, ferodoxin and takes part in the formation of chlorophyl.
Cu	Important in photosynthesis, metabolism of protein and carbohydrates.
Mn	Activates several enzymes and plays a role in the assimilation and metabolism of nitrogen.
Ni	Important for grain filling, seed viability, iron absorption and it supports the catalytic action of several enzymes.
B	Takes part in the formation of nucleic acids and cell division. It also activates certain dehydrogenase enzymes.
Mo	Plays a role in nitrogen fixation and assimilation. It also forms part of nitrogenase and nitrate reductase enzymes.
Co	Part of vitamin B_{12} and it is essential in nitrogen fixation.
Na	Aids in metabolism and synthesis of chlorophyll and improves the crop quality e.g. improves the taste of carrots by increasing sucrose.

Continuous cropping and harvesting of a field takes nutrients out of the soil leading to the increase in shortage of macronutrients. Many techniques have been devised to improve crop production which include the use of fertilisers. *Fertilisers* are mainly inorganic substances containing readily available plant nutrients. New advancements in the processing of the decomposed animal and plant waste has led to a separate class of fertilisers called the organic fertilisers. Manures (organic materials) and/or chemical fertilisers (inorganic compounds) are usually added to the soil in order to increase or maintain its fertility by replacing the nutrients taken out of it by plants. Generally, fertilisers are classified based on the nutrient availability and the sources to which the nutrients are obtained. Figure 4.6 shows the classes of fertilisers.

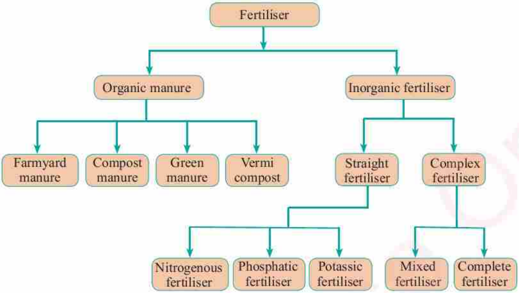


Figure 4.6 Classification of fertiliser

4.6.2 Inorganic fertiliser

The pressure of the ncreasing population has for a long time influenced the search for new methods that increase crop production. Food demand has been a growing challenge in many countries especially in the developing countries. The use of inorganic (chemical) fertilisers requires a good understanding of the land requirement and the properties of a particular type of fertiliser. The effective use of fertilisers takes into consideration the type, amount, correct material carrier and how to apply the fertilisers. Therefore, factors such as specific nutritional requirements of the crop to be planted, nutrient deficiencies of the soil, soil reaction and the amount that will provide the required amount of nutrients should be considered before applying fertilisers. In addition, correct timing (climate) and methods for applying the fertilisers have to be considered. The soil where fertiliser has to be applied needs to have a reasonable humus content to raise its cation exchange capacity and avoid fertiliser leaching.

Common fertiliser

Commonly available fertilisers can be classified according to the composition of the nutrients as straight fertilisers, mixed fertilisers and complete fertilisers.

Straight fertiliser

Usually, straight fertilisers contain only one of the three major (primary) nutrients namely nitrogen, phosphorus and potassium (N, P, K). They can be placed into three main groups, namely, nitrogeneous, phosphatic, and potassic fertilisers.

Nitrogenous fertiliser

Nitrogenous fertilisers are designed to supply only nitrogen as a primary macronutrient. The common nitrogenous fertilisers include ammonium sulphate (SA) i.e. ($(NH_4)_2SO_4$), ammonium sulphate nitrate ($(NH_4)_2SO_4 + NH_4NO_3$), calcium ammonium nitrate (CAN) i.e. ($Ca(NO_3)_2 + NH_4NO_3$) and urea ($(NH_2)_2CO$). The following are the properties of nitrogenous fertilisers:

(a) They are highly soluble in water therefore easily leached. As a result, they should be applied to growing crops.

(b) They do not remain in the soil for a long time, so they need to be applied frequently.

(c) They have high heat of solution hence they should not come into direct contact with any part of the plant especially leaves.

(d) They are hygroscopic, that is, they absorb moisture from the atmosphere.

(e) They are highly volatile such that under hot weather condition, they change into gaseous form and escape into the atmosphere.

(f) Most nitrogenous fertilisers are corrosive and therefore should not be handled with bare hands.

Phosphatic fertiliser

Phosphatic fertilisers only provide phosphorus as the primary macronutrient. The commonly used phosphatic fertilisers include super phosphate, double or triple super phosphate, ground rock phosphate and bone meal. Some of the properties of phosphatic fertilisers are:

(a) They are sparingly soluble in water, so they are not easily leached.

(b) They remain in the soil for a long time.

(c) They are lightly hot, therefore, they have to be mixed thoroughly with the soil to minimise the heat effect.

Potassic fertiliser

The common potassic fertilisers include potassium chloride (muriate of potash) and potassium sulphate. The potassic fertiliser are moderately hot and more soluble in water than phosphatic fertilisers but less soluble than nitrogenous fertilisers.

Complex fertiliser

Complex fertilisers are also known as compound fertilisers. They are made from mixing two or more fertilisers containing macronutrients. They may also be further blended with elements that provide some of the less common plant nutrients known as secondary or trace nutrients, such as sulphur, calcium and magnesium. Complex fertilisers can be packaged and distributed in liquid or granular form. They include mixed and complete fertilisers.

Mixed fertiliser

Mixed fertilisers contain two major plant nutrients. They are produced according to the needs of certain agricultural regions or farmers may mix them according to the recommended ratio. For example, diammonium phosphate (DAP) provides both N and P. However, it must be noted that not all fertilisers can be mixed because unwanted reactions may occur.

Complete fertiliser

Complete fertilisers are fertilisers which contain all the three major plant nutrients. The commonly available complete fertilisers in the market are the following:

(a) NPK − 10:15:10 which means there is 10% N, 15% P and 10% K in the mixture.

(b) NPK − 10:10:10 which means there is 10% N, 10% P and 10% K in the mixture.

(c) NPK − 10:20:15 which means a mixture containing 10% N, 20% P and 15% K in the mixture.

Sometimes, the composition of the complete fertilisers may include other nutritional elements besides N, P and K. In this case, the type and amount in percentages of the nutritional elements have to be stated on the bag containing the fertilisers.

Example 4.6

A farm requires 120 kg of nitrogen. What weight of urea fertiliser labelled 37-0-0 needs to be applied to the soil to meet this demand? Show clearly how you obtain your answer.

Given

The percentage of nitrogen in the fertiliser is 37.

No phosphorus

No potassium

Solution

Let the amount in kg of fertiliser needed to be applied to meet the demand of a farm be *x*, then 37 kg of nitrogen is contained in 100 kg of the fertiliser 120 kg of nitrogen will be contained in *x* kg of fertiliser;

$$x = \frac{120\text{ kg} \times 100\text{ kg}}{37\text{ kg}}$$

$$= 324.32\text{ kg}$$

Therefore, 324.32 kg of the fertiliser needs to be applied to meet the demand of a farm.

Example 4.7

A farmer was advised to supply 160 kg of N on the maize farm. Calculate the mass of the fertiliser with 80% by mass $Ca(NO_3)_2$ which a farmer has to buy in order to meet the nitrogen requirement for the farm.

Given

The molar mass of $Ca(NO_3)_2$ is 164 g mol^{-1} or 0.164 kg mol^{-1}

The mass of nitrogen in one mole of $Ca(NO_3)_2$ is 28 g or 0.028 kg

Solution

Thus, 0.028 kg of N is contained in 0.164 kg of $Ca(NO_3)_2$

160 kg of N will be contained in *x* kg of $Ca(NO_3)_2$

$$x = \frac{160\text{ kg} \times 0.164\text{ kg}}{0.028\text{ kg}}$$

$$= 937.14\text{ kg of } Ca(NO_3)_2$$

But 80% by mass $Ca(NO_3)_2$ means,

80 kg of $Ca(NO_3)_2$ is in 100 kg of the fertiliser.

What mass of fertiliser will contain 937.14 kg of $Ca(NO_3)_2$?

$$x = \frac{937.14\ \text{kg} \times 100\ \text{kg}}{80\,\text{kg}}$$

$x = 1171.42$ kg of the fertiliser

Therefore, 1171.42 kg of the fertiliser is required to meet the nitrogen requirement in the farm.

Advantages of chemical fertiliser

Chemical fertilisers are advantageous in that they:

(a) work immediately.

Chemical fertilisers dissolves easily and release essential nutrients into the soil and become easily absorbed.

(b) are nutrient specific.

They supply a particular nutrient hence specific chemical fertilisers can be selected. For example, super phosphate is used in a soil which is deficient in phosphorus.

(c) are convenient to use.

Chemical fertilisers are more pleasant to handle compared to manure.

(d) are not bulky.

They are easily stored, transported and supplied compared to manure.

Disadvantages of chemical fertiliser

Despite the advantages, chemical fertilisers have some shortcomings. Some of them include the following:

(a) Affecting micro-organisms living in the soil.

Using chemical fertilisers for a prolonged period of time upsets the pH of the soil, thus kills some of the beneficial microbes present in the soil.

(b) They can easily leach down to the soil without fully benefiting the plants.

Highly soluble fertiliser dissolves into the soil quite rapidly. Since plants can only absorb a certain amount of the nutrient at a time, much of the fertiliser leaches away. The leached fertilisers are detrimental to the ground water. Leaching will also require constant application of fertiliser in the soil, which is not economical.

(c) They may encourage plant diseases.

Fast-release chemical fertilisers have a high nutrient content compared to slow-release organic fertilisers. Over-abundance of some nutrients attracts pests and diseases. For example, when there is an over-abundance of nitrogen (N) in relation to phosphate (P), plants are more susceptible to fungal and bacterial infections.

(d) Producing agricultural products with lower nutritional value and poor flavour.

Repeated use of chemical fertilisers may cause toxic chemicals, like cadmium, arsenic and uranium to build up in the soil. These toxic chemicals can ultimately find their way into the growing crops, fruits and vegetables, lowering their nutritional values and flavour.

(e) May destroy the structure of the soil.

Some chemical fertilisers contain acids which dissolve soil crumbs, the material that holds rock particles together. When chemical fertilisers are used for a prolonged duration these cementing materials are destroyed leading to a compacted surface that prevents rain water from entering the soil.

(f) High cost

The manufacture of artificial fertiliser requires high technology which is expensive, thus increasing the cost of production hence the price of the fertiliser.

4.6.3 Organic manure

Manure is a decomposed organic matter that is added to the soil in order to improve or maintain soil fertility. It is derived from plants and animal remains that have been allowed to undergo decomposition. Organic manure is classified into four main types, namely farmyard manure, green manure, compost and vermi-compost manure. *Farmyard manure* (FYM) is the organic manure made from a mixture of excreta (dung) and urine of livestock like cattle, horses, goats and sheep along with feed left-overs (hay or fodder). This type of manure is rich in nitrogen, phosphorus and potassium, and it can directly be used for farming. A prolonged storage of farmyard manure results into the loss of ammonia that consequently results into the loss of essential nutrients. To avoid this problem, FYM is stored by burying the excreta into covered pits to retain the nutrients.

A *compost manure* is a decayed farm waste such as farm weeds, straw, sugarcane refuse, rotting vegetables, kitchen wastes, crop stubble, groundnuts and rice husks. These wastes are allowed to undergo a composting process in which they undergo both aerobic and anaerobic processes in a composite pit to form a compost. A well-made compost is rich in various macronutrients. G*reen manure* is made by ploughing green crops on the same piece of land *(insitu).* In most cases, the green crops are ploughed to the land soon after harvest. The green manure adds nitrogen, recycles the elements and improves soil aeration. *Vermi compost* refers to the manure that is made from the excreta of worms and other microorganisms. The worms and microorganisms are allowed to feed on organic compounds and cast their excreta which is mixed with soil.

Apart from the fact that manure contains about 97% of the nutrients which are required by plants, it has several advantages and disadvantages. For effective use of manure, an insight on their advantages and disadvantages is required in order to avoid some detrimental effects which can be produced as a result of improper applications.

Advantages of manure

The following are some of the advantages of manure:

(a) Manure improves the soil structure by gluing together soil particles, which provides pores for good aeration and water movement.

(b) Manure increases the water holding capacity of a soil by providing enough surface area where water molecules can be adsorbed.

(c) Manure slows down the rate of releasing of the nutrients hence it minimises the possibility of over-fertilising plants.

(d) Cation exchange capacity of the soil is increased as humus accounts for 30 to 90% of the CEC of mineral soils.

(e) Due to its high CEC, humus helps to hold nutrients, thus reduces the leaching of nutrients from the soil.

(f) Crude organic matter in the surface layer of the soil reduces the impact of rain drops and the surface run-off of water. Thus it reduces soil erosion.

(g) With the use of manure, there is no risk of accumulation of toxic chemicals in the soil.

(h) Manure is renewable, biodegradable and therefore eco-friendly.

(i) Manure holds soil particles together, hence it reduces water and wind erosions.

(j) Manure decreases the compactness and clustering of the soil.

(k) The soil colour is dark due to the organic matter. This increases the soil temperature due to the absorption of more sunlight.

Disadvantages of manure

The use of manure is accompanied with some challenges, some of which are:

(a) The availability of nutrients present in manure depends on the activities of microbes which require moisture. Seasonal variation may affect activities of the microbes, hence reducing the release of the nutrients.

(b) Manure produces bad odour and is too annoying to use on indoor plants.

(c) Fresh manure may contain microbes that may be dangerous.

(d) It is difficult to estimate the amount of manure required to be applied in a certain field because the composition of essential nutrients in manure is not consistent.

(e) If manure is applied incorrectly, it can contribute to surface and ground water contamination, and can create a nutritional imbalance in the soil, causing salt burns.

(f) Manure are too bulky to store, transport, and supply.

(g) Manure is associated with high nitrogeneous levels from the excreta. High levels of salt can damage or kill plants.

4.6.4 Similarities and differences between inorganic fertiliser and manure

The comparison between inorganic fertilisers and manure is made based on their application, composition and properties. Manure and fertilisers show the following similarities and differences:

Similarities between inorganic fertiliser and manure

Inorganic fertilisers and manure are similar in that both:

(a) provide plant nutrients.

(b) can lower the soil pH. Decomposition of organic matter produces organic (humic) acids while hydrolysis of some cations in mineral fertilisers such as NH_4^+ produces H_3O^+ ions.

Differences between inorganic fertiliser and manure

The following are some of the common differences between inorganic fertiliser and manure:

(a) Manure has high moisture content (about 50-80%) while most inorganic fertilisers are dry.

(b) Manure has low and variable composition of plant nutrients but the composition of nutrients in inorganic fertilisers are fixed and high in concentration.

(c) Manure improves soil structure and other properties whereas inorganic fertilisers do not improve soil structure.

(d) Essential nutrients in inorganic fertilisers are readily available while most of the nutrients in manure are in organic combination and become gradually available in small amounts due to *mineralisation* by microbial activity.

(e) Inorganic fertilisers are expensive whereas manure is cheap.

Revision exercise 4

1. (a) Explain the meaning and significance of soil colloids.
   (b) Describe the properties of soil colloids.
   (c) Explain how soil colloids facilitate plant nutrition.
2. (a) Summarise the mechanism of ion exchange in the soil.
   (b) Describe cation exchange capacity of a soil.
   (c) A certain soil contains 2.0 meq/100 g of Al^{3+} and 12.0 meq/100 g of H^+. If the cation exchange capacity of the soil is *24* meq/100 g of oven-dried soil, calculate the:

(i) total exchangeable base of the soil sample.

(ii) percentage base saturation.

3. (a) What do you understand by the term soil reaction?

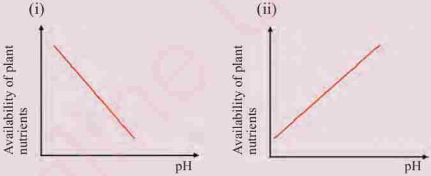
(b) Calculate the pH of the soil sample that contains 0.0001 g of active hydrogen ions per dm^3.

4. (a) Discuss the significance of soil pH.

(b) With the aid of chemical equations, show how Al^{3+} and microorganisms contribute to soil acidity.

(c) If a soil has the percentage base saturation of 60% and contains 8 meq of exchangeable hydrogen per 100 g of oven-dried soil, calculate the cation exchange capacity of the soil.

5. (a) Sketches (i) and (ii) show the relationship between soil pH and availability of plant nutrients.



With reasons, choose a sketch that represents the correct relationship between plant nutrient availability and soil pH.

(b) Ten grams (10 g) of oven-dried soil were shaken with 20 mL of 0.1 mol dm^{-3} hydrochloric acid solution. The mixture was then filtered and the soil thoroughly washed in distilled water. The filtrate and washings were neutralised by 12 mL of 0.1 mol dm^{-3} sodium hydroxide. If the CEC of the soil is 25 meq per 100 g of oven-dried soil, calculate the percentage base saturation of the soil.

6. (a) Enumerate the significance of liming.

(b) List four factors which determine the efficiency of liming materials.

(c) Water was added to 100 g of oven-dry soil and the mixture shaken thoroughly, filtered, and washed. 200 mL of the filtrate were obtained. If the filtrate had a pH of 3, calculate the amount of calcium hydroxide required to neutralise the soil sample.

7. (a) Explain:

   (i) one method that may be used to control low soil pH.

   (ii) two methods that may be used to control high soil pH.

   (b) How do the following processes contribute to the changes in the soil pH?

   (i) Microbial activity

   (ii) Decomposition of organic matter

   (iii) Leaching

   (c) Justify the statement that liming is a soil pH treatment.

8. (a) What are the advantages and disadvantages of manure compared to mineral fertiliser?

   (b) What are the negative effects of the following practices on the soil?

   (i) Repeated irrigation

   (ii) Over-liming

   (iii) Burning of vegetation

   (c) A farmer alters her agricultural practices to incorporate more organic matter into the soil. Explain some of the effects this process may have on inorganic reactions within the soil and the availability of nutrients to plants.

9. (a) Most soils in the humid tropics are acidic. Justify this statement.

   (b) Differentiate between potential and active soil acidity.

   (c) A farmer was advised to raise the pH of an acidic soil and decided to add lime to the field. Surprisingly, he recorded a drastic drop in crop harvests in the same year. What could be the cause of the observed drop in crop harvest?

10. (a) What do you understand by each of the following terms?

    (i) Straight fertiliser

    (ii) Mixed fertiliser

    (iii) Complete fertiliser

    (b) Below is a table showing the classification and sources of essential plant nutrients.

Macronutrients			Micronutrients
From air and water	Mostly from soil minerals	Mostly from organic matter	Mostly from soil minerals
1……………	1……………	1……………	1……4……..7……..
2……………	2……………	2……………	2……5……..8…….
3……………	3……………	3……………	3……6……..9…….

Use your knowledge of plant nutrients to fill in the blanks in the table above.

11. Explain how isomorphic exchange of central cations of soil colloids determines their net surface charge.

12. (a) Classify the following as straight fertiliser, mixed fertiliser or complete fertiliser:

    K_2SO_4, $(NH_2)_2CO$, $(NH_4)_2SO_4 + K_2SO_4$ and

    $(NH_2)_2CO + K_2SO_4 + Ca(H_2PO_4)_2.2H_2O$

    (b) If your soil is deficient in nitrogen, which nutrients supplement would you prefer to use between urea and manure? Give reason(s) for your choice.

    (c) Describe the detrimental effects of improper application of manure.

13. Justify the statement that applying fertilisers on a field without a good cropping system is often a wastage of money and efforts.

Chapter Five

Chemical analysis

Introduction

Chemical analysis is the study of the composition, structure, and properties of chemical materials. It is a collection of all methods and techniques used to discover the chemical information of a certain material. Through chemical analysis an analytical chemist will be able to know the quantity (amount) and quality of one or more constituents contained in a sample. In this chapter, you will learn about volumetric analysis, qualitative analysis, and the chemical analyses related to physical chemistry.

5.1 Volumetric analysis

Volumetric analysis is the determination of the concentration of an analyte in a solution by titration (procedures which are used to measure the volume of reagent needed to react with the analyte). It is also called *titrimetric analysis*. In titration, the reagent of a given concentration is called a *titrant*. The titrant is added drop-wise to the *analyte* until the reaction is complete. The titrant should not be in excess, but in an exact amount necessary for stoichiometric reaction with the analyte. The quantity of the titrant required for complete reaction with the analyte is used to calculate the quantity of the analyte present in the sample. The most common titrations are acid-base, oxidation-reduction (Redox), complex formation and precipitation titrations.

