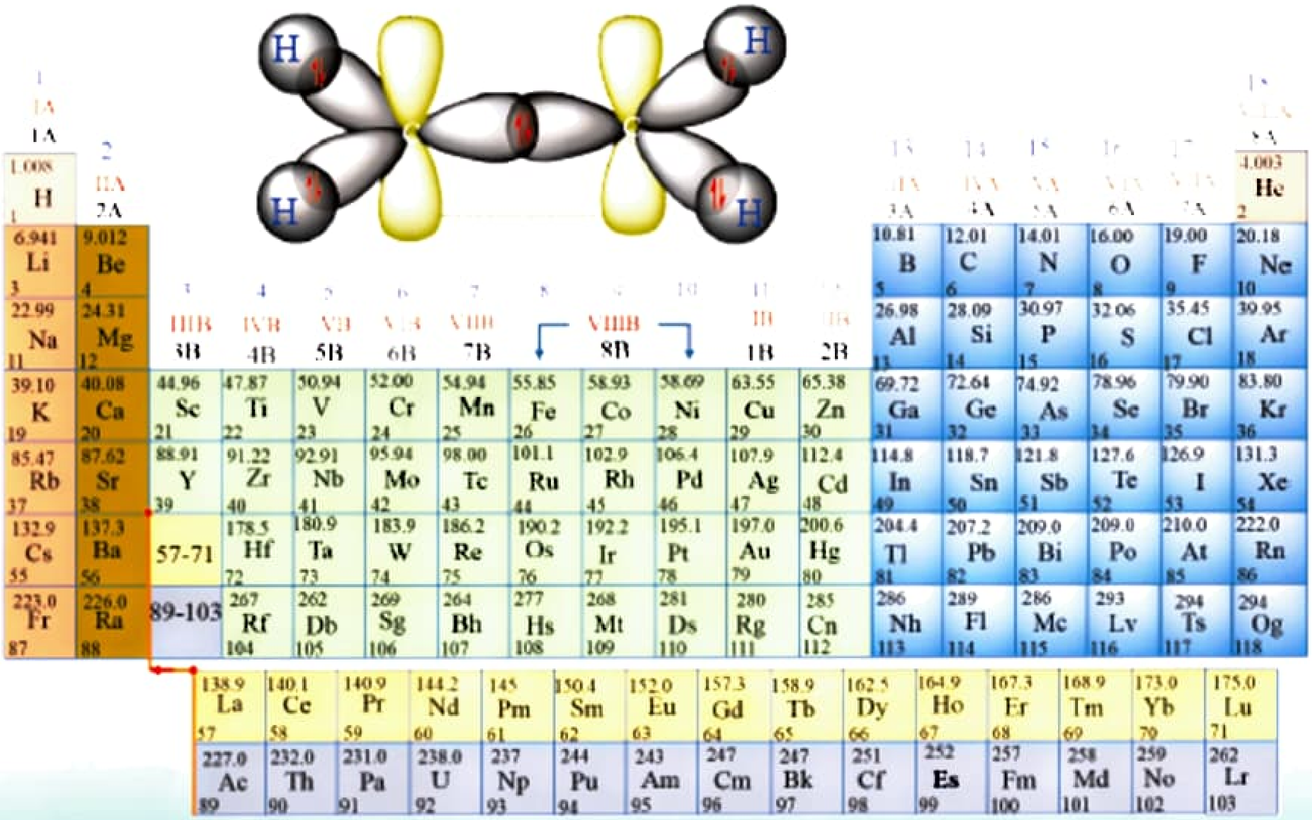
General and Inorganic Chemistry

for Advanced Secondary Schools

Student's Book

Form Five and Six



Tanzania Institute of Education

General and Inorganic Chemistry

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Student's Book
Form Five and Six

THE UNITED REPUBLIC OF TANZANIA
MINISTRY OF EDUCATION,
SCIENCE AND TECHNOLOGY

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Commissioner for Education

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Dr Aneth A. Komba

Director General

Tanzania Institute of Education

Preface

This textbook, General and Inorganic Chemistry for Advanced Secondary Schools, is written specifically for Form Five and Six students in the United Republic of Tanzania. The book is prepared in accordance with the 2023 Chemistry Syllabus for Advanced Secondary Education, Form V-VI, issued by the Ministry of Education, Science and Technology (MoEST). It is a new edition after merging the contents from General Chemistry for Advanced Level Secondary Schools Student's Book for Form Five and Six and Inorganic Chemistry for Advanced Level Secondary Schools Student's Book for Form Five and Six that were published in 2019 in accordance with the 2009 Chemistry syllabus issued by the then, Ministry of Education and Vocational Training (MoEVT).

The book consists of four chapters, namely: The atom, Chemical bonding, Periodic classification, and Transition elements. In addition to the contents, the chapters contain illustrations, activities, tasks, and exercises. You are encouraged to do all the activities and tasks, and attempt all questions in the exercises. You are also advised to do a project work in any theme from the covered chapters of this book. In addition you are required to prepared a portfolio to keep records of activities performed in different lessons. This will enhance your understanding and development of the intended competencies for this level.

Additional learning resources are available in the TIE e-Library at https://ol.tie.go.tz or ol.tie.go.tz

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Chapter One

The Atom

Introduction

Understanding the structure of an atom allows us to predict how atoms interact with each other. In this chapter, you will learn about atomic theories and their applications in determining of the electronic configurations of different elements. The competencies developed will enable you to advance your scientific knowledge of the structure and behaviours of matter.

Think

Matter without atoms

1.1 The concept of atom

Task 1.1

Employ educational online platforms to investigate the compositions of matter.

The concept of the atom is fundamental to our understanding of matter. The word atom comes from the Greek word *atomos*, meaning indivisible. Therefore, an atom is the smallest possible unit of matter. It originated from ancient Greek philosophers like Democritus and Leucippus who proposed that matter is made up of indivisible particles called atoms. The atomic theories largely developed by scientists like John Dalton, Joseph John Thomson, Ernest Rutherford and Niels Bohr in the 19th and early 20th centuries describe atoms as consisting of a nucleus composed of protons and neutrons surrounded by a cloud of electrons. The discovery of these subatomic particles, along with advancements in quantum mechanics, has provided deeper insights into the behaviours of atoms and the forces that govern them.

1.2 Dalton's atomic theory

The studies about matter started in early 1800s when John Dalton postulated his theory, the *Dalton's atomic theory*. The theory provided the first comprehensive explanation of the nature of matter and laid a foundation for further developments in atomic theories and chemistry in general.

1.2.1 Postulates of the Dalton's atomic theory

Dalton's atomic theory is summarised 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.

1.2.2 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 with the following postulates:

(a) Atoms are made up of small 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, which are called *isotopes*. For example, protium ($^{1}_{1}H$), deuterium ($^{2}_{1}H$) and tritium ($^{3}_{1}H$) are isotopes of the hydrogen element. 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

Aim: To investigate the composition of matter

Requirements: 1 g of anhydrous copper(II) sulfate or potassium permanganate, distilled water, 50-mL beakers (5 pieces), measuring cylinders and glass rod

Procedure

1. Put about 0.5 g of either anhydrous copper(II) sulfate or potassium permanganate into a beaker.
2. Add a small amount of distilled water into a beaker and stir using glass rod until all the contents dissolve.
3. Transfer about 1 mL of the solution prepared in step 2 into another separate beaker and top up with distilled water.
4. Transfer about 1 mL of the solution from step 3 into another separate beaker and top up with distilled water.
5. Continue with the dilution process into separate beakers 4 and 5.

Question

How does the colour intensity of the solutions demonstrate some postulates of the Dalton's atomic theory?

1.2.3 Discovery of the fundamental particles of an atom

The amendments of the Dalton's atomic theory indicates that atoms consist of three sub-atomic particles, which are protons, neutrons, and electrons. The discovery of these sub-atomic particles is very important to the current understanding of the atomic structure.

The discovery of electrons

The existence of electrons in an atom was first suggested by J. J. Thomson when 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 rays called *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 pressure of the gas in the discharge tube is lowered to a certain level for example 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 as shown in Figure 1.1, they are deflected towards a positively charged plate. Cathode rays consist of moving particles with definite mass and velocity that produce heat when they strike a material surface and cause some changes such as ions formation.

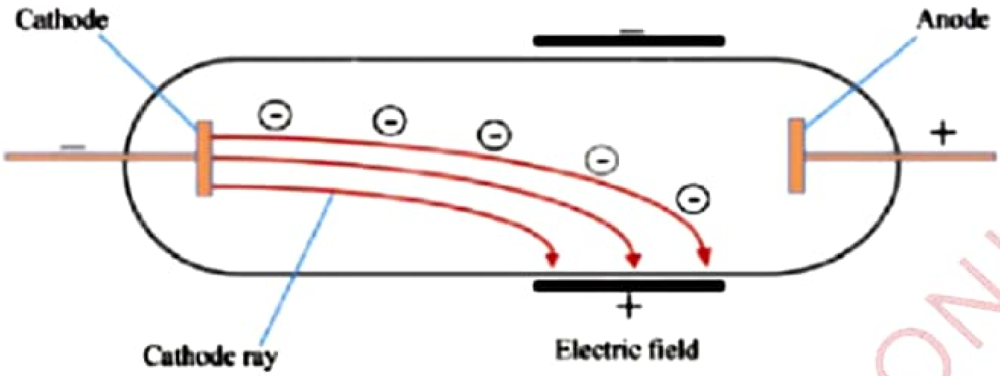


Figure 1.1: **Cathode rays production using a discharge tube**

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, 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, cause 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 called **canal rays** and later were renamed as positive rays. In 1910, Geiger and Marsden (Mueller) bombarded a thin sheet of gold foil with a beam of alpha (α)-particles 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 shows positive rays production using a discharge tube.

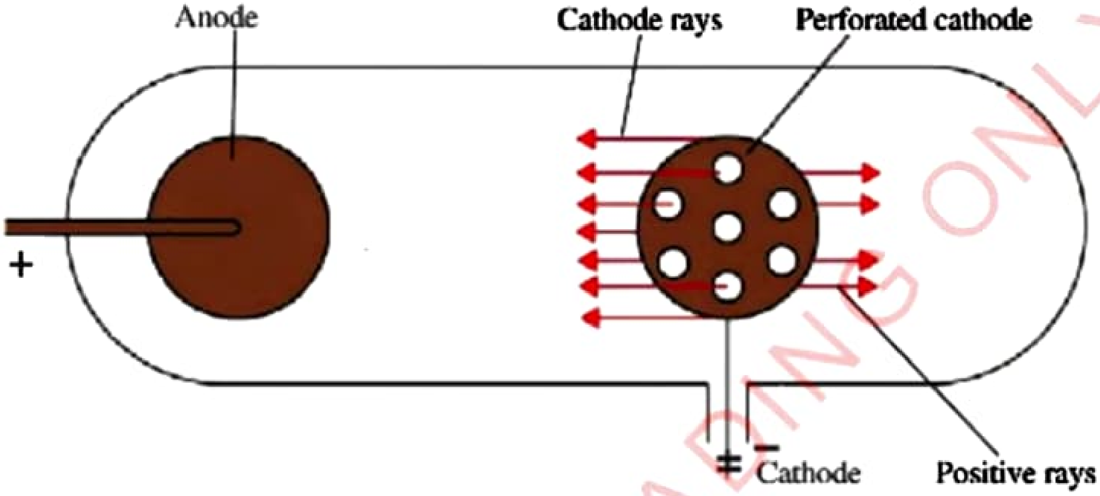


Figure 1.2: *Positive rays production using a discharge tube*

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 cause mechanical motion in the mica wheel, which indicates the particle nature of these rays.

(c) They 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 the electrons.

(e) When the charge on the positive particles of hydrogen 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 called it a proton.

The discovery of neutrons

In 1932, a 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:

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

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 hydrogen atom or protium.

1.2.4 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 the concept of the atomic structure.

J. J. Thomson's atomic model

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.

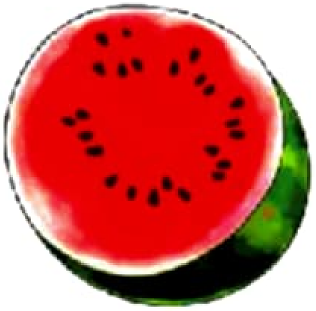


Figure 1.3: *Cross-section of a watermelon showing distribution of the seeds*

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 (Figure 1.4).

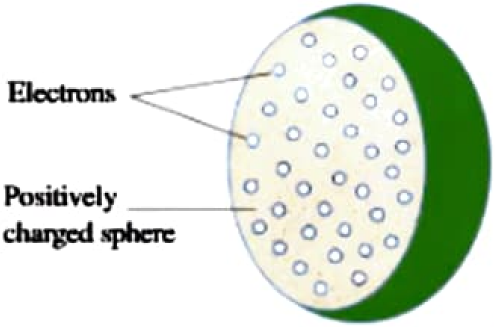


Figure 1.4: *J. J. Thomson's plum pudding atomic model*

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 1.2

Aim: To investigate the arrangements of particles as suggested by J. J. Thomson atomic model.

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

Procedure

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

Questions

1. How can the arrangements of seeds in the fruits be used to explain the J.J Thomson's atomic model?
2. What does the flesh part of the fruits represent?

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.

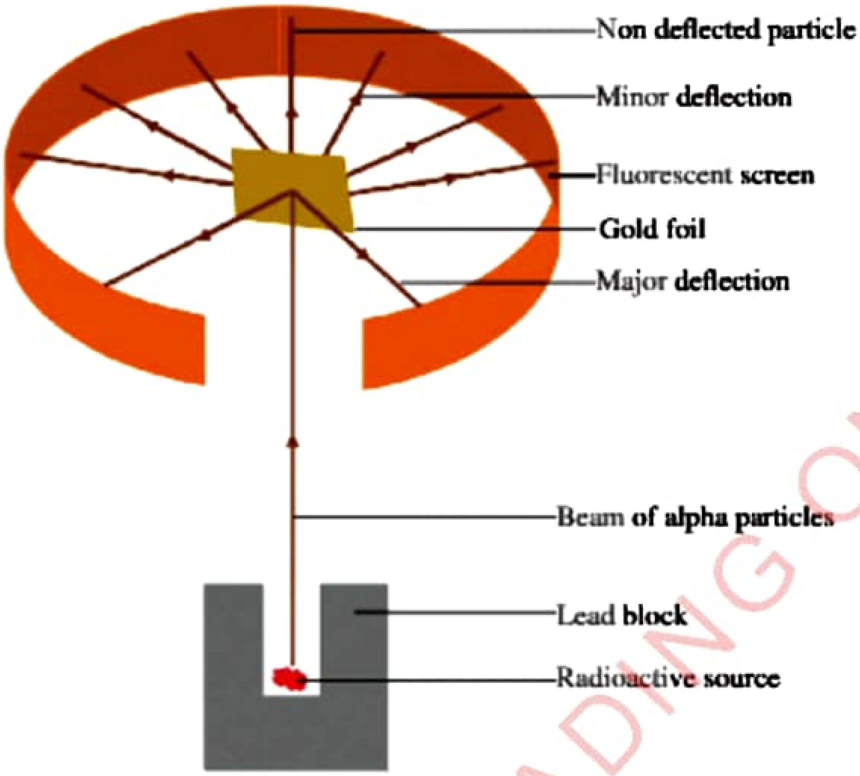


Figure 1.5: *Rutherford's gold foil experiment*

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 α-particles were deflected through small angles, and others were deflected through large angles.

(c) Very few α-particles completely rebounded 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 could 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 could have been some repulsion due to like charges, the momentum could have overcome the repulsive effect, and the particles could have deflected slightly or gone straight through.

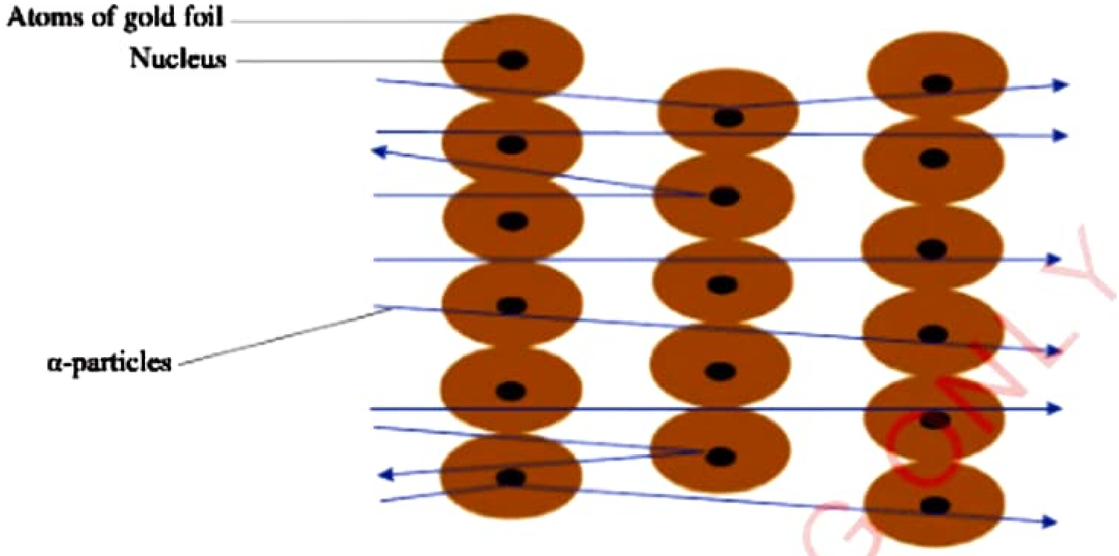


Figure 1.6: *Observations from Rutherford's experiment*

Interpretations of Rutherford's observations

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 α-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 observations 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.

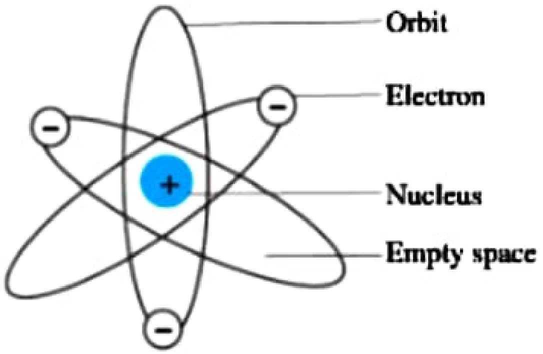


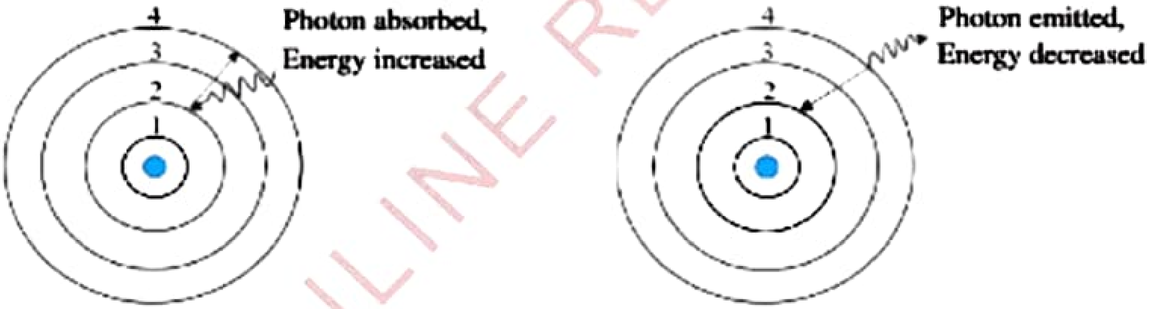
Figure 1.7: *Distribution of positive and negative charges in an atom*

Success and limitations 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 and the arrangement of electrons in 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 got attracted to the nucleus. Therefore, Rutherford's atomic Model could not account for the stability of an atom as well as explain the emissions 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 revolve 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. Similarly, 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 absorption and emission of photons by electrons with their corresponding transitions.



(a)
Absorption

(b)
Emission

Figure 1.8: *Electron movements between energy levels due to absorption and emission of energy (photons)*

Activity 1.3

Aim: To demonstrate how small particles of matter take part in chemical reactions.

Requirements: Vinegar, baking soda, a flat-bottomed flask, measuring cylinder and glass rod

Success and limitations of Rutherford's atomic model

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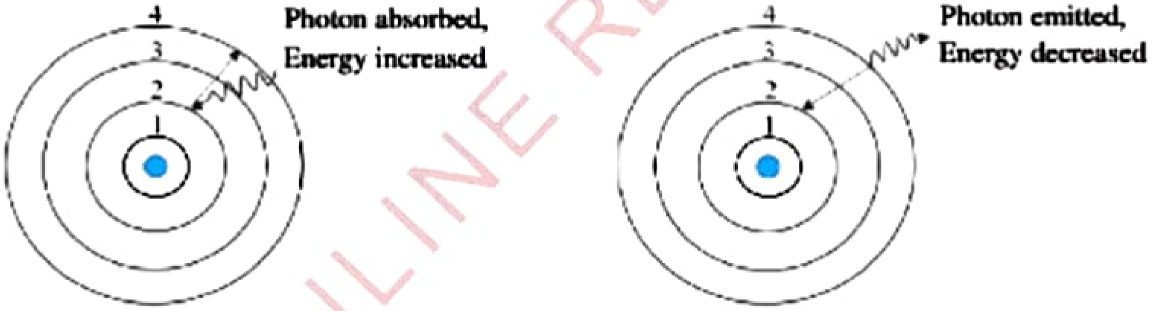


(a)
Absorption

(b)
Emission

Figure 1.8: *Electron movements between energy levels due to absorption and emission of energy (photons)*

Activity 1.3

Aim: To demonstrate how small particles of matter take part in chemical reactions.

Requirements: Vinegar, baking soda, a flat-bottomed flask, measuring cylinder and glass rod

Procedure

1. Transfer about 1 g of baking soda into a conical flask.
2. Slowly add vinegar to the flask. Be careful, as the mixture will fizz up.
3. Stir the mixture with a glass rod.

Questions

1. What reaction equation is involved in this experiment?
2. How do the results in the experiment show the presence of small particles involved in chemical reaction?
3. Which test can be employed to demonstrate the presence of small particles in the products?

Exercise 1.1

1. Explain the important contributions of Dalton's atomic theory towards the development of the structure of the atom.
2. Which statements in Dalton's atomic theory are now considered to be incorrect? Explain
3. (a) How were the three sub-atomic particles discovered?
   (b) Explain the characteristics of each of the sub-atomic particles.
4. Describe J. J. Thomson's model of the atom and its contribution to the structure of matter.
5. Using Dalton's atomic theory, explain the fact that potassium sulfate from Tanzania and that from other countries has the same mass percentages of potassium, sulfur and oxygen.
6. Describe Rutherford's observations that:
   (a) the nucleus has a relatively smaller, diameter than that of an atom.
   (b) most of the mass of an atom is concentrated in the nucleus.
7. Explain the fact that Rutherford's observations challenged the Thomson's model of the atom.
8. Explain the advancement of J. J. Thomson's model over Dalton's atomic theory.

1.3 Bohr's atomic theory

After exploration and proposition of the atomic model, Niels Bohr put forward a model for hydrogen atom, which predicted the existence of line spectra. The line spectra are formed as a result of transition of electrons. The theory is instrumental in explaining the structure of hydrogen atom and provides an understanding of the atomic spectra as well as behaviours of electrons in atoms.

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,

$$mvr = \frac{nh}{2\pi} \quad (1.1)$$

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 when it is in its stationary state. That is, the atom does not change energy while the electron is moving within an orbit.

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

$$\Delta E = E_2 - E_1 = h\upsilon \quad (1.2)$$

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.

1.3.1 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.

1.3.2 Nature of electromagnetic radiation

An electromagnetic radiation is an array of wavelengths which results 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 Physicist about quantisation of energy is the basis for the modern understanding of the atomic structure. The scholar explained the relationship between energy and frequency of electromagnetic radiation.

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, amplitude and wavenumber. 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.

$$\lambda \propto \frac{1}{\upsilon}$$

$$\lambda = \frac{c}{\upsilon} \qquad (1.3)$$

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

Thus, the speed of light,

$$c = \upsilon\lambda$$

All the types of electromagnetic radiations travel in the vacuum at the same speed of $2.99 \times 10^{8}\ \text{m s}^{-1}$. *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.

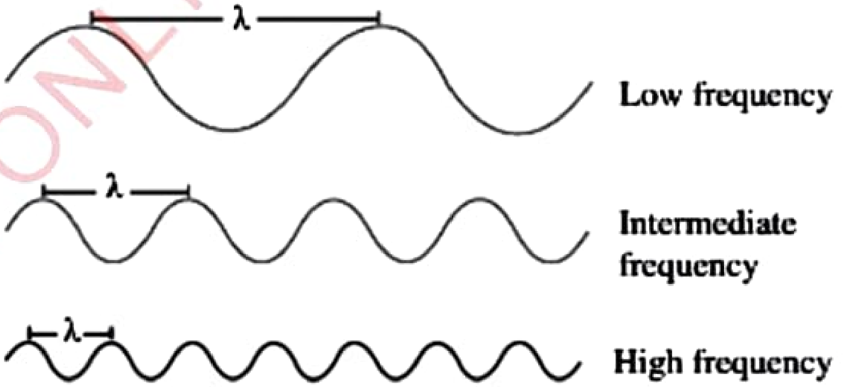


Figure 1.9: *Variations of frequencies with wavelengths of electromagnetic radiations*

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.

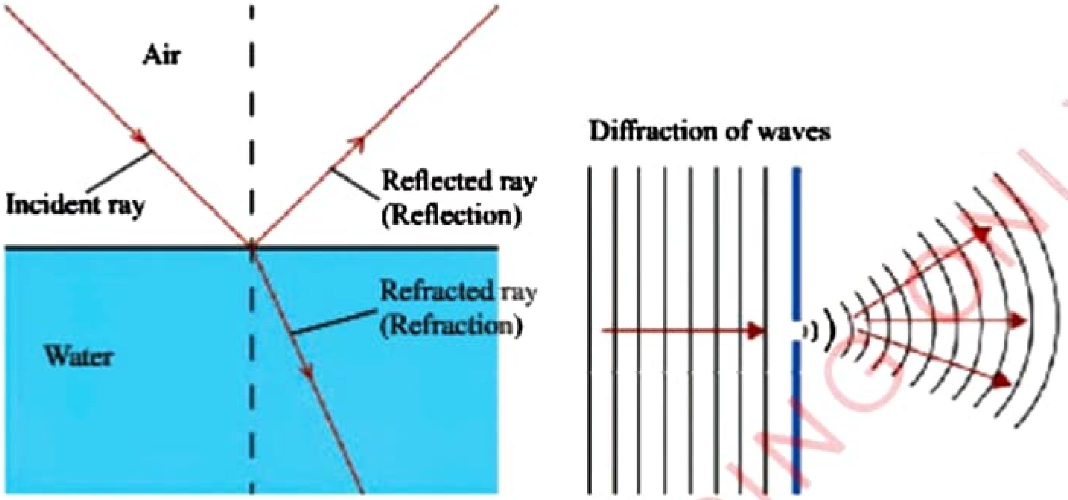


Figure 1.10: *Refraction, reflection and diffraction of waves*

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 whose 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).

$$E \, \alpha \, \upsilon$$

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

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 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 Physicist Albert Einstein (1879–1955) in his photon theory which explained the 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 more energy than the minimum required threshold level, it is ejected from the material.