Equivalence point and end point

Equivalence point is the stoichiometric point at which chemically equivalent quantities of reactants have been mixed. The equivalence point is an ideal result which is rarely obtained in titration experiments. What is obtained during actual titration is the *end point* which is the apparent sudden change in a physical property such as colour of the solution. For example, in the redox reaction of permanganate ion and oxalate ion, 2 moles of permanganate ion react stoichiometrically with 5 moles of oxalate ion in hot acidic solution.

$$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \longrightarrow 10CO_2(g) + 2Mn^{2+}(aq) + 8H_2O(l)$$

Titrant (Purple) Analyte (Colourless) (Colourless)

Theoretically, if the unknown solution contains 0.60 moles of $C_2O_4^{2-}$, the equivalence point is reached when 0.24 moles of MnO_4^- solution have been added. In the actual titration involving permanganate and oxalate ions, an end point is the sudden appearance of the faint pink colour of permanganate ions in the flask. Prior to the equivalence point, all permanganate ions are consumed by oxalic acid and the titration solution remains colourless. After the equivalence point, the unreacted permanganate ions start to accumulate until they are enough for one to see. The first trace of purple colour is the end point. Only few people with good sight obtain the measured end point that is closer to the true equivalence point, and not all the times they perform titration experiments. Therefore, for titrations involving colour change the end point cannot exactly be equal to the equivalence point because a little extra of the titrant is required for titration solution to exhibit colour.

Detection of the end point

The end point of a titration is detected visually by a sudden change in some properties of a reaction mixture, in many cases by change in colour. The observed colour change may be a result of the titrant as self-indicator or colour change of the added indicator. Indicators are substances at equivalent point that produce some changes which can be easily seen. For example, in titrating a solution containing Fe^{2+} with that of $KMnO_4$, the $KMnO_4$ is a self-indicator. Fe^{2+} ions are converted to Fe^{3+} and addition of an extra drop of $KMnO_4$ solution after the equivalence point imparts a pink colour to the reaction mixture.

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

Titrant (Purple) Analyte (Colourless) (Colourless)

In acid-base titrations, both the acid and base are always colourless, so it is difficult to tell when the reaction between acid and base is completed. An indicator is added to the analyte solution in order to detect the end point of the reaction by following the colour change of the indicator. For example, in the titration of HCl solution with NaOH solution, methyl orange or phenolphthalein are commonly used as indicators. Methyl orange has a yellowish colour in NaOH (basic) solution. After the completion of the reaction (*i.e.* after equivalence point), an extra drop of HCl solution turns the reaction mixture orange. Phenolphthalein indicator is pink in NaOH so after the equivalence point additional drop of HCl will turn the reaction mixture colourless.

Acid-base indicators

The success of any titration depends upon how accurately the equivalence point is judged. If the end point coincides with the equivalence point, it is an ideal condition. Acid-base indicators are those substances which possess different colours at different hydrogen ion concentrations (pH) of the solution. When a small amount of an indicator is added to an acid solution it possesses an *acid colour*, and when it is added to a base solution it has a different colour called *base colour*. For example, acid colour of methyl red is red while its base colour is yellow. This colour change is not sudden, but takes place gradually and spreads over a pH range of about 2 units. The pH range during which this colour change takes place is called *colour change interval*. In the case of methyl red, the colour is clear red at pH 4.2 (or less) and distinct yellow at pH 6.3 (or more). In the pH range between 4.2 and 6.3, the indicator colour is a mixture of red and yellow. Therefore, the colour change interval for methyl red is from pH 4.2 to 6.3. Table 5.1 shows the colour changes and pH ranges of common indicators.

Table 5.1 Colour changes and pH ranges of common indicators

Acid-Base Indicator	Colours		pH Range
	Acid	Base	
Phenolphthalein	Colourless	Pink	8.3 – 10.0
Methyl orange	Red	Yellow	3.1 – 4.4
Methyl red	Red	Yellow	4.2 – 6.3
Methyl yellow	Red	Yellow	2.9 – 4.0
Bromophenol red	Yellow	Red	5.2 – 6.8
Neutral red	Red	Orange	6.8 – 8.0
Cresol red	Red	Yellow	0.2 – 1.8
Thymol blue	Yellow	Blue	8.0 – 9.6
Nitramine	Colourless	Orange	10.8 – 13.0
Congo red	Blue	Red	3.0 – 5.5

Choice of indicators

The colour change of a good indicator must take place as close as possible to the equivalence point of the titration. Suppose the reaction between an analyte and a titrant is just complete (equivalence point) when 20.00 mL of titrant solution is added to the analyte. If the indicator used for this titration shows a colour change when 20.10 mL of titrant solution has been added, then there is a difference of

0.10 mL in the equivalence point (theoretical end point) and the actual end point. This difference is called the *indicator error*. The most suitable indicator for this titration will be the one which will show a colour change when exactly 20.00 mL of the reagent solution has been added. The choice of a suitable indicator for an acid-base titration depends upon the nature of the acid and the base involved.

Indicators for titration of a strong acid with a strong base

Consider the reaction between HCl and NaOH which is represented as:

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

Table 5.2 shows the data obtained during titration of 0.10 M NaOH with 0.10 M HCl solution whose plot gives a sigmoid curve as shown in Figure 5.1.

Table 5.2 pH changes for gradual addition of NaOH in HCl

Volume of NaOH (mL)	pH
0.00	1.00
10.00	1.18
20.00	1.37
40.00	1.96
49.90	4.00
50.00	7.00
50.10	10.00
51.00	11.00
55.00	11.68
60.00	11.96

Figure 5.1 shows that in the initial stages of the titration, pH increases very slowly even when large volumes of NaOH solution are added. However, close to the equivalence point (pH 7), the addition of very small amount of NaOH causes relatively much greater rise in pH. For example, when the volume of NaOH is

increased from 0.00 to 49.90 mL, the increase in pH is from 1.00 to 4.00, *i.e.* 3 pH units. But when the volume is further increased from 49.90 to 50.00 mL, *i.e.* only 0.10 mL, the pH rises from 4.00 to 7.00, *i.e.* yet same 3 pH units.

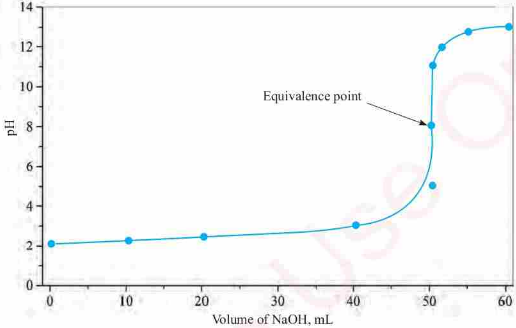


Figure 5.1 Titration curve for the titration of 0.10 M NaOH against 0.10 M HCl

It is also obvious from Figure 5.1 that, when 49.90 mL of NaOH solution has been added, 99.8% of the reaction is complete and the pH change is from 1.00 to 4.00. If a certain indicator shows a colour change at pH 4.00 the titration error will be only 0.2%. Likewise, if the indicator used shows a colour change at pH 10.00, the titration value will be 50.10 mL instead of 50.00 mL (the equivalence point) corresponding to the titration error of 0.2%. Therefore, although the pH at the equivalence point of the titration is 7, it is not necessary that the indicator used should show a colour change at pH 7. Any indicator which shows a colour change between pH 4.00 to 10.00 can be used because the error introduced will not be greater than ± 0.2%. For example, from Table 5.1, methyl orange, congo red, methyl red, bromophenol red, thymol blue, neutral red and phenolphthalein can be used as indicators in this titration because their colour change intervals fall within the pH limit of 4.00 to 10.00. Consider three sets of titration experiments in which the concentrations of NaOH and HCl were varied as shown below:

- 1.00 M NaOH with 1.00 M HCl.
- 0.10 M NaOH with 0.10 M HCl.

- 0.01 M NaOH with 0.01 M HCl.

After performing the required titrations, the data obtained are as summarised in Table 5.3 and their plots are as shown in Figure 5.2. From Table 5.3 and Figure 5.2, when 1.00 M solution of a strong base is titrated with 1.00 M solution of a strong acid, the sharp rise in pH is observed from pH 3.3 to 10.7, which is a wide range of 7.4 pH units. Thus, any indicator which shows a colour change between this pH range is suitable.

Table 5.3 pH changes when the concentrations of NaOH and HCl are varied

Added Volume of NaOH (mL)	pH		
	1.00 M solution	0.10 M solution	0.01 M solution
0.00	0.00	1.00	2.00
50.00	0.50	1.50	2.50
90.00	1.30	2.30	3.30
99.00	2.30	3.30	4.30
99.80	3.00	4.00	5.00
99.90	3.30	4.30	5.30
100.00	7.00	7.00	7.00
100.10	10.70	9.70	8.70
100.20	11.00	10.00	9.00
101.00	11.70	10.70	9.70
110.00	12.70	11.70	10.70
200.0	13.4	12.50	11.50

When 0.10 M solution of a strong base is titrated with 0.10 M solution of a strong acid, the rise is observed from pH 4.3 to 9.7, *i.e.* 5.4 pH units. Here the pH range has been reduced. Thus, any indicator which shows colour change between this pH range is suitable . You can realise that cresol red, methyl yellow and nitramine are not suitable for this titration. When 0.01 M solution of a strong base is titrated with 0.01 M solution of a strong acid, the rise is further reduced from pH 5.3 to 8.7, *i.e.* only 3.4 pH units. Here the pH range is much narrow. Thus, any indicator which shows a colour change between this pH range suitable. It is observed that the pH rise becomes narrow and narrow as the concentrations of strong acid and strong base are reduced. This is an important point that must be considered when selecting an indicator for strong solutions of bases and acids.

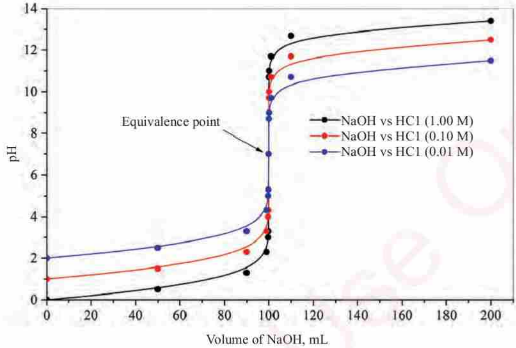


Figure 5.2 Titration curves for different concentrations of NaOH and HCl solutions

Indicators for the titration of a weak acid with a strong base

In the titration of weak acid against strong base, the pH at equivalence point is more than 7. This is due to the hydrolysis of the salt formed. For example, in the titration of acetic acid (CH_3COOH) with sodium hydroxide (NaOH), the salt formed is sodium acetate (CH_3COONa) which is hydrolysed as

$$CH_3COONa(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + Na^+(aq) + OH^-(aq)$$

Due to hydrolysis of the salt formed, $[OH^-]$ in the solution is greater than $[H^+]$ hence, the solution is alkaline, *i.e.* its pH is greater than 7. From the degree of hydrolysis and hydrolysis constant of a weak electrolyte, an expression for the pH at equivalence point for the titration of a weak acid with a strong base is given by

$$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log C \qquad (5.1)$$

where, $K_w = 1.0 \times 10^{-14}$ (the ion product of water),

K_a = the dissociation constant of a weak acid, and

C = the concentration of salt.

For example, if 50.00 mL solution of 0.10 M NaOH is gradually added to 50.00

mL solution of 0.10 M CH_3COOH the total volume will become 100.00 mL and therefore the concentration of CH_3COONa formed will be 0.05 M. Thus,

$$K_w = 1.0\times10^{-14},\ \log K_w = -14,\ pK_w = 14,\ \frac{1}{2}pK_w = 7$$

$$K_a = 1.8\times10^{-5},\ \log K_a = -4.76,\ pK_a = 4.76,\ \frac{1}{2}pK_a = 2.38$$

$$C = 0.05\ \text{M};\ \log C = -1.30,\ \frac{1}{2}\log C = -0.65$$

Substituting the values in the expression $pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a + \frac{1}{2}\log C$ gives

$$pH = 7.00 + 2.38 + (-0.65) = 8.73$$

Therefore, when 0.10 M NaOH is titrated with 0.10 M CH_3COOH the pH at equivalence point = 8.73 (Table 5.4 and Figure 5.3) and not 7.00 as was observed in the titration of 0.10 M NaOH with 0.10 M HCl.

Table 5.4 pH changes when a strong base is added to either a strong or weak acid

Added volume of NaOH (mL)	pH	
	HCl	CH_3COOH
0.00	1.00	2.87
10.00	1.18	4.14
20.00	1.37	4.57
30.00	1.60	4.92
40.00	1.96	5.35
45.00	2.27	5.70
49.00	3.00	6.43
49.90	4.00	7.44
50.00	7.00	8.73
50.10	10.20	10.00
51.00	11.00	11.00
55.00	11.68	11.58
60.00	11.96	11.76

Figure 5.3 shows that, the range of sharp increase for the titration of 0.10 M NaOH with 0.10 M CH_3COOH is from pH 7.8 to 9.7. Thus, from Table 5.1, cresol red, methyl yellow, methyl orange, congo red, methyl red, bromophenol

red and nitramine are not suitable indicators for this titration. Neutral red, thymol blue and phenolphthalein fall within the pH range and are therefore suitable for this titration.

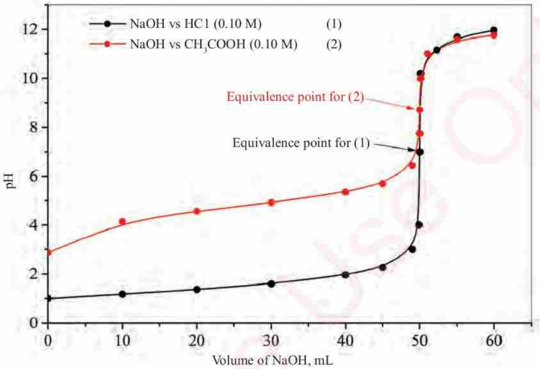


Figure 5.3 Titration curves for the titration of NaOH with HCl and CH_3COOH

Indicators for the titration of a weak base with a strong acid

An example of this type of titration is the titration of 0.10 M aqueous ammonia solution with 0.10 M HCl. The reaction involved is represented by:

$$NH_4OH(aq) + HCl(aq) \longrightarrow NH_4Cl(aq) + H_2O(l)$$

The salt produced undergoes hydrolysis to form H_3O^+.

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

Due to the formation of H_3O^+ ions, the solution at the equivalence point will be slightly acidic as shown by the following expressions:

Suppose 50.00 mL of 0.10 M NH_3 solution is titrated with 0.10 M HCl solution. An expression for the pH at equivalence point for titration of a weak base with a strong acid is given by:

$$pH = \frac{1}{2}pK_w - \frac{1}{2}pK_b - \frac{1}{2}\log C \qquad (5.2)$$

where, K_b is the dissociation constant of a weak base, and

c is the concentration of salt.

Given that at equivalence point, C = 0.05, thus:

$$K_w = 1.0 \times 10^{-14},\ \log K_w = -14,\ pK_w = 14,\ \frac{1}{2}pK_w = 7$$

$$K_b = 1.8 \times 10^{-5},\ \log K_b = -4.76,\ pK_b = 4.76,\ \frac{1}{2}pK_b = 2.38$$

$$C = 0.05\text{ M},\ \log C = -1.30,\ \frac{1}{2}\log C = -0.65$$

Substituting the values in the expression $pH = \frac{1}{2}pK_w - \frac{1}{2}pK_b - \frac{1}{2}\log C$ gives pH = 3.97.

Consider the data for the titration of 0.10 M NH_3 solution with 0.10 M HCl solution, as shown in Table 5.5. The reaction between 0.10 M NH_3 and 0.10 M HCl results into a sharp increase in pH from 3.0 to 6.5.

Table 5.5 pH changes when a weak base is added to a strong acid

Volume of NH_3 solution added (mL)	pH
0	1.00
5	1.32
10	1.53
20	2.00
28	3.00
30	6.6
33	7.75
40	8.66
50	8.73

In Figure 5.4, the graph clearly shows an increase in pH. In this situation, indicators such as methyl orange, congo red and methyl red can be used.

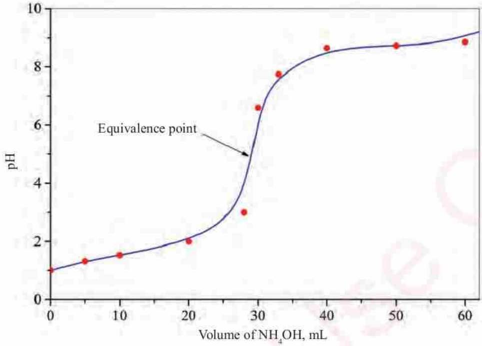


Figure 5.4 Titration curve for the titration of 0.10 M NH_3 with 0.10 M HCl

Indicators for the titration of a weak acid with a weak base

To exemplify this type of titration, consider the reaction between 0.10 M CH_3COOH and 0.10 M NH_3 solution.

$$CH_3COOH(aq) + NH_3(aq) \longrightarrow CH_3COONH_4(aq)$$

The salt CH_3COONH_4 undergoes hydrolysis as

$$CH_3COONH_4(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + NH_3(aq) + H_2O(l)$$

The water molecules on the two sides cancel each other, remaining with the equation,

$$CH_3COONH_4(aq) \rightleftharpoons CH_3COOH(aq) + NH_3(aq)$$

As it can be seen, the hydrolysis reaction is the reverse of the titration reaction. Therefore, the pH at the equivalence point depends on the relative values of K_a (dissociation constant of acid, CH_3COOH) and K_b (dissociation constant of base, NH_3 solution). If $K_a = K_b$, the pH at equivalence point will be 7; if $K_a > K_b$, the pH at equivalence point will be less than 7, and if $K_a < K_b$, the pH at equivalence point will be greater than 7. Consider the titration data shown in Table 5.6.

Table 5.6 pH changes for the titration of weak base with weak acid

Volume of 0.10 M NH_3 solution added (mL)	pH	Volume of 0.10 M NH_3 solution added (mL)	pH
0.00	1.00	150.00	4.82
10.00	1.53	160.00	5.21
20.00	1.62	170.00	5.98
30.00	1.96	175.00	6.52
40.00	2.01	178.00	7.30
50.00	2.36	182.00	8.10
70.00	2.74	185.00	8.22
90.00	2.95	190.00	8.43
110.00	3.19	192.00	8.56
130.00	3.75	195.00	8.61

Table 5.6 and Figure 5.5 show that there is no shap change in pH at any volume of the base NH_4OH despite the type of an indicator used. Under this situation it is very difficult to judge the colour change at the end point and accurate results are seldom.

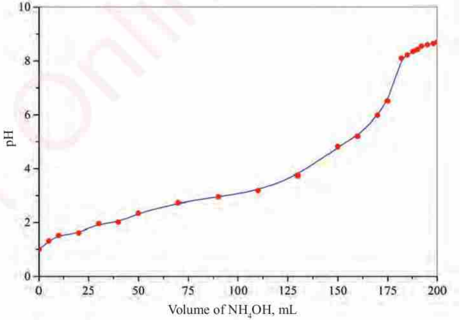


Figure 5.5 Titration curve for the titration of weak base with weak acid

The standard solution

Standard solution is the solution whose concentration is known. The solution is important because it is used to determine the concentration of the analyte. A precisely measured amount of standard solution is added from the burette to a known volume of the solution of unknown concentration until the equivalence point is reached.

Preparation of standard solutions

As stated previously, a solution whose concentration is accurately known is called a *standard solution*. Standard solution can be prepared by either direct or indirect method.

Direct method

In this method, an exactly weighed amount of a substance of definite and known composition is dissolved and made up to known volume in a volumetric flask. From the known weight and volume, the concentration of the solution is calculated. Preparation of a standard solution by direct method can be done using only those substances which fulfil the following conditions:

(a) The substance must be either 100% pure or at least of known purity. For example, if 0.10 g Na_2CO_3 is weighed and it is known that its purity is 98.5%, then the actual weight of Na_2CO_3 in the sample will be

$$0.10\ \text{g} \times \frac{98.5}{100} = 0.0985\ \text{g}$$

(b) The impurity must neither react with the analyte nor the reagent. For example, if in the above example the impurity is NaCl and since it does not react with Na_2CO_3 or HCl, Na_2CO_3 sample can be used as a reagent for titrating HCl.

(c) There should be available tests for knowing the impurities present in the substance.

(d) Before weighing, the substance is dried to remove moisture. The substance should be stable during drying at the oven temperature.

(e) The substance should not absorb moisture, react with oxygen or carbon dioxide during weighing.

(f) The reaction of the substance with the analyte should be fast, simple, complete and stoichiometric.

A substance which fulfils the above conditions is called a *primary standard* and in most cases is used to prepare secondary standards. Secondary standards are substances which do not fulfil the above conditions.

Indirect method

Numerous substances which can be used as titrants are not primary standards. Therefore, their standard solutions cannot be prepared directly by weighing. For example, in the case of hydrated sodium thiosulphate ($Na_2S_2O_3.5H_2O$) there is always some uncertainty about its water content, so its standard solution cannot be prepared by direct method. A solution of appropriate concentration of $Na_2S_2O_3$ is first prepared by weighing and then it is titrated with a standard solution of KIO_3, which is a primary standard. Through this titration, the exact concentration of a thiosulphate solution can be calculated. This process is known as *standardisation.*

Standardisation of HCl by anhydrous Na_2CO_3

If HCl solution whose concentration is about 0.20 M requires to be standardised using Na_2CO_3, stoichiometric calculations are needed so as to know the mass of Na_2CO_3 to be weighed that is enough to prepare its standard solution for the standardisation process.

Consider the chemical equation,

$$Na_2CO_3(aq) + 2HCl(aq) \longrightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$$

Stoichiometrically, since two moles of HCl require one mole of Na_2CO_3, the given HCl solution of about 0.20 M will require Na_2CO_3 of the concentration equal to half that of HCl solution, *i.e*. about 0.10 M. If Na_2CO_3 has to be dissolved in 250 mL, its mass required to prepare 0.10 M Na_2CO_3 solution is calculated as shown below:

$$M = \frac{n\,(\text{mol})}{V\,(\text{L})} \tag{5.3}$$

where, M = molar concentration,

n = number of moles, and

v = volume of solution.

$$0.10 = \frac{n}{0.25}$$

$$n = 0.025 \text{ ml}$$

$$\text{But } n = \frac{\text{mass}}{\text{Molar mass}}$$

$$\text{Mass} = 0.025\ \text{mol} \times 106\ \text{g mol}^{-1} = 2.65\ \text{g}$$

Preparation of about 0.10 M Na_2CO_3 standard solution and the standardisation process can be demonstrated by Activity 5.1.

Activity 5.1

Standardisation of HCl solution using Na_2CO_3 as the standard base

Requirements: Beakers, burette, pipette, conical flasks, 250 mL volumetric flask, glass rod, funnel, watch glass, retort stand, white tile and water bottle, Na_2CO_3, 0.2 M HCl, and methyl orange.

Procedure

1. Weigh about 2.65 g of anhydrous sodium carbonate powder in a watch glass and record its mass (e.g. 2.68 g).
2. Transfer the powder completely into a 250 mL beaker. Add about 50 mL distilled water. Wash the watch glass thoroughly by using a water bottle and transfer all the washings into the beaker. Add more water to dissolve the remaining solid. Use a glass rod to stir the solution in order to facilitate the dissolution process.
3. Carefully, transfer the resulting solution into a 250 mL volumetric flask by means of a funnel and a glass rod. Rinse the beaker, glass rod and the inner surface of the funnel with distilled water and transfer all the washings to the volumetric flask. Repeat this process to make sure that all the Na_2CO_3 has been transferred to the volumetric flask.
4. Add distilled water to the volumetric flask up to the mark. Stopper the flask and homogenise the solution by shaking.
5. Fill the burette with HCl solution and record its initial volume.
6. Pipette 25.00 mL of the sodium carbonate solution into a conical flask, add few drops of methyl orange indicator and put the flask on top of the white tile.
7. Titrate against the hydrochloric acid solution.
8. Record the titre volume in tabular form and repeat the titration to obtain three more readings.

Questions

1. What was the colour change of the solution at the end point?
2. Determine the concentration of Na_2CO_3 solution in mol L^{-1} and g L^{-1}.
3. Determine the molarity of hydrochloric acid solution.

The results in Table 5.7 and calculations are given as an example.

Experimental results

Volume of pipette used is 25.00 mL

Table 5.7 Titration results for the standardisation of HCl by anhydrous Na_2CO_3

Volume of HCl (mL)	Titrations			
	Pilot	1	2	3
Final burette reading	27.50	27.00	32.10	26.40
Initial burette reading	0.00	0.50	5.50	0.00
Volume used (titre volume)	27.50	26.50	26.60	26.40
Average titre volume	26.50 mL			

The average titre value is obtained by:

$$V = \frac{V_1 + V_2 + V_3}{3}$$

$$= \frac{26.50 + 26.60 + 26.40}{3}$$

$$= 26.50 \text{ mL}$$

Therefore, from the titration, 25.00 mL of Na_2CO_3 solution required 26.50 mL of HCl solution for complete reaction.

Answers to questions

1. At the end point the solution colour changed from yellow to orange.
2. To calculate the accurate concentration of Na_2CO_3 prepared, the weighed mass of 2.68 g and the volume of 250 mL are used.

$$\text{Molar concentration, M} = \frac{n\,(\text{mol})}{V\,(\text{L})} = \frac{2.68 \text{ g} \,/\, 106 \text{ g mol}^{-1}}{0.25 \text{ L}} = 0.1011 \text{ M}$$

$$\text{Mass concentration, g L}^{-1} = \frac{\text{mass (g)}}{V\,(\text{L})} = \frac{2.68}{0.25 \text{ L}} = 10.72 \text{ g L}^{-1}$$

3. From the balanced chemical equation,

$$2HCl(aq) + Na_2CO_3 \longrightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$$

the exact concentration of HCl solution can be calculated from the relation:

$$\frac{M_a \times V_a}{n_a} = \frac{M_b \times V_b}{n_b} \tag{5.4}$$

where, M_a = molarity of acid solution,

M_b = molarity of base solution,

V_a = titration volume of acid solution,

V_b = titration volume of base solution,

n_a = stoichiometric value for an acid, and

n_b = stoichiometric value for the base.

In this example, M_a is not known,

$M_b = 0.1011$ M,

$V_a = 26.50$ mL,

$V_b = 25.00$ mL,

$n_a = 2$, and

$n_b = 1$

The given relation is rearranged to $M_a = \frac{M_b \times V_b}{n_b} \times \frac{n_a}{V_a}$, and substituting the known values with their corresponding units gives:

$$M_{HCl} = \frac{0.1011\,\text{M} \times 25.00\,\text{mL}}{1} \times \frac{2}{26.50\,\text{mL}} = 0.1907\,\text{M}$$

Therefore, the molarity of HCl solution is 0.1907 M.

The given HCl solution has been standardised and its accurate concentration is 0.1907 M.

Standardisation of a base using oxalic acid

Basic (alkaline) solution can be standardised using oxalic acid as the primary standard. Oxalic acid is available as a pure, non-hygroscopic and crystalline solid that can be accurately weighed. Oxalic acid sample of known mass (known moles) can be titrated with NaOH solution to determine very precisely the concentration of the NaOH. This procedure is called standardisation of NaOH solution. Suppose that a NaOH solution with the concentration of approximately 0.10 M is provided for standardisation using $H_2C_2O_4 \cdot 2H_2O$. Activity 5.2 demonstrates how the standardisation process can be achieved.

Activity 5.2

Standardisation of NaOH using oxalic acid

Requirements: Beakers, burette, pipette, conical flasks, 250 mL volumetric flask, glass rod, funnel, watch glass, retort stand, white tile water bottle, $H_2C_2O_4.2H_2O$, about 0.10 M NaOH, and phenolphthalein indicator.

Procedure

1. Use stoichiometric calculations to determine the concentration of $H_2C_2O_4.2H_2O$ needed to react with about 0.10 M NaOH.
2. Calculate the mass of oxalic acid required to prepare 250 mL of its standard solution needed for standardising about 0.10 M NaOH solution.
3. Weigh the calculated mass (step 2) in a watch glass, transfer it in a beaker and dissolve it with distilled water. Follow the same procedure as step 2 and 3 from Activity 5.1 to prepare 250 mL standard solution of oxalic acid.
4. Fill the burette with NaOH solution, pipette 25.00 mL aliquots of $H_2C_2O_4$ in a conical flask, add 2−3 drops of phenolphthalein indicator, put the flask on top of the white tile and titrate it with NaOH solution.
5. Repeat the titration to obtain at least three readings and tabulate your results as shown in Table 5.8.

Table 5.8 Titration results for a standardisation of a base using oxalic acid

Volume of NaOH (mL)	Titrations			
	Pilot	1	2	3
Final burette reading				
Initial burette reading				
Titre volume				
Average titre volume				

Questions

1. Write the balanced chemical equation for the reaction between oxalic acid and NaOH.

2. Calculate the molar concentration of the prepared $H_2C_2O_4$.
3. Determine the exact concentration of the given NaOH solution.

5.1.1 Acid-base titration

You have learnt that the choice of an indicator in acid-base titration depends on the strength of the acid and the base. In a strong acid-strong base titration, a bromothymol blue indicator is used, In weak acid-strong base reactions a phenolphthalein indicator is used, while methyl orange is used for strong acid-weak base reactions. However, there are reactions in which determination and analysis of the amount and concentration of acids or bases is done at two end points. These are called double indicator titrations.

Acid–base titrations using double indicators

Reaction between HCl and Na_2CO_3

Sodium carbonate is a salt of carbonic acid (H_2CO_3), a dibasic acid which dissociates in two steps.

$$H_2CO_3(aq) \rightleftharpoons HCO_3^-(aq) + H^+(aq) \qquad pK_1 = 6.38$$

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^-(aq) \qquad pK_2 = 10.32$$

In aqueous solution, Na_2CO_3 hydrolyses as:

$$Na_2CO_3(aq) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2CO_3(aq)$$

Sodium carbonate (Na_2CO_3) reacts with hydrochloric acid (HCl) in two stages. In the first step, one mole of $NaHCO_3$ is produced from one mole of Na_2CO_3 and HCl. The sodium bicarbonate formed reacts with the HCl still in the solution to produce NaCl, CO_2 and water.

$$\text{Step 1: } Na_2CO_3(aq) + HCl(aq) \longrightarrow NaHCO_3(aq) + NaCl(aq)$$

$$\text{Step 2: } NaHCO_3(aq) + HCl(aq) \longrightarrow NaCl(aq) + CO_2(g) + H_2O(l)$$

Assume that 50.00 mL of 0.10 M Na_2CO_3 solution is titrated with 0.10 M HCl solution. By the time 50.00 mL of 0.10 M HCl solution has been added, the reaction is complete. The pH at this point is given by:

$$\frac{1}{2}\text{p}K_1+\frac{1}{2}\text{p}K_2=\frac{1}{2}(6.38+10.32)=8.35.$$

Therefore, the first end point can be detected using phenolphthalein indicator. At the completion of the first step the solution is acidic with a pH of about 3.94 and methyl orange can be used as an indicator. For this titration process, phenolphthalein indicator indicates half way end point of volume of HCl reacted with sodium carbonate during titration. The other half end point volume of HCl remained for complete reaction is indicated by methyl orange indicator added to the same solution. The approach for determination of the volume of HCl used when Na_2CO_3 is titrated against HCl using phenolphthalein and methyl orange indicators is demonstrated by Activity 5.3.

Activity 5.3

Determination of the volume of HCl used for the titration with Na_2CO_3 using phenolphthalein and methyl orange indicators

Requirements: Beakers, pipettes, burettes, retort stand, white tile, conical flasks, 0.05 M Na_2CO_3 solution, 0.10 M HCl solution, methyl orange (MO) indicator, and phenolphthalein (POP) indicator.

Procedure

1. Pipette 25.00 mL of Na_2CO_3 solution into a conical flask.
2. Add 2–3 drops of phenolphthalein indicator.
3. Put HCl into the burette and take the initial reading.
4. Titrate HCl solution against Na_2CO_3 solution until a colour change is observed and record the first titre value.
5. Add 2–3 drops of methyl orange indicator to the same solution in the titration flask and continue titrating until a colour change is observed, then record the second titre value.
6. Repeat the procedure to obtain three readings and record the results in a tabular form as shown in Table 5.9.

Table 5.9 Titration results for the reaction between Na_2CO_3 and HCl

Volume of HCl (mL)	Titrations			
	Pilot	1	2	3
Initial burette reading				
Final burette reading after using POP				
Final burette reading after using MO				
Titre volume when POP was used				
Titre volume when MO was used				

Questions

1. Calculate the average titre value when:
   (a) POP was used.
   (b) MO was used.
2. Write the balanced chemical equations when:
   (a) POP was used as an indicator.
   (b) MO was used as an indicator.
3. Write the overall balanced chemical equation for the reaction between hydrochloric acid and sodium carbonate.
4. Calculate the total volume of HCl solution used for complete reaction with Na_2CO_3.

Reaction between HCl and a mixture of Na_2CO_3 and NaOH

Determination of the composition of sodium carbonate and sodium hydroxide in a mixture is useful in the analysis of commercial caustic soda. Two methods can be used for this analysis. In the first method the total alkali (carbonate and hydroxide) is determined by titration with standard acid, using methyl orange or other suitable indicators. In the second portion of solution, the carbonate is precipitated with a slight excess of barium chloride solution. The resulting mixture is then titrated with standard acid using phenolphthalein indicator. This titration gives the hydroxide content and by subtracting this from the first titration, the volume of acid required for the carbonate is obtained. The second method utilises two indicators in the same mixture. It has been stated earlier that the pH of half-neutralised sodium carbonate, that is, at the sodium hydrogen carbonate stage, is about 8.35. The second end point for complete neutralisation is slightly acidic, so a different indicator has to be used. In this case, phenolphthalein and methyl orange indicators are employed. Consider the chemical reaction of the mixture of sodium carbonate and sodium hydroxide with hydrochloric acid given below:

$$Na_2CO_3(aq) + HCl(aq) \longrightarrow NaCl(aq) + NaHCO_3(aq)$$

$$NaHCO_3(aq) + HCl(aq) \longrightarrow NaCl(aq) + CO_2(g) + H_2O(l)$$

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

The pH of the solution closer to the equivalence point of the reactions between Na_2CO_3 and HCl, and $NaHCO_3$ and HCl is alkaline, so phenolphthalein indicator is used to indicate the end points of these reactions. On the other hand, the pH of the solution closer to the equivalence point of the reaction between NaOH and HCl is acidic, thus, methyl orange is used to indicate the end point of this reaction. The experimental determination of the percentage composition of sodium carbonate in the mixture can be demonstrated in Activity 5.4.

Activity 5.4

Determination of the percentage composition of sodium carbonate in the mixture.

Requirements: Beakers, pipettes, burettes, retort stand, white tile, conical flasks, a solution containing 4.94 g of a mixture of sodium carbonate and sodium hydroxide in 1 dm^3 of aqueous solution, 0.10 M pure hydrochloric acid, methyl orange, and phenolphthalein indicators.

Procedure

1. Pipette 25.00 mL of a solution containing a mixture of Na_2CO_3 and NaOH into a conical flask.
2. Add 2–3 drops of phenolphthalein indicator.

3. Fill the burette with HCl solution and take the initial reading.
4. Titrate HCl solution against a solution containing a mixture of Na_2CO_3 and NaOH until a colour change is observed and record the first titre value.
5. Add 2–3 drops of methyl orange indicator to the same solution in the titration flask and continue to titrate until a colour change is observed. Record the second titre value.
6. Repeat the procedure three times and record the results in tabular form as shown in Table 5.10.

Table 5.10 Titration results for the reaction between HCl and a mixture of Na_2CO_3 and NaOH

Volume of HCl (mL)	**Titrations**			
	Pilot	**1**	**2**	**3**
Initial burette reading				
Final burette reading after using POP				
Final burette reading after using MO				
Titre volume when POP was used				
Titre volume when MO was used				

Questions

1. Determine the volume of HCl which reacted completely with Na_2CO_3 in the mixture.
2. Determine the volume of HCl which reacted completely with NaOH in the mixture.
3. Calculate the concentration in g dm^{-3} of Na_2CO_3 and NaOH in the mixture.
4. Calculate the percentage of Na_2CO_3 in the mixture.

5.1.2 Redox titration

In physical chemistry the concepts of redox reaction and redox titration are discussed. In this sub-section the knowledge acquired in balancing redox reactions is experimentally employed to determine the unknown concentration of the analyte through redox titration.

Standardising $Na_2S_2O_3$ using potassium permanganate or potassium iodate

During the redox titration, potassium permanganate or potassium iodate of known concentration first reacts quantitatively with acidified potassium iodide solution to liberate iodine:

$$10I^-(aq) + 2MnO_4(aq) + 16H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 5I_2(aq) + 8H_2O(l)$$

$$5I^-(aq) + IO_3^-(aq) + 6H^+(aq) \longrightarrow 3I_2(aq) + 3H_2O(l)$$

In both cases, the liberated iodine is titrated with sodium thiosulphate through which its concentration can be calculated. The reaction involved between thiosulphate and iodine is as shown hereunder.

$$2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

The steps involved in the standardisation of sodium thiosulphate using potassium permanganate or potassium iodate are demonstrated by Activities 5.5 and 5.6, respectively.

Activity 5.5

Standardisation of sodium thiosulphate using potassium permanganate

Requirements: Beakers, pipettes, burettes, retort stand, white tile, conical flasks, 0.02 M $KMnO_4$ solution, $Na_2S_2O_3$ solution of unknown concentration, 10% KI, 1.00 M H_2SO_4, and starch indicator.

Procedure

1. Pipette 25.00 mL of $KMnO_4$ solution into a conical flask.
2. To the conical flask, add 20.00 mL of KI solution followed by 20.00 mL of H_2SO_4 solution.
3. Fill the burette with $Na_2S_2O_3$ solution and titrate it with the liberated iodine until the solution becomes pale yellow.
4. Add about 1–2 mL of starch indicator and continue titrating until a colour change is just observed (from dark blue to colourless), and record the final volume used.

5. Repeat the procedure to obtain at least three readings and record your results in tabular form as shown in Table 5.11.

Table 5.11 Titration results for the standardisations of $Na_2S_2O_3$ using $KMnO_4$

Volume of $Na_2S_2O_3$ (mL)	Titrations			
	Pilot	1	2	3
Final burette reading				
Initial burette reading				
Titre volume				
Average titre volume				

Questions

1. Write down the balanced half reaction equations to show the oxidation and reduction processes for the reaction in step (2). Identify the oxidant and reductant in the two equations.
2. Calculate the concentration of $Na_2S_2O_3$ in mol dm^{-3}.

Activity 5.6

Standardisation of sodium thiosulphate using potassium iodate

Requirements: Beakers, pipettes, burettes, retort stand, white tile, conical flasks, 0.02 M KIO_3 solution, $Na_2S_2O_3$, solution of unknown concentration, 10% KI, 1.00 M H_2SO_4, and starch indicator.

Procedure

Follow the procedure in Activity 5.5 but add KIO_3 in a place of $KMnO_4$ and record the results in a tabular form as shown in Table 5.12.

Table 5.12 Titration results for the standardisations of $Na_2S_2O_3$ using KI

Volume of $Na_2S_2O_3$ (mL)	Titrations			
	Pilot	1	2	3
Final burette reading				
Initial burette reading				
Titre volume				
Average titre volume				

Questions

1. Write down half reaction equations and the overall equation for the reaction between KIO_3 and acidified KI.
2. Calculate the molarity of $Na_2S_2O_3$.
3. 25.00 mL of the potassium iodate solution were added to about 15 mL of a 15% solution of potassium iodide (ensuring excess iodide ion). On acidification, the liberated iodine needed 24.10 mL of 0.05 mol dm^{-3} sodium thiosulphate solution to titrate it. Calculate the concentration of potassium iodate in g dm^{-3}.

Reaction of oxalic acid with potassium permanganate

The reaction between oxalic acid and potassium permanganate occurs in acidic medium. Potasium permanganate ion is a powerful oxidasing agent in an acidic medium. In this reaction, dilute sulphuric acid is added so as to create an acidic environment. Potassium permanganate in this case acts as a self-indicator.

$$2KMnO_4(aq) + 3H_2SO_4 + 5H_2C_2O_4 \longrightarrow 2MnSO_4(aq) + K_2SO_4(aq) + 10CO_2(g) + 8H_2O(l)$$

$$2MnO^-_4(aq) + 6H^+(aq) + 5H_2C_2O_4(aq) \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2(g)$$

5.1.3 Precipitation titration

Precipitation titrations are a form of titration useful in the determination of halides such as chlorides, bromides, and iodides. They involve the use of precipitating agents such as copper(II) sulphate, potassium thiosulphate, and silver nitrate.

Volumetric estimation of copper in copper(II) sulphate

Experimentally, the estimation of copper in copper(II) sulphate can be done through iodometric titration. In this titration, the appearance or disappearance of elemental iodine indicates the end point of the reaction as for Activities 5.5 and 5.6. The method involves indirect titration of iodine liberated by the reaction with the analyte. In the volumetric estimation of copper in copper(II) sulphate, the analyte ($CuSO_4$) first reacts with potassium iodide (KI) to liberate iodine.

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

The liberated iodine is titrated with the known concentration of sodium thiosulphate using starch indicator (Activity 5.7).

$$2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

Results from the titration process are helpful in determining the concentration of the analyte taking into account that stoichiometrically, $2Cu^{2+} \equiv I_2 \equiv 2S_2O_3^{2-}$.

Activity 5.7

Volumetric estimation of copper in copper(II) sulphate

Requirements: Beakers, retort stand, pipettes, burettes, conical flasks, 0.1 M $Na_2S_2O_3$ solution, $CuSO_4$ solution of unknown concentration, 10% KI, and starch indicator.

Procedure

Follow the procedure of Activity 5.5 but put $CuSO_4$ in a place of $KMnO_4$ and KI in a place of acidified KI. Record the titration results in a tabular form as shown in Table 5.13.