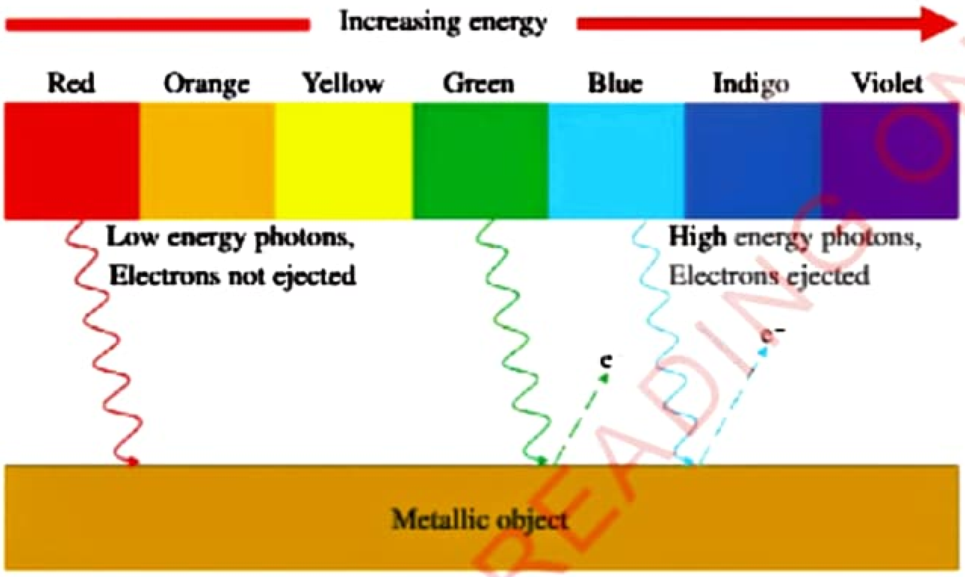


Figure 1.11: *Ejection of electrons from a metallic object when hit by high energy photons*

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 in 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 depends on the energy of individual photons and not on the intensity of incoming light. 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 = planck's 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,

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

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

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.

1.3.3 Atomic spectra

Atomic spectra are the emitted light in the form of series of coloured lines with dark spaces in between which occur 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 be therefore 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 for producing and observing 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 spectrum and emission spectrum.

Absorption spectrum

It is a type of spectrum formed when light of a particular wavelength is absorbed by passing through a substance. In this process, black lines are formed in the spectrum corresponding to the wavelength of the light absorbed, as shown in Figure 1.12.

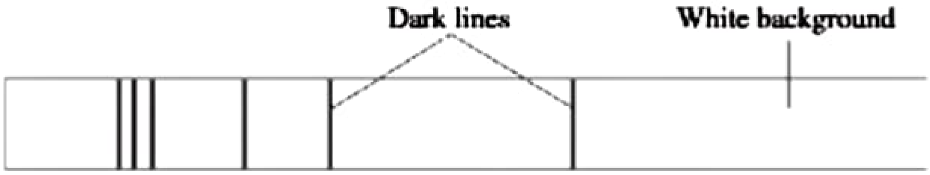


Figure 1.12: *Absorption spectrum*

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 whose 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 wavelengths or frequencies over a wide range of wavelength or 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 visible light.

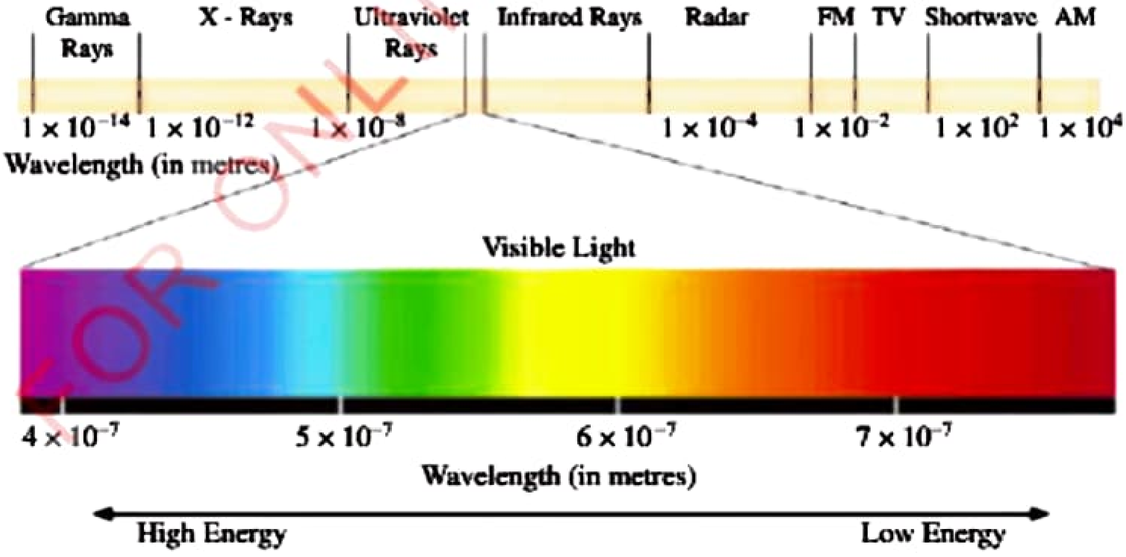


Figure 1.13: *Continuous spectrum of the visible light*

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: *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 with varying intensity are emitted by an element if electricity passes 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. Figure 1.15 represents a line spectrum.

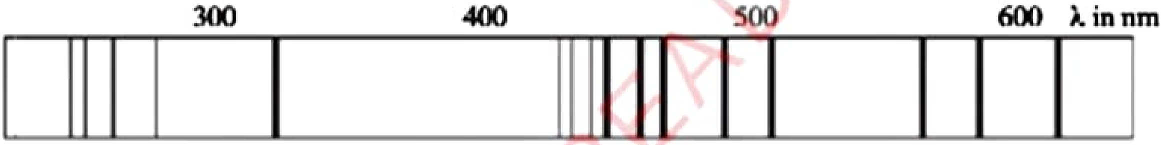


Figure 1.15: *Line spectrum*

1.3.4 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.

Energy levels

According to the Bohr's theory, when hydrogen atoms absorb light, 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 $n = 1$). He further showed that the energies that an eletron in hydrogen atom can occupy are given by $E_n = -R_H(\frac{1}{n^2})$, where R_H is the Rydberg's constant.

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 $E_2 - E_1$ (ΔE). Thus, a greater energy is associated with a shorter wavelength of radiation in the ultraviolet region. This happens because the energy change is inversely proportional to the wavelength of radiation. This concept can lead to the relationship between Planck's quantum energy and wavenumber equation.

$$\Delta E \, \alpha \, \frac{1}{\lambda}$$

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

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

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

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 wavenumber ($\bar{v}$).

Therefore, the wavenumber and the Rydberg energy of the the transitions give 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 (= 1.09737×10^7 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 of an electron moving in the orbit (or principal quantum number n_1 and n_2) is given by Equation 1.8.

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

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

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

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

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

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

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, $\Delta E = 2.178\times 10^{-18}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)\text{J}$ (1.9)

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

$$E = \frac{-13.6\text{ eV}}{n^2} \tag{1.10}$$

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

The negative sign indicates that the energy of an electron within the orbit is 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

Sodium atom emits a yellow-line radiation with a wavelength of 589 nm. Calculate the energy associated with such radiation.

Solution

Convert 589 nm into metres, then use the equation to calculate the energy

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

The energy of the atom is 3.37×10^{-19} J.

Hydrogen spectrum

Hydrogen spectrum is one of the simplest emission lines spectrum observed for atomic hydrogen. It is obtained when electric charge passes 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 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 of 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.

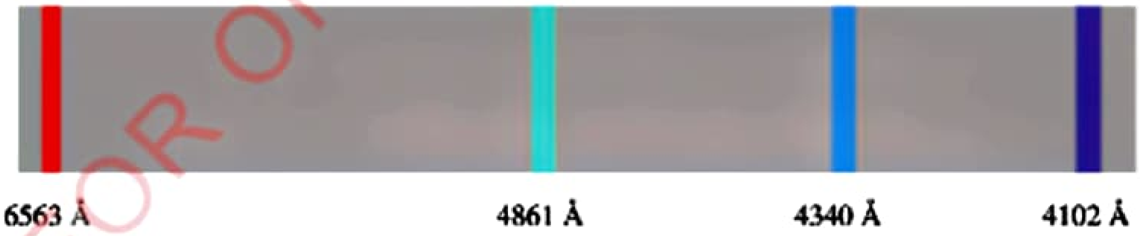


Figure 1.16: *Spectrogram of the visible lines in the Balmer series of hydrogen*

In 1885, J. J. Balmer discovered empirically 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.

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

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

$n_2 = 3, 4, 5.....$

In addition to the Balmer series, four other spectral lines were discovered in the infrared and ultraviolet regions of the hydrogen spectrum. All the series were named after their discoverers as 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......	Ultraviolet
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, ... 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 and converge to a certain limit above which the electron is 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 directly jump from the excited state to the ground state or they may move in steps hence different lines are produced.

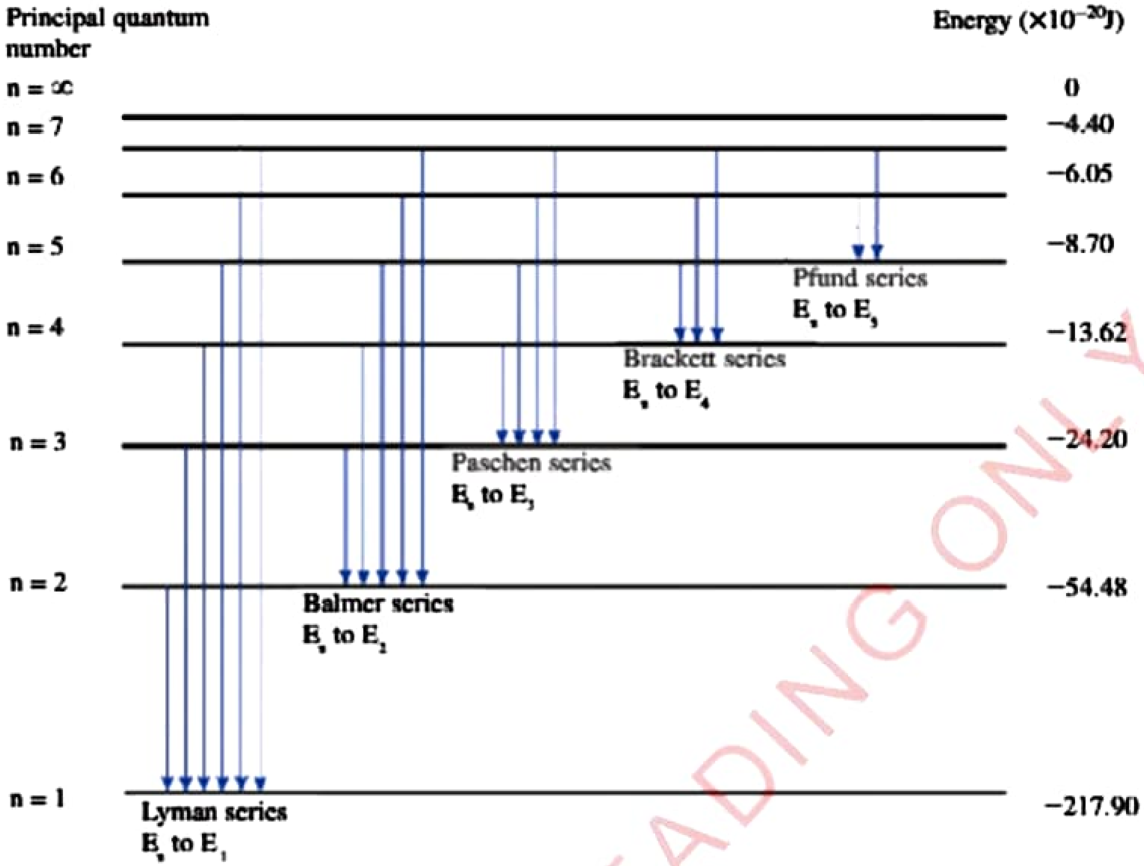


Figure 1.17: *Energy level diagram for hydrogen atom*

Exercise 1.2

1. Explain the three types of emission spectra.
2. (a) Some of the cell phones are said to operate at 900 MHz. Calculate the wavelength and energy of these waves.

   (b) Can such cell phones operate at a wavelength of 360 nm? Explain.
3. The arrangement of the seven colours in the visible light spectrum is in fixed order. Explain.
4. The electron in the ground state of hydrogen atom absorbs a photon of wavelength 97.20 nm. What energy level does the electron move to?
5. Why does the hydrogen spectrum have a large number of lines even though hydrogen has only one electron?

6. Which of the following electron transitions correspond to the absorption or emission of energy? Explain your answer.
   - (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. (a) Compare absorption spectrum and emission spectrum.
   (b) Which one between the two in (a) Bohr worked on?
8. (a) Explain the Bohr's atomic theory.
   (b) Explain the success of Bohr's atomic theory in exploring the structure of hydrogen atoms.
9. (a) Calculate the wavelength of light that corresponds to the transition of the electron from $n = 4$ to $n = 2$ state of the hydrogen atom.
   (b) With reasons, comment whether the transition in (a) is absorption or emission.
10. The medical and pharmaceutical industry has encountered a challenge in detecting toxic metals in urine and blood samples. How can the atomic spectrum address this challenge?
11. Identify the wavelength for the electromagnetic radiation with 3.0×10^{12} Hz and calculate the energy of its photon.

1.4 Atomic mass

Atomic mass is the mass of an atom of an element. It is expressed in atomic mass unit. The atomic mass of an atom is mainly determined by the masses of its protons and neutrons. Electrons contribute very little to the overall mass of an atom.

Task 1.2

Use any reliable educational source to explore the nature of an atom and how its sub-atomic particles behave.

1.4.1 Fundamental particles of an atom

An atom is a neutral, spherical entity which is composed of a positively charged 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 +1 unit charge and 1 unit mass. The neutron (n°) has no charge but has 1unit mass. The positive charge of the nucleus emanates from 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}
Proton	1.67262×10^{-27}	1.00727	+1	$+1.60218 \times 10^{-19}$
Neutron	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 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 numbers 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 could 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).

1.4.2 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*. 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.

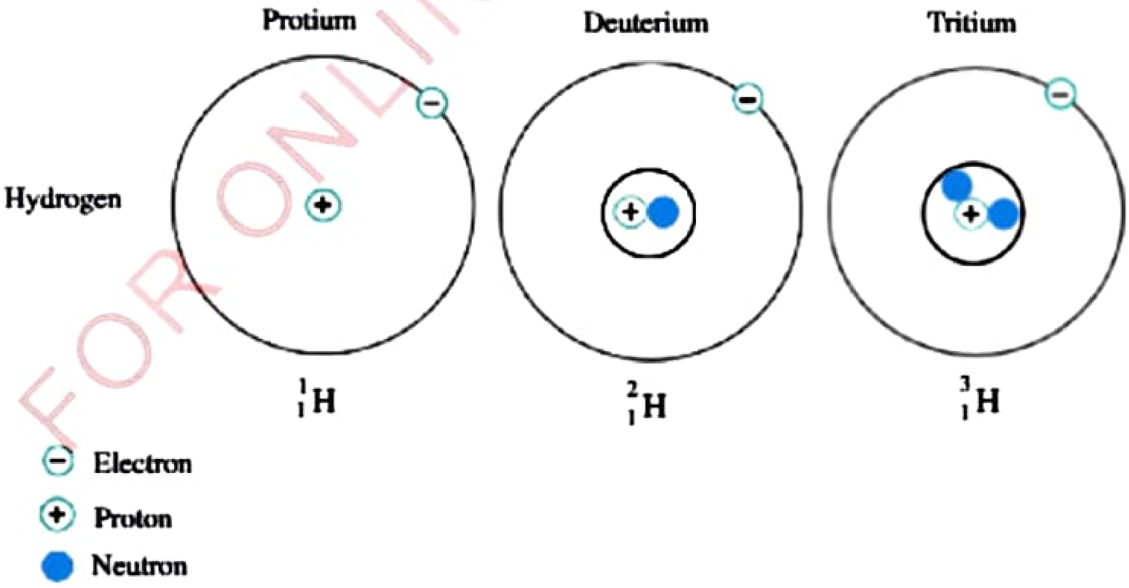


Figure 1.18: *Isotopes of hydrogen*

All isotopes of an element have nearly identical chemical behaviours, 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. Mass spectrometry is 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

$$\frac{\text{Mass of } ^{28}\text{Si atom}}{\text{Mass of } ^{12}\text{C atom}} = 2.\dot{3}$$

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 that 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

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

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

Example 1.3

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

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

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

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 a.m.u. + 52.45 a.m.u.

= 107.87 a.m.u.

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

Significance of isotopes

The isotopes have significant applications in various fields. Isotopic properties are applied in fields such as 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.

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.

1.4.3 Mass spectrometry

Mass spectrometry is a technique used for measuring the relative masses of particles in a sample. This happens by creating charged particles and separating them according to their mass to charge ratios. 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 (Figure 1.19).

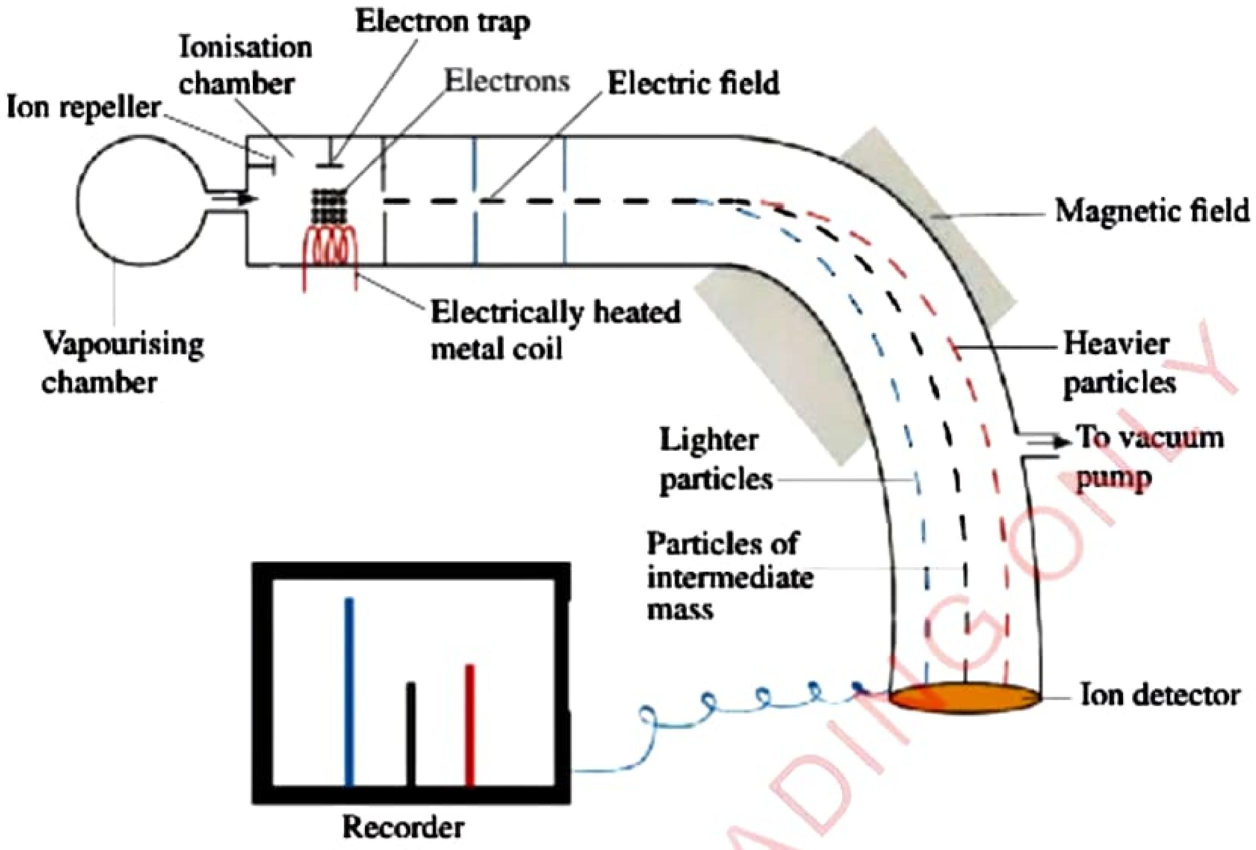


Figure 1.19: *Sketch of a mass spectrometer*

Working mechanism of mass spectrometer

The sample is introduced into the vapourisation chamber and vapourised (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 ratios (*m/e* or *m/z*).

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).

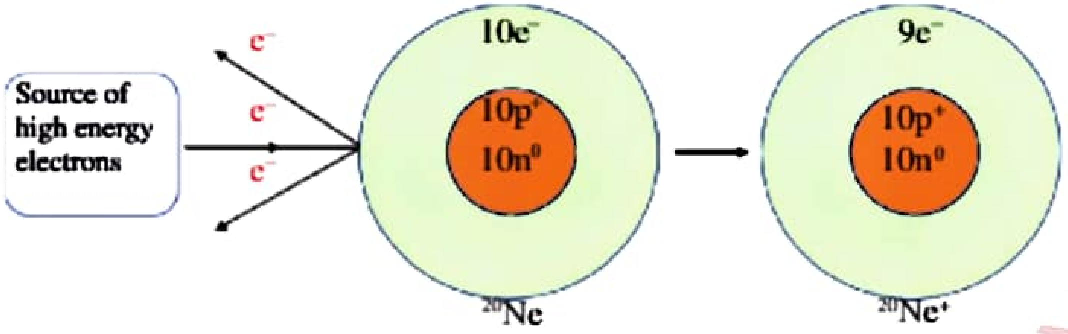


Figure 1.20: *Ionisation of neon (Ne) by using high energy electron source*

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 for identifying the masses of different isotopes of an element. The mass spectrometry is also used for identifying 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 abundances 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 mass or mass number. The number of peaks equals the number of isotopes. For example, chlorine has two naturally occurring isotopes; ^{35}Cl and ^{37}Cl (Figure 1.21). When a sample of chlorine molecule is fragmented into different isotopes in the mass spectrometer, it gives two ions, ^{35}Cl (75%) and ^{37}Cl (25%). The ^{35}Cl gives a mass reading at a mass to charge ratio of 35, and ^{37}Cl gives 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 is 3:1.

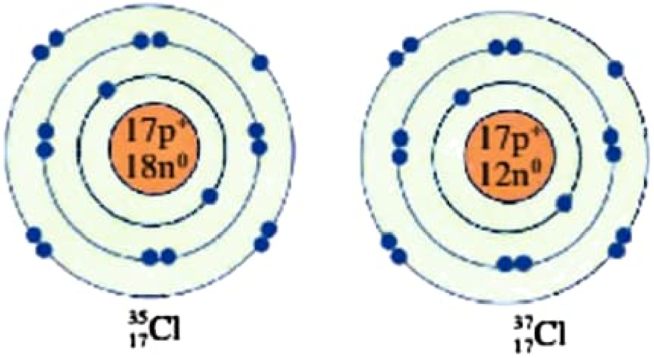


Figure 1.21: *Isotopes of chlorine atom*

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

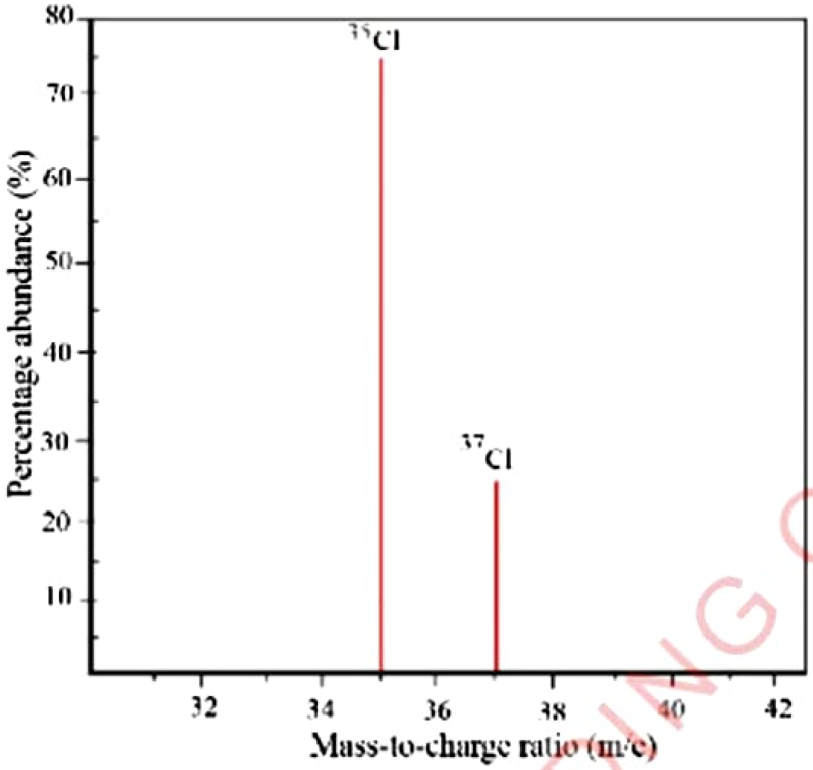


Figure 1.22: *Percentage abundances of chlorine isotopes*

Example 1.4

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

(a) determine 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 1.5

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 is 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 $^{63}\text{Cu} = 0.675$

Then,

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

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

The percentage abundance of $^{63}\text{Cu} = 0.675 \times 100\% = 67.5\%$

The percentage abundance of $^{65}\text{Cu} = 0.325 \times 100\% = 32.5\%$

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

Task 1.3

Use online sources to explore the contribution of isotopes in the world's development.

Exercise 1.3

1. How the concepts of atomic number and atomic mass have contributed to the success of chemists?
2. Why the mass number of an element can vary without affecting its chemical properties?
3. Explain the practical application of isotopes.
4. 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.
5. (a) Calculate 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 (a).

6. Silicon (Si) has three naturally occurring isotopes; ^{28}Si, ^{29}Si, and ^{30}Si.
   (a) Determine the number of protons, neutrons and electrons in each isotope.
   (b) Comment on the variations in the number of protons, neutrons, and eletrons in relation to the properties of the element.

7. 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. The 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.

8. Gold appears in two isotopic compositions of 50% gold–197 and 50% gold–198. Comment on the physical properties of the two isotopes.

9. The following are three isotopes of an element:
   $^{12}_{6}E$, $^{13}_{6}E$, and $^{14}_{6}E$.
   (a) How many protons and neutrons are in the first isotope?
   (b) How many protons and neutrons are in the second isotope?
   (c) How many protons and neutrons are in the third isotope?

10. Iodine has three major isotopes; ^{127}I, ^{126}I, and ^{128}I with the abundance of 80%, 17%, and 3%, respectively.
   (a) Calculate the average atomic mass of iodine.
   (b) What is the significance of calculating the atomic mass of iodine?
   (c) Comment on the contribution of each isotope based on their physical and chemical properties.

1.5 Quantum Theory

Niels Bohr succeeded in giving the first quantitative model of an atom. The model presents the idea that electrons move in a fixed circular orbit. However, the quantum theory reject it. 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.

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 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. de Broglie 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 equation 1.14

$$E = h\nu$$

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

$$E = mc^2 \qquad (1.14)$$

where, c is the velocity of radiation.

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

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

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

$$mc = \frac{h}{\lambda} \qquad (1.15)$$

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,

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

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, while the 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 they are insignificant. Therefore, the equation works only to microscopic particles that their radii are smaller than their wavelengths.

Example 1.6

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, $\mathbf{m} = 6.7 \times 10^{-25}$ 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, $\mathbf{mc} = \frac{\mathbf{h}}{\lambda}$,

Then,

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

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

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

Therefore, the wavelength of the alpha particle is 9.88×10^{-13} m.

1.5.1 Heisenberg's uncertainty principle

A large moving particle has a definite location at any instance 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 Physicist Werner Heisenberg (1901–1976) anticipated how difficult it was to characterise the physical behaviours 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. This is because 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 1.17.

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

or

$$\Delta x m \Delta v \geq \frac{h}{4\pi} \tag{1.17}$$

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 become insignificant.

Example 1.7

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,

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

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

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

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

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

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

Example 1.8

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

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

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

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

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

Exercise 1.4

1. How the Heisenberg's Uncertainty Principle is used to determine 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 the radius of 0.53 Å. Calculate the minimum uncertainty in its speed.
4. Explain de Broglie's wave theory of wave-particle duality and give its equation.
5. The alpha particles emitted from radium have an energy of 4.8 eV. What is the de Broglie's wavelength? Hint: 1 eV = 1.6×10^{-19} J.
6. A radiotherapy machine emits an alpha particle with mass of 6.6×10^{-27} kg moving with a velocity of 105 cm s^{-1}.
   (a) Calculate the wavelength of this particle.
   (b) What is the energy associated with this emission?
   (c) Is the machine favourable for cancer therapy of a 67 kg patient if the curing needs a total dose of 200 Joules which has to be administered in four different doses? Explain.