Table 5.13 Titration results for the estimation of Cu in CuSO4 using $Na_2S_2O_3$

Volume of $Na_2S_2O_3$ (mL)	Titrations			
	Pilot	1	2	3
Initial burette reading				
Final burette reading				
Titre volume				
Average titre volume				

Questions

1. Stoichiometrically, determine the mole ratio between $CuSO_4$ and NaS_2O_3.
2. Calculate the concentration of $CuSO_4$ and estimate the amount of copper in $CuSO_4$ solution.

5.2 Qualitative analysis

Qualitative analysis is a method used for identification of ions or compounds in a sample. It aims at determining substances present in a mixture but not their quantities. By conducting appropriate tests and applying logic, the identities of ions present in an unknown solution can be determined. The analyses to be performed are based upon the idea that no two ions produce the same set of chemical reactions as each ion reacts on its own characteristic way. In qualitative analysis several types of chemical reactions have to be monitored which are revealed through colour change, evolution of a gas, production of sound, increase in temperature of the reaction vessel and the formation of the precipitate (a solid product). In many cases, qualitative analysis will also involve the separation of ions or compounds in a mixture. Examples of qualitative tests would include ion precipitation reactions (solubility tests) and chemical reactivity tests.

5.2.1 Preliminary tests

There are separate procedures for detecting cations and anions called the *cation* and *anion analysis*, respectively. In order to identify the ions present in the sample, the first thing to perform is preliminary tests. These tests may consist of physical examination (colour, texture and smell), dry heating the sample to detect the presence of some constituents such as carbon (marked by the appearance of smoke or char) or water (marked by the appearance of moisture). It may also involve introducing the sample into a flame and noting the colour produced as certain elements may be identified by means of their characteristic flame colours. Other preliminary tests include the action of dilute and concentrated acids as well as solubility in water. The analytical procedures, experiments/ tests performed have to be recorded in tabular form with three columns titled experiment, observation and inference. The experimental column summarises the test performed to the unknown sample. This has to be reported in a simple past tense. For example, "a small amount of the sample was picked with a clean spatula to the test tube where a small amount of water was added." The changes observed when the sample is tested have to be written in the observation column. Examples of the observations include the colour change, evolution of gases, smell, flame colour, sound and formation of precipitates. The suggestions from the observation is written in the inference column. Table 5.14 summarises some of the preliminary tests for different ions.

Table 5.14 Preliminary tests for cations and anions

S/N	Experiment to be performed	Observation	Inference
1.	**Appearance of the sample** (i) Colour	White/colourless	Absence of transition metals
		Blue	Cu^{2+} may be present
		Orange	$Cr_2O_7^{2-}$ may be present

S/N	Experiment to be performed	Observation	Inference
		Green	Fe^{2+}, Cu^{2+}, Ni^{2+} and Cr^{3+} may be present
		Yellow	Fe^{3+} and CrO_4^{2-} may be present
		Brown	Fe^{3+} may be present
		Black	Oxides or sulphides may be present
		Pink	Mn^{2+} or Co^{2+} may be present
	(ii) Texture	Crystalline	NO_3^-, SO_4^{2-}, Cl^-, $C_2O_4^{2-}$, CrO_4^{2-}, NO_2^-, CH_3COO^- and $Cr_2O_7^{2-}$ or hydrated salts may be present
		Powder	CO_3^{2-} and HCO_3^- or anhydrous salts may be present except CO_3^{2-} of NH_4^+, K^+ and Na^+
	(iii) Odour	Solid with a chocking smell (urine smell)	NH_4^+ may be present
		Solid with a smell of vinegar	CH_3COO^- may be present
	(iv) Deliquescence	Absorbs water to form a solution	NO_3^-, SO_4^{2-} and Cl^- may be present
2.	**Flame test** Pick up a small amount of the sample using a wet wire/glass rod or base of the test tube and heat it on a non-luminous flame. Use conc. HCl in a watch glass to wet the wire/glass rod or base of the test tube.	Bright yellow/golden yellow	Na^+ may be present
		Brick red (orange)	Ca^{2+} may be present
		Pale green	Ba^{2+} may be present
		Lilac (light purple/ violet)	K^+ may be present
		Crimson (blood red)	Sr^{2+} may be present
		Blue-green	Cu^{2+} may be present
		Blue-grey	Pb^{2+} and Sb^{2+} may be present
		Yellow sparks	Fe^{2+} and Fe^{3+} may be present

S/N	Experiment to be performed	Observation	Inference
3.	**Solubility of the solid sample** Take about 0.5 g of a sample in a clean test-tube.	Soluble in cold distilled water	(i) NO_3^-, CH_3COO^-, HCO_3^- may be present (ii) SO_4^{2-} may be present except those of Ba^{2+}, Sr^{2+}, Ca^{2+}, and Pb^{2+}
	Add enough amount of distilled water to dissolve it.		(iii) Cl^- may be present except those of Ag^+ and Pb^{2+}
	If the sample does not dissolve, warm the contents.		(iv) Na^+, K^+, NH_4^+ may be present (v) CO_3^{2-} and $C_2O_4^{2-}$ of Na^+, K^+, NH_4^+ may be present
		Soluble in hot distilled water	$PbCl_2$ may be present
		Insoluble in cold and hot distilled water	(i) SO_4^{2-} of Ba^{2+}, Sr^{2+}, Ca^{2+} and Pb^{2+} may be present (ii) Cl^- of Ag^+ may be present (iii) CO_3^{2-} and $C_2O_4^{2-}$ may be present except those of Na^+, K^+, NH_4^+
4.	**Action of heat on a solid sample** Put about 0.5 g of a sample in a clean and dry test tube and heat the content.	Colourless droplets forming on the cooler part of the test-tube which turn white anhydrous $CuSO_4$ blue	Hydrated salt may be present

S/N	Experiment to be performed	Observation	Inference
		NH_3 gas: Colourless gas with a chocking smell, turns red litmus paper blue and forms dense white fumes with HCl	NH_4^+ may be present
		HCl gas: Colourless gas with a pungent smell, turns wet blue litmus paper red and forms dense white fumes with NH_3	Cl^- may be present
		O_2 gas: Colourless gas evolves, which re-lights a glowing wooden splint	NO_2^- of Na^+ and K^+ may be present
		NO_2 gas: Brown fumes evolve, which turn wet blue litmus paper red and a gas which re-lights a glowing wooden splint	NO_3^- may be present except those of Na^+ and K^+ NO_2^- may be present
		CO_2 gas: Colourless gas evolves, which turns lime water milky.	CO_3^{2-} or HCO_3^- may be present
		SO_2 gas: Colourless gas with pungent smell evolves, which turns wet blue litmus paper red or wet potassium dichromate paper green or decolourises the solution of potassium permanganate	SO_4^{2-} or SO_3^{2-} may be present except those of Na^+ and K^+
		Colourless vapour with a smell of vinegar evolves	CH_3COO^- may be present

S/N	Experiment to be performed	Observation	Inference
		CO gas: Colourless and odourless gas evolves, neutral to litmus paper and burns with a blue flame	$C_2O_4^{2-}$ may be present
		H_2 gas: Colourless and odourless gas evolves, neutral to litmus paper and burns with a 'pop' sound	$HCOO^-$ may be present
		HBr/Br_2 gas: Greenish yellow gases, turn wet blue litmus paper red and condenses to red liquid	Br^- may be present
		I_2 gas: Violet vapour	I^- may be present
		Cracking sound with evolution of brown gas	$Pb(NO_3)_2$ may be present
		Cracking sound with no gas evolving	Chlorides of Na^+ or K^+ may be present
		White sublimate	NH_4^+ may be present
		Black/purple sublimate	I^- may be present
		Residue that are reddish brown when hot and yellow when cold (PbO)	Pb^{2+} may be present
		Residue that is yellow when hot and white when cold (oxides of Zn, Sn and Sb)	Zn^{2+}, Sn^{2+} or Sb^{2+} may be present
		Black residue	Cu^{2+} may be present
		Reddish-brown when hot and pale yellow when cold	Fe^{3+} may be present
		Changes from red to blue	Co^{2+} may be present
		Changes from green to yellow	Ni^{2+} may be present

S/N	Experiment to be performed	Observation	Inference
5.	**Action of dilute HCl or H_2SO_4 on a solid sample** Treat a pinch of the salt in a clean dry test tube with dil. HCl or H_2SO_4 and identify the gas evolved. If no reaction warm gently.	**CO_2 gas**: Effervescence of a colourless gas which turns lime water milky	CO_3^{2-} or HCO_3^- may be present
		NO_2 gas: Brown fumes evolve, which turn wet blue litmus paper red	NO_2^- may be present
		No gas evolves	SO_4^{2-} or Cl^- may be present
		H_2S gas: A gas with a rotten egg smell evolves	S^{2-} may be present
		SO_2 gas evolves	SO_3^{2-} may be present
		Colour change from yellow to orange	CrO_4^{2-} may be present
6.	**Action of concentrated H_2SO_4 on a solid sample** ***Safety Precautions:*** [*Concentrated H_2SO_4 is corrosive. Handle with care and do not boil*].	Colourless gas with irritating smell evolves, which turns wet blue litmus paper red and forms dense white fumes with ammonia gas (HCl gas)	Cl^- may be present

S/N	Experiment to be performed	Observation	Inference
	Put about 0.5 g of a sample in a clean and dry test tube. Add a small amount of concentrated H_2SO_4. If no reaction warm the contents gently.	Brown fumes evolve, which turn wet blue litmus paper red, and intensify on addition of copper turnings	NO_3^- may be present
		Colourless vapour with vinegar smell evolves	CH_3COO^- may be present
		Upon warming, effervescence of a colourless gas evolves that turns lime water milky and burns with a blue flame.	$C_2O_4^{2-}$ may be present
		Effervescence of a colourless gas which turns lime water milky	CO_3^{2-} or HCO_3^- may be present
		Reddish brown gases, turn wet blue litmus paper red	Br^- may be present
		Blue crystals turn white	$CuSO_4.5H_2O$ may be present
		Turn starch/iodine paper blue black and bleaches blue litmus paper	I^- may be present

From the preliminary tests under Table 5.14, the following can be deduced:

(a) The action of heat on hydrated salts forms colourless droplets on the cooler parts of the test tube.

$$CuSO_4 \cdot 5H_2O(s) \xrightleftharpoons{\text{heat}} CuSO_4(s) + 5H_2O(l)$$

(b) Ammonium chloride salts sublime upon heating but ammonia gas is given off when they are further heated.

$$NH_4Cl(s) \xrightarrow{\text{heat}} NH_3(g) + HCl(g)$$

(c) The action of heat on nitrate salts of sodium and potassium produce nitrite salts and oxygen gas.

$$2KNO_3(s) \xrightarrow{\text{heat}} 2KNO_2(s) + O_2(g)$$

(d) Metal nitrates except those of Na^+, K^+, and NH_4^+ decompose to form metal oxide, nitrogen dioxide and oxygen gas upon heating.

$$2Pb(NO_3)_2(s) \xrightarrow{\text{heat}} 2PbO(s) + 4NO_2(g) + O_2(g)$$

(e) Silver nitrate decomposes to give silver metal, nitrogen dioxide and oxygen gas.

$$2AgNO_3(s) \xrightarrow{\text{heat}} 2Ag(s) + 2NO_2(g) + O_2(g)$$

(f) Ammonium nitrate decomposes to nitrous oxide and water vapour.

$$NH_4NO_3(s) \xrightarrow{\text{heat}} N_2O(g) + 2H_2O(g)$$

(g) The action of heat on metal nitrites gives brown fumes of NO_2.

$$2NaNO_2(s) \xrightarrow{\text{heat}} Na_2O(s) + NO_2(g) + NO(g)$$

(h) The action of heat on carbonates of most metals except sodium and potassium, produces carbon dioxide gas and metal oxides.

$$MgCO_3(s) \xrightarrow{\text{heat}} MgO(s) + CO_2(g)$$

(i) The action of heat on bicarbonate salts of most metals except sodium and potassium, produces carbon dioxide gas, metal oxides and water.

$$Mg(HCO_3)_2(s) \xrightarrow{\text{heat}} MgO(s) + 2CO_2(g) + H_2O(l)$$

(j) The decomposition of silver and ammonium carbonates gives different products.

$$2Ag_2CO_3(s) \xrightarrow{\text{heat}} 4Ag(s) + 2CO_2(g) + O_2(g)$$

$$(NH_4)_2CO_3(s) \xrightarrow{\text{heat}} 2NH_3(g) + H_2O(g) + CO_2(g)$$

Group I and II sulphates do not decompose on heating. Other metal sulphates decompose to metal oxides and sulphur trioxide on heating. Fe(II) sulphate gives both SO_3 and SO_2 upon heating as Fe(II) changes to Fe(III). Ammonium sulphate first sublimes when heated but further heating decomposes the salt to ammonia and hydrogen sulphate.

$$CuSO_4(s) \xrightarrow{\text{heat}} CuO(s) + SO_3(g)$$

$$2FeSO_4(s) \xrightarrow{\text{heat}} Fe_2O_3(s) + SO_3(g) + SO_2(g)$$

$$(NH_4)_2SO_4(s) \xrightarrow{\text{heat}} 2NH_3(g) + H_2SO_4(g)$$

For the action of dil. H2SO4 or HCl on the unknown samples, the acid decomposes carbonates, sulphides, sulphites and nitrites in cold to give gases. Identification of these gases will indicate the nature of the anion present in the salt as indicated in the following reactions:

(a) *Carbonates/hydrogen carbonates*: On treating the carbonates/hydrogen carbonates with dil. H_2SO_4 or HCl, carbon dioxide gas (CO_2) is given off with the brisk effervescence.

$$Na_2CO_3(aq) + H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + H_2O(l) + CO_2(g)$$

$$NaHCO_3(aq) + HCl(aq) \longrightarrow NaCl(aq) + CO_2(g) + H_2O(l)$$

(b) *Sulphides:* When sulphides are treated with dil. H_2SO_4 or HCl, hydrogen sulphide gas (H_2S) is given off.

$$ZnS(s) + H_2SO_4(aq) \longrightarrow ZnSO_4(aq) + H_2S(g)$$

$$ZnS(s) + 2HCl(aq) \longrightarrow ZnCl_2(aq) + H_2S(g)$$

(c) *Sulphites*: Sulphite salts react with dil. H_2SO_4 or HCl to evolve SO_2 gas.

$$Na_2SO_3(s) + H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + H_2O(l) + SO_2(g)$$

(d) *Nitrites*: The reaction of solid nitrite with dil. H_2SO_4 or HCl evolves nitric oxide (NO) gas through HNO_3 which readily reacts with oxygen from air to give brown fumes of NO_2.

$$2KNO_2(s) + H_2SO_4(aq) \rightarrow K_2SO_4(aq) + 2HNO_2(aq)$$

$$3HNO_2(aq) \rightarrow HNO_3(aq) + 2NO(g) + H_2O(l)$$

$$\underset{\text{Colourless}}{2NO(g)} + O_2(g) \rightarrow \underset{\text{Brown fumes}}{2NO_2(g)}$$

(e) *Chromates*: Chromate salts react with dil. H_2SO_4 or HCl to form dichromate.

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightarrow Cr_2O_7^{2-}(aq) + H_2O(l)$$

For the action of concentrated H_2SO_4 on the unknown salts, the acid is used to identify the class of anions. These are chlorides (Cl^-), fluorides (F^-), bromides (Br^-), iodides (I^-), sulphites (SO_3^-), nitrates (NO_3^-), carbonates (CO_3^-), bicarbonates (HCO_3^-), acetates (CH_3COO^-) and oxalates $(COO)_2^{2-}$. Examples of the reactions involved include:

(a) *Chlorides and fluorides*: Electrochemically, chlorides and fluorides are not strong reducing agents to reduce sulphuric acid to SO_2 and H_2S compared to bromide and iodide. Similarly, sulphuric acid is not a strong oxidising agent to oxidise chlorides and fluorides. Consequently, chloride and fluoride salts react with conc. H_2SO_4 to evolve hydrogen chloride (HCl) and hydrogen fluoride (HF) gases, respectively.

$$NaCl(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HCl(g)$$

$$NaF(s) + H_2SO_4(l) \rightarrow NaHSO_4(s) + HF(g)$$

(b) *Bromides*: Bromide salts give off bromine and sulphur dioxide gases when they react with conc. H_2SO_4. During the reaction bromide is oxidised to bromine while the H_2SO_4 is reduced to SO_2.

$$KBr(s) + H_2SO_4(l) \rightarrow KHSO_4(s) + HBr(g)$$

$$2HBr(g) + H_2SO_4(l) \rightarrow SO_2(g) + Br_2(g) + 2H_2O(l)$$

(c) *Iodides*: Iodine and H_2S vapours evolve when iodide salts react with conc. H_2SO_4. This is because iodide is a stronger reducing agent compared to bromide so it reduces H_2SO_4 directly to H_2S.

$$KI(s) + H_2SO_4(l) \rightarrow KHSO_4(s) + HI(g)$$

$$8HI(g) + H_2SO_4(l) \rightarrow H_2S(g) + 4I_2(g) + 4H_2O(l)$$

(d) *Sulphites*: Sulphite salts evolve SO_2 upon reacting with conc. H_2SO_4.

$$Na_2SO_3(s) + H_2SO_4(l) \longrightarrow Na_2SO_4(aq) + H_2O(l) + SO_2(g)$$

(e) *Nitrates*: Reaction of concentrated sulphuric acid with nitrate salts gives off NO_2 gas.

$$NaNO_3(s) + H_2SO_4(l) \longrightarrow NaHSO_4(s) + HNO_3(l)$$

$$HNO_3(l) + H_2SO_4(l) \longrightarrow SO_2(g) + NO_2(g) + 3H_2O(l)$$

(f) *Carbonates/bicarbonates*: Carbonate/bicarbonate salts react with conc. H_2SO_4 to give metal sulphate, water and carbon dioxide.

$$Na_2CO_3(s) + H_2SO_4(l) \longrightarrow Na_2SO_4(aq) + H_2O(l) + CO_2(g)$$

$$2NaHCO_3(s) + H_2SO_4(l) \longrightarrow Na_2SO_4(aq) + 2H_2O(l) + 2CO_2(g)$$

(g) *Acetates*: Acetates produce acetic acid vapour upon reaction with conc.

$$CH_3COONa(s) + H_2SO_4(l) \longrightarrow NaHSO_4(s) + CH_3COOH(g)$$

(h) *Oxalates*: Oxalates evolve carbon dioxide and carbon monoxide gases upon the action of conc. H_2SO_4.

$$Na_2C_2O_4(s) + H_2SO_4(l) \longrightarrow Na_2SO_4(aq) + H_2O(l) + CO_2(g) + CO(g)$$

5.2.2 Group separation and confirmatory tests for cations

After doing preliminary tests on a salt or the mixture of salts, experimental procedures have to be performed to confirm the ions present. Tests carried under this case are called *confirmatory tests*. These tests are done in aqueous solutions of salts or on dry samples, and they require specific reagents. This sub-section deals with the anions, and cations separately.

Preparation of solution for confirmatory tests of cations

The important step in this case is to prepare a clear and transparent solution of the salt under investigation. For this purpose, the following solvents are tested one after another in a systematic order until a proper solvent is obtained.

- Distilled water (cold or hot).
- Dilute HCl (cold or hot).
- Conc. HCl (cold or hot).
- Dilute HNO_3.

- Concentrated HNO_3.
- Aqua regia (3 parts concentrated HCl and 1 part concentrated HNO_3).

In case the salt does not dissolve in a particular solvent even on heating, try the next solvent.

Group separation

Cations are divided into six groups depending on solubility of their compounds and their similarities in chemical reactions with certain reagent(s). Each group has a common reagent which is used to precipitate its cations out of the solution. Since some ions of an earlier group may also react with the reagent of a later group, the separation is done sequentially. This avoids ambiguity as to which ions are present in the solution.

Groups in group separation are categorised based on values of solubility product constant (K_{sp}) and colours of precipitates or solutions formed.This classification of groups is different from that of the periodic table. From the knowledge of solubility and solubility products, it is known that most metal chloride salts are soluble in water except chlorides of Ag^+, Pb^{2+}, and Hg_2^{2+}. Thus, the first step in the separation of cations into their respective groups is to add dilute HCl thereby causing Group I cations to precipitate out as AgCl, $PbCl_2$, and/or Hg_2Cl_2. If no precipitate forms, then these cations are not present in significant amounts. The precipitate can be collected by filtration or centrifugation. After the chloride group precipitate is removed, the remaining solution is treated with H_2S gas in an acidic medium of HCl. Under these conditions, only Group II metal ions that form insoluble sulphides (Bi^{3+}, Cd^{2+}, Cu^{2+}, Sb^{3+}, and Sn^{2+}) precipitate as their sulphide salts. Group III cations such as Fe^{2+}/Fe^{3+}, Al^{3+}, and Cr^{3+} are precipitated as hydroxides after addition of ammonia solution followed by solid ammonium chloride to the supernatant from Group II.

Next, the solution containing the remaining cations is treated with hydrogen sulphide or ammonium sulphide in alkaline medium. This treatment removes any remaining cations that form insoluble sulphides in basic media. These are Group IV divalent metal ions which include Co^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+}. Treatments of the Group IV filtrates with CO_3^{2-} salts yield Group V precipitates, which consist of the carbonates of Ca^{2+}, Sr^{2+} and Ba^{2+}. At this point, all the metal ions that form water-insoluble chlorides, sulphides or carbonates have been precipitated out. The only common ions that might remain are Group VI cations which include Na^+, K^+, Mg^{2+}, and NH_4^+. The consecutive precipitation steps are summarised in Figure 5.6.

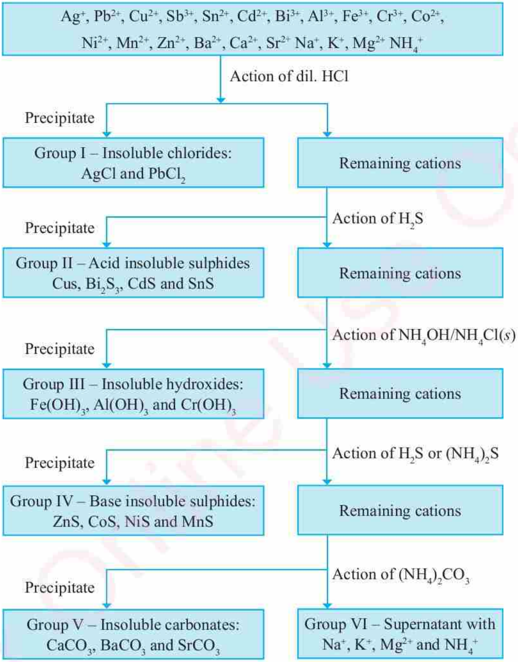


Figure 5.6 Schematic presentation of cation group separation

Group analysis and confirmatory tests for cations

After separation of cations into their respective groups, the presence of each cation in a group has to be verified by other characteristic reactions through cation analysis as shown in Table 5.15.

Table 5.15 Group analysis and confirmatory tests

Group I analysis		
Experiment	**Observation**	**Inference**
Add enough water to cover the precipitate obtained during group I separation, boil and then add ammonia solution.	Precipitate soluble in warm water	Pb^{2+} may be present
	Precipitate insoluble in warm water	Ag^{+} may be present
	Precipitate soluble in ammonia solution	Ag^{+} may be present
	Precipitate insoluble in ammonia solution	Pb^{2+} may be present
Confirmatory tests for Pb^{2+}		
(i) Add K_2CrO_4 to the solution of the sample. $CrO_4^{2-}(aq) + Pb^{2+}(aq) \longrightarrow \underset{\text{Yellow ppt}}{PbCrO_4(s)}$	Yellow precipitate is formed	Pb^{2+} confirmed
(ii) Add KI solution to the solution of the sample. Warm and cool the mixture. $2I^{-}(aq) + Pb^{2+}(aq) \longrightarrow \underset{\text{Yellow ppt}}{PbI_2(s)}$	Yellow precipitate is formed which disappears on warming but re-appears on cooling	Pb^{2+} confirmed
Confirmatory tests for Ag^{+}		
(i) To about 1 mL of the sample solution, add excess dilute HCl. $Ag^{+}(aq) + Cl^{-}(aq) \longrightarrow \underset{\text{White ppt}}{AgCl(s)}$	White precipitate is formed	Ag^{+} confirmed

(ii) To about 1 mL of the sample solution, add K_2CrO_4. $CrO_4^{2-}(aq) + 2Ag^+(aq) \longrightarrow \underset{\text{Brick red ppt}}{Ag_2CrO_4(s)}$	Brick red precipitate is formed.	Ag^+ confirmed.
Group II analysis		
Group two cations can be separated into sub-group IIA and IIB to simplify the confirmatory tests.		
Wash the precipitate obtained in group II separation by adding enough water to cover it, centrifuge and then decant. Add sodium hydroxide followed by few drops of ammonium sulphide.	Precipitate insoluble in ammonium sulphide is formed	Group IIA (Pb^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}) may be present
	Precipitate soluble in ammonium sulphide	Group IIB (Sb^{3+} and Sn^{2+}) may be present
Group IIA analysis		
Cover the precipitate with water and warm, followed by addition of concentrated HNO_3, then do the following tests:		
(i) Filter any precipitate and to the filtrate add dilute H_2SO_4.	White precipitate is formed	Pb^{2+} may be present
(ii) To the filtrate add concentrated ammonia solution.	White precipitate is formed	Bi^{3+} may be present
	Blue solution is formed	Cu^{2+} may be present
(iii) To the filtrate add concentrated ammonia solution followed by H_2S gas.	Colourless solution which forms yellow precipitate on addition of H_2S gas	Cd^{2+} may be present

Confirmatory tests for Bi^{3+}		
(i) Add potassium iodide solution to the solution of the sample. $3I^-(aq) + Bi^{3+}(aq) \longrightarrow \underset{\text{Dark-brown ppt}}{BiI_3(s)}$	Dark-brown precipitate which on dilution forms an orange precipitate	Bi^{3+} confirmed
(ii) Add excess dilute HCl to the solution of the sample. $Bi^{3+} + Cl^-(aq) + H_2O(l) \longrightarrow \underset{\text{White ppt}}{BiOCl(s)} + 2H^+(aq)$ $\underset{\text{White ppt}}{BiOCl(s)} + \underset{\text{Excess}}{2HCl(aq)} \longrightarrow BiCl_3(aq) + H_2O(l)$	White precipitate soluble in excess dilute HCl	Bi^{3+} confirmed
(iii) Add sodium hydroxide drop-wise until in excess to the solution of the sample. $3OH^-(aq) + Bi^{3+}(aq) \longrightarrow \underset{\text{White ppt}}{Bi(OH)_3(s)}$	White precipitate which turns faint yellow on heating	Bi^{3+} confirmed
Confirmatory tests for Cd^{2+}		
(i) Add dilute HCl to the solution of the sample followed by H_2S gas. $S^{2-}(aq) + Cd^{2+}(aq) \longrightarrow \underset{\text{Yellow ppt}}{CdS(s)}$	Yellow precipitate insoluble in ammonium sulphide	Cd^{2+} confirmed
(ii) Add dilute ammonia solution to the solution of the sample. $Cd^{2+}(aq) + 2NH_3(aq) + 2H_2O(l) \longrightarrow \underset{\text{White ppt}}{Cd(OH)_2(s)} + 2NH_4^+(aq)$	White precipitate soluble in excess ammonia solution	Cd^{2+} confirmed

$Cd(OH)_2(s) + 4NH_3(aq) \rightleftharpoons \underset{\text{Light yellow}}{[Cd(NH_3)_4]^{2+}(aq)} + 2OH^-(aq)$		
Confirmatory tests for Cu^{2+}		
(i) Add excess ammonia solution to the solution of the sample. $Cu(NO_3)_2(aq) + 4NH_4OH(aq) \longrightarrow \underset{\text{Deep blue}}{[Cu(NH_3)_4](NO_3)_2(aq)} + 4H_2O(l)$	Blue precipitate soluble in excess ammonia forming a deep blue solution	Cu^{2+} confirmed
(ii) Add potassium hexacyanoferrate(III) solution to the solution of the sample. $2CuSO_4(aq) + K_4[Fe(CN)_6](aq) \longrightarrow \underset{\text{Brown-red ppt}}{Cu_2[Fe(CN)_6](s)} + 2K_2SO_4(aq)$	Brownish-red gelatinous precipitate is formed	Cu^{2+} confirmed
Group IIB analysis		
(i) Acidify the supernatant obtained in the 1st step of group II analysis using dilute HCl.	Precipitate is formed	Sn^{2+} may be present
	No ppt formed	Sb^{3+} may be present
(ii) Dissolve the precipitate obtained in (i) with hot concentrated HCl acid and divide the resulting solution into two portions.	Solution is formed	Sb^{3+}, Sn^{2+} may be present
To the first portion add equal volume of water followed by H_2S gas.	Orange precipitate is formed	Sb^{3+} may be present
To the second portion add a clean iron wire.	White precipitate which may turn grey is formed	Sn^{2+} may be present

Confirmatory tests for Sn^{2+}		
(i) To the solution of the sample, add excess sodium hydroxide solution followed by silver nitrate solution. $2OH^-(aq) + Sn^{2+}(aq) \longrightarrow \underset{\text{White ppt}}{Sn(OH)_2(s)}$ $\underset{\text{White ppt}}{Sn(OH)_2(s)} + 2AgNO_3(aq) \longrightarrow \underset{\text{Black ppt}}{2AgOH(s)} + Sn(NO_3)_2(aq)$	Black precipitate of silver is formed	Sn^{2+} confirmed
(ii) To the solution of the sample add dilute H_2SO_4 followed by ammonium molybdate(VI).	Blue precipitate is formed	Sn^{2+} confirmed
Confirmatory tests for Sb^{3+}		
(i) To the solution of the sample add ammonium sulphide followed by small amount of solid oxalic acid. $3S^{2-}(aq) + 2Sb^{3+}(aq) \longrightarrow \underset{\text{Orange ppt}}{Sb_2S_3(s)}$	Orange precipitate is formed	Sb^{3+} confirmed
(ii) To the solution of the sample add potassium iodide solution. $3I^-(aq) + Sb^{3+}(aq) \longrightarrow \underset{\text{Orange}}{SbI_3(aq)}$	Orange solution is formed	Sb^{3+} confirmed
Group III analysis		
(a) Wash the precipitate obtained in Group III separation with warm water. Add sodium hydroxide followed by H_2O_2 and warm.	Brown precipitate is formed	Fe^{3+} may be present
	Solution is formed	Cr^{3+}, Al^{3+} may be present

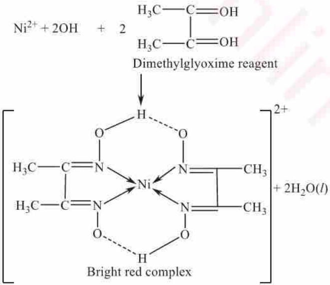
(b) Divide the solution obtained in (a) into two portions. (i) In the first portion, add dilute ethanoic acid and few drops of lead(II) ethanoate.	Yellow precipitate is formed	Cr^{3+} may be present
(ii) Acidify the second portion with dilute HCl followed by one drop of litmus solution. Add ammonia solution to make the resulting solution slightly alkaline.	White precipitate which decolourises litmus dye is formed	Al^{3+} may be present
Confirmatory test for Fe^{2+}		
To the solution of the sample add few drops of potassium hexacyanoferrate(III) (Potassium ferricyanide). $\underset{}{3Fe^{2+}(aq) + 2[Fe(CN)_6]^{3-}(aq)} \longrightarrow \underset{\text{Dark blue}}{Fe_3[Fe(CN)_6]_2(s)}$	Dark blue precipitate is formed	Fe^{2+} confirmed
Confirmatory tests for Fe^{3+}		
(i) Add few drops of potassium hexacyanoferrate(II) (Potassium ferrocyanide) into the solution of the sample. $4Fe^{3+}(aq) + 3[Fe(CN)_6]^{4-}(aq) \longrightarrow \underset{\text{Dark blue}}{Fe_4[Fe(CN)_6]_3(aq)}$	Dark blue solution is formed	Fe^{3+} confirmed
(ii) To the solution of the sample add few drops of potassium or ammonium thiocyanate solution. $Fe^{3+}(aq) + SCN^-(aq) \longrightarrow \underset{\text{Deep red}}{[Fe(SCN)]^{2+}(aq)}$	Deep red colouration is formed	Fe^{3+} confirmed

Confirmatory test for Al^{3+}		
Acidify the solution with dilute HCl acid and add few drops of litmus solution followed by ammonia solution. $AlCl_3(aq) + 3NH_4OH(aq) \xrightarrow{\text{Litmus solution}} 3NH_4Cl(aq) + \underset{\text{Blue colour adsorbs on this ppt}}{Al(OH)_3(s)}$	Blue lake precipitate is formed	Al^{3+} confirmed
Confirmatory Tests for Cr^{3+}		
(i) To the solution of the sample add excess dilute NaOH until all grey precipitate dissolves, and then add dilute H_2O_2 solution followed by dilute H_2SO_4. Shake gently. $Cr^{3+}(aq) + 3OH^-(aq) \longrightarrow \underset{\text{Greyish green ppt}}{Cr(OH)_3(s)}$ $2Cr(OH)_3(s) + 4NaOH(aq) + 3H_2O_2(aq) \longrightarrow \underset{\text{Yellow}}{2Na_2CrO_4(aq)} + 8H_2O(l)$ $Na_2CrO_4(aq) + H_2SO_4(aq) + 2H_2O_2(aq) \longrightarrow Na_2SO_4(aq) + \underset{\text{Blue}}{CrO(O_2)_2.2H_2O(aq)} + 2H_2O(l)$	Blue solution is formed	Cr^{3+} confirmed
(ii) To the solution of the sample add excess dilute NaOH followed by dilute H_2O_2 solution. $Cr_2(SO_4)_3(aq) + 10NaOH(aq) + 3H_2O_2(aq) \longrightarrow \underset{\text{Yellow}}{2Na_2CrO_4(aq)} + 3Na_2SO_4(aq) + 8H_2O(l)$	Yellow solution is formed	Cr^{3+} confirmed
(iii) To the solution obtained in (ii) add dilute acetic acid followed by few drops of lead acetate. $Na_2CrO_4(aq) + (CH_3COO)_2Pb(aq) \longrightarrow \underset{\text{Yellow ppt}}{PbCrO_4(s)} + 2CH_3COONa(aq)$	Yellow precipitate is formed	Cr^{3+} confirmed

Group IV analysis		
(i) Wash the precipitate obtained in group IV separation by adding enough water to cover it, warm, centrifuge and decant. Then, add water to the precipitate followed by dilute HCl.	Solution is formed	Mn^{2+}, Zn^{2+} may be present
	Black residue is formed	Ni^{2+}, Co^{2+} may be present
(ii) To the solution in (i) add excess NaOH solution.	White precipitate, which turns brown on exposure to air	Mn^{2+} may be present
	White precipitate soluble in excess NaOH solution	Zn^{2+} may be present
(iii) To the residue in (i) add concentrated HCl followed by crystals of $KClO_3$. Heat until all crystals have dissolved, then evaporate to nearly dryness.	Green-yellow solution depositing yellow crystals	Ni^{2+} may be present
	Pink solution depositing blue crystals	Co^{2+} may be present

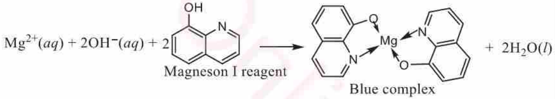
Confirmatory Tests for Mn^{2+}		
(i) To the solution of the sample, add dilute NaOH solution. $Mn^{2+}(aq) + 2OH^-(aq) \rightarrow \underset{\text{White ppt}}{Mn(OH)_2(s)}$	White precipitate which darkens on exposure to air is formed	Mn^{2+} confirmed
(ii) To the solution of the sample add sodium bismuthate(V) solution followed by concentrated HNO_3 drop-wise. $2Mn^{2+}(aq) + 5BiO_3^-(aq) + 4H^+(l) \rightarrow \underset{\text{Purple}}{2MnO_4^-(aq)} + 5BiO^+(aq) + 2H_2O(l)$	Purple solution is formed	Mn^{2+} confirmed
(iii) Boil the solution of the sample. Add solid lead dioxide and concentrated HNO_3. $2Mn^{2+}(aq) + 5PbO_2(s) + 4H^+(l) \rightarrow \underset{\text{Purple}}{2MnO_4^-(aq)} + 5Pb^{2+}(aq) + 2H_2O(l)$	Purple solution is formed	Mn^{2+} confirmed
Confirmatory tests for Zn^{2+}		
(i) To the solution of the sample add potassium hexacyanoferrate(II) solution. $2Zn^{2+}(aq) + [Fe(CN)_6]^{4-}(aq) \rightarrow \underset{\text{White ppt}}{Zn_2[Fe(CN)_6](s)}$	White precipitate is formed	Zn^{2+} confirmed
(ii) To the solution of the sample add dilute NaOH solution until in excess. $Zn^{2+}(aq) + 2OH^-(aq) \rightarrow \underset{\text{White ppt}}{Zn(OH)_2(s)}$	White precipitate soluble in excess	Zn^{2+} confirmed

$Zn(OH)_2(s) + 2OH^-(aq) \longrightarrow [Zn(OH)_4]^{2-}(aq)$ White ppt Excess		
Confirmatory tests for Co^{2+}		
(i) To the neutral or acidic solution of the sample add ammonium thiocyanate. $Co^{2+}(aq) + 2OH^-(aq) \longrightarrow Co(OH)_2(s)$ Blue ppt	Blue solution is formed	Co^{2+} confirmed
(ii) To the solution of the sample add NaOH, warm and then add ammonia solution. $Co^{2+}(aq) + 2OH^-(aq) \longrightarrow Co(OH)_2(s)$ Blue ppt $Co(OH)_2(s) + 6NH_3(aq) \longrightarrow [Co(NH_3)_6]^{2+}(aq) + 2OH^-(aq)$ Blue ppt	Blue precipitate which turns pink upon warming. The precipitate is soluble in ammonia solution	Co^{2+} confirmed
(iii) To the neutral solution of the sample add concentrated KNO_2 solution. $Co^{2+}(aq) + 6NO_2^-(l) \longrightarrow [Co(NO_2)_6]^{3+}(s)$ Yellow ppt	Yellow precipitate is formed	Co^{2+} confirmed
Confirmatory Tests for Ni^{2+}		
(i) To the solution of the sample add sodium hydroxide solution followed by ammonia solution. $Ni^{2+}(aq) + 2OH^-(aq) \longrightarrow Ni(OH)_2(s)$ Green ppt	Green precipitate is formed which dissolves in ammonia solution	Ni^{2+} confirmed

$Ni(OH)_2(s) + 6NH_3(aq) \longrightarrow [Ni(NH_3)_6]^{2+}(aq) + 2OH^-(aq)$ Green ppt Blue	to give a deep blue solution	
(ii) To the solution of the sample, add dilute ammonia solution until just alkaline, followed by dimethylglyoxime reagent.  Bright red complex	Red precipitate is formed	Ni^{2+} confirmed
(iii) To the solution of the sample add ammonia solution until in excess. $Ni^{2+}(aq) + 6NH_3(aq) \longrightarrow [Ni(NH_3)_6]^{2+}(aq)$ Excess Blue	Green precipitate, which dissolves in excess ammonia solution forming a blue solution	Ni^{2+} confirmed

Group V analysis		
Wash the precipitate obtained in Group V separation with hot water. Dissolve the precipitate in small amount of ethanoic acid.		
(i) To the prepared sample solution add potassium chromate(VI) solution. Leave it to stand for few minutes.	Yellow precipitate is formed	Ba^{2+} may be present
(ii) To the prepared sample solution, add saturated $CaSO_4$ solution. Leave it to stand for few minutes.	White precipitate is formed	Sr^{2+} may be present
(iii) To the prepared sample solution, add dilute H_2SO_4 until in excess, centrifuge and discard any residue. To the supernatant add dilute ammonia solution to neutralise excess acid followed by ammonium oxalate.	White precipitate is formed	Ca^{2+} may be present
Confirmatory Tests for Ba^{2+}		
(i) To the solution of the sample add potassium chromate(VI) solution. $CrO_4^{2}\ (aq) + Ba^{2+}(aq) \longrightarrow \underset{\text{Yellow ppt}}{BaCrO_4(s)}$	Yellow precipitate is formed	Ba^{2+} confirmed
(ii) To the solution of the sample add dilute NaOH solution followed by ammonium oxalate solution and ethanoic acid. $C_2O_4^{2-}(aq) + Ba^{2+}(aq) \longrightarrow \underset{\text{White ppt}}{BaC_2O_4(s)}$ $2CH_3COOH(aq) + \underset{\text{White ppt}}{BaC_2O_4(s)} \longrightarrow (CH_3COO)_2Ba(aq) + H_2C_2O_4(l)$	White precipitate soluble in ethanoic acid is formed	Ba^{2+} confirmed

(iii) Perform flame test.	Green flame	Ba^{2+} confirmed
Confirmatory Tests for Sr^{2+}		
(i) To the solution of the sample add calcium sulphate solution or dilute H_2SO_4 acid. $SO_4^{2}(aq) + Sr^{2+}(aq) \longrightarrow \underset{\text{White ppt}}{SrSO_4(s)}$	White precipitate is formed	Sr^{2+} confirmed
(ii) Perform flame test.	Red flame	Sr^{2+} confirmed
Confirmatory Tests for Ca^{2+}		
(i) To the solution of the sample add excess ammonia solution followed by ammonium oxalate. $C_2O_4^{2}(aq) + Ca^{2+}(aq) \longrightarrow \underset{\text{White ppt}}{CaC_2O_4(s)}$	White precipitate is formed	Ca^{2+} confirmed
(ii) Perform flame test.	Brick red flame	Ca^{2+} confirmed
Group VI analysis		
To the solution of the sample from group VI separation, add aqueous ammonium oxalate, then filter and discard any precipitate.		
Confirmatory Tests for Mg^{2+}		
(i) To the prepared sample solution, add dilute ammonia solution, solid ammonium chloride and disodium hydrogen phosphate. $MgCl_2(aq) + NH_3(aq) + Na_2HPO_4(aq) \longrightarrow \underset{\text{White ppt}}{Mg(NH_4)PO_4(s)} + 2NaCl(aq)$	White precipitate is formed	Mg^{2+} confirmed

(ii) To the prepared sample solution add 2-3 drops of magneson I reagent followed by excess NaOH solution drop-wise.  	Sky-blue precipitate is formed	Mg^{2+} confirmed
Confirmatory Tests for K^+ and Na^+		
Evaporate the supernatant to dryness and use the residue formed to perform flame test.	Lilac/light purple flame	K^+ confirmed
	Yellow flame	Na^+ confirmed
Confirmatory Test for NH_4^+		
To a small amount of a solid sample add dilute NaOH and warm. Pass wet litmus paper to the mouth of the test tube containing the mixture. Dip a glass rod in concentrated HCl and pass it to the mouth of a test tube containing the mixture. $NH_4^+(aq) + OH^-(aq) \longrightarrow NH_3(g) + H_2O(l)$	Colourless gas evolves, which turns wet red litmus paper blue and forms white fumes with concentrated HCl	NH_4^+ confirmed

Example 5.1

You are provided with sample R containing a mixture of two salts with two different cations and common anion. Carry out a systematic qualitative analysis recording your observations and deductions to identify the ions present in the salts.