7. (a) What part of Bohr's theory of the atom is considered unrealistic as a result of Heisenberg's uncertainty principle?

   (b) The Heisenberg's uncertainty principle or wave nature of particles is not a practical way of examining the behaviours of macroscopic objects, but it is the most significant in describing the behaviours of electrons or systems on a very small scale. Explain.

1.5.2 Quantum numbers

The wave equations developed in quantum mechanics are used for describing 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 for describing 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. A 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 $n = 2,3,...$ orbitals.

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 has values of 0 and 1; for $n = 3$, l has values of 0, 1 and 2, for $n = 4$, l has values of 0, 1, 2 and 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 $l = 1$ has three possible values of m_l, which are -1, 0 and +1. This means that this orbital has 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 has 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 spin quantum number

The spin quantum number (s) designates the direction of the electron spin and may have a spin of +½ which corresponds to spin up (↑) and –½ which corresponds to spin down (↓). Unlike l and m_l, the spin quantum number does not depend on other quantum numbers. The spin quantum number helps to determine whether an atom has the ability to generate a magnetic field or not. Table 1.3 summarises the relationships of the four quantum numbers.

Table 1.3: *Relationships of the n, l, m_l and s*

n	l	m_l	s	Number of electrons ($2n^2$)
1	0	0	+½, –½	2
2	0	0	+½, –½	8
	1	-1	+½, –½	
		0	+½, –½	
		+1	+½, –½	

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 $2n^2$. For an orbital with $n = 1$, the number of electrons is 2, and for $n = 2$, the total number of electrons is 8, and for $n = 3$, the total number of electrons is 18.

1.5.3 Atomic orbitals and electronic configuration

The wave mechanical theory of the atom developed the concept of electron cloud in the atom. The concept 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 $m_l = 0$. This means the probability of finding an electron in the *s*-orbital is equal in all directions, thus, appears in 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.

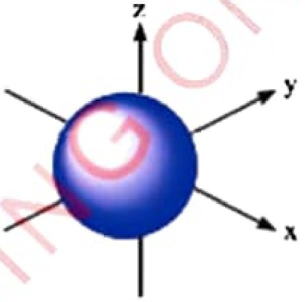


Figure 1.23: *Shape of an s-orbital*

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 orientations 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 orientations in space are called *degenerate orbitals*. The three orientations of *p*-orbitals are shown in Figure 1.24.

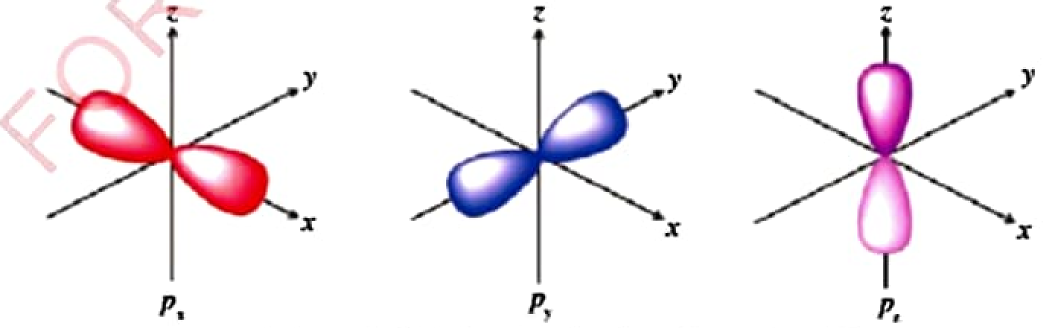


Figure 1.24: *Shapes and orientations of p-orbitals*

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. These 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 the fourth *d*-orbital ($d_{x^2-y^2}$) are directed along the x and y axes. The fifth *d*-orbital (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.

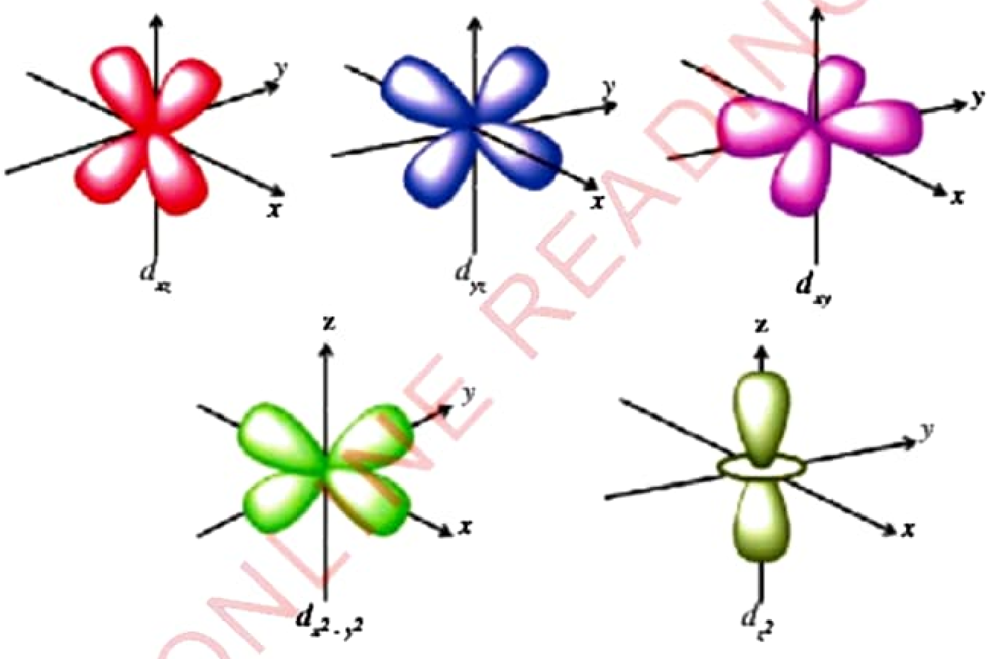


Figure 1.25: *Shapes and orientations of d-orbitals*

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 arrangements of electrons in atomic orbitals. The electronic configuration can be used for describing the orbitals of an atom in its ground state, in excited state, or ionised state. The unique electronic configurations of elements account 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 for representing the 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) Box method

(b) Line diagram method

Figure 1.26: *Methods of representing orbitals*

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

1.5.4 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 Aufbau principle, Pauli's exclusion principle, and 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 whose values of $n + l$ are 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 1.27. Start at 1*s* and move along the arrow.

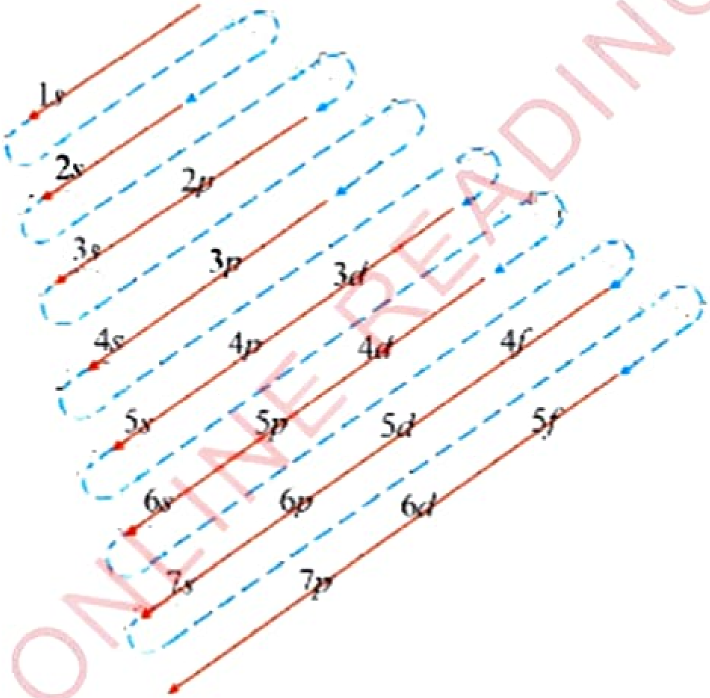
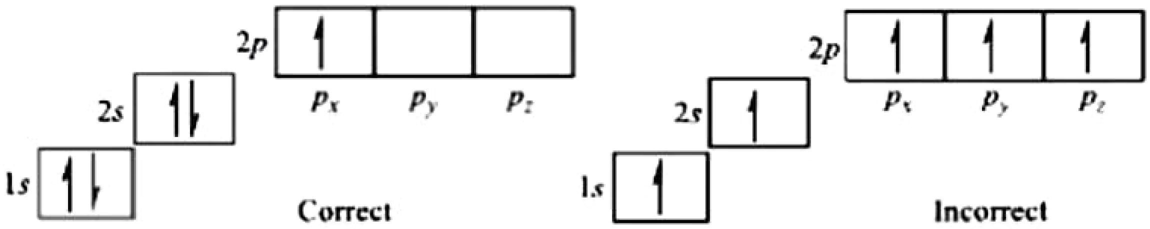


Figure 1.27: *Order of filling electrons in atomic orbitals*

Figure 1.27 shows the order of filling electrons in atomic orbitals according to Aufbau Principle. The trend in electronic configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$ 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 1.28.



Correct

Incorrect

Figure 1.28: *Filling of electrons in orbitals of different energy levels as per Aufbau principle*

The Pauli's exclusion principle

Pauli's exclusion principle was named after the 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 1.29.

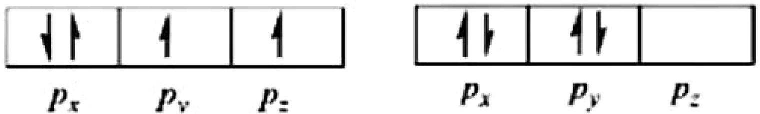
Correct

Incorrect

Figure 1.29: *Pairing of electrons as per Pauli exclusion principle*

The Hund's rule

The Hund's rule was named after the physicist Friedrich Hund (1896−1997). The rule guides 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 1.30.



Correct Incorrect

Figure 1.30: *Filling of electrons in degenerate p-orbitals as per Hund's rule*

You have seen that three rules govern the way in which electrons are filled in the atomic orbitals, namely Aufbau principle, Pauli's exclusion principle and Hund's rule. However, some configurations may seem too long, and thus, condensation is done to shorten. Besides, some elements have peculiar behaviours, and therefore, they need a special way of assigning electronic configurations.

The condensed electronic configuration

The condensed electronic configuration is used for shortening the electronic configurations 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 configurations of some elements

The electronic configurations of some elements such as chromium and copper are 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 configurations of Cu and Cr is attributed by *full-filled 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 electronic configurations is also applicable in elements with f^7 and f^{14} half-filled and full-filled configurations, respectively.

Table 1.4 shows the electronic configurations 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*

Elements	*spdf* notation	orbital diagram
$_{2}He$	$1s^2$	[↑↓] 1s
$_{6}C$	$1s^22s^22p^2$	[↑↓] [↑↓] [↑][↑][ ] 1s 2s 2p
$_{10}Ne$	$1s^22s^22p^6$	[↑↓] [↑↓] [↑↓][↑↓][↑↓] 1s 2s 2p
$_{12}Mg$	$1s^22s^22p^63s^2$	[↑↓] [↑↓] [↑↓][↑↓][↑↓] [↑↓] 1s 2s 2p 3s
$_{14}Si$	$1s^22s^22p^63s^23p^2$	[↑↓] [↑↓] [↑↓][↑↓][↑↓] [↑↓] [↑][↑][ ] 1s 2s 2p 3s 3p
$_{20}Ca$	$1s^22s^22p^63s^23p^64s^2$	[↑↓] [↑↓] [↑↓][↑↓][↑↓] [↑↓] [↑↓][↑↓][↑↓] [↑↓] 1s 2s 2p 3s 3p 4s
$_{22}Ti$	$1s^22s^22p^63s^23p^64s^23d^2$	[↑↓] [↑↓] [↑↓][↑↓][↑↓] [↑↓] [↑↓][↑↓][↑↓] [↑↓] [↑][↑][ ][ ][ ] 1s 2s 2p 3s 3p 4s 3d
$_{25}Mn$	$1s^22s^22p^63s^23p^64s^23d^5$	[↑↓] [↑↓] [↑↓][↑↓][↑↓] [↑↓] [↑↓][↑↓][↑↓] [↑↓] [↑][↑][↑][↑][↑] 1s 2s 2p 3s 3p 4s 3d
$_{28}Ni$	$1s^22s^22p^63s^23p^64s^23d^8$	[↑↓] [↑↓] [↑↓][↑↓][↑↓] [↑↓] [↑↓][↑↓][↑↓] [↑↓] [↑↓][↑↓][↑↓][↑][↑] 1s 2s 2p 3s 3p 4s 3d

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 the 3*d*-orbitals. In case of ionisation, the electrons are first lost from the 4*s*-orbital which is the outermost shell then from the 3*d* which is the inner shell.

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. Which of the following electronic configurations are incorrect. Give reasons for the incorrect configurations.

   (a) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$ (b) $1s^2 2s^2 2p^6 3s^3 3d^8$

   (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-filled 3rd energy level.

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

   (c) contains three electrons in the 2*p* sub-shell.

   (d) has $4s^2$ outer energy sub-shell.

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

5. Which of the following pair of quantum numbers determines the energy of an electron in an orbital? Give reasons for 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 allowed?

   (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? Deduce your answer.

(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) Explain the existence of orbitals in atoms.

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

9. Explain 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.

Task 1.4

Use the locally available materials to construct models representing different theories of the atomic structure and compare them with the available pieces of works of literature. Use the atoms containing more than 4 electrons.

Revision exercise 1

1. According to Dalton's atomic theory, an element is made up of tiny indivisible particles called atoms. Explain by either supporting or rejecting the statement.

2. A 1.008 g of hydrogen combines with 35.453 g of chlorine to form 36.463 g of pure hydrogen chloride. Explain the Dalton's explanation for this combination.

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%, respectively.

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 180?

5. Hydrogen is 99% ^{1}H, 0.8% ^{2}H and 0.2% ^{3}H.
   (a) Calculate its average atomic mass.
   (b) What is the significance of each isotope of hydrogen?
   (c) What is the significance of the average atomic mass?

6. Explain the medical and environmental advantages of the existence of isotopes in elements.

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 $5.09 \times 10^{14}\ s^{-1}$. Calculate the energy of photons in this radiation.

9. Bohr rectified the drawbacks of Rutherford's model. Justify this statement.

10. Explain the equation that describes the Heisenberg's uncertainty principle.

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

12. (a) Calculate the de Broglie's wavelength of a baseball of mass 0.17 kg that is thrown with a velocity of $30\ m\ s^{-1}$.
    (b) Compare your answer with that obtained for the de Broglie's wavelength of the electron in question 11.

13. Complete the following table:

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

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

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

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

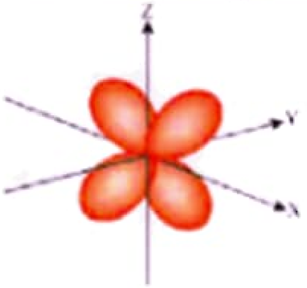
(c) $3p: n =$ ___, $l =$ ___, $m_l =$ ___

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

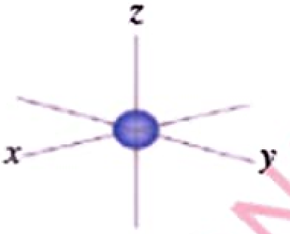
15. Electron clouds in atomic orbitals are fundamental for understanding chemical reactions. Explain.

16. (a) Identify the orbital presented below as *s*, *p* or *d*.

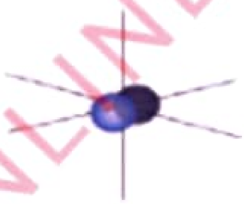
(b) Can this type of orbital be found in the $n = 2$ energy level? Explain.

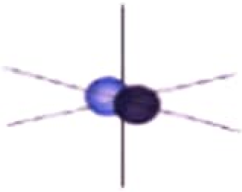


17. Observe the following images and answer the questions that follow:



(i)


(ii)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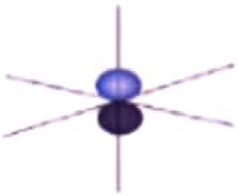
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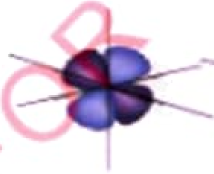
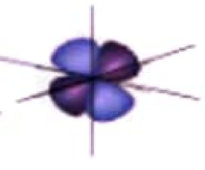

(v)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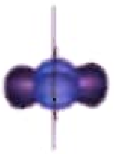
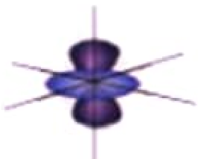
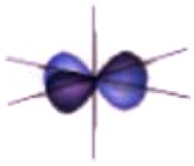

(vii)


(viii)


(ix)

(a) Use the axes in (i) as references to name the orbitals labelled (i) – (ix).

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

18. The Aufbau principle, Pauli's exclusion principle, and Hund's rule are applied in determining the electronic configurations. Explain.

19. 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.

20. How the isotopes of carbon are used in radioactive dating?

Chapter Two

Chemical bonding

Introduction

Chemical bonding is a fundamental process that reinforces the formation of matter around us. From the water we drink, food we eat to the materials we use for building our world, chemical bonding is at the heart of all. In this chapter, you will learn about the concept of chemical bonding and the interaction of atoms in forming different types of molecules. The competencies developed will enable you to predict the properties and behaviours of substances leading to the creation of various products with different properties.

Think

Products without chemical bonding

2.1 The concept of chemical bonding

Task 2.1

Conduct site visits to various workshops and perform an investigation on how different methodologies are employed in joining various materials to form products.

Chemical bonding is the interaction process that results into the association of atoms to form molecules, ions crystals, and any other stable substances. It is the glue that holds atoms together. The bonding involves the interaction of electrons, leading to the formation of products.

2.2 Types of chemical bonds

Task 2.2

Use online sources to simulate the formation of different types of bonds. Compare the simulated results with those from different literature.

There are two main types of chemical bonds, which are intramolecular bonding and intermolecular bonding. Intramolecular bonding refers to the forces of attraction that exist between bonds within (inside) a molecule or compound. Intermolecular bonding refers to interactions between molecules of a compound. These chemical bonds can be classified into ionic (electrovalent) bonds, covalent bonds, metallic bonds, hydrogen bonding and van der Waals forces.

2.2.1 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 cation and anion 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 such as 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 bonds by the loss of electrons at certain ionisation energies (IEs).

$$\mathrm{Na}(s) \longrightarrow \mathrm{Na}(g) \qquad \mathrm{SE} = +109\ \mathrm{kJ\ mol^{-1}}$$
$$\mathrm{Na}(g) \longrightarrow \mathrm{Na^+}(g) + e^- \qquad \mathrm{IE} = +495\ \mathrm{kJ\ mol^{-1}}$$
$$\mathrm{Mg}(s) \longrightarrow \mathrm{Mg}(g) \qquad \mathrm{SE} = +150\ \mathrm{kJ\ mol^{-1}}$$
$$\mathrm{Mg}(g) \longrightarrow \mathrm{Mg^+}(g) + e^- \qquad \mathrm{IE} = +736\ \mathrm{kJ\ mol^{-1}}$$
$$\mathrm{Mg^+}(g) \longrightarrow \mathrm{Mg^{2+}}(g) + e^- \qquad \mathrm{IE} = +1448\ \mathrm{kJ\ mol^{-1}}$$

Sublimation energy (SE) is the energy required to transform a substance from its solid phase directly into its gas phase without passing through a liquid phase. *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. For example,

$$\tfrac{1}{2}\mathrm{Cl_2}(g) \longrightarrow \mathrm{cl}(g)$$
$$\mathrm{Cl}(g) + e^- \longrightarrow \mathrm{Cl^-}(g)$$
$$\tfrac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{O}(g)$$
$$\mathrm{O}(g) + 2e^- \longrightarrow \mathrm{O^{2-}}(g)$$

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:

$$Cl(g) + e^- \longrightarrow Cl^-(g) \qquad EA = -349\ kJ\,mol^{-1}$$

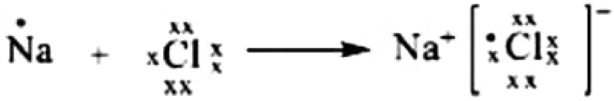
$$Br(g) + e^- \longrightarrow Br^-(g) \qquad EA = -324\ kJ\,mol^{-1}$$

$$I(g) + e^- \longrightarrow I^-(g) \qquad EA = -295\ kJ\,mol^{-1}$$

Thus, the cations and anions 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,

$$Na^+(g) + Cl^-(g) \longrightarrow NaCl(s) \qquad LE = -786\ kJ\,mol^{-1}$$

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



$$\dot{Na} + \overset{xx}{\underset{xx}{{}_x Cl {}^x_x}} \longrightarrow Na^+ \left[\overset{xx}{\underset{xx}{{}^{\bullet}_{x} Cl {}^x_x}} \right]^-$$

Characteristics of ionic compounds

Compounds formed by ionic bonds are called *ionic compounds*. These have several characteristics, which include:

(a) They are crystalline solids at room temperature.

(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.

2.2.2 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 has 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 between the positively charged atomic nuclei and the negatively charged shared electrons. 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 for predicting whether a chemical bond is covalent or ionic depending on the charge and the relative sizes of cations and anions. The number of covalent bonds formed by an atom in a molecule is called the *covalency*. 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.

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 compounds. The characteristics include 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 temperature.

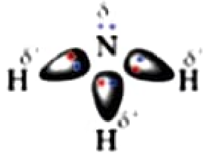
(d) do not conduct electricity.

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 difference 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 between atoms 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 the 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 bonding electrons are withdrawn away from its nucleus. Other examples of polar covalent compounds include hydrogen chloride (HCl), ammonia (NH_3), and water (H_2O).



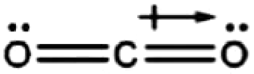
The geometry of water molecule is bent because of the repulsive effect of lone pair of electrons on the oxygen atom.

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). Sharing of electrons in covalent bonding can be represented using the Lewis structure (a). However, some of the 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 180° away from each other, making the molecule non-polar as shown in structure (b).

Chlorine

(a)



Carbon dioxide

(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 does 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 stable noble gas structure of argon. This can be shown by the electronic configurations of aluminium and covalent bond formation between aluminium and three chlorine atoms as illustrated in Figure 2.1.

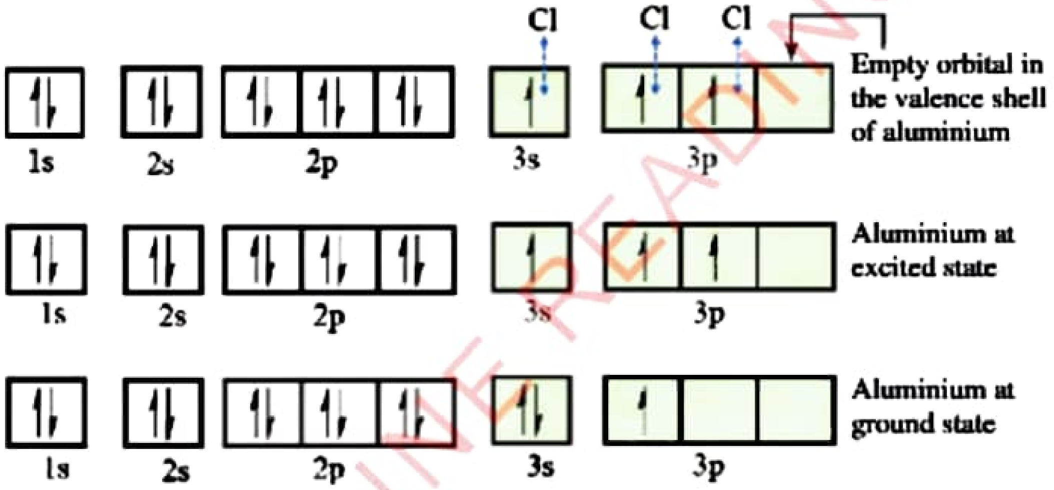
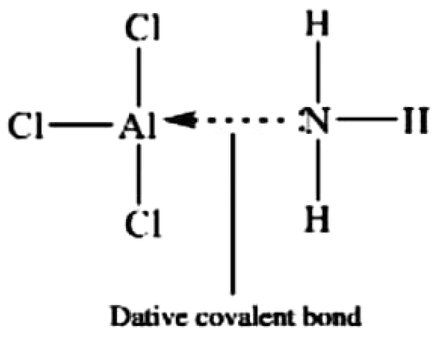


Figure 2.1: *Formation of covalent bond between aluminium and three chlorine atoms*

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



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

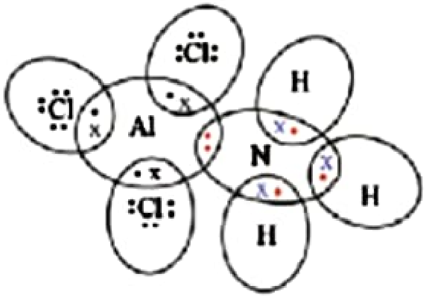
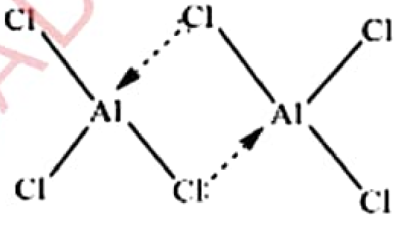


Figure 2.2: *Dative covalent bond between aluminium and nitrogen in $AlCl_3$*

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

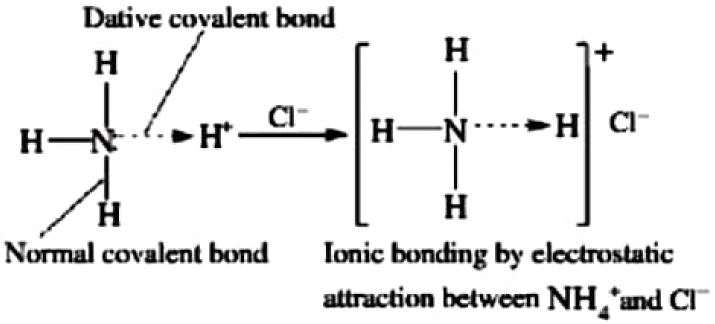
When anhydrous aluminium chloride ($AlCl_3$) is cooled, the molecule dimerises to form molecules of Al_2Cl_6. The two monomers of $AlCl_3$ are held together in Al_2Cl_6 dimers by dative bonding.



Al_2Cl_6

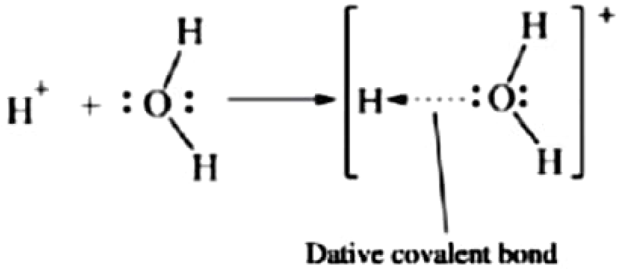
Ammonium ion (NH_4^+) and ammonium chloride (NH_4Cl)

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 with chloride ions by electrovalent bond to form ammonium chloride. Ammonium chloride therefore, shows all the three common bonds (electrovalent or ionic bond, dative bond, 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.



Strengths and lengths of ionic and covalent bonds

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.

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. 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.

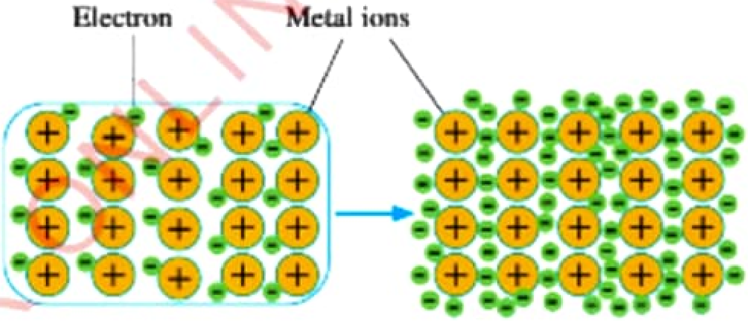
Table 2.1: *Average bond lengths and bond energies for some common bonds*

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

Bond	Bond length (nm)	Bond energy (kJ/mol)
H—N	0.100	389
H—O	0.097	464
H—F	0.092	565
H—Cl	0.127	431
H—Br	0.141	364
H—I	0.161	297
N—N	0.145	163
N=N	0.123	418
N≡N	0.109	946

2.2.3 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.



Localised electrons

Delocalised electrons

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,

Figure 2.4: *Examples of objects in which atoms are linked together by metallic bonding*

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 electrical installation. Examples of metallic objects are shown in Figure 2.4.

Exercise 2.1

1. Compare ionic compounds and covalent compounds.
2. Describe the concept of dative covalent bonding.
3. Use a ChemDraw software to draw the Lewis structures of the following substances:
   - (a) Nitrogen
   - (b) Hydrogen sulfide
   - (c) Sodium fluoride
4. With reason(s), identify the polar and non-polar compounds in the following list:
   - (a) Cl_2
   - (b) BeF_2
   - (c) CO
   - (d) SO_2

5. Compare a coordinate covalent bond with a non-polar covalent bond.
6. Explain the formation of covalent bonds with reference to carbon tetrachloride.
7. (a) Describe 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 structures of hydrogen chloride and ammonium chloride.
9. Explain the unique properties exhibited by metals due to metallic bonding.
10. The balance between different types of forces governs the behaviours of matter in our universe. If the intermolecular forces were stronger than intramolecular species, what differences could be observed in the world?

2.2.4 Hydrogen bonding

Hydrogen bonding is a special type of bonding formed by dipole-dipole forces between a hydrogen atom covalently bonded to a more electronegative atom with another highly electronegative atom that possesses lone pair(s) of electrons.

Conditions for the formation of a hydrogen bond

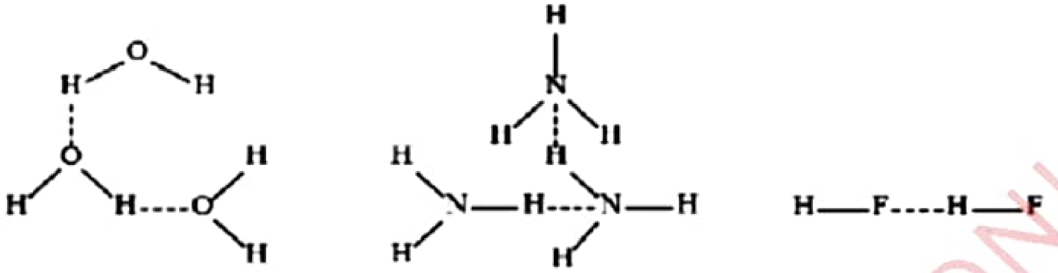
Apart from forming a normal covalent bond, under certain conditions, hydrogen can form a hydrogen bond with other elements within the same or different molecules. The following are the necessary conditions for the formation of a hydrogen bond:

(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.

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 dashed line (----) in the molecules 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*

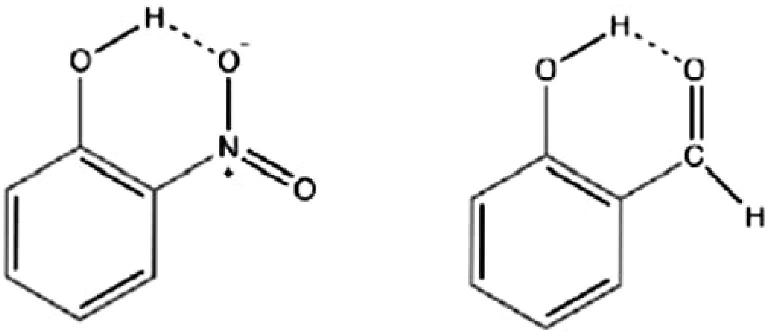
Types of hydrogen bonds

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 it 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.

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

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) (b)

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

(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 it appears 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 points

Under normal circumstances, the melting points (*mp*) and boiling points (*bp*) of compounds in a group of the periodic table increase with increase in molecular weights. However in the case of groups 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.

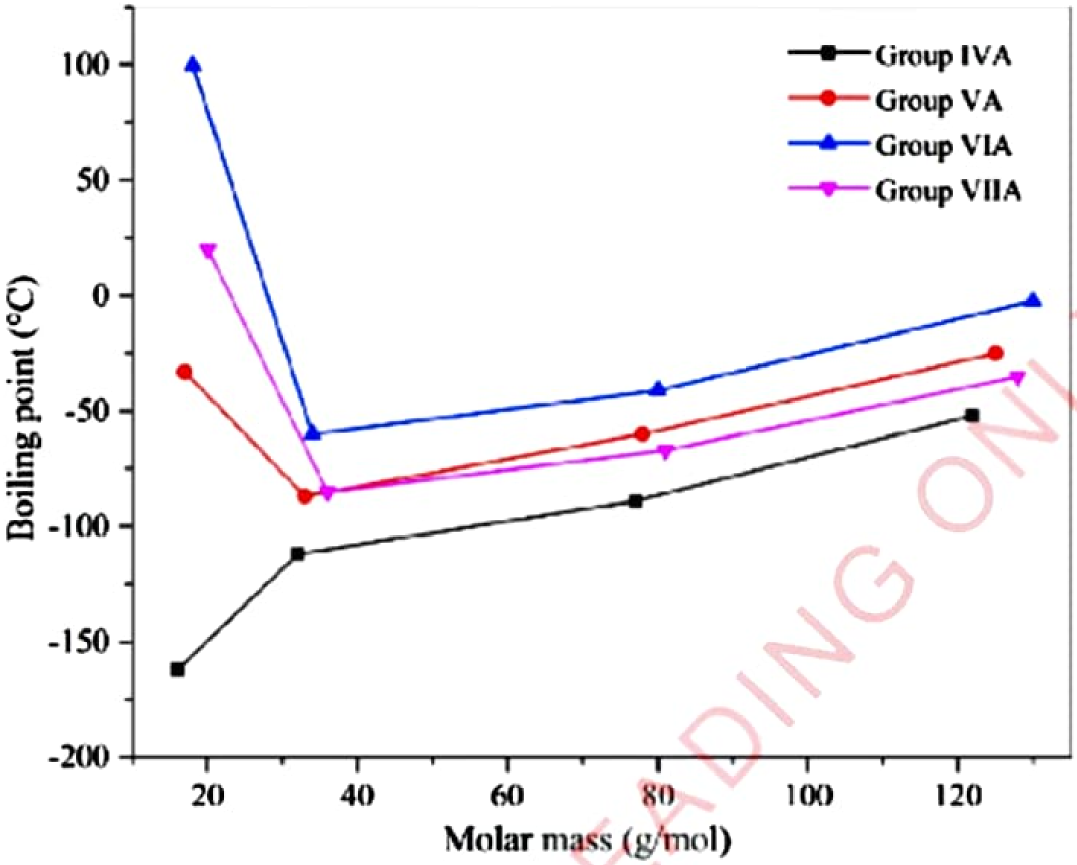


Figure 2.7: *Plot of boiling points of hydrides of groups IVA, VA, VIA, and VIIA against molar masses*

Solubility

Hydrogen bond 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 (e.g. 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 bonds. The molecular masses of such compounds are found to be doubled as compared to those calculated from their simple formulae. For example, the molecular mass of the dimer of acetic acid is 120. The molecular structure of the dimer of acetic acid is shown in Figure 2.8.

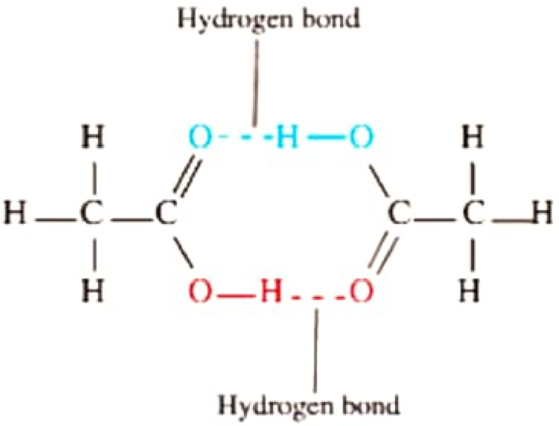


Figure 2.8: *Molecular structure of acetic acid dimer*

Hydrogen bond in ice

The oxygen atom in water consists of two lone pairs of electrons that can participate in hydrogen bond formation. Therefore, each water molecule has two hydrogen bonds and two covalent 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, its 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, and hence, the volume decreases.

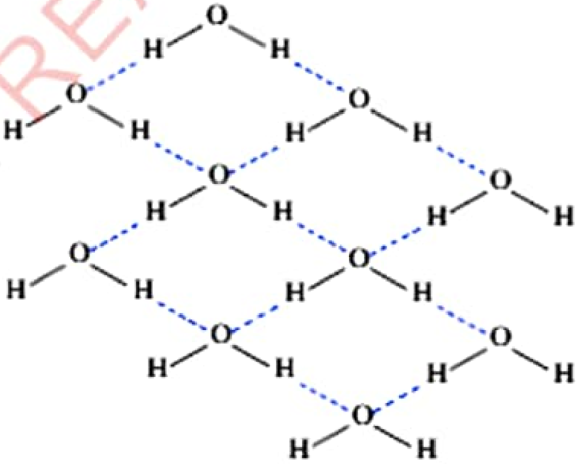


Figure 2.9: *Hydrogen bonding in ice*

Activity 2.1

Aim: To investigate the effect of hydrogen bonding in water

Requirements: Water, deep-freezer or refrigerator or ice cubes, 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. Put the two plastic beakers filled with water into the deep-freezer or refrigerator and allow the water in it to freeze.
3. Measure 500 mL of water and pour it into a 1000 mL beaker.
4. Remove the ice blocks from the plastic beakers and put them into a 1000 mL beaker containing 500 mL of liquid water and note the observations.

   N.B. If you have ice cubes, take some into the beaker containing water and note your observations.

Questions

1. What have you observed in terms of the position of ice in water?
2. Why ice water has displayed different physical properties from those of liquid water?

2.2.5 The van der Waals forces

The van der Waals forces were named after the 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 interactions 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 interactions between molecules which have permanent dipoles. Examples 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.

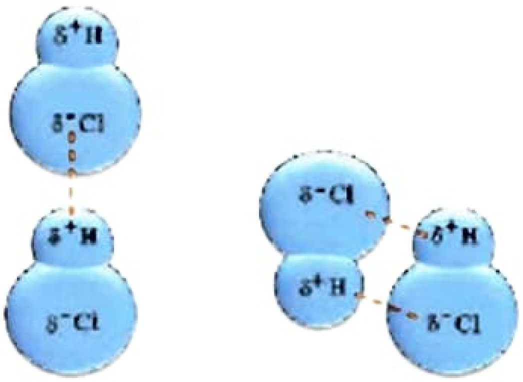


Figure 2.10: *Dipole–dipole interactions in HCl*

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.

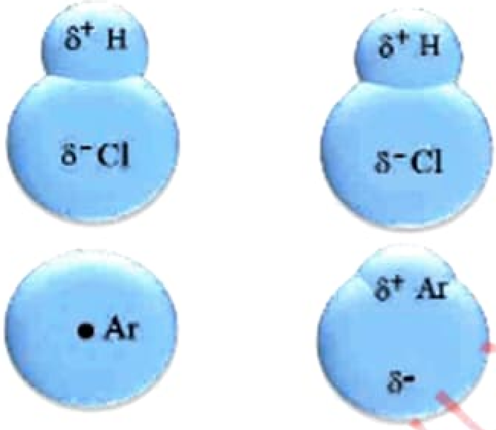


Figure 2.11: *Induced dipole attraction*

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 symmetrical.

Yet at any given instance 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.

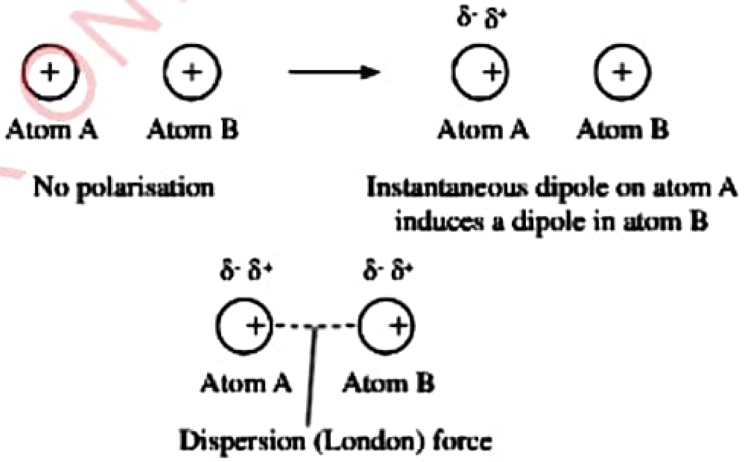


Figure 2.12: *Dispersion forces*

Exercise 2.2

1. (a) With examples, show that hydrogen bonding is formed by dipole-dipole forces between hydrogen atoms and more electronegative atoms of neighbouring molecules.
   (b) Explain the necessary conditions for the formation of hydrogen bonding
2. Account for the impact of intramolecular hydrogen bonds in molecules.
3. Ice floats on water. Explain.
4. By giving reasons, assess the occurrence of hydrogen bonding in the following compounds in their liquid state:
   (a) CaF_2 (b) CH_3OH
   (c) NaH (d) C_3H_8
   (e) HCO(OH)
5. Arrange the compounds HF, H_2O, and HBr in order of the increasing strength of the hydrogen bonding.
6. Describe the effects of hydrogen bonding in some of the molecules in which it exists.
7. Consider the boiling points of hydrides shown in Figure 2.7 and explain the possible causes of some hydrides of group VA and VIIA displaying relatively similar boiling points.
8. What factors affect the strength of van de Waals forces?

2.3 Hybridisation of atomic orbitals

Hybridisation of atomic orbitals is a key concept in molecular chemistry, providing a comprehensive explanation for the shapes of molecules. Atoms undergo hybridisation to increase the combining capacity of the formed hybrid orbitals.

2.3.1 Atomic orbitals involved in hybridisation process

During the hybridisation process, atomic orbitals of similar energies on the same atom mix to produce new orbitals of equal energies. These new orbitals are known as *hybrid orbitals*. They have characteristics of the original orbitals but allow for the formation of more stable bonds. These explain the observed molecular geometries that cannot be described by a simple application of Valence Shell Electron Pair Repulsion (VSEPR) Theory. The concept of hybridisation was introduced by Linus Pauling, a renowned chemist, to elucidate the structures and bonding of molecules.

2.3.2 Lewis theory of hybridisation of atomic orbitals

The Lewis theory of hybridisation of atomic orbitals provides a framework for understanding the bonding in covalent molecules. According to the theory, atoms can undergo hybridisation of their atomic orbitals to form new hybrid orbitals, which can better accommodate the sharing of electrons in covalent bonds. The Valence Shell Electron Pair Repulsion (VSEPR) model successfully explains the 3-D arrangements of atoms in a molecule. The valence bond theory (VB), on the other hand, explains the strength of the bonds in a molecule.

Valence Shell Electron Pair Repulsion (VSEPR) Theory

The VSEPR theory is based on the repulsion between the electron pairs in the valence shell of atoms of the molecule. It is used for predicting 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 the molecule. These electrons tend to be far apart from each other to minimise the repulsion forces 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 bonding electron pairs that have no lone pairs around the central atom are connected to additional atoms by a single or double bonds to form a linear shape at an angle of 180°. Examples of such molecules are $BeCl_2$, C_2H_2, and CO_2. Molecules with three bonding electron pairs or two bonding electrons and one lone pair form trigonal planar shape. Examples of such molecules are BCl_3 and BF_3. The molecular geometries of BCl_3, CO_2, and C_2H_2 are shown in Figures 2.13 and 2.16.

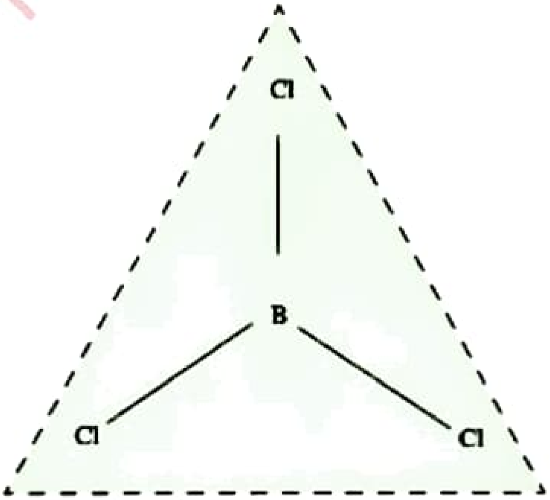
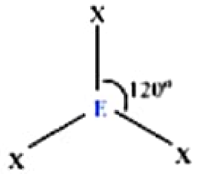
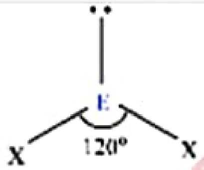
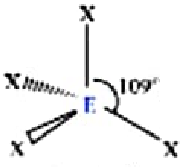
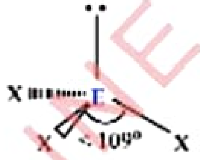
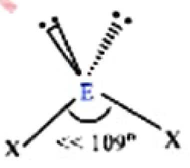
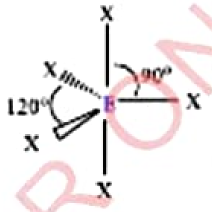
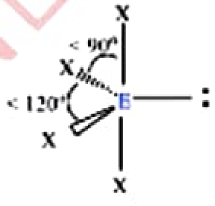
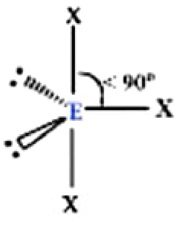
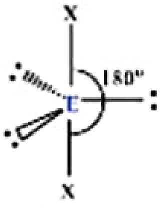
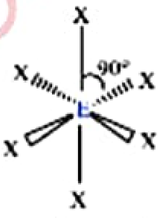
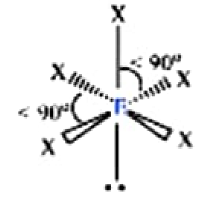
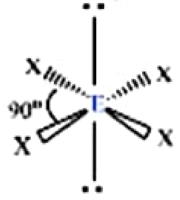
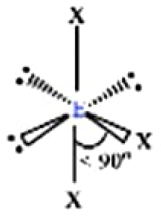
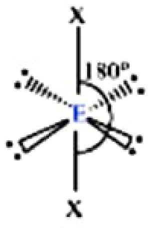


Figure 2.13: *Molecular geometry of BCl_3*

Molecules having four pairs of electrons around the central atom, for example, NH_3, NH_4^+, and H_2O experience mutual repulsion of the bonding and the lone pairs of electrons. Hence, geometrical distribution of electron pairs (arrangement of valence electron pairs) is tetrahedral. The arrangement of atoms in methane (CH_4) and ammonium ion (NH_4^+) 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°). Molecules with five bonding electron pairs for example, PCl_5 are arranged in a trigonal bipyramid with bond angles of 120° in plane and 90° perpendicular to the plane. Six bonding electron pairs are organised in an octahedral arrangement with bond angle of 90°, for example, SF_6.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 the VSEPR theory.

Table 2.2: *Geometries of various compounds based on the 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

Valence bond theory

Valence bond theory is used for explaining how atoms bond to form molecules. It focuses on the role of atomic orbitals and the overlapping of these atomic orbitals to form chemical bonds.

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 relationships 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. For instance, when a molecule of H_2 forms, 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.

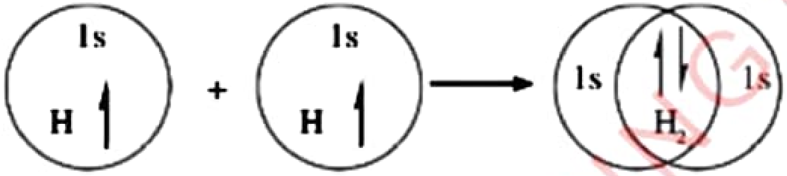


Figure 2.14: *Orbital overlap in hydrogen molecule*

The stability of the bond mainly depends 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 maximise the overlap. This is because there is more electron density in one direction. The combinations of different atomic orbitals to maximise the overlap form new atomic orbitals. This is because the valence atomic orbitals in the molecule are different from those in the isolated atoms. The spatial orientations of these newly formed orbitals lead 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* orbitals. The types of hybrid orbitals vary with the type of atomic orbitals mixed, but their number equals to the number of mixed orbitals. For the hybridisation process to occur, there must be a promotion of energy and electrons, and a vacant orbital within the same energy level.

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 numbers of hybrid orbitals.
4. The hybrid orbitals tend to be scattered in space and farthest apart.
5. The hybrid orbitals are stronger than the non-hybrid orbitals.
6. During hybridisation, the number of combined orbitals is as per requirements of the bonding atoms.

2.3.3 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.

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 (${}_4Be$) atom can be used for explaining the formation of beryllium chloride as illustrated in Figure 2.15.

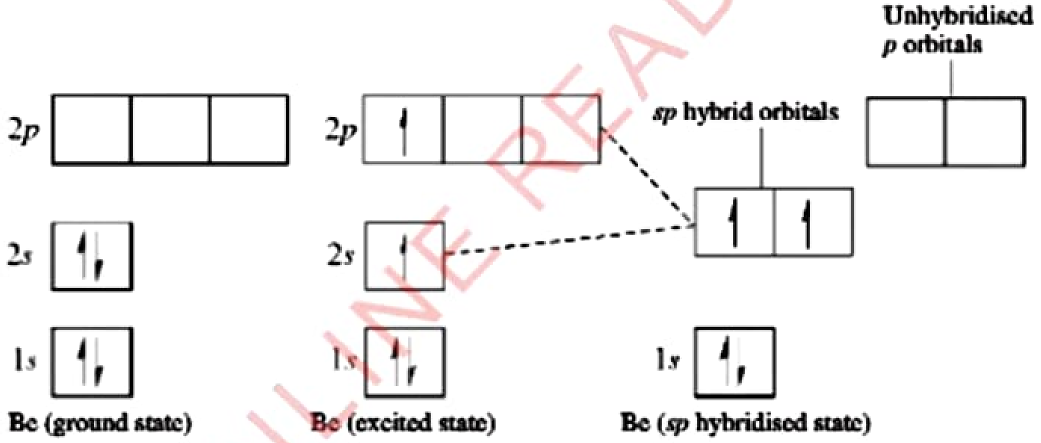


Figure 2.15: *sp hybridisation of beryllium*

One electron from the 2*s* orbital, is promoted to 2*p* orbital 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 empty and unhybridised. Examples of other molecules with *sp* hybridisation are carbon dioxide (CO_2) and ethyne (C_2H_2). The *sp* hybridised molecules have linear shapes as shown in Figure 2.16.

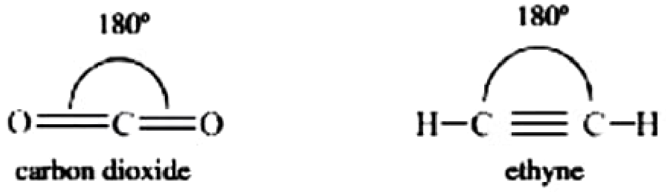


Figure 2.16: *Molecular geometries of carbon dioxide and ethyne*

sp^2 hybridisation

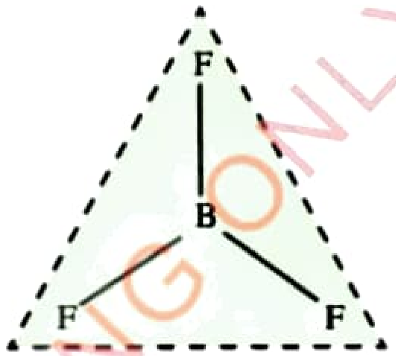


Figure 2.17: *Trigonal planar shape of boron trifluoride*

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 ($AlCl_3$), and iron(III) chloride ($FeCl_3$). 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 for explaining the formation of boron trifluoride (BF_3).

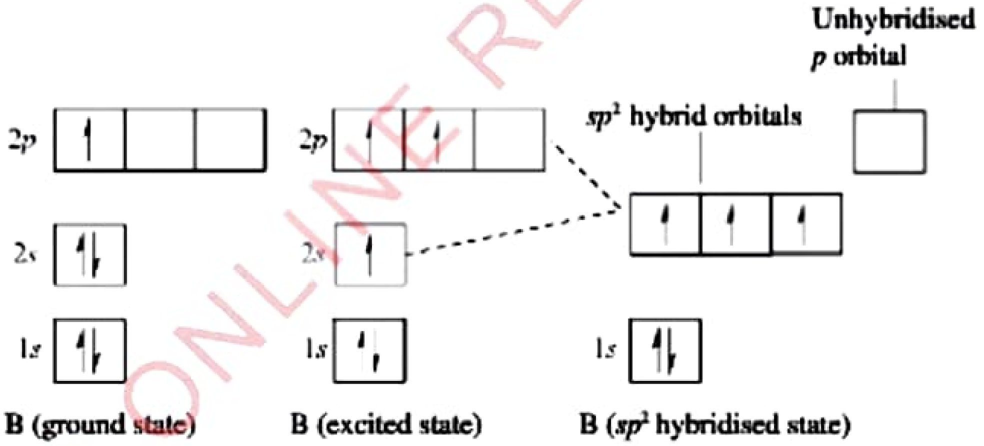


Figure 2.18: *sp^2 hybridisation of boron atom*

The 2*s* orbital 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 the F atom. The three sp^2 hybrid orbitals of B lie at 120° apart, and the unhybridised 2*p*-orbitals are 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. For example, the four hybrid orbitals of carbon 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.

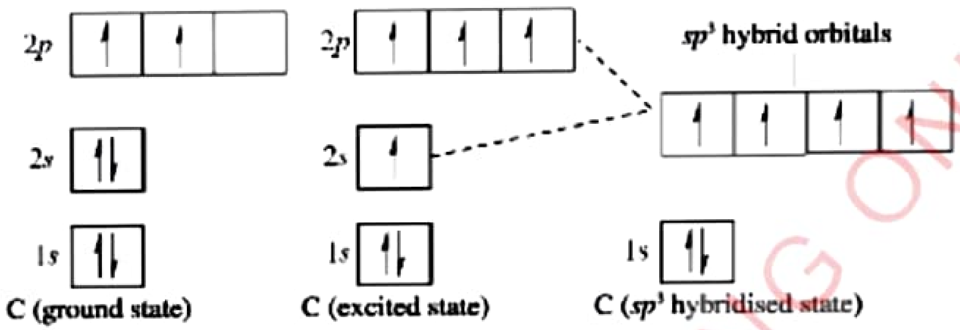


Figure 2.19: *sp^3 hybridisation of carbon atom*

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.

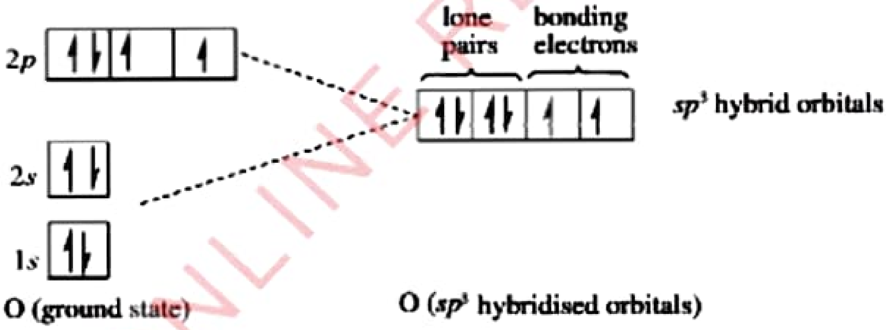


Figure 2.20: *sp^3 hybridisation of oxygen*

Normally, pure hybrid orbitals which include bonding hybrid orbitals have more *p*-characters than those involving a lone pair of electron. The latter, 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.