Solution

The solution for this task is as per Tables 5.16, 5.17 and 5.18

Table 5.16 Systematic analysis for a sample

S/N	Experiment performed	Observation	Inference
1.	**Appearance of the sample** (i) Colour	White	Absence of transition metals
	(ii) Texture	Crystalline	NO_3^-, SO_4^{2-}, Cl^-, $C_2O_4^{2-}$, CrO_4^{2-}, NO_2^-, CH_3COO^- and $Cr_2O_7^{2-}$ or hydrated salts may be present
	(ii) Deliquescence	Absorbed water to form a solution	NO_2^-, SO_4^{2-} and Cl^- may be present
2.	**Flame test** A small amount of the sample on a base of the test tube wetted with conc. HCl was heated on a non-luminous flame.	Brick red (orange) flame observed	Ca^{2+} may be present
3.	**Solubility of the solid sample** To the small amount of the sample in clean test tube distilled water was added to dissolve it.	Soluble in cold distilled water	NO_3^-, CH_3COO^- or HCO_3^- may be present SO_4^{2-} may be present except those of Ba^{2+}, Sr^{2+}, Ca^{2+} and Pb^{2+} Cl^- may be present except those of Ag^+ and Pb^{2+} CO_3^{2-} and $C_2O_4^{2-}$ of Na^+, K^+, NH_4^+ may be present

4.	**Action of heat on a solid sample** About 0.5 g of a sample in a clean and dry test tube was heated.	No colourless droplets formed on the cooler part of the test tube	Absence of hydrated salts
		Brown fumes evolved which turned wet blue litmus paper red and a gas which re-lighted a glowing wooden splint	NO_3^- may be present except those of Na^+ and K^+
5.	**Action of dilute HCl or H_2SO_4 on a solid sample** A pinch of the salt in a clean dry test tube was treated with dil. H_2SO_4.	No gas evolved	SO_4^{2-}, Cl^-, NO_3^- or CH_3COO^- may be present
6.	**Action of concentrated H_2SO_4 on a solid sample** A pinch of the salt in a clean dry test tube was treated with concentrated H_2SO_4.	Brown fumes evolved, which turned wet blue litmus paper red and intensified on addition of copper turnings	NO_3^- may be present
Confirmatory test for NO_3^-			
	About 1 mL of the sample solution was transferred into the test tube. Then a freshly prepared $FeSO_4$ solution was added followed by concentrated H_2SO_4.	Brown ring formed at the junction of the liquids	NO_3^- confirmed

Table 5.17 Cation group separation

Experiment	Observation	Inference
Group I		
Dilute HCl was added to the sample solution.	No precipitate formed	Group I cations are absent
Group II		
Hydrogen sulphide gas was passed through the solution in the presence of dil. HCl.	No precipitate formed	Group II cations are absent
Group III		
Few drops of concentrated HNO_3 were added to the sample solution, warmed, and then cooled. Then solid NH_4Cl was added to the solution followed by ammonia solution.	White precipitate formed	Al^{3+} may be present
Group IV		
The filtrate from Group III was warmed and then cooled and hydrogen sulphide gas was passed through it for few minutes.	No precipitate formed	Group IV cations are absent
Group V		
The solution from Group IV was warmed and $(NH_4)_2CO_3$ solution was added.	White precipitate formed	Ba^{2+}, Ca^{2+} and Sr^{2+} may be present

Table 5.18 Cation group analysis

Group III analysis		
Experiment	**Observation**	**Inference**
The precipitate obtained in Group III separation was washed with warm water, followed by addition of sodium hydroxide and H_2O_2 solutions.	No brown precipitate formed	Fe^{3+} absent
	Solution formed	Cr^{3+} and Al^{3+} may be present
The solution obtained above was divided into two portions. (i) Into the first portion, dilute ethanoic acid and few drops of lead(II) ethanoate were added.	No yellow precipitate formed	Cr^{3+} is absent
(ii) The second solution was acidified with dilute HCl followed by one drop of litmus solution and then ammonia solution was added to make the solution slightly alkaline.	White precipitate which decolourised the litmus dye formed	Al^{3+} may be present
Confirmatory test for Al^{3+}		
The solution was acidified with dilute HCl followed by one drop of litmus solution and then ammonia solution was added.	Blue lake precipitate formed	Al^{3+} confirmed
Group V analysis		
(i) To the prepared sample solution, potassium chromate(VI) solution was added and left to stand for few minutes.	No yellow precipitate formed	Ba^{2+} absent
(ii) To the prepared sample solution, saturated $CaSO_4$ solution was added.	No white precipitate formed	Sr^{2+} absent
(iii) To the prepared sample solution, excess dilute H_2SO_4 was added and the residue was discarded. To the filtrate excess dilute ammonia solution was added followed by ammonium oxalate.	White precipitate formed	Ca^{2+} may be present
Confirmatory Test for Ca^{2+}		
To the solution of the sample excess ammonia solution was added followed by ammonium oxalate.	White precipitate formed	Ca^{2+} confirmed

Conclusion: The anion present is NO_3^-

The cations present are Al^{3+} and Ca^{2+}

Therefore, the unknown salts are $Al(NO_3)_3$ and $Ca(NO_3)_2$

5.2.3 Confirmatory tests for anions

Preparations of the aqueous solution for analysis of anions

The anions of the salts are made soluble in water by converting them into sodium salts using sodium carbonate, that is, while the anions are solubilised, the cations are precipitated as carbonates. In a clean 100 mL beaker, mix about 1 g of the sample with about 2.00 g of solid sodium carbonate. Add 50 mL of distilled water to the mixture. Boil the content in the beaker for few minutes. Filter or centrifuge the mixture to remove the precipitate formed. The supernatant/ extract obtained contains sodium salts of the anions and is used for their analysis by following the procedures shown in Table 5.19.

Table 5. 19 Confirmatory test for anions

S/N	Experiment to be done	Observation	Inference
1.	**Confirmatory tests for SO_4^{2-}**		
	(i) Transfer about 1 mL of the extract prepared above into the test-tube. Add barium chloride solution followed by dilute HCl or barium nitrate solution followed by dilute HNO_3. $Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow \underset{\text{White ppt}}{BaSO_4(s)}$	White precipitate is formed	SO_4^{2-} confirmed
	(ii) Transfer about 1 mL of the extract into the test-tube. Add ethanoic acid followed by lead ethanoate. Divide the resulting mixture into two portions. In one portion add dilute HCl and in another add ammonium ethanoate solution. $Pb^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow \underset{\text{White ppt}}{PbSO_4(s)}$ $\underset{\text{White ppt}}{PbSO_4(s)} + 2CH_3COO^-(aq) \longrightarrow (CH_3COO)_2Pb(aq) + SO_4^{2-}(aq)$	White precipitate insoluble in dilute HCl but soluble in the solution of ammonium ethanoate formed	SO_4^{2-} confirmed
2.	**Confirmatory test for Cl^-, Br^- and I^-**		
	(i) To 1 mL of the solution add $AgNO_3$ slowly followed by dilute HNO_3. $Ag^+(aq) + Cl^-(aq) \longrightarrow \underset{\text{White ppt}}{AgCl(s)}$	White precipitate soluble in ammonia solution is formed	Cl^- confirmed

	$Ag^+(aq) + Br^-(aq) \longrightarrow \underset{\text{Cream ppt}}{AgBr(s)}$	Cream colour ppt, sparingly soluble in NH_3 solution	Br^- confirmed
	$Ag^+(aq) + I^-(aq) \longrightarrow \underset{\text{Yellow ppt}}{AgI(s)}$	Yellow ppt insoluble in NH_3 solution	I^- confirmed
	(ii) Transfer about 0.5 g of the original solid sample into the test-tube. Add potassium dichromate solution followed by a few drops of concentrated H_2SO_4. $Cr_2O_7^{2-}(aq) + 6Cl^-(aq) + 14H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 3Cl_2(g) + 7H_2O(l)$	Red orange vapour is observed	Cl^- confirmed
	(iii) Transfer about 0.5 g of the original solid sample into the test tube. Add equal amount of solid MnO_2 followed by few drops of concentrated H_2SO_4. $MnO_2(s) + 2Cl^-(aq) + 4H^+(aq) \longrightarrow Mn^{2+}(aq) + Cl_2(g) + 2H_2O(l)$	Greenish yellow gas evolves, which bleaches moist red litmus paper	Cl^- confirmed
3.	**Confirmatory tests for NO_2^-** (i) Transfer about 1 mL of the extract into the test tube. Add dilute H_2SO_4 followed by freshly prepared $FeSO_4$ solution. $2KNO_2(aq) + H_2SO_4(aq) \longrightarrow K_2SO_4(aq) + 2HNO_2(aq)$ $3HNO_2(aq) \longrightarrow HNO_3(aq) + 2NO(g) + H_2O(l)$ $\underset{\text{Colourless}}{NO(g)} + FeSO_4(aq) \longrightarrow \underset{\text{Brown solution}}{FeSO_4.NO(aq)}$	Brown solution is formed	NO_2^- confirmed

	(ii) Transfer about 1 mL of the extract into the test tube. Add dilute H_2SO_4 followed by KI solution then add few drops of starch. $2KI(s) + 2H_2SO_4(aq) + 2KNO_2(aq) \longrightarrow 2K_2SO_4(aq) + I_2(s) + 2NO(g) + 2H_2O(l)$ $I_2(s) + \text{starch} \longrightarrow$ Blue black complex	Dark brown precipitates turn dark blue after addition of starch	NO_2^- confirmed
4.	**Confirmatory tests for NO_3^-** (i) Transfer about 1 mL of the extract into the test tube. Add freshly prepared $FeSO_4$ solution followed by careful addition of concentrated H_2SO_4 along the side of the test tube. $KNO_3(aq) + H_2SO_4(l) \longrightarrow KHSO_4(aq) + HNO_3(aq)$ $6FeSO_4(aq) + 3H_2SO_4(l) + 2HNO_3(aq) \longrightarrow 3Fe_2(SO_4)_3(aq) + 4H_2O(l) + 2NO(g)$ $FeSO_4(aq) + 5H_2O(l) + NO(g) \longrightarrow \underset{\text{Brown ring}}{[Fe(NO)(H_2O)_5]SO_4}$	Brown ring is formed at the junction of the liquids	NO_3^- confirmed
	(ii) Transfer about 0.5 g of the original solid sample into the test tube. Add copper turnings followed by concentrated H_2SO_4 then warm. $KNO_3(s) + H_2SO_4(l) \longrightarrow KHSO_4(s) + HNO_3(l)$ $4HNO_3(l) + Cu(s) \longrightarrow Cu(NO_3)_2(aq) + 2H_2O(l) + 2NO_2(g)$	Brown fumes evolve	NO_3^- confirmed

5.	**Confirmatory tests for $C_2O_4^{2-}$** (i) Transfer about 1 mL of the extract into the test tube. Add about 1 mL of $CaCl_2$ solution drop-wise and warm. Divide the resulting mixture into two portions. In one portion add dilute ethanoic acid. In another portion add dilute HCl or dilute HNO_3. $(NH_4)_2C_2O_4(aq) + CaCl_2(aq) \rightarrow \underset{\text{White ppt}}{CaC_2O_4(s)} + 2NH_4Cl(aq)$ $\underset{\text{White ppt}}{CaC_2O_4(s)} + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + H_2C_2O_4(aq)$	White precipitate, insoluble in dilute ethanoic acid but soluble in dilute HCl acid or HNO_3 acid forms	$C_2O_4^{2-}$ confirmed
	(ii) Transfer about 1 mL of the extract into the test tube. Add dilute H_2SO_4 followed by one drop of potassium permanganate solution and warm. $(Na)_2C_2O_4(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + H_2C_2O_4(aq)$ $\underset{\text{Purple}}{2KMnO_4(aq)} + 5H_2C_2O_4(aq) + 3H_2SO_4(aq) \rightarrow$ $\underset{\text{Colourless}}{2MnSO_4(aq)} + K_2SO_4(aq) + 10CO_2(g) + 8H_2O(l)$	Solution colour disappears	$C_2O_4^{2-}$ confirmed
	(iii) Transfer about 1 mL of the extract into the test tube. Add $AgNO_3$ solution. If precipitate is formed, add dilute ammonia solution. $(Na)_2C_2O_4(aq) + AgNO_3(aq) \rightarrow 2NaNO_3(aq) + \underset{\text{White ppt}}{Ag_2C_2O_4(s)}$ $\underset{\text{White ppt}}{Ag_2C_2O_4(s)} + 4NH_3(aq) \rightarrow 2[Ag(NH_3)_2]^+(aq) + C_2O_4^{2-}(aq)$	White precipitate, soluble in dilute ammonia solution is formed	$C_2O_4^{2-}$ confirmed

	(iv) Transfer about 1 mL of the extract into the test-tube. Add concentrated H_2SO_4. $Na_2C_2O_4(aq) + H_2SO_4(l) \longrightarrow Na_2SO_4(aq) + CO_2(g) + CO(g) + H_2O(l)$	Colourless gas which turns lime water milky and burns with a blue flame evolves	$C_2O_4^{2-}$ confirmed
	(v) Transfer about 1 mL of the extract into the test-tube. Add $BaCl_2$ or $Ba(NO_3)_2$ solution. If precipitate is formed, add dilute ammonium chloride or dilute HCl. $Na_2C_2O_4(aq) + BaCl_2(aq) \longrightarrow \underset{\text{White ppt}}{BaC_2O_4(s)} + 2NaCl(aq)$ $\underset{\text{White ppt}}{BaC_2O_4(s)} + 2HCl(aq) \longrightarrow BaCl_2(aq) + H_2C_2O_4(aq)$	White precipitate soluble in dilute ammonium chloride or dilute HCl is formed	$C_2O_4^{2-}$ confirmed
6.	**Confirmatory tests for CrO_4^{2-}** Transfer about 1 mL of the extract into the test tube. Add dilute HNO_3 followed by ammonia solution until the solution becomes neutral then boil. (i) To the neutral solution, add $BaCl_2$ solution followed by dilute HCl. $Na_2CrO_4(aq) + BaCl_2(aq) \longrightarrow \underset{\text{Yellow ppt}}{BaCrO_4(s)} + 2NaCl(aq)$ $\underset{\text{Yellow ppt}}{BaCrO_4(s)} + 2HCl(aq) \longrightarrow BaCl_2(aq) + H_2CrO_4(aq)$	Yellow precipitate soluble in dilute HCl	CrO_4^{2-} confirmed
	(ii) To the neutral solution, add $Pb(CH_3COO)_2$ or $Pb(NO_3)_2$ solution. $Na_2CrO_4(aq) + Pb(NO_3)_2(aq) \longrightarrow \underset{\text{Yellow ppt}}{PbCrO_4(s)} + 2NaNO_3(aq)$	Yellow precipitate is formed	CrO_4^{2-} confirmed

	(iii) To the original 1 mL of the extract add dilute sulphuric acid. $\underset{\text{Yellow}}{2K_2CrO_4(aq)} + H_2SO_4(aq) \rightarrow \underset{\text{Orange}}{K_2Cr_2O_7(aq)} + K_2SO_4(aq) + H_2O(l)$	The yellow solution turns orange	CrO_4^{2-} confirmed
7.	**Confirmatory test for $Cr_2O_7^{2-}$** Transfer about 1 mL of the extract into the test tube. Add few drops of dilute NaOH solution. $\underset{\text{Orange}}{K_2Cr_2O_7(aq)} + 2NaOH(aq) \rightarrow \underset{\text{Yellow}}{Na_2CrO_4(aq)} + \underset{\text{Yellow}}{K_2CrO_4(aq)} + H_2O(l)$	The solution changes from orange to yellow	$Cr_2O_7^{2-}$ confirmed
8.	**Confirmatory tests for CO_3^{2-} and HCO_3^-** (i) Transfer about 1 mL of the original sample solution into a test tube. Add few drops of $MgSO_4$ solution. If no precipitate is formed, warm the contents. $Na_2CO_3(aq) + MgSO_4(aq) \rightarrow Na_2SO_4(aq) + \underset{\text{White ppt}}{MgCO_3(s)}$ $NaHCO_3(aq) + MgSO_4(aq) \rightarrow Na_2SO_4(aq) + Mg(HCO_3)_2(aq)$ $Mg(HCO_3)_2(aq) \xrightarrow{\text{heat}} MgCO_3(s) + H_2O(l) + CO_2(g)$	White precipitate is formed before warming	CO_3^{2-} confirmed
		White precipitate is formed after warming	HCO_3^- confirmed
	(ii) Transfer about 1 mL of the solution of the original sample into a test tube. Add few drops of $CaCl_2$ solution. If no precipitate is formed warm the contents. $Na_2CO_3(aq) + CaCl_2(aq) \rightarrow 2NaCl(aq) + \underset{\text{White ppt}}{CaCO_3(s)}$	White precipitate is formed before warming	CO_3^{2-} confirmed

	$2NaHCO_3(aq) + CaCl_2(aq) \rightarrow 2NaCl(aq) + Ca(HCO_3)_2(aq)$ $Ca(HCO_3)_2(aq) \xrightarrow{heat} CaCO_3(s) + H_2O(l) + CO_2(g)$	White precipitate is formed after warming	HCO_3^- confirmed
	(iii) Transfer about 1 mL of the solution of the original sample into a test-tube. Add $BaCl_2$ solution. If the precipitate forms, add dilute HCl. $Na_2CO_3(aq) + BaCl_2(aq) \rightarrow \underset{\text{White ppt}}{BaCO_3(s)} + 2NaCl(aq)$ $\underset{\text{White ppt}}{BaCO_3(s)} + 2HCl(l) \rightarrow BaCl_2(aq) + H_2O(l) + CO_2(g)$	White precipitate soluble in dilute HCl is formed	CO_3^{2-} confirmed
9.	**Confirmatory Tests for CH_3COO^-** Transfer about 1 mL of the extract into the test tube. Add dilute HNO_3 followed by ammonia solution until the solution becomes neutral then boil. (i) To the neutral solution, add $FeCl_3$ solution. $3CH_3COONa\ (aq) + FeCl_3(aq) \rightarrow 3NaCl(aq) + \underset{\text{Deep red}}{(CH_3COO)_3Fe(aq)}$	Deep red colour is observed	CH_3COO^- confirmed
	(ii) To the neutral solution, add concentrated H_2SO_4 followed by ethanol solution. $CH_3COONa\ (aq) + H_2SO_4(l) \rightarrow NaHSO_4(aq) + CH_3COOH(aq)$ $CH_3COOH(aq) + C_2H_5OH(aq) \rightarrow \underset{\text{Fruity smell}}{CH_3COOC_2H_5(aq)} + H_2O(l)$	Fruity scent is felt	CH_3COO^- confirmed

10.	**Confirmatory tests for $HCOO^-$** (i) To the neutral solution as in 9 above add $FeCl_3$ $3HCOONa\,(aq) + FeCl_3(aq) \longrightarrow 3NaCl(aq) + \underset{\text{Red}}{(HCOO)_3Fe(aq)}$	Red colouration	$HCOO^-$ confirmed
	(ii) To a sample solution add $AgNO_3$ solution $HCOONa\,(aq) + AgNO_3(aq) \longrightarrow NaNO_3(aq) + \underset{\text{White ppt}}{HCOOAg(s)}$ $\underset{\text{White ppt}}{2HCOOAg(s)} \xrightarrow{\text{heat}} \underset{\text{Black}}{Ag_2O(s)} + 2CO(g) + H_2O(l)$	White ppt turning black on warming	$HCOO^-$ confirmed
11.	**Confirmatory tests for SO_3^{2-}** (i) To the sample solution add $BaCl_2$ followed by dilute HCl solution. $Na_2SO_3(aq) + BaCl_2(aq) \longrightarrow 2NaCl(aq) + \underset{\text{White ppt}}{BaSO_3(s)}$ $\underset{\text{White ppt}}{BaSO_3(s)} + 2HCl(aq) \longrightarrow BaCl_2(aq) + SO_2(g) + H_2O(l)$	White ppt soluble in dilute HCl	SO_3^{2-} confirmed
	(ii) To the sample solution add few drops of potassium manganate(VII) and immediately add dil. H_2SO_4. $\underset{\text{Purple}}{2KMnO_4(aq)} + 5Na_2SO_3(aq) + 3H_2SO_4(aq) \longrightarrow$ $K_2SO_4(aq) + \underset{\text{Colourless}}{2MnSO_4(aq)} + 5Na_2SO_4(aq) + 3H_2O(l)$	Solution decolourised	SO_3^{2-} confirmed

5.2.4 Guided qualitative analysis

For guided qualitative analysis the following tests (Table 5.20) can be done in the solution of the sample to identify the cations present.