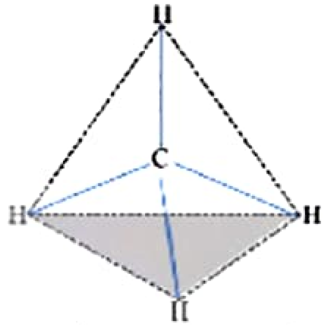


Figure 2.21: *Tetrahedral shape of methane*

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 3*s*-orbital, three of 3*p*-orbitals and one 3*d*-orbital form five sp^3d^1 hybrid orbitals. Examples of molecules whose central atoms form sp^3d^1 hybridisation are PCl_5, SF_4, ClF_3, and XeF_2. Figure 2.22 shows the hybridisation of phosphorus ($_{15}P$) atom, which can be used in the formation of phosphorus pentachloride.

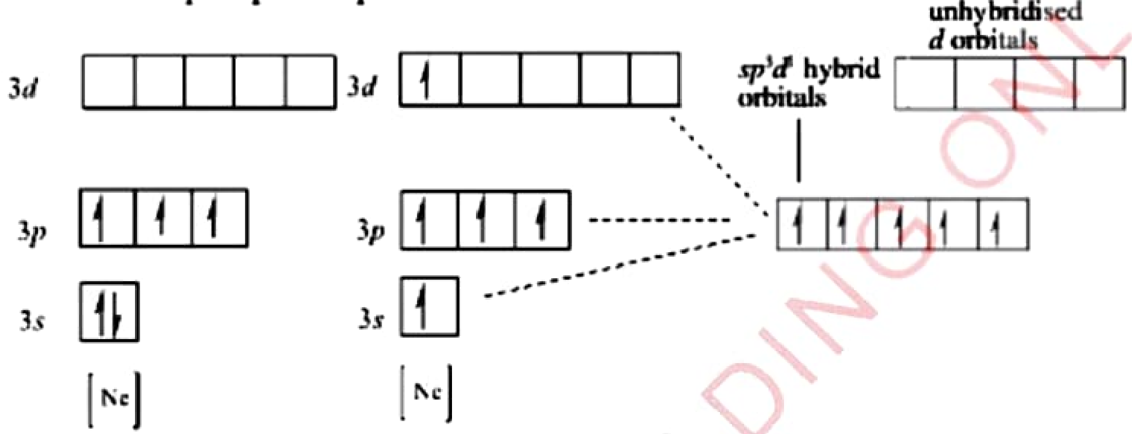


Figure 2.22: *sp^3d^1 hybridisation phosphorus*

The molecular shape in sp^3d^1 is 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 slightly change. For example, the shapes of PCl_5, SF_4, ClF_3, and XeF_2 are trigonal bipyramid, irregular tetrahedral, T-shaped, and linear, respectively.

Task 2.3

1. Use online sources to determine the type of hybridisation and geometrical shapes of the following molecules:
   (a) SiO_2
   (b) SO_2
   (c) SO_3
   (d) H_2SO_4
2. Use an appropriate software to draw the geometrical shapes of the molecules in question 1.

2.3.4 Overlapping of hybrid orbitals

Task 2.4

Use online simulators to create two compounds which are covalently bonded by either sigma bonds only or a mixture of sigma and π-bonds. Compare the simulated properties with those of works of literature.

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 worthwhile to understand the types of overlaps based on the orientations of the orbitals and their influence on the strengths 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 bonds. These are *s-s, s-p*, and *p-p* as shown in Figure 2.23.

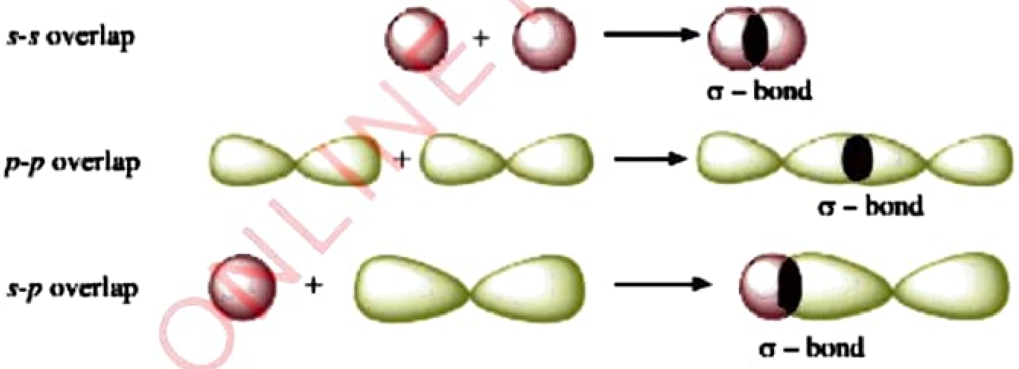


Figure 2.23: *Types of overlaps of atomic orbitals which result into σ bond formation*

The *pi* (π) bond

This type of bond is formed by the side by side overlap, which occurs perpendicular to the internuclear axis. The sideway orientations 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.

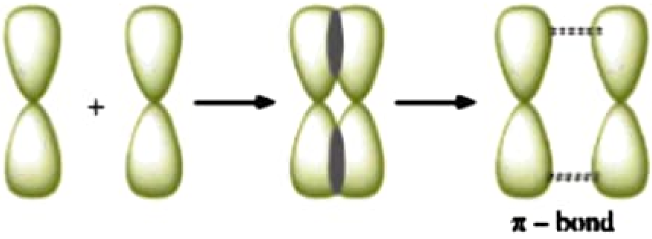


Figure 2.24: *pi bond formation by side by side overlap*

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 forms 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 bonds.

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 by 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.

Activity 2.2

Aim: To investigate the strength of chemical bonds

Requirements: Molecular models, manila papers, and marker pens

Procedure

1. Use the models to construct ethane molecule, place on the manila card and label it A.

2. Construct the second model for ethene and label it B.
3. Construct the third model for ethyne and label it C.
4. Test the flexibility of atoms in each model.
5. Measure the bond length between H-C and C-C atoms.
6. Break the bonds between atoms by pulling them.

Questions

1. Which model display flexibility in all bonds?
2. What is the relationship between the bond length and the number of bonds connecting the two atoms?
3. Which bonds need less energy for them to break? Explain.
4. How does the C-C bonds differ in each molecule in terms of;
   - (a) hybridisation of their atomic orbitals?
   - (b) bond angles?
   - (c) molecular geometries?

The overlap of atomic orbitals in carbon compounds

Carbon atom is among the elements which exhibit several types of hybridisation of atomic orbitals to form different molecular geometries.

sp hybridisation

In this type of hybridisation, the 2*s* orbital and only one of the 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.

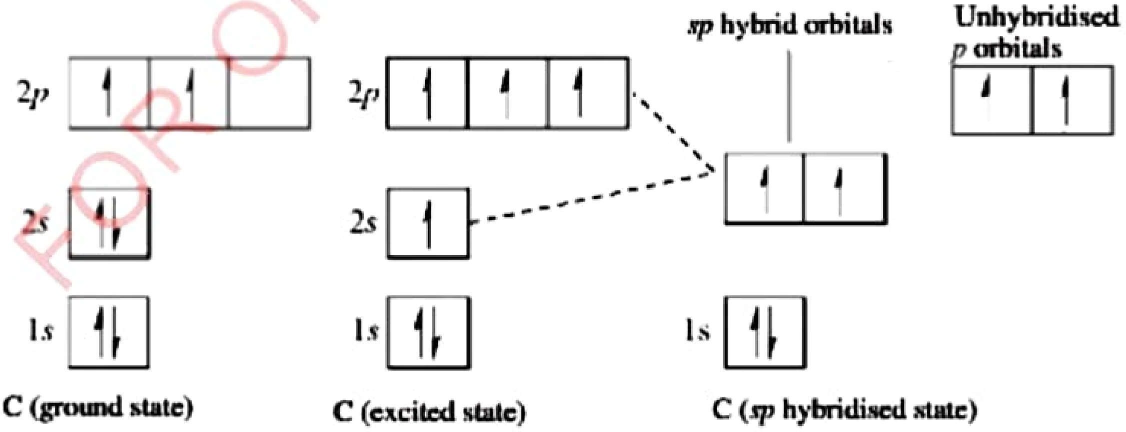


Figure 2.25: *sp hybridisation of carbon atom*

The unhybridised $2p$-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 ethyne (acetylene)

The C-C sigma bond in ethyne 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 ($C \equiv C$) 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.

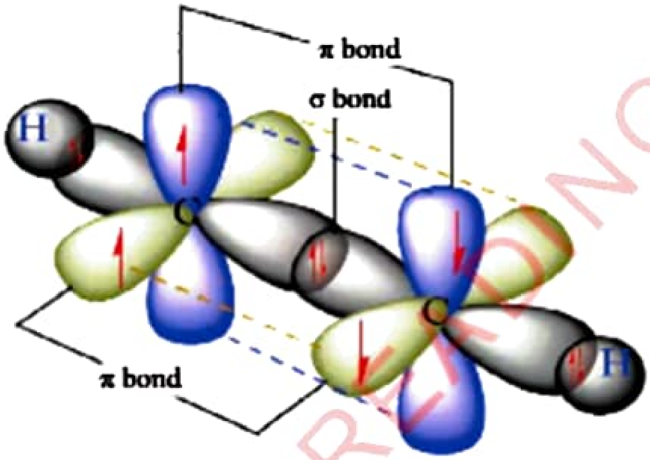


Figure 2.26: *Formation of sigma and pi bonds in ethyne (acetylene)*

sp^2 hybridisation

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

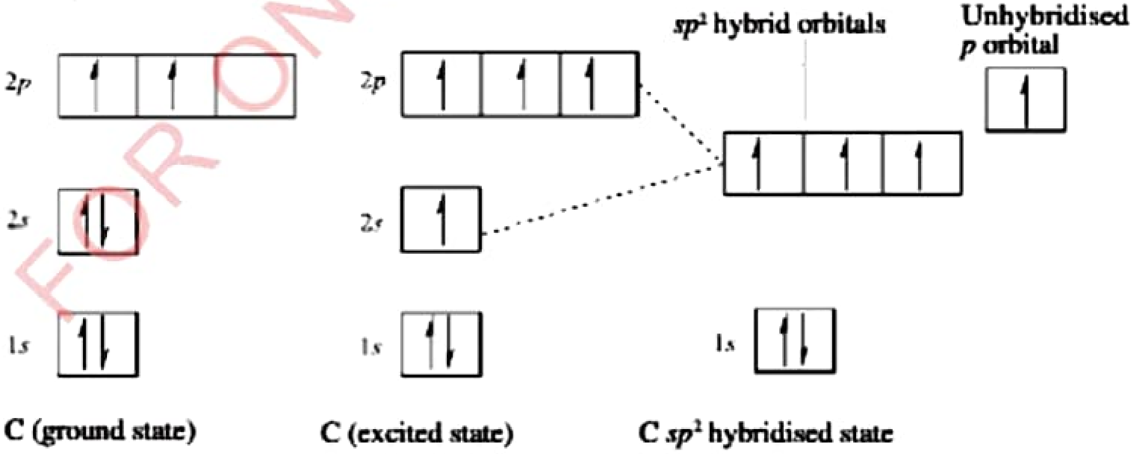


Figure 2.27: *sp^2 hybridisation of carbon atom*

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).

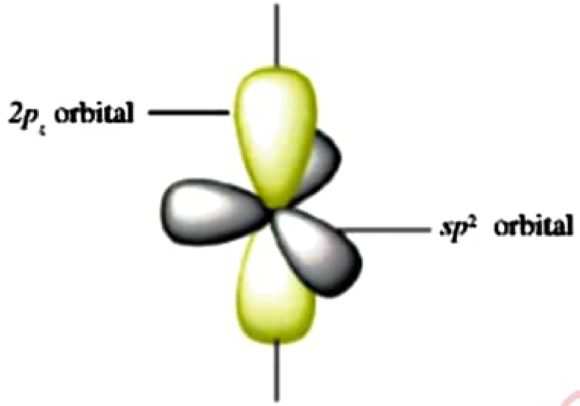


Figure 2.28: *The unhybridised $2p_z$ orbital*

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 a strong σ bond. The two unhybridised orbitals ($2p_z$) from two carbon atoms undergo sideway overlap to form a weak pi (π) bond. This bond has two regions of electron density, one above and one below the σ bond axis. The π bond holds two electrons that moves through both regions of the bond. Therefore, one σ bond and one π bond constitute the double bond of ethene (Figure 2.29).

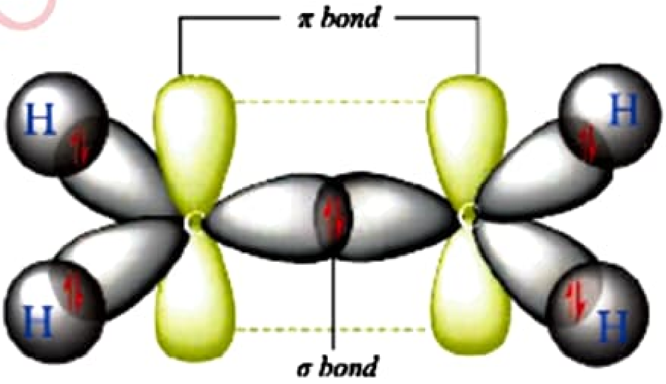


Figure 2.29: *Formation of π and σ bond in ethene*

sp^3 hybridisation

The $2s$ orbitals and three $2p$-orbitals hybridise to form four sp^3 hybrid orbitals as in Figure 2.19.

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

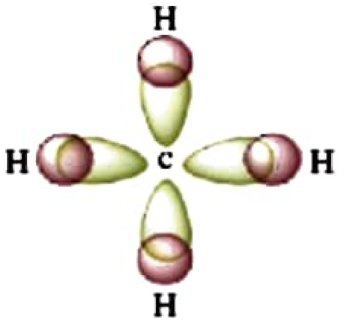


Figure 2.30: *sp^3 hybrid orbitals overlap in methane*

Exercise 2.3

1. Using examples, describe the process of hybridisation of atomic orbitals.
2. The bond angles in ammonia (107.3°) and methane (109.5°) differ, although they both have tetrahedral electron geometry. Explain.
3. In each of the following, identify the type of hybridisation, and hence, give the geometrical shape.

   (a) H_2S (b) CS_2

   (c) Cl_2O (d) NH_3

4. Identify the stronger bond between each of the following pairs. Give reasons in each case.

   (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

Revision exercise 2

1. Explain the forces necessary for the formation of ionic and covalent bonds.
2. Explain any three applications of the ionic compounds.

3. Ammonium chloride exhibits three types of chemical bonds. Justify this statement with the aid of chemical structures.

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

5. 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				
CF_4				
H_2O				
$AlCl_3$				

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

7. Account for the following observations:
   (a) Although CO_2 and SO_2 have the same empirical formulae, CO_2 is non-polar while SO_2 is polar.
   (b) The physical properties of water are mostly influenced by hydrogen bonding.

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

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

9. Use the VSEPR theory to compare the molecular geometries of SO_2 and CO_2.

10. Some molecules undergo similar hybridisation, yet they show different geometrical shapes. Justify this statement with any three examples.

11. Draw the molecular geometries of the following molecules using the VSEPR theory:

   (a) SF_4

(b) ClF_4

(c) BrF_5

(d) SO_4^{2-}

(e) PCl_5

12. Explain the importance of hydrogen bonding in real-life situations.

Chapter Three

Periodic classification

Introduction

Elements are organised based on the similarities and differences in their physical and chemical properties to form a periodic table, which simplifies their study. Studying the physical and chemical trends in the behaviours of elements in the periodic table enables chemists to explore the relationships and reactions involving the elements. Such knowledge is advantageous in various applications, including the selection of alternative elements for specific uses. In this chapter, you will learn the development of the periodic table and periodic trends of elements in the modern periodic table and analyse the periodic trends of elements in relation to their physical and chemical properties. The competencies developed from this chapter will enable you to describe the properties and uses of elements based on their observed reactions.

Think

Chemistry without a periodic table

3.1 Concept of periodicity

The concept of *periodicity* of elements is fundamental to the study of chemistry. Periodicity refers to the recurring patterns observed in the properties of elements when they are arranged in order of increasing atomic number. Periodicity is beautifully captured in the periodic table as a systematic arrangement of elements that serves as a roadmap for understanding the behaviours of different elements. Periodicity gives the basis for the composition of matter and its implications for the chemical behaviours of elements. It sets the benchmark for a deeper exploration of the relationships between elements and the underlying principles that govern their interactions.

3.1.1 Development of the modern periodic table

Task 3.1

Conduct an online search to determine the origin of the modern periodic table.

The modern periodic table is a result of efforts of some prominent scientists who utilised their time to learn how best they could arrange the elements based on similar physical and chemical properties. The development of the modern periodic table is therefore associated with several ideas of different scientists.

Johann Wolfgang Döbereiner (1780-1849)

In 1829, a Chemist Johann Wolfgang Döbereiner noticed that many of the known elements could be grouped in a set of three elements that have similar properties. These sets of elements were called *triads*. Examples of the Döbereiner's triads are shown in Table 3.1.

Table 3.1: *Döbereiner's triads*

Element	Relative atomic mass	Element	Relative atomic mass	Element	Relative atomic mass	Element	Relative atomic mass
Li	7	Ca	40	Cl	35.5	S	32
Na	23	Sr	88	Br	80	Se	79
K	39	Ba	137	I	127	Te	128

Johann Wolfgang Döbereiner suggested that all the elements could be grouped in forms of triads. Later attempts to expand the Döbereiner's concept were unsuccessful. However, it is currently known that some portions of the periodic table, for example, sulfur, selenium, and tellurium in group VIA, or aluminium, gallium, and indium in group IIIA have significant similarities in their chemistry. Döbereiner also discovered that the relative atomic mass of the middle elements in each triad, were close to the average of the relative atomic masses of the other two elements. This discovery provided a significant clue to other scientists on the importance of relative atomic masses when arranging the elements.

John Alexander Newlands (1837–1898)

In 1863, a Chemist John Alexander Newlands observed that, if elements are arranged in the order of increasing atomic masses, the eighth element starting from a given one was almost a repetition of the first in terms of structure and chemical properties. This finding was comparable to the eighth note of the music notes, hence the use of the word octave. Newlands called it the *law of octaves*. The Newlands' arrangement of the elements in the order of increasing relative atomic masses is shown in Table 3.2.

Table 3.2: *Parts of the Newlands' arrangement of elements into octaves*

H	Li	Be	B	C	N	O
F	Na	Mg	Al	Si	P	S
Cl	K	Ca	Cr	Ti	Mn	Fe
Co, Ni	Cu	Zn	Y	In	As	Se

The Newlands' arrangement of the elements worked well for the first 17 elements. Thus, the law of octaves was not well received and was ignored for years.

The increasing number of the known elements was a motivation for scientists to work hard towards the stable periodic table based on the arrangement of the elements according to their properties. As a result, the Chemists Julius Lothar Meyer and Dmitri Ivanovich Mendeleev created the first periodic table at almost the same time while working independently. Both Meyer and Mendeleev focused on the relationships between atomic masses and various physical and chemical properties. These two scientists can be considered as the co-creators of the modern periodic table, though Mendeleev received more credits.

Julius Lothar Meyer (1830-1895)

In 1864, Meyer produced the first periodic table of only 28 elements, which were organised by their valences. The table showed elements with similar properties often shared the same valence. Between 1864 and 1870, Meyer produced several versions of the periodic table. In 1869, Meyer compiled a periodic table, which consisted of 56 elements based on regular repeating patterns of physical properties such as molar volume. The periodic table according to Meyer is shown in Table 3.3. The question marks in some elements indicate that those elements were likely to exist, but they were not discovered by that time.

Table 3.3: *The periodic table as suggested by Julius Lothar Meyer*

I	II	III	IV	V	VI	VII	VIII	IX
	B (11)	Al (27.3)	–	–	–	? In (113.2)	Tl (202.7)	
				–				
	C (11.97)	Si (28)				Sn (117.8)		Pb (206.4)
			Ti (48)		Zr (89.7)			
	N (14.01)	P (30.9)		As (74.9)		Sb (122.1)		Bi (207.5)
			V (51.2)		Nb (93.7)		Ta (182.2)	
	O (15.96)	S (31.98)		Se (78.0)		Te (128?)		
			Cr (52.4)		Mo (95.6)		W (183.5)	
	F (19.1)	Cl (35.38)		Br (79.85)		I (126.5)		
			Mn (54.8)		Ru (103.5)		Os (198.6?)	
			Fe (55.9)		Rh (104.1)		Ir (196.7)	
			Co & Ni (58.9)		Pd (106.2)		Pt (196.7)	
Li (7.01)	Na (22.96)	K (39.04)		Rb (85.2)		Cs (132.7)		
			Cu (63.3)		Ag (107.66)		Au (196.2)	
Be (9.3)	Mg (23.9)	Ca (39.9)		Sr (87.0)		Ba (136.8)		
			Zn (64.9)		Cd (111.6)		Hg (199.8)	

The molar volume or atomic volume was obtained by dividing the molar mass (atomic mass) in grams per mole by the density of the elements in grams per cubic centimetres as shown in the following formula:

$$\text{Molar volume (cm}^3\text{/mol)} = \frac{\text{Molar mass (g/mol)}}{\text{Density (g/cm}^3\text{)}}$$

The variations in molar volumes against atomic numbers as per Meyer's plot are shown in Figure 3.1. Alkali metals appear to have the highest molar volumes. Non-metals appear in the rising parts of the graph, while metals appear at the top, bottom, and on the down slope.

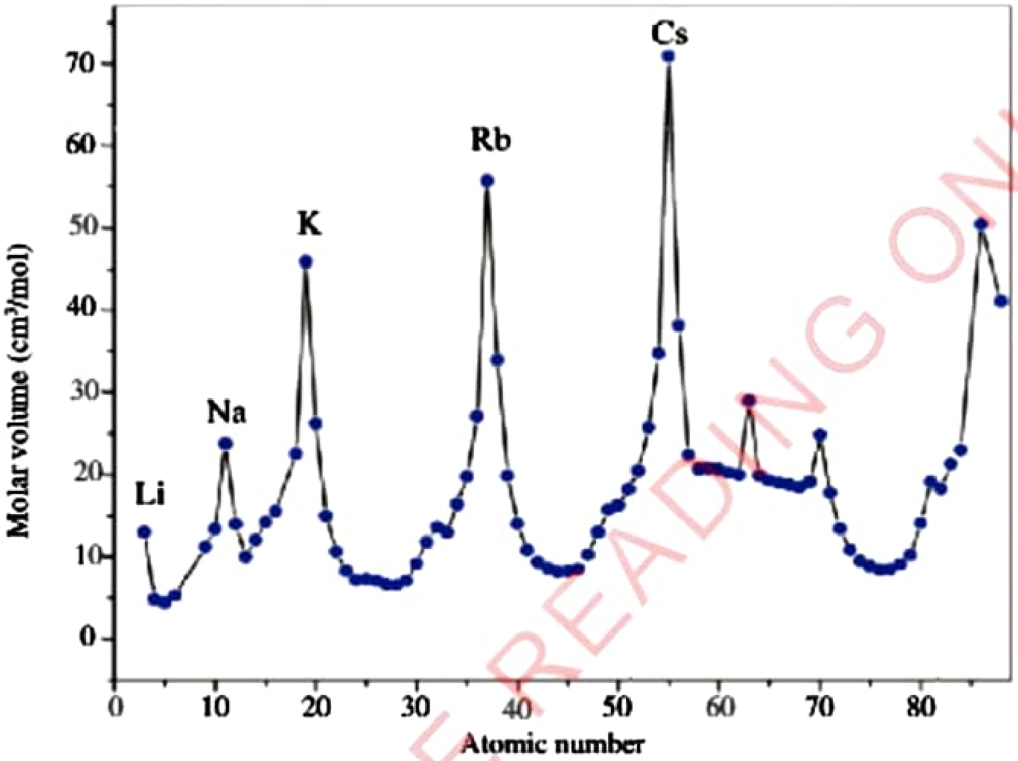


Figure 3.1: *Graph of molar volumes of atoms (cm^3mol^{-1}) against atomic numbers*

Although Meyer failed to classify the elements correctly, he made a very significant contribution towards the development of the modern periodic table.

Dmitri Ivanovich Mendeleev (1834–1907)

In 1869, Dmitri Ivanovich Mendeleev compiled the periodic table of the known elements in ascending order of their atomic weights. Mendeleev developed the Newlands' idea by placing elements with similar properties into groups and periods. He put forward the periodic law, which states that the properties of the elements are a periodic function of their atomic weights. Mendeleev predicted the existence and properties of new elements and left the gaps for unknown elements. For instance, Mendeleev left a gap below silicon and called the yet undiscovered element as eka-silicon. Similarly, this scholar named scandium as eka-boron and gallium as eka-aluminium. Most of the Mendeleev's predictions were proved correct when the elements in question were subsequently discovered. Table 3.4 shows the Mendeleev's periodic table based on the original table of 1871. In this table, the spaces marked with dash lines represent the elements that Mendeleev deduced their existence but were not known by that time, so, he left spaces where they can best fit. The question marks before symbol indicate the uncertainty in the name of some elements.

Table 3.4: *Mendeleev`s 1871 periodic table*

Period	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
1	H = 1							
2	Li = 7	Be = 9.4	B = 11	C = 12	N = 14	O = 16	F =19	
3	Na = 23	Mg = 24	Al = 27.3	Si = 28	P = 31	S = 32	Cl = 35.5	
4	K = 39	Ca = 40	--- = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Co = 59,
5	(Cu = 63)	Zn = 65	--- = 68	--- = 72	As = 75	Se = 78	Br = 80	Ni = 59, Cu = 63.
6	Rb = 85	Sr = 87	?Yt = 88	Zr = 90	Nb = 94	Mo = 96	--- = 100	Ru =104, Rh = 104,
7	(Ag =108)	Cd = 112	In = 133	Sn =118	Sb = 122	Te = 125	J = 127	Pd =106, Ag = 108.
8	Cs = 133	Ba = 137	?Di =138	?Ce =140	---	---	---	--- --- --- ---
9	(---)	---	---	---	---	---	---	
10	---	---	?Er =178	?La =180	Ta = 182	W = 184	---	Os = 195, Ir = 197
11	(Au = 199)	Hg = 200	Ti = 204	Pb = 207	Bi = 208	---	---	Pt = 198, Au = 199
12	---	---	---	Th = 231	---	U = 240	---	--- --- --- ---

Features of the Mendeleev's periodic table

The Mendeleev's periodic table of elements consists of twelve horizontal rows of elements called *periods*, and eight vertical columns called *groups*. The Mendeleev's work is summarised in the following statements:

(a) If the elements are arranged according to their atomic weights, they exhibit an apparent periodicity of properties.

(b) Elements which are similar in chemical properties have atomic weights which are similar in values or which increase regularly.

(c) The arrangements of the elements or groups of the elements in the order of their atomic weights correspond to their valences.

(d) Elements with small atomic weights diffuse widely, and the magnitude of their atomic weights determines their properties.

(e) It was expected that there could be discoveries of new elements that were not yet known, for example, elements that are analogous to aluminium and silicon whose atomic weights would be between 65 and 75.

(f) The atomic weight of an element may sometimes be amended based on the knowledge of the closely related elements.

Usefulness of the Mendeleev's periodic table

The Mendeleev's classification of elements was useful in various ways. Elements with similar chemical properties appeared in the same group. For example, the groups for halogens, alkali metals, and alkaline earth metals were already identified. The table was also useful in predicting the existence and properties of the elements, which were not yet discovered. The positions of such elements in the table were left empty. The table was also useful in checking the relative atomic masses of the elements. Although some elements had more than one valence, particular valences were associated with particular groups. The valences and the equivalent weights were used to check the correctness of several doubtful atomic masses.

Shortcomings of the Mendeleev's periodic table

The following are the shortcomings of the Mendeleev's periodic table:

(a) Mendeleev failed to assign a correct position for hydrogen in his periodic table because it resembles the elements of group IA as well as elements of group VIIA.

(b) The 14 rare earth metals were placed in the same group (group VIII) even though they have different atomic weights.

(c) Some pairs of elements had to be included in inverse order of their relative atomic masses so as to maintain the correct relationships of the elements. Examples of these pairs were argon (39.9) and potassium (39.1), cobalt (58.9) and nickel (58.7), tellurium (128) and iodine (127).

These shortcomings called for modifications that resulted into the development of the modern periodic table.

Henry Gwyn Moseley (1887–1915)

Henry Gwyn Moseley was a Physicist who developed the application of x-ray spectra to study atomic structure. The Moseley's discoveries resulted in a more accurate positioning of the elements in the periodic table by atomic numbers. In 1913, Moseley published the results which showed that the ordering of the wavelengths of the x-ray emissions of the elements corresponded to the ordering by their atomic numbers. This discovery revealed that the properties of the elements in the periodic table varied periodically with atomic numbers and not atomic weights as proposed by Mendeleev, Meyer, and others. The arrangements of the elements in the order of increasing atomic numbers eliminated the shortcomings of the Mendeleev's periodic table. The Moseley's work led to the formulation of the modern periodic table and the periodic law based on the atomic numbers. The modern periodic law states that, the chemical and physical properties of elements are the periodic functions of their atomic numbers.

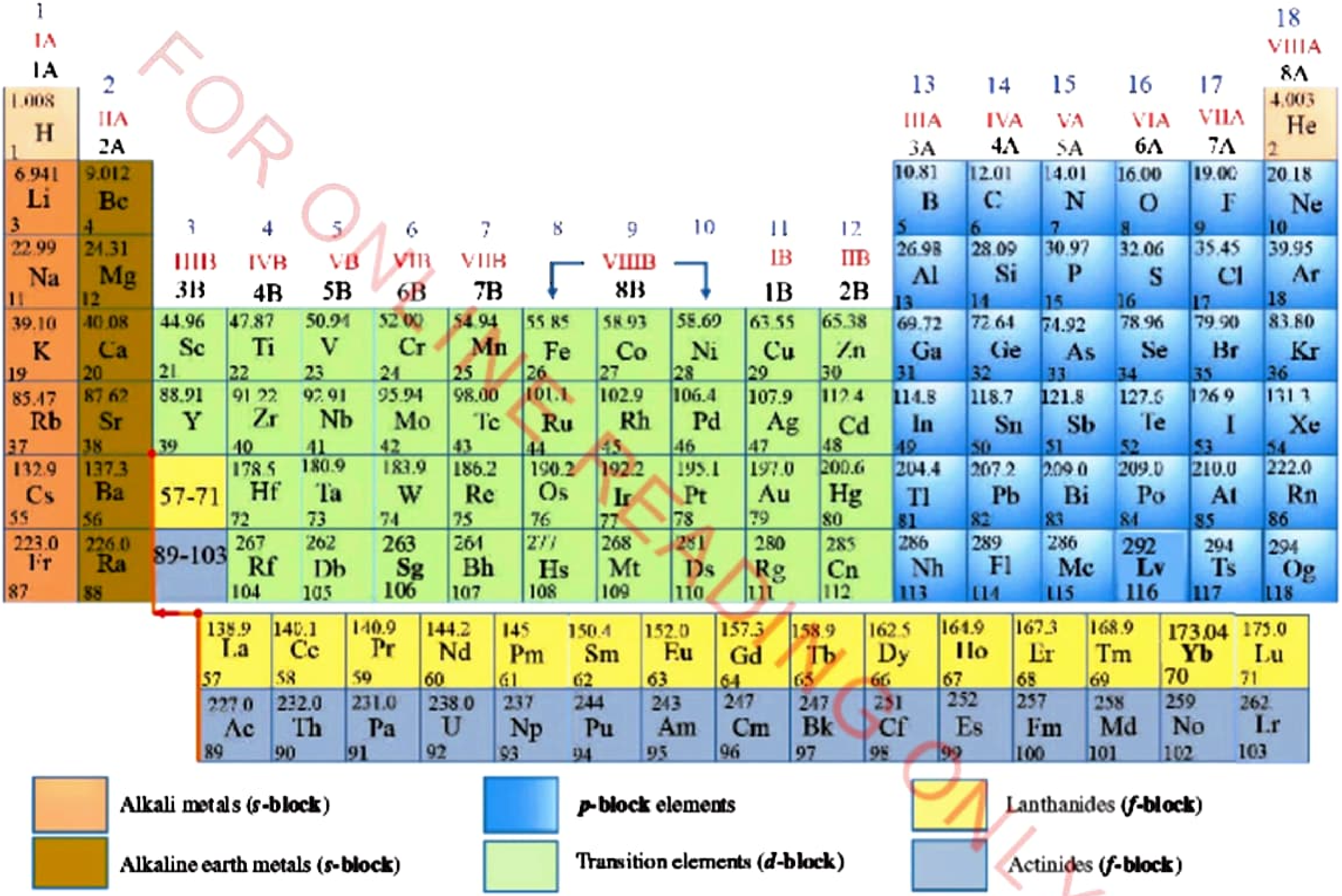
3.1.2 Features of the modern periodic table

The modern periodic table consists of seven horizontal rows called *periods* and eighteen vertical columns called *groups*. A group in the periodic table is a set of elements which have the same numbers of electrons in their outermost shells and hence, have similar properties. On the basis of Table 3.5, the first group (group IA) consists of elements known as *alkali metals,* which have one electron in their outermost shells. The second group (group IIA) consists of elements known as *alkaline earth metals,* which have two electrons in their outermost shells. The elements in groups IIIA, IVA, VA, and VIA have three, four, five, and six electrons, respectively in their outermost shells. The group VIIA consists of elements which have seven electrons in their outermost shells, these elements are known as *halogens*. The elements in group VIIIA have eight electrons in their outermost shells and are collectively known as *noble gases*. The elements in groups IA, IIA to VIIIA are called main group elements. The elements from group 3 (group IIIB) to group 12 (group IIB) are called *transition elements*.

A period in the periodic table is a set of elements which have the same number of electron shells and whose atomic numbers increase by one unit from one atom to another. In the period, elements are arranged in order of increasing atomic numbers. The number of electron shells increases from one period to another down the group. Within the period, the number of protons and electrons increase by one when moving from one group to another.

In the modern periodic table, the first period is the shortest with only two elements, which are hydrogen and helium. The second and third periods consist of eight elements each, which start from Li to Ne and Na to Ar, respectively. The fourth and the fifth periods are long with 18 elements each, which start from K to Kr and Rb to Xe, respectively. The sixth and seventh periods are incomplete periods of elements which are radioactive, including rare earth elements (atomic numbers 57 to 71). Elements with atomic numbers from 93 to 105 are only synthetic, discovered during atomic research. The structure of the modern periodic table is presented in Table 3.5.

Table 3.5: *Modern periodic table*



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
IA	IIA	IIIB	IVB	VB	VIB	VIIB		VIIIB		IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1A	2A	3B	4B	5B	6B	7B		8B		1B	2B	3A	4A	5A	6A	7A	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)
- Alkaline earth metals (*s*-block)
- *p*-block elements
- Transition elements (*d*-block)
- Lanthanides (*f*-block)
- Actinides (*f*-block)

Blocks of the modern periodic table

Depending on the types of orbitals occupied by the electrons in the outermost shells, the periodic table is divided into four main blocks, namely *s*-block, *p*-block, *d*-block, and *f*-block. The letters *s*, *p*, *d*, and *f* were coined from the properties of spectral lines observed from the hydrogen atom, which were sharp (*s*), principal (*p*), diffuse (*d*), and fundamental (*f*). The division of the periodic table into blocks is shown in Figure 3.2.

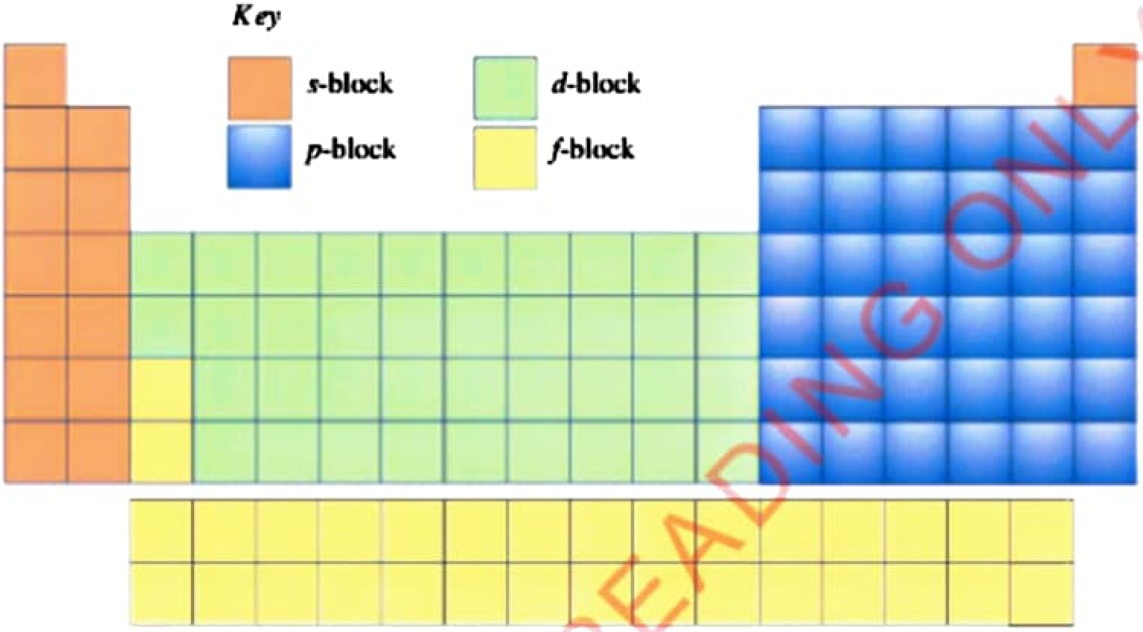


Figure 3.2: Sketch of the periodic table showing location of the s, p, d, and f-blocks

The *s*-block consists of elements whose outermost electrons occupy the *s*-orbitals. It constitutes the elements in groups IA and IIA, and helium (He), which is found in group VIIIA. The *p*-block consists of elements whose outermost electrons occupy the *p*-orbitals and constitutes the elements in groups IIIA to VIIIA with the exception of helium (He).

The *s* and *p*-blocks collectively form the main group elements whose general outer electronic configurations are $ns^{1\text{ to }2}$ and $ns^2np^{1\text{ to }6}$, respectively. Groups IB to VIIIB form *d*-block elements whose outermost electrons occupy the *d*-orbitals. These elements have the general outer electronic configuration of $(n\text{-}1)\,d^{1\text{ to }10}\,ns^{1\text{ to }2}$.

Similarly, *f*-block consists of elements whose outermost electrons occupy the *f* orbitals. Elements in the *f*-block include lanthanides (atomic numbers 57 to 71) and actinides (atomic number 89 to 103) whose general outermost electronic configuration is $(n\text{-}2)f^{1\text{ to }14}\,(n\text{-}1)\,d^{1\text{ to }10}\,ns^{1\text{ to }2}$. The *d* and *f*-block elements are collectively known as ***transition elements*** as they exhibit transition behaviours between *s* and *p*-block elements. Transition elements can be further classified into outer transition (*d*-block) and inner transition elements (*f*-block).

3.1.3 Comparison between the Mendeleev's and the modern periodic tables

The arrangements of elements using atomic masses and atomic numbers resulted into differences and similarities in the study of elements in the periodic table. The use of atomic weights in arranging the elements resulted into the Mendeleev's periodic table. The modern periodic table arose due to the placement of the elements by considering their atomic numbers. The following are the similarities between the Mendeleev's and modern periodic tables:

(a) Both used columns and rows to classify elements.

(b) Both tables aimed at simplifying the study of the elements.

(c) Both tables indicated periodicity properties of the elements.

The differences between the Mendeleev's and modern periodic tables are presented in Table 3.6.

Table 3.6: *Differences between the Mendeleev's and the modern periodic table*

Mendeleev's periodic table	Modern periodic table
Elements were arranged in order of increasing atomic weights.	Elements are arranged in order of increasing atomic numbers.
The table consisted of gaps for unknown elements.	There are no gaps in the modern periodic table
Elements with different properties were placed together.	Elements with different properties are placed in different groups and periods.
Rows of inner transition elements were not included.	Rows of inner transition elements are included.
Failed to locate the position of hydrogen.	Hydrogen is placed on top of group one.
Elements with higher atomic masses were placed before the elements with lower atomic masses. For example, argon (atomic mass 39.9) was placed before potassium (atomic mass 39.1).	The anomalies of having higher atomic masses of elements before elements with lower atomic masses are resolved.
Isotopes of the same elements were placed differently.	Isotopes of the same elements are placed together.

Activity 3.1

Aim: To design a simple modern periodic table

Requirements: Manila sheets of five different colours, pair of scissors, glue or office pins, marker pens, ruler, and pencil

Procedure

1. Prepare 30 small cards in four different colours from manila sheets.
2. Label the cards with respective element symbols starting from the 1st to the 30th.
3. Design a modern periodic table by fixing on the manila sheet the labelled cards on the appropriate positions using office pins or glue.
4. Present your designed periodic table by giving reasons for the placements of elements in such trends.

Questions

1. What do the colours indicate in the periodic table?
2. How is your design useful in explaining the physical and chemical properties of the elements?

Exercise 3.1

1. Explain the merits of the modern periodic table over others.
2. How was the law of octaves used in creating a periodic table?
3. Explain the Meyer's classification of elements.
4. What is the contribution of the Mendeleev's periodic law in the development of the modern periodic table?
5. The arrangement of elements in the periodic table is periodic. Explain.
6. Explain the significance of the periodic table in chemistry.
7. Describe the basis for classifying elements into different blocks in the modern periodic table.
8. What would be the impacts on the existing periodic table if new elements are discovered?

3.2 Periodic trends in properties of elements

Periodic trend is a regular variation in the properties of the elements with increasing atomic number, caused by regular variations in the atomic structures of the elements. The arrangement of elements using the atomic numbers in the modern periodic table makes it easy to study the trends of the physical and chemical properties of the elements across the periods and down the groups of the periodic table.

3.2.1 Periodic trends in physical properties of elements

The major periodic trends in physical properties include atomic size, ionisation energy (IE), electron affinity (EA), electronegativity, metallic character, melting points (mp), and boiling points (bp). The following are trends of the physical properties of elements down the group and across the period:

Atomic size

Atomic size is determined by the atomic radius, which is one-half the distance between the nuclei of two covalently bonded atoms. For monoatomic elements such as noble gases, the atomic size is simply the diameter of the whole atom, which is equal to two times the radius of the isolated atom (also called van der Waals radius). In general, the atomic radius is determined by two factors, which are the effects of the nuclear charge and the screening effect.

Effect of nuclear charge

The nuclear charge is the attractive force that pulls all the electrons closer to the nucleus. The higher the nuclear charge, the smaller the atomic radius. The atomic radii decrease from left to right of the period. This is due to the increase in effective nuclear charge caused by an increase in the number of protons, while the number of shells remains the same. Down the group, the atomic radii increase. This happens due to the decrease in the effective nuclear charge caused by an increase in the number of shells.

Screening (shielding) effect

Screening effect is the tendency of the innermost electrons to prevent the outermost electrons from receiving full influence of proton from the nucleus. The shielding effect is caused by the repulsion force between the electrons in the inner shell and those in the outer shell. This effect lowers the effective nuclear charge to the outermost shell, causing the increase in the atomic radius. The higher the number of shells, the stronger the screening effect and vice versa.

Generally, the atomic sizes decrease from left to right across the period (Figure 3.3). This is due to an increase in the number of electrons and protons, resulting in the effective nuclear charge, which then pulls the outer electrons closer. Despite the fact that the number of protons increases proportionally to the number of electrons across the periods, the sizes of the atoms decrease because the number of shells remains constant. This in turn increases the effective nuclear charge, which outweighs the screening effect. Appendix 1 shows both the empirical and calculated atomic radii for most of the elements.

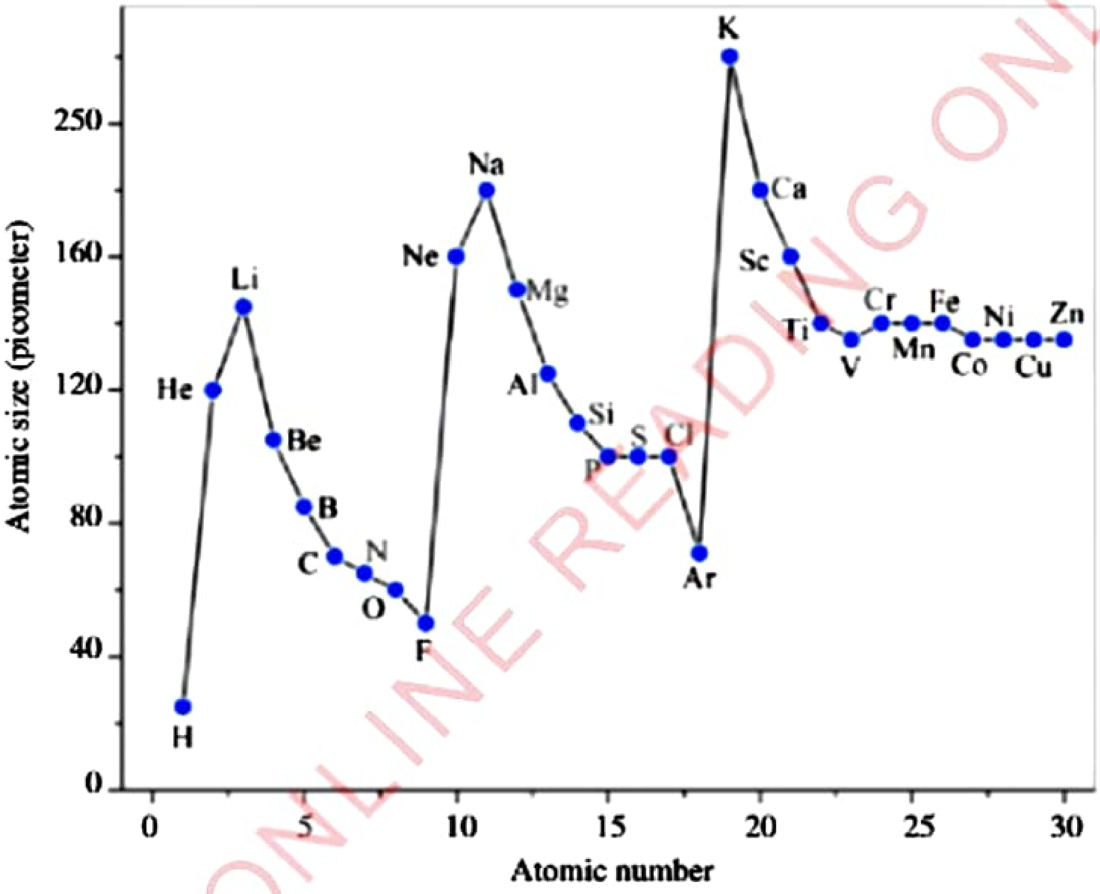


Figure 3.3: *Periodic trend in atomic sizes*

On the other hand, the atomic sizes increase down the group. This happens because an increase in the number of shells makes the outer electrons to be far away from the nucleus. Atomic sizes increase down the group due to the increase in the number of shells. The increase in the number of shells increases both the distance between the outer electrons and the nucleus as well as the number of inner electrons. The increased number of electrons causes an increase in the screening effect to the outer electrons, which decreases the effective nuclear charge and therefore, increasing the atomic sizes.

Ionic radii

The ionic radius is half the distance between two ions that are barely touching each other. Depending on the electronic charge of an ion, the ionic radius may be larger or smaller than the atomic radius (the radius of a neutral atom). Neutral atoms have larger atomic radii than their corresponding cations. This is because electrons are removed, and the remaining fewer electrons in cation experience stronger nuclear attractive forces.

For the atoms that consist of only one electron in the outermost shell, the removal of one electron during ionisation is accompanied by the loss of the shell, causing smaller ionic radii. Additionally, when an electron is removed from the outermost shell, the remaining fewer electrons experience a weaker electron-electron repulsion and therefore, are strongly attracted to the nucleus. An anion has a larger ionic size than a neutral atom because the addition of electron increases the size of the electron cloud.

Moreover, in anions, the nuclear attractive force is distributed to a larger number of electrons. As a result, the electrons experience weaker nuclear attractive forces than a neutral atom. These weaker nuclear attractive forces are also attributed to an increase in the electron-electron repulsion due to the additional electrons. Therefore, the general trend in ionic radii is the same as that of the atomic radii, which decrease across the period due to the increased effective nuclear charge, and increases down the group because of an increase in the number of shells.

Ionisation energy

In order to remove an electron from an atom, energy must be applied to overcome the electrostatic forces of attraction between the electron and the nucleus. This energy is called *ionisation energy* (IE). The ionisation energy is the minimum amount of energy required to completely remove one mole of the electrons from one mole of a gaseous atom or ion. It is expressed in kilojoules per mole (kJ/mol). The lower the ionisation energy, the more easily the atom becomes a cation and vice versa. Ionisation energy is determined by the atomic size, nuclear charge, screening or shielding effect, electron locality in orbitals, and electronic configuration.

Atomic size

As the size of an atom increases, the distance between the nucleus and valence electrons also increases. As a result, the force of attraction between the nucleus and valence electrons decreases. This makes the valence electrons to be loosely held and therefore, require smaller energy to remove an electron. Thus, the ionisation energy decreases with increase in the atomic sizes (down the group) and increases with the decrease in the atomic sizes (along the period).

Nuclear charge

An increase in the nuclear charge causes an increase in the force of attraction between the nucleus and valence electrons. This makes it difficult to remove an electron from a valence shell. Therefore, an increase in the nuclear charge causes the ionisation energy to increase.

Screening or shielding effect

Electrons that are present in the shells between the nucleus and the valence shell reduce the electrostatic attractions between the nucleus and the outermost electrons. The larger the number of electrons in the inner shells, the greater the screening effect and hence, the easier the removal of an electron (lower ionisation energy).

Electron locality in orbitals

Within the same energy level, the *s*-electrons are closer to the nucleus than the *p*-electrons, *d*-electrons, and lastly *f*-electrons. Hence, electrons in *s*-orbitals experience more attraction from the nucleus than those in the *p, d*, and *f*-orbitals. Therefore, ionisation energy within a certain energy level decreases in the trend $s > p > d > f$. This means that the *s*-electrons have the highest ionisation energies, and the *f*-electrons have the lowest ionisation energies.

Electronic configuration

Atoms whose orbitals are full-filled or half-filled with electrons have stable electronic configurations. Therefore, these atoms have a low tendency of losing electrons, hence high ionisation energies. It is important to note that it is possible to remove more than one electron from an atom. In this case, there are different types of ionisation energies starting from the 1st, 2nd, 3rd to the nth ionisation energy, depending on the valence of an atom.

First ionisation energy (1st IE) is the energy which is required to remove one mole of the most loosely held electrons from one mole of a gaseous atom to produce one mole of gaseous ion with a charge of positive one (+1).

$$X(g) \longrightarrow X^{+}(g) + e \qquad 1^{st}\ IE$$

Second ionisation energy (2nd IE) is the energy which is needed to remove a second electron from one mole of a unipositive gaseous ion to form a *di*-positive gaseous ion.

$$X^{+}(g) \longrightarrow X^{2-}(g) + e^{-} \qquad 2^{nd}\ \text{IE}$$

If an atom has two or more electrons in the valence shell, the amount of energy needed to remove the 2nd, 3rd and nth electrons increases steadily. That is, the 1st ionisation energy is always lower than the 2nd and subsequent ionisation energies. This is because when the first electron is removed (1st IE), the remaining fewer electrons experience stronger nuclear attractive effects. In addition, the attractive effects between the electrons in the valence shell and the positive charge created by the 1st ionisation make it difficult for the second electron to be removed, and hence needs higher second ionisation energy (2nd IE). The first and the other successive ionisation energies for Na, Mg, and Al are shown in Table 3.7.

Table 3.7: *Ionisation energies for Na, Mg, and Al in kJ mol^{-1}*

Element	1st IE	2nd IE	3rd IE	4th IE
Na	496	4565	6912	9540
Mg	738	1450	7732	10550
Al	577	1816	2744	11580

For sodium (Na), the 1st IE involves the removal of one electron from the outer 3*s*-orbital, but the second should be removed from the full-filled inner 2*p*-orbitals, which have a stable configuration. In magnesium, the 2nd IE involves the removal of an electron from the charged magnesium ion (Mg^{+}), which has an extra nuclear charge, hence needs higher ionisation energy. To remove a third electron (3rd IE) is even more difficult because the electron should come from the full-filled inner 2*p*-orbitals. The same argument holds during the formation of aluminium ion (Al^{3+}).

Task 3.2

Use a software to create graphical representations of the first, second, third, and fourth ionisation energies as listed in Table 3.7. Employ these graphs to analyse shared patterns and variations.

Periodic trends in the ionisation energies

Generally, the ionisation energies (IEs) increase from left to right across a period . This is due to the increase in the effective nuclear charge, which holds the electrons tightly. The IEs decrease down the group due to the increase in the number of shells and hence, increasing the electron distance from the nucleus, which lowers the attraction for the electrons. Despite this general trend, there is a large discrepancy in the IEs for the various elements in the periodic table. Figure 3.4 shows a sketch of the 1st IEs against the atomic numbers. The discrepancy in the trends of the IEs is observed between beryllium (Be) and boron (B), and nitrogen (N) and oxygen (O) in period 2, and between magnesium (Mg) and aluminium (Al), and phosphorus (P) and sulfur (S) in period 3.

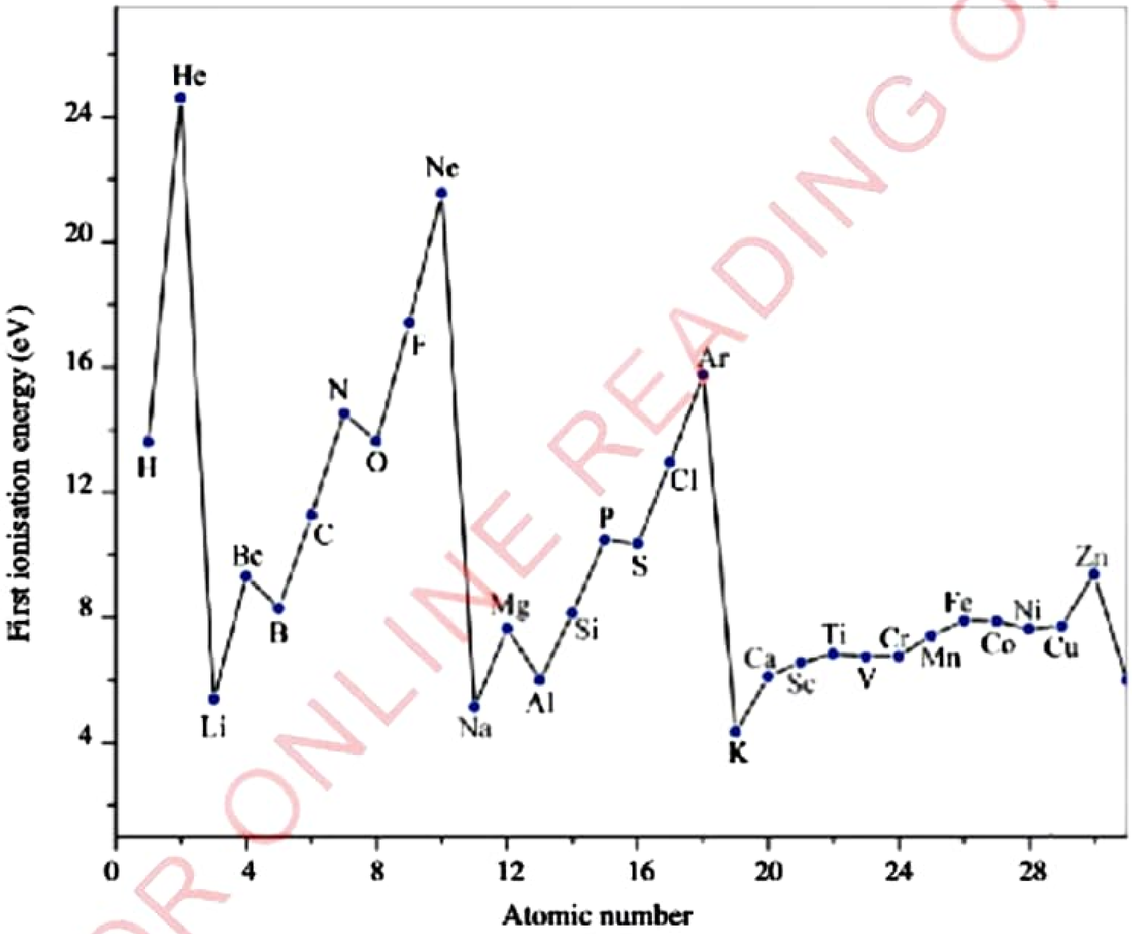


Figure 3.4: *First ionisation energies for some elements*

Explanation of the observed trends

Beryllium and boron

The decrease in IEs across the period from beryllium (Be) to boron (B) does not follow the general trend of increasing the IEs across the period from left to right.