Table 5.20 Action of excess NaOH and NH_4OH solutions on the sample solution

S/N	Experiment	Expected observation	Inference
1.	**Action of NaOH solution** To a sample solution add NaOH solution drop-wise, slowly until in excess.	White ppt insoluble in excess NaOH, which turns yellow on heating	Bi^{3+} may be present
		White ppt, which rapidly turns brown and insoluble in excess NaOH	Mn^{2+} may be present
		White ppt insoluble in excess NaOH	Mg^{2+}, Ca^{2+}, Ba^{2+} or Cd^{2+} may be present
		Light-blue ppt, which is insoluble in excess NaOH and turns pink on heating	Co^{2+} may be present
		Pale-blue ppt, which is insoluble in excess NaOH and turns black on heating	Cu^{2+} may be present
		Light-green ppt, which is insoluble in excess NaOH and unaffected by heat	Ni^{2+} may be present
		Redish-brown ppt, which is insoluble in excess NaOH	Fe^{3+} may be present
		Brown ppt, which is insoluble in excess NaOH	Ag^{+} may be present
		Grey-green ppt, which dissolves in excess NaOH to give a green solution	Cr^{3+} may be present
		Dirty-green ppt, which is insoluble in excess NaOH and turns brown when exposed to air	Fe^{2+} may be present

S/N	Experiment	Expected observation	Inference
		White ppt, which is soluble in excess NaOH	Zn^{2+}, Al^{3+}, Pb^{2+} or Sn^{2+} may be present
		No ppt formed and no gas evolved	Na^+ and K^+ may be present
		On warming, a gas is evolved which turns red litmus paper blue	NH_4^+ may be present
2.	**Action of NH_3 solution** To a sample solution add NH_3 solution slowly until in excess.	White ppt, which is soluble in excess NH_3 solution	Ca^{2+}, Zn^{2+}, Cd^{2+}, Sr^{2+}, Ba^{2+} may be present
		No ppt formed	K^+, Na^+ may be present
		White ppt, which is insoluble in excess NH_3 solution	Mg^{2+}, Al^{3+} or Pb^{2+} may be present
		Dark brown ppt, which is insoluble in excess NH_3 solution	Ag^+ may be present
		Dirty-green ppt, which is insoluble in excess NH_3 solution	Fe^{2+} may be present
		Reddish-brown ppt, which is insoluble in excess NH_3 solution	Fe^{3+} may be present
		Pale-blue ppt, which turns black on heating and soluble in excess NH_3 solution	Cu^{2+} may be present
		White ppt, which turns brown on exposure to air and insoluble in excess NH_3 solution	Mn^{2+} may be present
		Grey-green/ blue precipitate, which turns pink on heating and insoluble in excess NH_3 solution	Cr^{3+} may be present
		Pale-green precipitate, which dissolves in excess NH_3 solution to give a green solution	Ni^{2+} may be present

5.3 Chemical analysis related to physical chemistry

Physical-chemical analysis focuses on the application of physical methods in chemical analysis. In this sub-section, experimental determinations of the order of reaction, activation energy, heats of reaction and establishment of the distribution of a substance between two phases of immiscible liquids using the partition law are discussed.

5.3.1 Determination of the order of reaction

In *chemical kinetics*, a number of methods employed in the determination of rate laws are discussed. In this section, the knowledge gained from chemical kinetics is experimentally used to determine the order of reactions and the rate constants as exemplified by Activities 5.8 and 5.9.

Activity 5.8

Determination of order of reaction for the reaction between $Na_2S_2O_3$, KI and H_2O_2 using a graphical method

Hydrogen peroxide reacts with iodide ions in acidic medium to form iodine. The iodine produced then reacts with thiosulphate ions as indicated in the following reactions:

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \longrightarrow I_2(aq) + 2H_2O(aq)$$

$$2S_2O_3^{2-}(aq) + 2I^-(aq) \longrightarrow S_4O_6^{2-}(aq) + I^-(aq)$$

The initial rate of oxidation of iodide ions by hydrogen peroxide in acidic solution is found by measuring the time taken to liberate sufficient iodine to react with the thiosulphate ions present and then produce a blue colour with starch solution. The rate law for the reaction can be written as rate = $k[H_2O_2]^a [H^+]^b [I^-]^c$. By varying the concentration of each reactant independently, the orders a, b and c of the reaction can be determined.

Requirements: Beakers, pipettes, burettes, conical flasks, stop watch, A 0.10 M hydrogen peroxide, 0.25 M H_2SO_4, 0.05 M sodium thiosulphate, 0.30 M KI, starch solution, and distilled water.

Procedure

1. Measure 10 mL of H2O2 solution, 25 mL of H2SO4 solution, and 5 mL of Na2S2O3 solution into a 100 mL beaker.

2. Add approximately 1 mL of starch solution.
3. Pipette 5 mL of KI solution into another beaker and add 20 mL of distilled water. Label this mixture A.
4. Add mixture A to the first beaker and start a stop watch/clock. Swirl the content to mix thoroughly. Tabulate the time taken for the blue colour to appear.
5. Repeat the steps (1) to (4), but this time using mixture A with the composition as indicated in the table below:

	Composition	
	KI, mL	**Water, mL**
Mixture A	10	15
	15	10
	20	5
	25	0

Questions

1. Plot a graph of log(1/t) against log (volume) of KI.
2. Calculate the gradient of the graph and interpret the information obtained.
3. Determine the order of reaction with respect to KI.

Activity 5.9

Determination of the order of reaction for the reaction between $Na_2S_2O_3$ and HCl by isolation method

The purpose of this activity is to investigate the effect of the concentration of sodium thiosulphate on the rate of reaction when it reacts with hydrochloric acid. Sodium thiosulphate reacts with dilute acid to produce sulphur dioxide, sulphur and water. Sulphur dioxide is a soluble gas that dissolves completely in aqueous solution. The sulphur formed however, is insoluble and exists in the mixture as a pale yellow precipitate that gives a milky appearance and makes the solution opaque. Therefore, the rate of the reaction can be studied by monitoring the opaqueness of the reaction through measuring the time needed for the reaction mixture to become opaque. The results will be mathematically analysed to determine the order of reaction.

$$S_2O_3^{2-}(aq) + 2H^+(aq) \longrightarrow S(s) + SO_2(g) + H_2O(l)$$

$$\text{Rate} = \frac{-d[S_2O_3^{2-}]}{dt} = \frac{d[S]}{dt} = k[S_2O_3^{2-}]^m[H^+]^n \qquad (5.5)$$

where, m is the order of reaction with respect to sodium thiosulphate,

n is the order of reaction with respect to the acid, and

k is the rate constant.

Requirements: Beakers, pipettes, burettes, conical flasks, measuring cylinder, a piece of white paper marked "+" and stop watch, 0.15 M sodium thiosulphate, 0.10 M hydrochloric acid, and distilled water.

Procedure

1. Place a small beaker (100 mL by volume) on top of the "+" mark on the white paper.
2. Measure out 50 mL of sodium thiosulphate using a measuring cylinder into the beaker placed on the marked paper.
3. Using another measuring cylinder, measure out 50 mL of hydrochloric acid. Then, add the measured acid into the beaker containing sodium thiosulphate and immediately start the stop watch.
4. In a tabular form record the time taken for the precipitation to obscure the mark on a piece of white paper marked "+".
5. Repeat the procedure by using other concentrations as shown in the table below:

Exp.	Volume of $Na_2S_2O_3$, mL	Volume of H_2O, mL	Volume of HCl, mL
1.	50	0.00	50.00
2.	40	10.00	50.00
3.	30	20.00	50.00
4.	20	30.00	50.00

Questions

1. Write the ionic equation for the reaction that takes place in this experiment.
2. Given that the volumes of individual solutions are directly proportional to their concentrations, calculate the order of reaction with respect to sodium thiosulphate.
3. If the value of $n = 2$, calculate the value of k.

Determination of activation energy, E_a

Arrhenius equation discussed in chemical kinetics suggests that there is an exponential relationship between the rate constant and temperature.

$$k = Ae^{\frac{-E_a}{RT}} \tag{5.6}$$

where, A = pre-exponential factor,

E_a = activation energy,

R = universal gas constant,

T = temperature, and

k = rate constant.

The logarithmic form of Arrhenius equation, $\ln k = \frac{-E_a}{RT} + \ln A$, is very useful in determining the activation energy from the plot of ln k versus $\frac{1}{T}$. In Activity 5.10 the time taken for the completion of reaction at different temperatures is recorded from which activation energy can be determined.

Activity 5.10

Determination of activation energy of the reaction

In acidic medium oxalic acid is oxidised by $KMnO_4$ and completion of the reaction is indicated by the disappearance of the purple colour of the permanganate ion.

Requirements: Beakers, measuring cylinder, boiling tubes, conical flasks, Bunsen burner, thermometer and stop watch. A solution of 0.02 M $KMnO_4$, solution of 0.05 M oxalic acid in 0.50 M H_2SO_4.

Procedure

1. Put about 250 mL of water into a 300 mL beaker and warm. Use this as.
2. Measure 10 mL of $KMnO_4$ solution and 10 mL of 0.05 M oxalic acid solution in 0.50 M H_2SO_4 and put them into separate boiling tubes.
3. Put a thermometer into a boiling tube containing $KMnO_4$ solution and heat the boiling tube in a water bath, allow the content to warm at 50 ºC.
4. Pour the hot solution of $KMnO_4$ into a boiling tube containing acidified oxalic and immediately start a stop watch. Record the time taken for the purple colour to disappear.

5. Repeat the experiment at 60 ºC, 70 ºC and 80 ºC temperatures.
6. Record your results in a tabular form.

Questions

1. Write the half ionic and overall equations for the reaction in this experiment.
2. Plot a graph of log t (s) against $\frac{1}{T}(K^{-1})$.
3. Calculate the slope of the graph and hence determine the activation energy of the reaction.

5.3.2 Determination of heat of reactions

Heat of reaction can either be endothermic or exothermic depending on the nature of the reaction. In endothermic reaction, heat is absorbed from the surroundings while in exothermic reaction heat is released to the surroundings. According to the first law of thermodynamics, during a chemical reaction heat is neither created nor destroyed. In practice, the heat lost becomes equal to the heat gained if the heat exchange can be sufficiently insulated from the surroundings so that not much heat escapes to the surroundings. A vessel that provides adequate heat insulation from its surroundings and in which temperature changes are measured in order to determine heats of chemical reactions is called a *calorimeter*. A perfect calorimeter is expected neither to absorb heat from the solution that it contains nor to lose any heat to the surroundings. The method which is used to determine the heat of reaction is known as *calorimetry*. There are several heats of reactions such as heat of formation, heat of combustion, heat of solution, and heat of neutralisation. Since the heat given off or absorbed during a chemical reaction occurs at constant pressure, the heat of the reaction is equal to the change in the enthalpy of the system. Activities 5.11–5.13 demonstrate how the enthalpies of combustion, formation, dissolution and neutralisation can be determined experimentally.

Activity 5.11

Determination of enthalpy of formation

Requirements: Beakers, thermometer, stirring rod, 0.40 g magnesium ribbon, 2.00 g magnesium carbonate, and 1.00 M hydrochloric acid.

Procedure

1. Measure 60 mL of HCl solution into a 100 mL beaker and record the initial temperature, T_1.
2. Add magnesium ribbon into a beaker with HCl in step (1), swirl the mixture and record the final reaction temperature, T_2.
3. Again measure out 60 mL of HCl solution into another 100 mL beaker and record the initial temperature, T_3.
4. Add magnesium carbonate into a beaker with HCl in step (3), swirl the mixture and record the final temperature, T_4.

Questions

1. Calculate the heat evolved during the reaction from steps (1) to (2) and (3) to (4) assuming that there is no change in the volume of the solution and neglect heat absorbed by the container. (Specific heat capacity of solution = 4.2 J g^{-1} K^{-1} and the density of solution = 1.0 g cm^{-3}).
2. Calculate the molar enthalpy of formation of magnesium carbonate ($MgCO_3$) given that ΔH_f (CO_2) = –394 kJ mol^{-1} and ΔH_f(H_2O) = –286 kJ mol^{-1}.

Activity 5.12

Determination of the enthalpy of solution

Requirements: Beakers, thermometer, stirring rod, distilled water and 2.00 g of each of ammonium nitrate, calcium chloride, sodium hydroxide, and sodium chloride.

Procedure

1. Measure 50 mL of distilled water into a 100 mL beaker and record its initial temperature, T_1.
2. Add 2.00 g of ammonium nitrate in the same beaker, swirl the mixture and record the final temperature, T_2.
3. Repeat the procedure for the rest of the sample salts.

Questions

1. For each salt, state whether the process is endothermic or exothermic.
2. Calculate the heat change of reaction during the dissolution of the salt samples. Assume that there is no change in the volume of the solution and neglect tha heat absorbed by the container. (Specific heat capacity of solution = 4.2 J g^{-1} K^{-1}, density of solution = 1.0 g cm^{-3}).
3. Calculate the molar enthalpy of solution for each of the sample salt.

Activity 5.13

Determination of the enthalpy of neutralisation

Requirements: Beakers, measuring cylinder, thermometer and stirring rod, 0.10 M HCl, and 0.10 NaOH

Procedure

1. Use a thermometer to measure the temperature of the two solutions separately and record as T_1 for the first solution and T_2 for the second solution.
2. Determine the average temperature of the two solutions. This is your initial temperature of the solution.
3. Measure 25 mL of 0.10 M NaOH solution into a 100 mL beaker and put a thermometer in it.
4. Measure 25 mL of 0.10 M HCl solution and pour into the beaker containing NaOH in step 3. Mix the contents and record the maximum temperature. This is your final temperature of the reaction.

Questions

1. Determine the temperature difference of the reaction.
2. Calculate the molar heat of the neutralisation reaction given that the specific heat capacity of the solution = 4.2 J g^{-1} K^{-1} and the density of the solution = 1.0 g cm^{-3}. Neglect the heat loss to the surroundings.

5.3.3 Distribution of a solute between two liquid phases

The partition law expresses the relation between the concentrations of a given substance in two liquid phases that are in equilibrium with each other. The law states that when a solute is added to two immiscible liquids in both of which the solute is soluble, the solute distributes itself between the two liquids in a definite manner depending upon its solubility. When the equilibrium is reached, the ratio of the concentrations of the solute in the two liquids is constant at a given temperature, and is called the *partition coefficient* or *distribution coefficient*.

$$\frac{C_1}{C_2} = \text{Constant}(K_d) \tag{5.6}$$

where, C_1 is the concentration of a solute in solvent 1,

C_2 is the concentration of a solute in solvent 2, and

K_d is the distribution (partition) coefficient.

For experimental verification of the partition law, different quantities of the solute are added in different quantities of two solvents. If the value of the partition coefficient for each experiment remains the same then the data follows the partition law. In this section, the partition law is verified by the distribution of ammonia between water and chloroform (Activity 5.14) and distribution of iodine between water and isobutyl alcohol (Activity 5.15).

Activity 5.14

Distribution of ammonia between water and chloroform

Requirements: Separating funnel with its stopper, measuring cylinder, pipette, burette, beakers, conical flasks, 0.50 M HCl, 0.05 M HCl, 1.00 M ammonia solution, methyl orange indicator, and chloroform.

Procedure

1. Measure 25 mL of ammonia solution into a clean separating funnel.
2. Add 75 mL of chloroform into the separating funnel containing ammonia solution, stopper the separating funnel, mix the contents thoroughly and leave them to settle.
3. Empty the two layers into separate clean beakers.
4. Pipette 25.00 mL of the lower layer into a clean conical flask, add 2–3 drops of methyl orange indicator.

5. Fill the burette with 0.05 M HCl and record the initial volume.
6. Titrate the contents in the burette against the contents in the flask, record the volume used when the colour changes from yellow to orange.
7. Repeat the procedure but in step 4 pipette 20.00 mL of the upper layer into the conical flask and titrate against 0.50 M HCl. Record your results in a tabular form.

Questions

1. Calculate the molarity of ammonia present in aqueous and chloroform layers.
2. Calculate the distribution coefficient of ammonia between the aqueous layer and the chloroform layer.
3. In which layer do you think ammonia dissolves more? Explain your answer.
4. The partition coefficient for ammonia distributed between aqueous and chloroform layers is approximately 25. If 25.00 mL sample of the aqueous ammonia layer requires approximately 24.50 mL of 0.50 mol dm^{-3} sulphuric acid for complete neutralisation, calculate the concentration (mol dm^{-3}) of ammonia in chloroform layer.

Activity 5.15

Distribution of iodine between water and isobutyl alcohol

Requirements: Separating funnel with its stopper, measuring cylinder, pipette, burette, beakers, conical flasks, 1.524 g of iodine in 1 dm^3 of water, 0.001 M sodium thiosulphate solution, isobutyl alcohol, and starch indicator.

Procedure

1. Measure 50 mL of iodine solution into a clean separating funnel.
2. Add 50 mL of isobutyl alcohol into the separating funnel containing iodine solution, stopper the separating funnel, mix the contents thoroughly and leave them to settle.
3. Empty the two layers into separate clean beakers.

4. Pipette 25.00 mL of the lower layer into a clean conical flask, add 2−3 drops of starch indicator.
5. Fill the burette with 0.001 M $Na_2S_2O_3$ and record the initial volume.
6. Titrate the contents in the burette against the contents in the flask, record the volume used when the blue colour just appears.
7. Repeat the procedure but in step 4 pipette 20.00 mL of the upper layer into the conical flask and record your results in a tabular form.

Questions

1. Write a balanced equation for the reaction that occurs in the titration process.
2. Calculate the concentration of iodine in the aqueous layer.
3. Calculate the K_d of iodine for the two solvent system.

Answers for Some Questions

Chapter One

Exercise 1.2

2. $\lambda = 0.33$ m, $E = 5.96 \times 10^{-25}$ J

4. $n_2 = 4$

6. (a) Absorption (b) emission
   (c) emission (d) absorption

9. 4.86×10^{-7} m, emitted.

Exercise 1.3

3. (a) M = 14, N = 26 (b) M = 7, N = 12

4. (a) (i) p = 5, n = 6, e = 5
   (ii) p = 20, n = 21, e = 20
   (iii) p = 53, n = 78, e = 53

5. ^{28}Si (p = 14, n = 14, e = 14) ^{29}Si (p = 14, n = 15, e = 14) ^{30}Si (p = 14, n = 16, e = 14).

6. ^{10}B = 51.1% and ^{11}B = 48.9%

7. 197.5

8. (a) carbon (b) atomic number
   (c) atomic mass (d) 6 protons, 6 neutrons
   (e) 6 protons, 7 neutrons (f) 6protons, 8 neutrons

9. 126.86 a.m.u

Exercise 1.4

3. 1.09×10^{6} m s^{-1}

5. 2.58×10^{-7} m

6. 1.0039×10^{-10} m or 1.0039×10^{-8} cm

Revision exercise 1

3. 6.94 a.m.u   4. 178.6 a.m.u

5. 1.012 a.m.u   8. 3.37×10^{-19} J

11. 7.27×10^{-10} m   12. 1.299×10^{-34} m

Chapter Four

Exercise 4.1

4. 50 meq/100 g   5. 0.375 meq/100 g

6. pH = 3

Exercise 4.2

2. (a) 119.05%   (b) 109%   (c) 86%

Revision exercise 4

2. (c) (i) ΣEB = 10 meq/100 g   (ii) PBS = 41.66%

3. (b) pH = 4

4. (c) CEC = 20 meq/100 g

5. (b) PBS = 32%

6. (c) 0.0185 g of $Ca(OH)_2$.