The 1st IE of Be involves the removal of an electron from the 2*s*-orbital that is full-filled with electrons. Meanwhile, the 1st IE of B involves the removal of an electron from the 2*p*-orbital that is partially filled (with one unpaired electron). Therefore, the higher IE of Be relative to that of B can be explained by two factors. First, the electrons in the 2*s*-orbital are closer to the nucleus than the electrons in the 2*p*-orbital. Therefore, they experience stronger nuclear attractive forces. Secondly, the electronic configuration of Be is full-filled with 2 electrons in 2*s*-orbitals and therefore is stable, while B is partially filled with only one electron in 2*p*-orbital of the outer most shell. This makes it easier to lose one electron and acquire stability leading to its low IE.

Nitrogen and oxygen

The decrease in the 1st IEs across the period from nitrogen to oxygen also does not follow the general trend of increasing IEs across the period from left to right. Nitrogen consists of 3 unpaired electrons in the 2*p*-orbital, which is a half-filled configuration and therefore stable. To remove an electron from this stable configuration needs a higher energy, hence higher IE. In oxygen, the outer 2*p*-orbital consists of 2 unpaired electrons and one pair of electrons. This configuration is unstable as it is neither half-filled nor full-filled. Therefore, it requires less energy to remove an electron due to the lower stability, causing its low first IE.

Magnesium and aluminium

The decrease in the 1st IE across the period is also observed when moving from magnesium (Mg) to aluminium (Al). This does not follow the general trend of the increase in 1st IEs across the period. In Mg, the 1st IE involves the removal of an electron from a set of paired electrons from 3*s*-orbital, which is full-filled hence becomes more stable. This orbital also experiences high nuclear attractive forces because it is closer to the nucleus than 3*p*. Therefore, it requires higher energy to remove the electron leading to higher 1st IE. For the case of Al, the 1st IE involves the removal of an electron from the 3*p*-orbital, which is partially filled with only one electron in 3*p*-orbital, and is higher in energy than the 3*s*-orbital. As a result, the electron is removed more easily, leaving a stable configuration, hence, low 1st IE.

Phosphorus and sulfur

Phosphorus has higher IE than sulfur due to its half-filled electronic configuration which is stable, hence, to remove an electron from phosphorus, high IE is needed. This is contrary to sulfur which has unstable electronic configuration caused by single and double occupancy of electrons in the degenerate 3*p*-orbitals, which makes it easy to remove electrons.

Activity 3.2

Aim: To investigate the variations in ionisation energies of metals through a flame test

Requirements: Glass rod or nichrome wire, Bunsen burner, beaker, watch glass, concentrated hydrochloric acid, 2g of sodium chloride, anhydrous copper(II) sulfate, magnesium chloride, calcium chloride, aluminium chloride, zinc sulfate, iron(II) chloride, and iron(III) chloride

Procedure

1. Dip the glass rod or nichrome wire into a beaker containing concentrated hydrochloric acid and heat it on a non-luminous flame of the Bunsen burner until no distinctive flame colouration is observed.
2. Dip the cooled glass rod/nichrome wire from step 1 into concentrated hydrochloric acid, pick a small amount of solid sample of sodium chloride and heat the rod/wire on a non-luminous flame. Record the colour of the resulting flame.
3. Clean the glass rod/nichrome wire using distilled water and repeat step 1 and 2, while replacing sodium chloride with another salt until all the samples are tested.
4. Tabulate the salts with the respective flame colours.

Questions

1. Why nichrome wire is dipped in concetrated hydrochloric acid?
2. Which salts gave positive flame tests?
3. How do you relate the observations made and factors affecting the ionisation energy of elements?

Electron affinity

The electron affinity (EA) of an atom or molecule is the amount of energy change when one mole of electrons is added to one mole of a gaseous atom or ion to form one mole of gaseous ions. EA is expressed in units of kJ/mol and is represented by the following general equation:

$$X(g) + ne^{-} \longrightarrow X^{n}(g) \qquad EA = \text{......} \ kJ/mol$$

Just like IE, electron affinity can be first, second, third up to the nth electron affinity depending on the valence of an atom. The first EA is the energy released when one mole of electrons is added to one mole of gaseous atom to form one mole of negative monovalent ions. For example, addition of one mole of electrons to one mole of gaseous oxygen atom.

$$O(g) + e^- \longrightarrow O^-(g) \qquad EA = -142 \text{ kJ/mol}$$

The second EA is the energy absorbed when one mole of electrons is added to one mole of negative monovalent ion to form one mole of negative divalent ions.

Example:

$$O^-(g) + e^- \longrightarrow O^{2-}(g) \qquad EA = +791 \text{ kJ/mol}$$

It is important to note that the first electron affinity is always negative because the electron is attracted to the atom's nuclear charge. The second and subsequent electron affinities are always positive. This is because the energy must be absorbed in order to overcome electrostatic repulsion and add another electron to a negative ion. In general, the electron affinity depends on the atomic size, screening or shielding effect, and electronic configuration.

Atomic size

As the sizes of atoms increase, the effective nuclear charge or the nuclear attraction for adding electron decreases. As a result, the tendency of an atom to attract additional electron towards itself decreases. Therefore, electron affinity is inversely related to the size of the atom and directly related to the effective nuclear charge.

Screening or shielding effect

Electrons closer to the nucleus of an atom hinder the nuclear attraction for the incoming electron. Therefore, the larger the number of electrons around the nucleus, the lower the electron affinity (more negative). This means that electron affinity is inversely related to the shielding effect.

Electronic configuration

Electron affinities are largely influenced by electronic configurations of the elements. If an atom has a full-filled or half-filled configuration of orbitals, its electron affinity will be low. This is because these configurations are stable and have less tendency to accept the incoming electrons, hence the lower the values of the electron affinity. If an atom has an electronic configuration that is neither half-filled nor full-filled, its electron affinity will be relatively higher because the atom is less stable and easily accepts an incoming electron to acquire stability.

Periodic trends in electron affinity

Generally, electron affinities increase (become more negative) across the period from left to right due to decrease in atomic sizes as a result of increase in the effective nuclear charge. This decrease in atomic sizes makes it possible for the nucleus to pull the incoming electrons more readily. The electron affinities decrease down the group due to an increase in the atomic sizes, which causes the decrease in the electron attraction to the nucleus.

However, the changes in electron affinities down the group are not as large as observed across the period. This is because the lower electron-nucleus attraction is counter-balanced by the lower electron-electron repulsion. This low electron-electron repulsion is caused by a large electron-electron distance due to a larger valence shell. Beside the general trend in electron affinities across the periods and down the groups, there are some observed discrepancies (Figure 3.5). Elements in group IA, namely Li, Na, K, Rb, and Cs have unexpected higher electron affinities than the corresponding elements in group IIA within the same period which are Be, Mg, Ca, Sr, and Ba, respectively. Group IA elements have one electron in the outermost *s*-orbitals, while group IIA elements have two electrons in the outermost *s*-orbitals (full-filled). Therefore, the incoming electron in group IA elements is filled in the outermost *s*-orbital having one electron, hence higher electron affinity (becomes more negative). For the case of group IIA elements, which have a full-filled outermost *s*-orbital, the incoming electron moves to the empty *p*-orbital, which is higher in energy and therefore, energetically unfavourable. As a result, these elements have lower electron affinities.

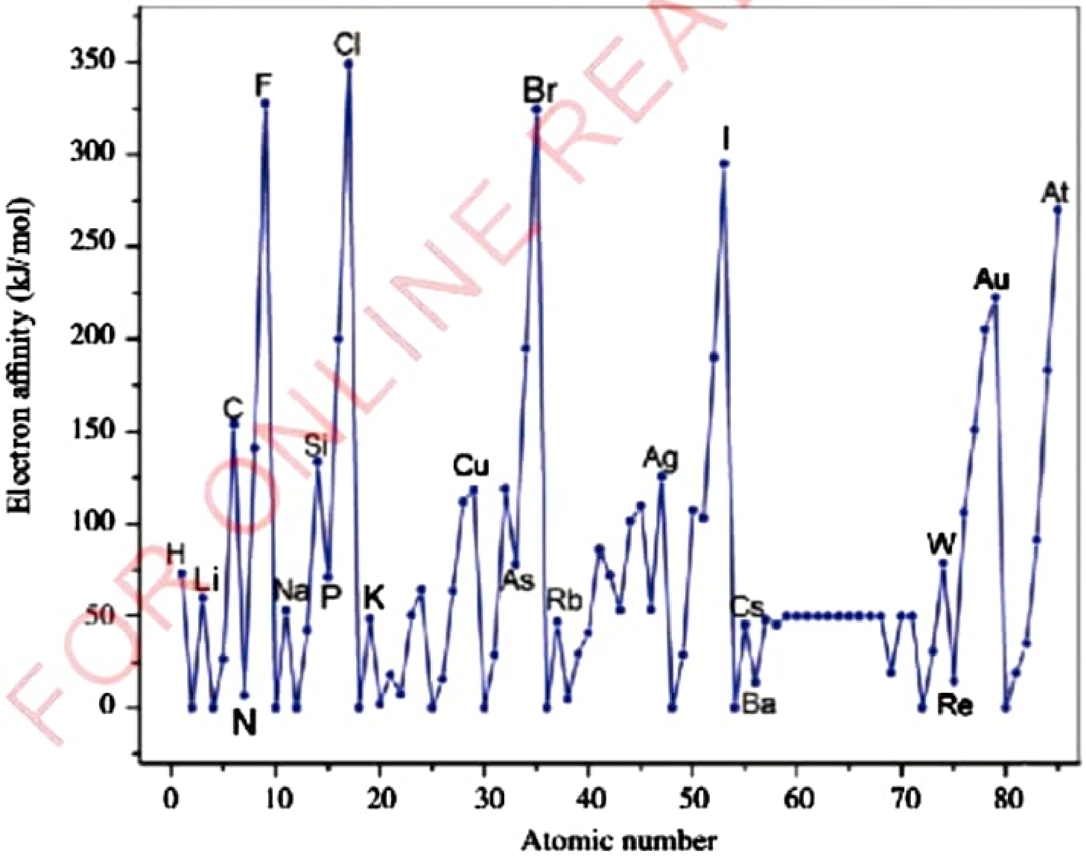


Figure 3.5: *Periodic trends in the electron affinities for main group elements as a function of atomic numbers*

Another discrepancy is observed between group IVA elements, namely C, Si, Ge, and Sn and the corresponding group VA elements, which are N, P, As, and Sb, respectively within the same period. Group IVA elements have two unpaired electrons in the outermost *p*-orbitals, and one empty *p*-orbital, while group VA have three unpaired electrons in the *p*-orbitals (half–filled), and therefore are stable. Group IVA elements need one electron to acquire half–filled configurations which are stable, and therefore, have higher electron affinities. For the case of group VA elements, the addition of one electron creates the first paired electrons in the *p*-orbital. Due to the electron-electron repulsion, this atom becomes less stable and therefore, energetically unfavourable. As a result, group VA elements have low electron affinities (less negative or more positive).

For the case of group VIIA, a discrepancy is observed between fluorine and chlorine. Electron affinity of fluorine is unexpectedly lower than that of chlorine; this is because fluorine has small size that makes electrons to accumulate within a small region of an atom (increased electron density). The incoming electrons experience more repulsion; thus, some amount of energy must be absorbed to overcome repulsion, and hence, energy released becomes smaller than expected.

Electronegativity

Electronegativity is the ability of an atom in a molecule to attract a bonding pair of electrons towards itself. An atom with high electronegativity has a strong tendency to attract electrons towards itself (high electron affinity), while resisting its electrons from being taken (high ionisation energy). Similarly, an atom with a positive electron affinity and a low ionisation energy has a very low electronegativity. This is because it does not want more electrons and can willingly give away its valence electrons. Therefore, electronegativity is closely related to ionisation energy and electron affinity.

Generally, the electronegativity increases from left to right across the period due to an increase in the effective nuclear charge. This increase in the effective nuclear charge makes it difficult for an atom to lose electrons hence leading to high ionisation energy and an increase in the electron affinity. Down the group, the electronegativity decreases due to a decrease in the effective nuclear charge. This decrease in the effective nuclear charge accounts for the decrease in the ionisation energy and a small decrease in the electron affinity. Just like other periodic properties, the trend in electronegativity shows some discrepancies in the transition elements. However, these discrepancies are not observed in the main group elements. The periodic trend in electronegativity as a function of atomic numbers is shown in Figure 3.6.

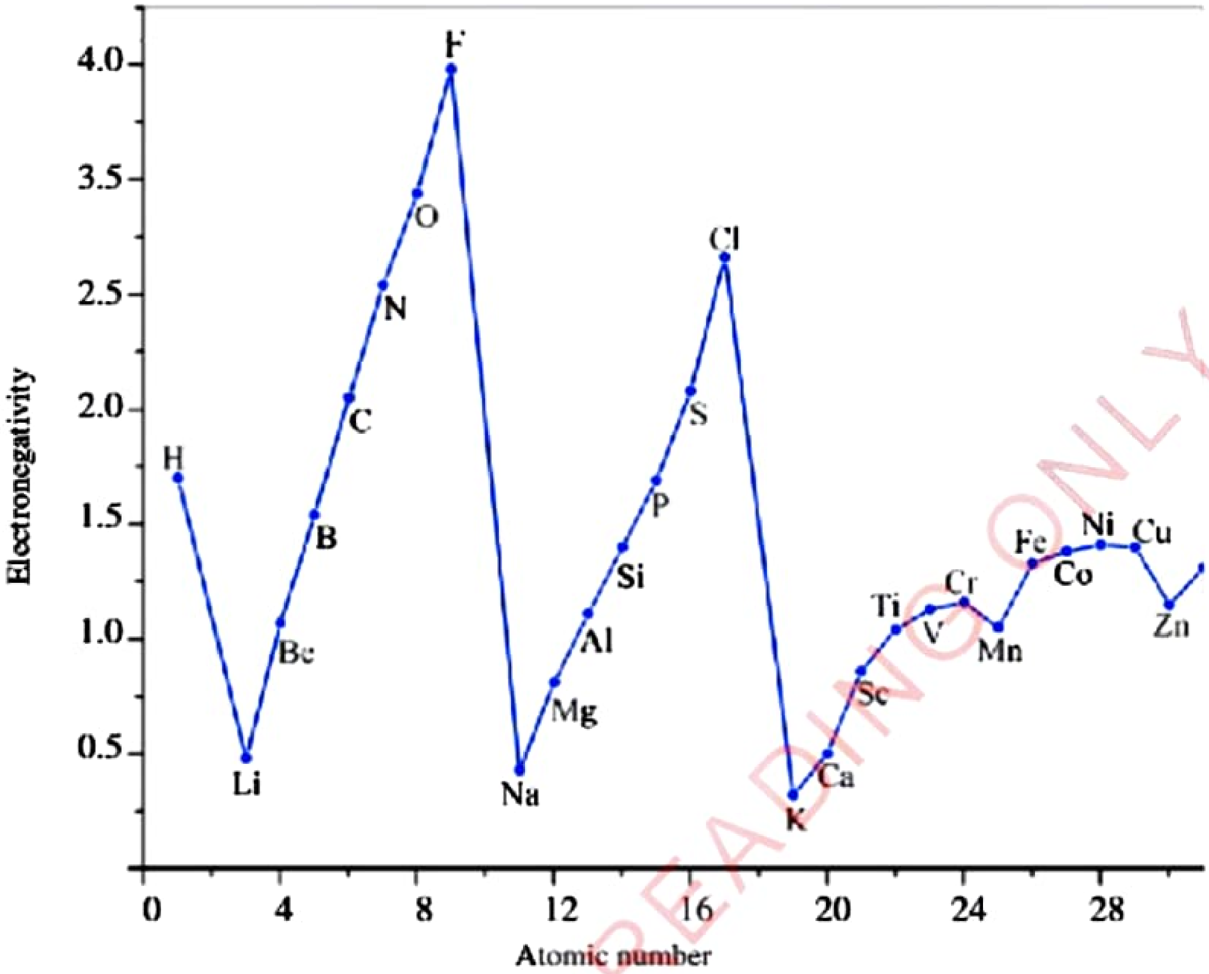


Figure 3.6: *Periodic trend in electronegativity*

Metallic character

Metallic character is referred to as a set of chemical properties that are associated with the elements classified as metals in the periodic table. This character depends on the ability of an element to lose its valence electrons. Generally, metals tend to lose electrons to form cations, while non-metals have a tendency of gaining electrons to form anions. Metals are easily oxidised and are strong reducing agents. Metallic character can also be accounted for in terms of various physical properties such as high density, high thermal conductivity, high electrical conductivity, shiny appearance, and malleability.

Periodic trends in metallic characters

Metallic characters decrease across the period from left to right. This is because the number of electrons in the valence shell increases. Therefore, the tendency of atoms to gain electrons and fill the valence shell increases relative to lose electrons and remove the unfilled shell. Metallic characters increase down the group from top to bottom. This is because, when moving down the group, the number of shells increases, resulting into low attraction between the nucleus and valence electrons. Therefore, the ability of an element to lose its valence electrons increases.

Periodic trends in melting and boiling points

Melting point is the temperature required to break bonds and change the physical state of a substance from solid to liquid. The stronger the bond, the higher the melting point. The trend in the melting points across the period in the periodic table is not consistent. Generally, metals have higher melting points than non-metals.

Boiling point is the temperature at which the vapour pressure of a substance is equal to the atmospheric pressure. The trend in the boiling points is closely related to that of the melting points, but the values of boiling points are generally higher than those of the melting points.

Periodic trends in physical properties across period 3

The physical properties of period 3 elements are similar to those discussed in the general trends, except density, melting, and boiling points, which show greater variations. The densities of period 3 elements increase from sodium to aluminium due to closely packed atoms, high atomic masses, and small atomic radii. The density decreases for silicon because the structure of silicon has more open spaces than closed packed aluminium structure, making it to have lower density. Other elements of period 3 have lower densities because they exist as molecules. The densities decrease from S_8, P_4 to Cl_2. Sulfur has relatively larger molecules than P_4 and Cl_2.

Generally, the melting points increase from sodium to silicon followed by a decrease towards argon with a slight increase from phosphorus to sulfur. Similarly, the boiling points increase from sodium to aluminium, then decrease towards argon with a slight increase from phosphorus to sulfur. The melting points and boiling points of period 3 elements are presented in Figure 3.7.

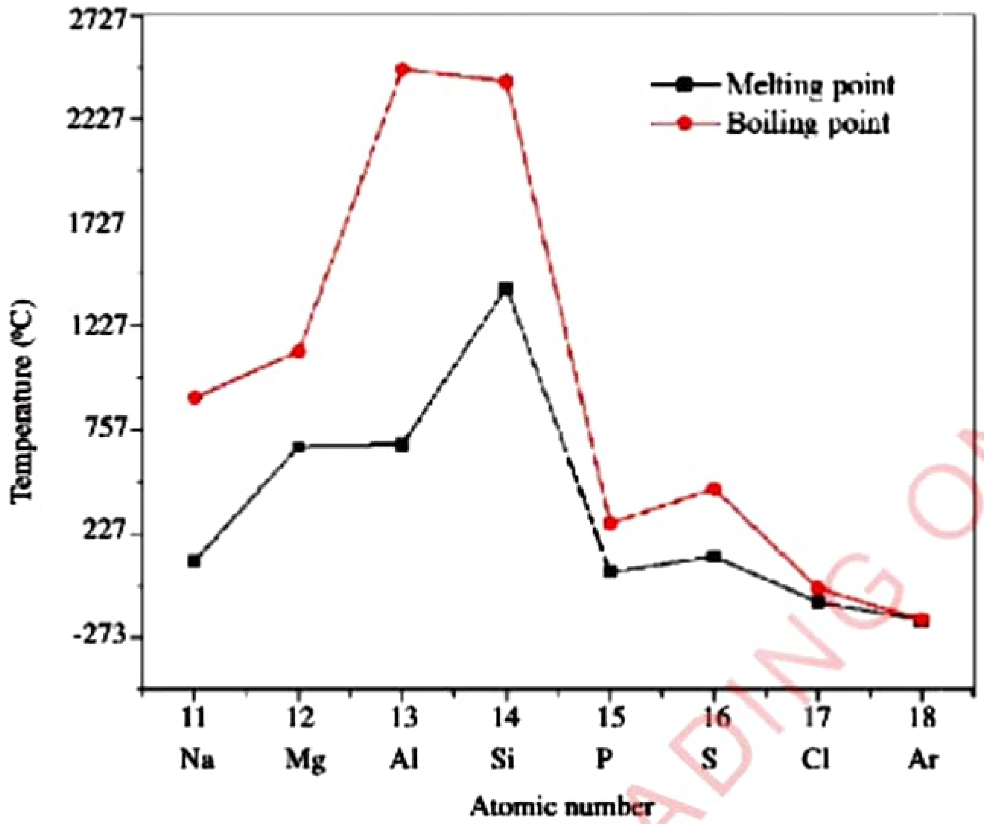


Figure 3.7: *Variations in melting and boiling points of period 3 elements*

Explanations of the observed trends

Sodium, magnesium, and aluminium are metals with a metallic bonding in which metal ions are attracted to the delocalised sea of electrons. The charges on the metal ions increase across the period from sodium (+1) to aluminium (+3). Since the number of delocalised electrons increases, the strength of metallic bonding also increases and hence, an increase in the melting and boiling points. Although aluminium ionises by losing three electrons due to its high total ionisation energies (1st IE, 2nd IE, and 3rd IE), it contributes only two electrons during formation of metallic crystal, hence, this accounts for the close melting point of magnesium, which also contributes two electrons in the metallic crystal.

Silicon is a metalloid that possesses non-metallic and metallic properties. It has a strong covalent bonding whereby each silicon is bonded to four other silicon atoms, forming a three dimensional giant molecule. Therefore, silicon has very high melting and boiling points because of the strong covalent bonds that need a large amount of energy to be broken.

On the other hand, phosphorus, sulfur, and chlorine are non-metals, which exist as small and separate molecules. Their atoms are held together by the van der Waals forces of attraction. Argon is also a non-metal that exists as separate atoms (monoatomic). These elements have low melting and boiling points. This is because the melting and boiling processes involve breaking the weak van der Waals forces, which require little energy.

Sulfur has higher melting and boiling points than phosphorus, chlorine, and argon. This is because it exists as S_8 molecules followed by phosphorus which exists as P_4 molecules, then chlorine which exists as Cl_2 and lastly the monoatomic argon (Ar) atoms. The strengths of the van der Waals forces decrease as the sizes of the molecules decrease and hence, decreasing the melting and boiling points in the order of $S_8 > P_4 > Cl_2 > Ar$.

Task 3.3

Use online sources to retrieve numerical data related to various periodic trends for the first thirty elements in the periodic table. Then, employ a software of your preference to create graphical representations of these trends. Give explanation on the observed variations.

Exercise 3.2

1. Understanding the trends of the atomic radius is essential in exploring the properties of elements. Explain.
2. Rank the following elements in the order of increasing ionisation energy: Explain your answer.
   (a) First IEs of Be, Li, K, and Al
   (b) Second IEs of Be, Na, Mg, and Al
3. (a) Why do the electronegativities generally decrease down the group?
   (b) Explain the variations of the ionisation energies and electron affinities with respect to the following:
      (i) Atomic size
      (ii) Effective nuclear charge

4. Explain each of the following terms as applied to characteristics of elements:
    (a) Electronegativity
    (b) Electron affinity
    (c) Screening effect

5. Arrange the following elements in the order of decreasing atomic sizes: Al, B, C, K, and Na. Give reason(s) for the arrangement.

6. Consider the following elements: Na, Mg, O and P.
    (a) Which element has the largest atomic radius? Why?
    (b) Which element has the highest electron affinity? Why?

7. Describe the criteria used in arranging elements in order of their increase in each of the following periodic trends:
    (a) Ionisation energy
    (b) Atomic size
    (c) Electron affinity

8. Using examples, explain the practical applications of physical trends in the periodic table to industrial aspects.

Periodic trends in physical properties of the elements in groups IA, IIA, and VIIA

Group IA

Group IA consists of metallic elements which are lithium, sodium, potassium, rubidium, caesium, and francium. These elements are soft and silvery white with lustre. They have low melting and boiling points due to their large atomic sizes and low charges, which lead to formation of weak metallic bonds. They have low densities due to lower molar masses and large atomic radii. The group IA elements have relatively lower densities than other elements of the same periods.

Group IIA

Group IIA elements consist of metallic elements which are beryllium, magnesium, calcium, strontium, barium, and radium. These elements have smaller atomic sizes and higher charges than those of group IA. They have higher melting and boiling points than those of group IA elements. The trends of melting and boiling points decrease down the group. Group IIA elements are more closely packed in their lattices making them to have strong metallic bond. They have lower densities but relatively higher than those of group IA.

Group VIIA (Halogens)

Group VIIA consists of fluorine, chlorine, bromine, iodine, and astatine elements. These elements have low melting and boiling points, which increase down the group. The trend is opposite to that of groups IA and IIA elements whose trends in melting and boiling points decrease down the groups. This is because the halogens exist as diatomic molecules that interact through van der Waals forces, which increase the strength as the atoms become large.

3.2.2 Periodic trends in chemical properties of elements

Periodic trends play a crucial role in chemical reactions. Elements that are close together in the periodic table tend to have similar reactivity due to their similar electronic configurations. Elements in the same group (vertical column) often undergo similar reactions. For example, alkali metals (Group I) are all highly reactive and readily lose an electron to form a +1 ion. On the other hand, noble gases (Group 18) are generally unreactive due to their full valence electron shells. Furthermore, trends in electronegativity influence the type of bonding (ionic or covalent) that occurs in reactions. Understanding these trends allows us to predict the behaviours of elements in chemical reactions.

Periodic trends in chemical properties are predictable patterns in chemical reaction observed in the element of the periodic table across the period and down the group. These trends are influenced by the electronic configuration and the effective nuclear charge experienced by the valence electron. Periodic chemical trends are useful in studying chemical bonding, reactivity, and properties of elements and compounds.

Reactions of group IA elements with oxygen

Group IA elements react with oxygen to form metal oxides, and their reactions are called oxidation. Group IA elements are very reactive, and they easily undergo oxidation when they come in contact with air. To prevent them from oxidation, they are stored in liquid oils, sealed glass tube, vacuum or in an inert gas. The reactivity of group IA elements increases down the group. Depending on the period of the metal and hence the reactivity, different types of oxides are formed when the metals are burnt in oxygen. The reactions of group IA elements in air are the same as in oxygen, except that oxygen reacts violently.