Glossary

Absorption spectrum	Type of spectrum formed when a light of a particular wavelength is absorbed by passing through a substance such that black lines are formed in the spectrum corresponding to the wavelength of the light absorbed
Active soil acidity	The concentration of hydrogen ions in the soil solution
Analyte	A substance whose chemical constituents are being identified and measured
Anion analysis	Procedures for detecting anions in a chemical substance
Atom	The smallest particle of matter that can take part in a chemical reaction
Atomic mass unit	The mass of a carbon–12 atom
Atomic number	The number of protons in the nucleus of an atom
Atomic radius	One-half the distance between nuclei of two covalently bonded atoms
Atomic symbol	A notation or representation which consists of one to three letters abbreviation for the name of an element (which can be in English, Latin or Greek)
Band spectrum	A type of emission spectrum which consist of well-defined number of groups of closely packed lines usually emitted by molecules
Biodegradable	A substance that can easily be decomposed by microorganisms and become less harmful to the environment
Bond energy	The average amount of energy which is required to break one mole of bonds of a particular type in gaseous covalent molecules
Bonding	The process of joining two or more things together
Calorimeter	A vessel that is used to determine heats of chemical reactions and which is able to provide adequate heat insulation

Calorimetry	The method of determining heat of reaction by using a calorimeter
Cation analysis	Procedures for detecting cations in a specific group of metal cations
Cation exchange capacity	The sum of exchangeable cations held in 100 g of the oven dried soil
Chemical analysis	The study of the composition, structure and properties of chemical substances
Chemical bonding	An interaction process that results into the association of atoms to form molecules, ions or crystals
Chemical equivalent	The formula weight of a substance divided by its valence
Chemical kinetics	The study of reaction rates and their mechanisms
Complete fertilisers	The fertilisers which contain all the three major plants' nutrients (nitrogen, phosphorus and potassium)
Complex compound	A molecule or ion composed of a central metal atom which is surrounded by ligands
Compost manure	Decayed farm wastes
Confirmatory tests	Experimental procedures performed after the preliminary tests on a salt or mixture of salts so as to approve the ions present
Continuous spectrum	The arrangement of all possible radiations of all frequencies over a wide range of frequencies
Coordinate covalent bond	The type of covalent bond in which the shared electron pair is donated by only one atom
Covalent bond	A chemical bond which is formed by sharing of electrons between two bonding atoms of non-metals
Degenerate orbitals	Are orbitals with the same energy, size and shape but differ in orientation in space
Electron affinity	The energy change when one mole of electrons is added to one mole of gaseous atom or ion

Electronegativity	The relative ability of an atom to attract the bonding electrons towards itself
Electronic configuration	The representation of the arrangement of electrons in atomic orbitals
Electrons	The negatively charged particle of an atom
Electrovalent bond	The chemical bond formed by the electrostatic forces of attraction between two opposite charged ions, namely cations and anions formed as a result of transfer of one or more electrons from one atom to another
End point	An indication of completeness of the titration reaction revealed by a sudden colour change of an indicator
Equivalence point	A point at which the amount of a titrant added is enough to neutralise an analyte during titration
Equivalent	The amount of a substance that reacts proportionally with a given amount of another substance in a chemical reaction
Exothermic reaction	The chemical reaction which involves the transfer of heat from the reaction system to the surroundings
Frequency	The number of complete oscillations per second
Fossil fuels	Fuels formed from gradual decay of animal or plant remains over millions of years
Fusion	A process of joining lighter nuclei to form heavier nuclei
Greenhouse effect	A heating effect resulting from the trapping of infrared radiation of longer wavelengths by carbon dioxide in the atmosphere
Group in a periodic table	A set of elements which have the same numbers of electrons in their outer most shell and hence have similar properties
Heat	A form of energy that flows between two objects or two parts of an object because of the difference in temperature

Hybridisation	The process of mixing orbitals to form stable bonds of molecular orbitals
Hydrogen bond	Special type of dipole-dipole forces between hydrogen atom which is covalently bonded to more electronegative atom with another highly electronegative atom that possesses lone pairs of electrons
Hydrogen spectrum	This is one of the simplest emission lines spectrum observed for atomic hydrogen. It is obtained by passing electric charge through a hydrogen gas contained in a discharge tube at low pressure.
Humus	Organic component of the soil formed by the decomposition of leaves and other materials by soil micro-organisms
Indicator	The substance which changes its colour according to pH change in the solution
Indicator error	The difference between the theoretical end point and the actual end point
Inorganic colloids	Are soil colloids derived from the weathering of primary clay minerals such as mica, feldspar and hornblende
Intramolecular hydrogen bond	The type of hydrogen bond that exists between hydrogen atom and a small, highly electronegative atom within the same molecule
Intermolecular hydrogen bonding	The type of hydrogen bonding that exists between hydrogen atom of one molecule and a small highly electronegative atom of another molecule
Ionic product	The product of the ionic concentrations in moles per litre each raised to its stoichiometric coefficient for a sparingly soluble salt
Ionic radius	Half the distance between two ions that are barely touching each other
Ionisation energy	The energy which is required to remove completely one mole of electrons from one mole of gaseous atoms or ions

Isotopes	Atoms of the same element having same atomic number but different mass number
Isotopy	The state of an element that exists into atoms with different number of neutrons
Land arrangement	The arrangement formed when four electrons groups maximise their separation around a central atom, when all four groups are bondings, the molecular shape is tetrahedral the bond angle is 109.5°
Land pollution	Contamination of land or soil with solid or liquid materials to the extent that exceeds permissible levels
Lattice energy	The energy required to separate one mole of a solid ionic compound into its component gaseous ions; or, the energy released when one mole of an ionic compound is formed from its gaseous ions.
Liming	The practice of adding basic substances to acidic soils with the purpose of neutralising acidity and creating favourable soil conditions for plant growth and microbial activity
Line spectrum	The type of spectrum which consist of separate lines with very little or no groupings at all
Lone pair of electrons	The outer most pair of electrons of an atom which do not take part in the normal covalent bond formation
Manure	A decomposed organic matter derived from plant and animal remains that is added to a soil in order to improve or maintain soil fertility
Mass number	The number of protons and neutrons in the nucleus of an atom
Mass spectrometer	A device used for measuring the relative masses of particles in a sample by creating charged particles and separating them according to their mass to charge ratio
Mass spectrometry	A method for measuring the relative masses and abundances of atomic particles

Matter	Anything that has mass and occupies space
Melting point	The temperature required to break bonds and change the physical state of a substance from solid to liquid
Metallic bonds	Are the electrostatic forces of attraction between positive metal ions and the negative delocalised electrons (sea of electrons)
Metallic character	Referred to as a set of chemical properties that are associated with the elements classified as metals in the periodic table
Molecularity of the reaction	The number of molecules (species) reacting in an elementary step
Momentum	A product of mass and velocity of a moving body
Neutrons	The sub-atomic particle of an atom that carry no charge
Non-polar covalent bond	A type of covalent bond formed between identical atoms, which have the same electronegativity
Nuclear charge	The attractive force that pulls all the electrons closer to the nucleus
Nucleus	The core of an atom consisting of protons and neutrons
Orbit	The path taken by an electron when revolving around the nucleus
Orbital	A three-dimensional region within an atom where there is a high probability of finding an electron within certain energy level
Organic colloids	Are colloids formed from the microbial decomposition of organic matter
Oxidation	Is the electron loss by a substance or increase in oxidation state of a substance or addition of oxygen to a substance or removal of hydrogen from a substance
Ozone layer	A region of the earth's stratosphere that is covered by ozone gas (O_3) that absorbs ultraviolet radiations from the sun, preventing them from reaching the earth's surface

Ozone layer depletion	The destruction of ozone layer by the reaction of the ozone gas in the stratosphere with chlorofluorocarbons and other halogenated compounds
Percentage base saturation	A ratio of the exchangeable basic cations to the total exchangeable cations of a dry soil sample
Period	A horizontal row of elements in the periodic table
Periodic table	A table of elements arranged in order of increasing atomic numbers
pH	A negative logarithm of hydrogen ions concentration
Plant macro-nutrients	Are elements needed by plants in large amount for growth and repair
Plant micro-nutrients	Are essential elements needed in small quantity by plants for growth and repair
Polar covalent bond	The covalent bond which is formed between atoms of different electronegativity because of unequal sharing of electrons
Polarising power	The ability of a cation to deform a negatively charged radical in a compound
Pollutant	Unwanted substances in the environment that affect normal life on earth
Pollution	Contamination of the environment with harmful substances by certain natural phenomena and anthropogenic activities
Potential soil acidity	The concentration of hydrogen ions attracted to the soil colloids before being released to the soil solution
Proton	The positively charged particles of an atom
Qualitative analysis	Determination of non-numerical composition of each chemical substance present in a sample
Quantitative analysis	The determination of the numerical composition of substances in a given sample

Quantum numbers	The numbers which are used to describe the properties of electrons in an atom
Rate constant	A constant which gives the relationship between the rate of reaction and concentrations of the reactants
Rate law	A mathematical expression which shows the dependence of the rate of chemical reaction on the concentration of the reactants
Redox reactions	The reactions which involve simultaneous oxidation and reduction of chemical species
Redox titration	The determination of the concentration of an analyte from the sample through redox reaction by measuring volumes of the analyte and titrant
Reduction	The electron gain by a substance or decrease in oxidation state of a substance or removal of oxygen from a substance or addition of hydrogen to a substance
Screening effect	The tendency of the inner most electron to protect the outer most electrons from the attractive influence of the nucleus
Self-indicator	A reactant which acts as an indicator due to its colour change at the end of the reaction
Soil acidity	A measure of the degree of concentration of hydrogen ions in the soil solution
Soil chemistry	A branch of chemistry which deals with the study of composition, properties and chemical interactions of the soil components
Soil colloids	Soil particles or single tiny aggregate of size ranging from 1.0 nanometre to 1000 nanometre suspended in soil medium
Soil microbial activities	Are processes for soil microorganisms to release minerals in the soil by decomposing organic matter
Soil reaction	The reaction that indicates the acidity or alkalinity of the soil

Solubility product	The product of the concentration of ions in moles per litre raised to their stoichiometric coefficient for a saturated sparingly soluble salt solution
Solubility	The maximum quantity in grams or moles that can dissolve to form one litre of a saturated solution
Spectrum	Arrangement of radiations in order of increasing or decreasing wavelength and frequency
Standard enthalpy of combustion	The heat or enthalpy change of a system when one mole of the substance is completely burnt in oxygen at standard conditions
Standard enthalpy of formation	The heat or enthalpy change when one mole of a substance is formed from its pure elements in their standard state under standard conditions (1 atm and 25 ºC)
Standard solution	A solution whose concentration is exactly known
Standardisation	Determination of the exact concentration of an analyte through titration with a standard solution
Stratosphere	The second major layer of the atmosphere just above the troposphere and below the mesosphere
Titrant	A solution of known concentration that is added (titrated) to another solution to determine the concentration of a second chemical species
Valence Shell Electron Pair Repulsion (VSEPR)	The model that explain the shape of molecules and ions to be determined by the electron pair repulsion around the central atom
Vermi compost	The manure that is made from the excreta of worms and other microorganisms
Volumetric analysis	The determination of the concentration of an analyte (unknown substance) in a solution by measuring volumes
Water pollution	Contamination of water with harmful substances which make it unfit for use
Wavelength	The distance between two successive crests (maxima) or troughs (minima) of a wave

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Appendix 1 The periodic table

1 IA 1A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 VIIIB 8B	10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1.008 H 1																	4.003 He 2
6.941 Li 3	9.012 Be 4											10.81 B 5	12.01 C 6	14.01 N 7	16.00 O 8	19.00 F 9	20.18 Ne 10
22.99 Na 11	24.31 Mg 12											26.98 Al 13	28.09 Si 14	30.97 P 15	32.06 S 16	35.45 Cl 17	39.95 Ar 18
39.10 K 19	40.08 Ca 20	44.96 Sc 21	47.87 Ti 22	50.94 V 23	52.00 Cr 24	54.94 Mn 25	55.85 Fe 26	58.93 Co 27	58.69 Ni 28	63.55 Cu 29	65.38 Zn 30	69.72 Ga 31	72.64 Ge 32	74.92 As 33	78.96 Se 34	79.90 Br 35	83.80 Kr 36
85.47 Rb 37	87.62 Sr 38	88.91 Y 39	91.22 Zr 40	92.91 Nb 41	95.94 Mo 42	98.00 Tc 43	101.1 Ru 44	102.9 Rh 45	106.4 Pd 46	107.9 Ag 47	112.4 Cd 48	114.8 In 49	118.7 Sn 50	121.8 Sb 51	127.6 Te 52	126.9 I 53	131.3 Xe 54
132.9 Cs 55	137.3 Ba 56	57-71	178.5 Hf 72	180.9 Ta 73	183.9 W 74	186.2 Re 75	190.2 Os 76	192.2 Ir 77	195.1 Pt 78	197.0 Au 79	200.6 Hg 80	204.4 Tl 81	207.2 Pb 82	209.0 Bi 83	209.0 Po 84	210.0 At 85	222.0 Rn 86
223.0 Fr 87	226.0 Ra 88	89-103	267 Rf 104	262 Db 105	263 Sg 106	264 Bh 107	277 Hs 108	268 Mt 109	281 Ds 110	280 Rg 111	285 Cn 112	286 Nh 113	289 Fl 114	286 Mc 115	292 Lv 116	294 Ts 117	294 Og 118

138.9 La 57	140.1 Ce 58	140.9 Pr 59	144.2 Nd 60	145 Pm 61	150.4 Sm 62	152.0 Eu 63	157.3 Gd 64	158.9 Tb 65	162.5 Dy 66	164.9 Ho 67	167.3 Er 68	168.9 Tm 69	173.04 Yb 70	175.0 Lu 71
227.0 Ac 89	232.0 Th 90	231.0 Pa 91	238.0 U 92	237 Np 93	244 Pu 94	243 Am 95	247 Cm 96	247 Bk 97	251 Cf 98	252 Es 99	257 Fm 100	258 Md 101	259 No 102	262 Lr 103

🟧	Alkali metals (*s* – **block**)	🟦	***p* – block** elements	🟩	Transition elements (*d* – **block**)
🟫	Alkaline earth metals (*s* – **block**)	🟨	Lanthanides (*f* – **block**)	⬜	Actinides (*f* – **block**)

Appendix 2 Table of elements showing atomic numbers, atomic mass, and atomic radii

Name of the element	Symbol	Atomic number	Atomic mass	Empirical atomic radius	Calculated atomic radius
Actinium	Ac	89	227	195	-
Aluminium	Al	13	26.9815	125	118
Americium	Am	95	243	175	-
Antimony	Sb	51	121.75	145	133
Argon	Ar	18	39.948	71	71
Arsenic	As	33	74.9216	115	114
Astatine	At	85	210	-	127
Barium	Ba	56	137.34	215	253
Berkelium	Bk	97	247	-	-
Beryllium	Be	4	9.0122	105	112
Bismuth	Bi	83	208.980	160	143
Bohrium	Bh	107	264	-	-
Boron	B	5	10.811	85	87
Bromine	Br	35	79.909	115	94
Cadmium	Cd	48	112.40	155	161
Caesium	Cs	55	132.905	260	298
Calcium	Ca	20	40.08	180	194
Californium	Cf	98	251	-	-
Carbon	C	6	12.01115	70	67
Cerium	Ce	58	140.40	185	158
Chlorine	Cl	17	35.453	100	79
Chromium	Cr	24	51.996	140	166
Cobalt	Co	27	58.9332	135	152
Copernicium	Cn	112	285	-	-
Copper	Cu	29	63.54	135	145
Curium	Cm	96	247	-	-
Darmstadtium	Ds	110	281	-	-
Dubnium	Db	105	262	-	-
Dysprosium	Dy	66	162.50	175	228
Einsteinium	Es	99	252	-	-
Erbium	Er	68	167.26	175	226
Europium	Eu	63	151.96	185	231
Fermium	Fm	100	257	-	-
Flerovium	Fl	114	289	-	-
Fluorine	F	9	18.9984	50	42
Francium	Fr	87	223	-	-
Gadolinium	Gd	64	157.25	180	233
Gallium	Ga	31	69.72	130	136

Name of the element	Symbol	Atomic number	Atomic mass	Empirical atomic radius	Calculated atomic radius
Germanium	Ge	32	72.64	125	125
Gold	Au	79	196.967	135	174
Hafnium	Hf	72	178.49	155	208
Hassium	Hs	108	277	-	-
Helium	He	2	4.0026	120	31
Holmium	Ho	67	164.930	175	226
Hydrogen	H	1	1.00797	25	53
Indium	In	49	114.82	155	156
Iodine	I	53	126.904	140	115
Iridium	Ir	77	192.2	135	180
Iron	Fe	26	55.847	140	156
Krypton	Kr	36	83.80	-	88
Lanthanum	La	57	138.91	195	195
Lawrencium	Lr	103	262	-	-
Lead	Pb	82	207.19	180	154
Lithium	Li	3	6.939	145	167
Livermorium	Lv	116	293	-	-
Lutetium	Lu	71	174.97	175	217
Magnesium	Mg	12	24.312	150	145
Manganese	Mn	25	54.9380	140	161
Meitnerium	Mt	109	268	-	-
Mendelevium	Md	101	258	-	-
Mercury	Hg	80	200.59	150	171
Molybdenum	Mo	42	95.94	145	190
Moscovium	Mc	115	289	-	-
Neodymium	Nd	60	144	185	206
Neon	Ne	10	20.183	160	38
Neptunium	Np	93	237	175	-
Nickel	Ni	28	58.71	135	149
Nihonium	Nh	113	286	-	-
Niobium	Nb	41	93	145	198
Nitrogen	N	7	14.0467	65	56
Nobelium	No	102	259	-	-
Oganesson	Og	118	294	-	-
Osmium	Os	76	190	130	185
Oxygen	O	8	15.9994	60	48
Palladium	Pd	46	106.4	140	169
Phosphorus	P	15	30.9734	100	98
Platinum	Pt	78	195.09	135	177
Plutonium	Pu	94	244	175	-

Name of the element	Symbol	Atomic number	Atomic mass	Empirical atomic radius	Calculated atomic radius
Polonium	Po	84	209	190	135
Potassium	K	19	39.102	220	243
Praseodymium	Pr	59	141	185	247
Promethium	Pm	61	145	185	205
Protactinium	Pa	91	231	180	-
Radium	Ra	88	226	215	-
Radon	Rn	86	222	-	120
Rhenium	Re	75	186	135	188
Rhodium	Rh	45	102.905	135	173
Roentgenium	Rg	111	280	-	-
Rubidium	Rb	37	85.47	235	265
Ruthenium	Ru	44	101	130	178
Rutherfordium	Rf	104	261	-	-
Samarium	Sm	62	150	185	238
Scandium	Sc	21	44.946	160	184
Seaborgium	Sg	106	263	-	-
Selenium	Se	34	78.96	115	103
Silicon	Si	14	28.086	110	111
Silver	Ag	47	107.870	160	165
Sodium	Na	11	22.9898	180	190
Strontium	Sr	38	87.62	200	219
Sulphur	S	16	32.064	100	88
Tantalum	Ta	73	181	145	200
Technetium	Tc	43	98	135	183
Tellurium	Te	52	127.604	140	123
Tennessine	Ts	117	294	-	-
Terbium	Tb	65	159	175	225
Thallium	Tl	81	204.4	190	156
Thorium	Th	90	232.038	180	-
Thulium	Tm	69	169	175	222
Tin	Sn	50	118.71	145	145
Titanium	Ti	22	47.87	140	176
Tungsten	W	74	183.85	135	193
Uranium	U	92	238.03	175	-
Vanadium	V	23	50.942	135	171
Xenon	Xe	54	131.30	-	108
Ytterbium	Yb	70	173.04	175	222
Yttrium	Y	39	88.91	180	212
Zinc	Zn	30	65.38	135	142
Zirconium	Zr	40	91.22	155	206

Appendix 3 Table of some fundamental physical constants

Constant	Symbol	Value
Avogadro's number	N_A	6.02×10^{23} mol^{-1}
Charge of electron/proton	e	1.60×10^{-19} C
Coulomb constant	C	96500 C
Faraday Constant	F	9.65×10^{4} C mol^{-1}
Mass of a neutron	m_n	1.673×10^{-27} kg
Mass of a proton	m_p	1.673×10^{-27} kg
Mass of an electron	m_e	9.11×10^{-31} kg
Molar volume of ideal gas at S.T.P	V_m	2.24×10^{-2} m^3 mol^{-1}
Planck's constant	h	6.625×10^{34} J s
Rydberg constant	R	1.097×10^{7} m^{-1}
Speed of light	c	3×10^{8} m s^{-1}
Universal gas constant	R	8.314 J mol^{-1} K^{-1} 0.0821 L atm mol^{-1} K^{-1}

Appendix 4 Some conversion factors

1 cal	=	4.184 J		
1 kcal	=	10^3 cal		
1 Å	=	10^{-8} cm	=	10^{-10} m
1 L	=	1 dm^3	=	10^{-3} m^3
	=	1000 mL	=	1000 mL
1 nm	=	10^{-9} m		
1 eq	=	10^{-3} meq		
1 atm	=	1.01325×10^{5} Nm^{-2}		
	=	1.01325 bar		
	=	101325 Pa		
	=	760 mmHg		
	=	760 torr		

Index

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