Lithium

Lithium burns strongly with red flame when heated in air to form white lithium monoxide.

$$4Li(s) + O_2(g) \longrightarrow 2Li_2O(s)$$

Lithium is unique among the group IA elements as it reacts with nitrogen in the air to form lithium nitride.

$$6Li(s) + N_2(g) \longrightarrow 2Li_3N(s)$$

Sodium

Sodium burns in air with a bright yellow or golden yellow flame to form a white solid mixture of sodium oxide. However, if oxygen is present in excess, sodium peroxide is formed.

$$4Na(s) + O_2(g) \longrightarrow \underset{\text{sodium oxide}}{2Na_2O(s)}$$

$$2Na(s) + O_2(g) \longrightarrow \underset{\text{sodium peroxide}}{Na_2O_2(s)}$$

Potassium

Potassium burns in air to form potassium oxide. When oxygen is present in excess, potassium form a mixture of potassium peroxide and potassium superoxide. If small pieces of potassium are used, no flame is observed, and if large pieces are used, a lilac flame is observed.

$$2K(s) + O_2(g) \longrightarrow \underset{\text{potassium oxide}}{2K_2O(s)}$$

$$2K(s) + O_2(g) \longrightarrow \underset{\text{potassium peroxide}}{K_2O_2(s)}$$

$$K(s) + O_2(g) \longrightarrow \underset{\text{potassium superoxide}}{KO_2(s)}$$

Rubidium and caesium

Both rubidium and caesium burn in air with orange or yellow flame to form superoxides. Rubidium also shows a dark brown flame.

$$Rb(s) + O_2(g) \longrightarrow RbO_2(s)$$

$$Cs(s) + O_2(g) \longrightarrow CsO_2(s)$$

Reactions of group IA elements with water

All group IA elements react violently or explosively with water to form aqueous metal hydroxides and hydrogen gas, as shown in the following general equation:

$$2M(s) + 2H_2O(l) \longrightarrow 2MOH(aq) + H_2(g)$$

where, M represents any group IA metal.

Examples:

$$2Li(s) + 2H_2O(l) \longrightarrow 2LiOH(aq) + H_2(g)$$

$$2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$$

$$2K(s) + 2H_2O(l) \longrightarrow 2KOH(aq) + H_2(g)$$

Reactions of group IA elements with hydrochloric acid

Lithium

Lithium reacts violently with dilute hydrochloric acid to form lithium chloride salt and hydrogen gas.

$$2Li(s) + 2HCl(aq) \longrightarrow 2LiCl(aq) + H_2(g)$$

Sodium

Sodium reacts with dilute hydrochloric acid to form sodium chloride salt and hydrogen gas. The reaction is violent and finishes quickly. The sodium ignites, producing a bright flame.

$$2Na(s) + 2HCl(aq) \longrightarrow 2NaCl(aq) + H_2(g)$$

Potassium

Potassium reacts violently with dilute hydrochloric acid to produce potassium chloride salt and hydrogen gas. The reaction is very fast due to its position in the periodic table compared to Li and Na, though it can be affected by the strength of the acid. Potassium ignites when in contact with acid producing a bright lilac flame.

$$2K(s) + 2HCl(aq) \longrightarrow 2KCl(aq) + H_2(g)$$

Reactions of group IA elements with sulfuric acid

Lithium

Lithium reacts with dilute sulfuric acid to form lithium sulfate and hydrogen gas. When lithium is added to the dilute sulfuric acid, effervescence occurs as hydrogen gas is released. The colour of sulfuric acid turns yellowish as it is converted to lithium sulfate. As the reaction proceeds, the heat generated ignites the hydrogen gas, which is released and produces a reddish flame.

$$2Li(s) + H_2SO_4(aq) \longrightarrow Li_2SO_4(aq) + H_2(g)$$

Sodium

Sodium reacts with dilute sulfuric acid to give sodium sulfate and hydrogen gas.

$$2Na(s) + H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + H_2(g)$$

Potassium

Potassium reacts explosively with dilute sulfuric acid to give potassium sulfate and hydrogen gas.

$$2K(s) + H_2SO_4(aq) \longrightarrow K_2SO_4(aq) + H_2(g)$$

Reactions of group IA elements (alkali metals) with dilute nitric acid

Lithium

Lithium reacts with dilute nitric acid to form lithium nitrate, ammonium nitrate and water.

$$8Li(s) + 10HNO_3(aq) \longrightarrow 8LiNO_3(aq) + NH_4NO_3(aq) + 3H_2O(l)$$

Sodium

Sodium reacts with dilute nitric acid to produce sodium nitrate, water, nitrogen monoxide and dinitrogen monoxide.

$$11Na(s) + 14HNO_3(aq) \longrightarrow 11NaNO_3(aq) + 7H_2O(l) + NO(g) + N_2O(g)$$

The nitrogen monoxide then reacts with atmospheric oxygen to form nitrogen dioxide.

Potassium

Potassium reacts with dilute nitric acid to produce potassium nitrate, dinitrogen monoxide, nitrogen monoxide, nitrogen gas and water.

$$21K(s) + 26HNO_3(aq) \longrightarrow 21KNO_3(aq) + N_2O(g) + NO(g) + N_2(g) + 13H_2O(l)$$

Reactions of group IIA elements

Group IIA elements exhibit similar chemical and physical properties because they consist of two electrons in their outermost shells. The group IIA elements are strong reducing agents, because they strongly cause other species to be reduced (addition of electrons) and themselves become oxidised (lose electrons).

Reactions of group IIA elements with air or oxygen

All group IIA elements burn in air or oxygen to form metal oxides. Their reactions in pure oxygen are violent and produce white metal oxides. The general equation for combustion is given as follows:

$$2M(s) + O_2(g) \longrightarrow 2MO(s)$$

where M represents any group IIA metal.

Examples:

$$2Ca(s) + O_2(g) \longrightarrow 2CaO(s)$$

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

$$2Sr(s) + O_2(g) \longrightarrow 2SrO(s)$$

The burning of barium in air forms a peroxide (BaO_2).

$$Ba(s) - O_2(g) \longrightarrow BaO_2(s)$$

The burning of calcium in air produces a brick red flame, and magnesium burns with a brilliant white flame (no colour). Strontium and barium burn with bright-red and pale-green flames, respectively.

Reactions of group IIA elements with water

When group IIA elements react with water, they form hydroxides ($M(OH)_2$) and hydrogen gas (H_2). The general equation for the reactions of group IIA elements with water is

$$M(s) + 2H_2O(l) \longrightarrow M(OH)_2(aq) + H_2(g)$$

where M represents any group IIA metal.

The reactivity of group IIA elements increases down the group. Moving down the group, the reactions become more vigorous. Therefore, calcium, strontium, and barium elements react with cold water to form hydroxides and hydrogen gas.

$$Ca(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) - H_2(g)$$

$$Sr(s) + 2H_2O(l) \longrightarrow Sr(OH)_2(aq) - H_2(g)$$

$$Ba(s) + 2H_2O(l) \longrightarrow Ba(OH)_2(aq) \quad H_2(g)$$

Magnesium reacts slowly with cold water, but, when the steam is passed over heated magnesium, the reaction becomes violent and magnesium oxide is formed.

$$Mg(s) + H_2O(l) \longrightarrow MgO(s) + H_2(g)$$

Beryllium forms an oxide when it reacts with water at room temperature.

$$Be(s) + H_2O(l) \longrightarrow BeO(s) \quad H_2(g)$$

Reactions of group IIA elements with hydrochloric acid

Generally, group IIA elements react with hydrochloric acid to form metal chloride salts and hydrogen gas,

$$M(s) + 2HCl(aq) \longrightarrow MCl_2(aq) + H_2(g)$$

where M represents any group IIA metal. For example, magnesium reacts vigorously with hydrochloric acid to form magnesium chloride and hydrogen gas.

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

Similar reactions may occur between group IIA elements with dilute sulfuric acid to form corresponding salts and hydrogen gas. This is because these elements are highly electropositive and can easily displace hydrogen from acid solutions. Dilute nitric acid reacts with only magnesium to liberate hydrogen gas.

Reactions of group IIA elements with sodium hydroxide

All the elements of group IIA do not react with alkalis, except beryllium. Beryllium reacts with sodium hydroxide to form beryllates and hydrogen gas.

$$Be(s) + 2NaOH(aq) \longrightarrow \underset{\text{sodium beryllate}}{Na_2BeO_2(aq)} + H_2(g)$$

Activity 3.3

Aim: To investigate the reactions of Na, Mg, and Ca with dilute HCl and water.

Requirements: 1 g of Na, Mg, Ca metals, dilute HCl, distilled water, 3 beakers (100 cm^3) and 100 cm^3 measuring cylinder

Procedure

1. Measure 50 cm^3 of dilute HCl using a measuring cylinder and pour it into a beaker.
2. Add about 0.2 g of sodium metal and record your observations.
3. Repeat steps 1 and 2 using magnesium and calcium metals and record your observations.
4. Repeat steps 1 to 3 for all metals using distilled water instead of HCl and record your observations.

Questions

1. What physical observations were made on the experiment when the metals reacted with
   - (a) dilute HCl?
   - (b) distilled water?
2. How does the experiment explain the reactivity series of the three metals?

Task 3.4

Explore the uses of Group IIA elements in medical and construction industries.

Reactions of group VIIA elements

These elements are called *halogens,* and they exist as diatomic molecules, with weak intermolecular forces of attractions. Halogens consist of seven electrons in their outermost shells, which is one electron less than the next noble gas electronic configuration. This property makes them to be good oxidising agents because they tend to remove electrons from other substances during reactions. The reactivity of the halogens decreases down the group because of the increase in atomic radii and the shielding effect. Even though the nuclear charge increases down the group, its effects are largely cancelled out by the shielding effect and increased atomic radii.

Reactions of group VIIA elements with air

Halogens react with oxygen to form oxides. For example, fluorine reacts with oxygen to form oxygen difluoride (OF_2) and dioxygen difluoride (O_2F_2).

$$2F_2(g) + O_2(g) \longrightarrow 2OF_2(g)$$

$$F_2(g) + O_2(g) \longrightarrow O_2F_2(g)$$

The oxides of chlorine, namely dichlorine monoxide (Cl_2O) and chlorine dioxide (ClO_2) are unstable, hence they are not prepared directly from oxygen. The dichlorine monoxide is prepared by passing chlorine gas in the hydrated sodium carbonate at 20-30 °C.

$$2Cl_2(g) + 2Na_2CO_3(s) + H_2O(l) \longrightarrow Cl_2O(g) + 2NaHCO_3(aq) + 2NaCl(aq)$$

Reactions of group VIIA elements with water

Fluorine reacts violently with water vapour to form hydrogen fluoride and oxygen or ozone.

$$2F_2(g) + 2H_2O(g) \longrightarrow 4HF(g) + O_2(g)$$

$$3F_2(g) + 3H_2O(g) \longrightarrow 6HF(g) + O_3(g)$$

Chlorine disproportionates in water to form hypochlorous acid and hydrochloric acid.

$$Cl_2(g) + H_2O(l) \rightleftharpoons HClO(aq) + HCl(aq)$$

Hypochlorous acid decomposes slowly to give oxygen unless sunlight is present to accelerate the decomposition.

$$2HClO(aq) \longrightarrow 2HCl(aq) + O_2(g)$$

Disproportionation is a reaction in which a substance is simultaneously oxidised and reduced giving two different products.

Bromine also disproportionate in water to form hypobromous acid and hydrobromic acid.

$$Br_2(g) + H_2O(l) \longrightarrow HBrO(aq) + HBr(aq)$$

Iodine reacts slowly with water to form hypoiodous acid and hydroiodic acid.

$$I_2(g) + H_2O(l) \longrightarrow HIO(aq) + HI(aq)$$

These hypohalous acids are also called *oxo-acids*.

Reactions of group VIIA elements with sodium hydroxide

Fluorine gas reacts with dilute sodium hydroxide to form oxygen fluoride, sodium fluoride, and water.

$$2F_2(g) + 2NaOH(aq) \longrightarrow 2NaF(aq) + OF_2(g) + H_2O(l)$$

But, when fluorine gas reacts with concentrated sodium hydroxide, oxygen is formed instead of OF_2.

$$2F_2(g) + 4NaOH(aq) \longrightarrow 4NaF(aq) + O_2(g) + 2H_2O(l)$$

Chlorine gas reacts with cold dilute sodium hydroxide solution to form colourless solution of sodium chloride, sodium hypochlorite and water.

$$Cl_2(g) + 2NaOH(aq) \longrightarrow NaCl(aq) + NaOCl(aq) + H_2O(l)$$

Bromine liquid reacts with dilute sodium hydroxide to form sodium bromide, sodium hypobromite, and water.

$$Br_2(l) + 2NaOH(aq) \longrightarrow NaBr(aq) + NaOBr(aq) + H_2O(l)$$

This reaction is less reactive than the reaction between chlorine and sodium hydroxide. A solid iodine reacts slowly with dilute sodium hydroxide to form sodium iodide, sodium hypoiodite and water.

$$I_2(s) + 2NaOH(aq) \longrightarrow NaI(aq) + NaOI(aq) + H_2O(l)$$

This reaction is the least reactive compared to that of fluorine, chlorine, and bromine. If hot concentrated NaOH is reacted with some halogens (Br, Cl, and I), the general equation is given in the following equation:

$$3X_2(g) + 6NaOH(aq) \xrightarrow{60\ ^\circ C} 5NaX(aq) + NaXO_3(aq) + 3H_2O(l)$$

where X stands for Br, Cl, and I.

Reactions of halogens with acids

Fluorine reacts with dilute hydrochloric acid to form hydrogen fluoride and chlorine gas at room temperature.

$$F_2(g) + 2HCl(aq) \longrightarrow 2HF(aq) + Cl_2(g)$$

Fluorine reacts with sulfuric acid to form hydrogen fluoride and sulfuryl peroxide. The reaction occurs at a temperature near 0 °C.

$$F_2(g) + H_2SO_4(aq) \longrightarrow 2HF(aq) + \underset{\substack{\text{sulfuryl}\\\text{peroxide}}}{SO_2(O_2)(aq)}$$

Task 3.5

Consider the various items you use daily. Investigate their compositions and applications based on their physical and chemical characteristics. Place their constituent elements in respective groups in the periodic table.

Unique properties of fluorine

Fluorine differs in chemical and physical properties from other elements of group VIIA. These differences are due to its small atomic size, highest electronegativity, low bond dissociation energy, and the absence of *d*-orbitals in the valence shell.

These differences in properties are described as follows:

(a) *High chemical reactivity*

Fluorine is the most reactive element of all the halogens because the F–F bond is weak and hence, has low bond dissociation energy. The reason for the weakness of the F–F bond is that the F atom is small, with short F–F bond, which causes repulsion between the lone pairs of neighbouring F atoms. Fluorine is a very strong oxidising agent, which tends to oxidise other halogens lower in the group as shown in the following general equation.

$$F_2(g) + X_2(g) \longrightarrow 2XF(g)$$

where X represents halogens other than fluorine.

(b) *Strong hydrogen bonding in HF*

Hydrogen fluoride undergoes strong hydrogen bonding, while other halogen acids do not. This is because of the small atomic size and high electronegativity of fluorine. The following are the consequences of the strong hydrogen bonding in HF:

(i) HF is the weakest haloacid among all the halogen acids because of the strength of the H–F bond (does not easily dissociate).

(ii) HF is a liquid at room temperature, while other halogen acids are gases at room temperature. This is due to strong H–F bond that holds the molecules close to each other.

(iii) Due to strong hydrogen bonding, HF can form acidic salts of the type MHF_2; where M is a metal such as potassium (K), that is, $K^+[H-F-F]^-$. Other halogens do not form such kinds of salts.

(c) *Maximum ionic character*

Fluorides have the maximum ionic characters, for example, AlF_3 is ionic while other halides of Al are covalent. Due to high reactivity, HF cannot be stored in a glass bottle because it tends to react with silicates to form fluorosilicates. Other hydrogen halides do not react with silicates; hence, they can be stored in glass bottles.

$$Na_2SiO_3(g) + 6HF(l) \longrightarrow \underset{\text{sodium fluorosilicate}}{Na_2SiF_6(aq)} + 3H_2O(l)$$

(d) *Solubility in water*

Silver fluoride (AgF) is soluble in water, while other halides of silver such as AgCl and AgBr are insoluble in water.

(e) *Reaction of fluorine with water*

Fluorine reacts violently with water to form hydrogen fluoride and oxygen.

$$2F_2(g) + 2H_2O(l) \longrightarrow 4HF(aq) + O_2(g)$$

Other halogens such as Cl_2 and Br_2 undergo disproportionation reactions with water and form hydrogen halides (HX) and hypohalous acids (HXO).

Periodic trends in chemical properties along period 3

Periodic trends in chemical properties along period 3 are discussed by considering the reactions of hydrides, chlorides, hydroxides, and oxides of the elements in period 3. Period 3 includes the following elements: sodium, magnesium, aluminium, silicon, phosphorus, sulfur, chlorine, and argon.

Reactions of hydrides of period 3 elements with water

The hydrides are formed when elements react with hydrogen gas. Sodium and magnesium react with hydrogen to form ionic hydrides, which have basic characteristics. Many electronegative elements such as sulfur and chlorine react with hydrogen to form covalent acidic hydrides. The hydrides of sodium, magnesium, and aluminium are ionic. They react with water to form metal hydroxides and hydrogen gas.

$$NaH(s) + H_2O(aq) \longrightarrow NaOH(aq) + H_2(g)$$

$$MgH_2(s) + 2H_2O(l) \longrightarrow Mg(OH)_2(aq) + 2H_2(g)$$

Aluminium hydride, also called *alane* or *alumane*, reacts with water to form hydroxide and hydrogen gas.

$$AlH_3(s) + 3H_2O(l) \longrightarrow Al(OH)_3(aq) + 3H_2(g)$$

Lithium aluminium hydride dissolves in water to form lithium hydroxide, aluminium hydroxide and hydrogen gas.

$$LiAlH_4(s) + 4H_2O(l) \longrightarrow LiOH(aq) + Al(OH)_3(aq) + 4H_2$$

The hydride of silicon (SiH_4), which is known as *silane*, is partially ionic. The partial charges on the atoms are relatively small, hence, it dissolves in water to form silicon hydroxide and hydrogen gas in the presence of strong base as a catalyst.

$$SiH_4(s) + 4H_2O(l) \xrightarrow{NaOH} Si(OH)_4(aq) + 4H_2(g)$$

The hydride of phosphorus (PH_3), which is known as *phosphine*, does not react with water because the electronegativities of phosphorus and hydrogen are the same. Therefore, the partial charges on phosphine molecules are absent.

The hydrides of sulfur and chlorine are partially ionic, because sulfur and chlorine are more electronegative than hydrogen hence, they attract electrons from hydrogen. These hydrides react with water reversibly to form acidic solutions.

$$H_2S(g) + 2H_2O(l) \rightleftharpoons 2H_3O^+(aq) + S^{2-}(aq)$$

$$HCl(g) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

Reactions of chlorides of period 3 elements with water

The chlorides of sodium and magnesium are ionic or strong electrovalent compounds. They are not hydrolysed by water; they just ionise completely to form neutral solutions. This is because they have large ionic sizes and low charges compared to the other elements in the same period. They can also conduct electricity and undergo electrolysis when fused. Sodium chloride dissolves readily in water with a negligible heat change to form a colourless solution which contains Na^+ and Cl^- ions. The reaction does not involve hydrolysis.

$$NaCl(s) + H_2O(l) \longrightarrow Na^+(aq) + Cl^-(aq)$$

Magnesium chloride dissolves in water with a slightly heat change to form colourless solution, which contains Mg^{2-} and Cl^- ions.

$$MgCl_2(s) + H_2O(l) \longrightarrow Mg^{2+}(aq) + 2Cl^-(aq)$$

In a hydrated form, magnesium chloride is partially hydrolysed to form basic chloride Mg(OH)Cl.

$$MgCl_2 \cdot 6H_2O(s) \xrightarrow{\text{heat}} Mg(OH)Cl(s) + HCl(g) + 5H_2O(l)$$

Aluminium chloride ($AlCl_3$) has characteristics of covalent compounds and does not conduct electricity. It reacts vigorously with water to form a colourless solution containing $[Al(H_2O)_5(OH)]^{2+}$ and Cl^-. They undergo hydrolysis to form an acidic solution, which turns blue litmus paper to red.

$$Al_2Cl_6(s) + 12H_2O(l) \longrightarrow 2[Al(H_2O)_6]^{3+}(aq) + 6Cl^-(aq)$$

$$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \longrightarrow [Al(H_2O)_5OH]^{2+}(aq) + H_3O^+(aq)$$

Phosphorus chloride (PCl_3), silicon chloride ($SiCl_4$), and disulfur dichloride (S_2Cl_2) also undergo hydrolysis in water to form acidic solutions.

$$PCl_3(s) + 3H_2O(l) \longrightarrow H_3PO_3(aq) + 3HCl(aq)$$

$$SiCl_4(s) + 3H_2O(l) \longrightarrow H_2SiO_3(aq) + 4HCl(aq)$$

$$S_2Cl_2(s) + 3H_2O(l) \longrightarrow H_2S(aq) + 2HCl(aq) + H_2SO_3(aq)$$

Reactions of hydroxides of period 3 elements with water

In all the hydroxides of period 3, oxygen is more electronegative than the other period 3 elements. In sodium and magnesium hydroxides, hydrogen is more electronegative than a particular metal. In the hydroxides, oxygen attracts the bonding electrons more away from the metals than how it attracts the bond electron pair from hydrogen. As a result, a dipole moment is formed between oxygen and the metal of period 3 but not between oxygen and hydrogen.

Therefore, when sodium and magnesium hydroxides are dissolved in water, they form metal and hydroxyl ions, making their solutions basic.

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

$$Mg(OH)_2(aq) + H_2O(l) \longrightarrow Mg^{2+}(aq) + 2OH^-(aq)$$

Aluminium hydroxide is amphoteric because it has both basic and acidic properties. The reaction of aluminium hydroxide with water results in the formation of aqueous aluminium ions and hydroxide ions, though the process is not straightforward due to limited solubility of aluminium hydroxide in water.

$$Al(OH)_3(aq) + H_2O(l) \longrightarrow Al^{3+}(aq) + 3OH^-(aq)$$

This reaction occurs in a series of three steps with hydroxide ion being released in each step.

$$Al(OH)_3(aq) + H_2O(l) \longrightarrow Al(OH)_2^+(aq) + OH^-(aq) \qquad \text{Step 1}$$

$$Al(OH)_2^+(aq) + H_2O(l) \longrightarrow Al(OH)^{2+}(aq) + OH^-(aq) \qquad \text{Step 2}$$

$$Al(OH)^{2+}(aq) + H_2O(l) \longrightarrow Al^{3+}(aq) + OH^-(aq) \qquad \text{Step 3}$$

Aluminium hydroxide as an acid generates hydroxonium ions when dissolved in water. This reaction occurs in a series of steps as follows:

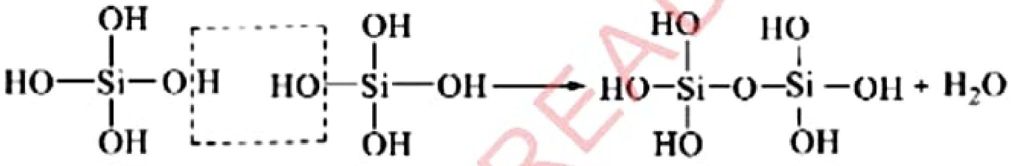
$$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(OH)(H_2O)_5]^{2+}(aq) + H_3O^+(aq)$$

$$[Al(OH)(H_2O)_5]^{2+}(aq) + H_2O(l) \rightleftharpoons [Al(OH)_2(H_2O)_4]^{+}(aq) + H_3O^+(aq)$$

$$[Al(OH)_2(H_2O)_4]^{+}(aq) + H_2O(l) \rightleftharpoons [Al(OH)_3(H_2O)_3](s) + H_3O^+(aq)$$

Silicon, phosphorus, sulfur, and chlorine in their hydroxides are electronegative and can withdraw electrons from O-H bond thus polarising it and facilitating the release of hydrogen as proton (H^+).

Silicic acid ($Si(OH)_4$) has a tendency of polymerising by releasing water molecules as by-products. The polymerisation process occurs when a molecule of $Si(OH)_4$ acts as an acid releasing H^+ ion, and another molecule acts as a base releasing OH^- ions. The process occurs when silicon hydroxide is dissolved in water. The formation of silicic acid polymer is shown as follows:



Other oxo-acids have acidities in the order $HClO_4 > H_2SO_4 > H_3PO_4$. Phosphoric(V) acid molecule ($OP(OH)_3$) has only one oxygen atom, hence, its electronegativity effect has to be shared by the three hydroxyl groups. This makes the phosphoric(V) acid weaker than sulfuric acid, which has two singly attached oxygen atoms. The chloric(VII) acid ($HClO_4$), commonly known as perchloric acid, has four oxygen atoms to one hydroxyl group, hence, it is stronger than sulfuric acid and phosphoric(V) acid.

Oxides of period 3 elements

Sodium and magnesium are strong metallic in properties whose oxides are ionic. Thus, their crystal structures are held strongly by ionic bonds, which lead into their high melting and boiling points. Sodium and magnesium oxides are strong bases, aluminium oxide (Al_2O_3) is amphoteric, and the oxides of the remaining metals are acidic. Silicon dioxide (SiO_2) and phosphorus pentoxide (P_2O_5) are covalent solids, while sulfur dioxide (SO_2) and chlorine(VII) oxide (Cl_2O_7) are gases.

The following are the reactions which show the amphoteric nature of aluminium oxide:

$$\text{As a base:}\quad Al_2O_3(s) + 6HF(aq) \longrightarrow \underset{\text{aluminium fluoride}}{2AlF_3(s)} + 3H_2O(l)$$

$$\text{As an acid:}\quad Al_2O_3(s) + 2NaOH(aq) \longrightarrow \underset{\text{sodium aluminate}}{2NaAlO_2(aq)} + H_2O(l)$$

Reactions of the oxides of period 3 elements with water

Sodium oxide (Na_2O) and magnesium oxide (MgO) are basic oxides as they react with water to form basic solutions.

$$Na_2O(s) + H_2O(l) \longrightarrow 2NaOH(aq)$$

$$MgO(s) + H_2O(l) \longrightarrow Mg(OH)_2(aq)$$

Aluminium oxide reacts with water to form aluminium hydroxide ($Al(OH)_3$).

$$Al_2O_3(s) + 3H_2O(l) \longrightarrow 2Al(OH)_3(aq)$$

The $Al(OH)_3$ formed behaves as an acid or a base.

$$Al(OH)_3(aq) + 3H^+(aq) \longrightarrow Al^{3+}(aq) + 3H_2O(l) \qquad \text{As a base}$$

$$Al(OH)_3(aq) + OH^-(aq) \longrightarrow [Al(OH)_4]^-(aq) \qquad \text{As an acid}$$

Silicon dioxide (SiO_2) does not react with water, because it is difficult to break up the giant covalent structure. It reacts with hot concentrated solution of NaOH.

$$SiO_2(s) + 2NaOH(aq) \xrightarrow{\text{heat}} Na_2SiO_3(s) + H_2O(l)$$

Phosphorus pentoxide reacts with water to form phosphoric acid.

$$2P_2O_5(s) + 6H_2O(l) \longrightarrow 4H_3PO_4(aq)$$

Sulfur dioxide (SO_2) and sulfur trioxide (SO_3) react with water to form sulfurous acid (H_2SO_3) and sulfuric acid (H_2SO_4), respectively.

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

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$$

Exercise 3.3

1. Describe the acidic and basic characteristics of the oxides of period 3 elements.
2. Explain with equations, the reactivity of the oxides of group IA with water.
3. The metallic characters of the elements change across a period. Illustrate this concept with reference to chlorides of the elements of period 3.
4. Use chemical equations to explain the following facts:
   (a) BeO is amphoteric. (b) MgO is a weak base.
   (c) CaO is basic. (d) BaO is extremely basic.
5. Explain the uses of oxides of alkali metals and alkaline earth metals.
6. What industrial applications do group I chlorides serve?

3.3 Diagonal relationships

Every first element in a group exhibits anomalous behaviours from the rest of the group members in the periodic table. Lithium, for example, exhibits properties, which distinguish it from other members of group I (Na, K, Rb, and Cs) and has similar properties to the second member of group II (Mg), which is located diagonal to it in period 3. This kind of similarity is called *diagonal relationship*. Diagonal relationship is the resemblance in properties whereby the first element in a particular group has similar properties diagonally with the second element in the next group. Other examples of elements that are related diagonally are Be, and Al, and B and Si. Table 3.8 indicates the positions of the elements in the periodic table, and those related diagonally are painted in the same colour.

Table 3.8: *Elements with diagonal relationships*

Period	Group			
	IA	IIA	IIIA	IVA
2	Li	Be	B	C
3	Na	Mg	Al	Si
4	K	Ca	Ga	Ge

Period 2 elements at the top of the main groups are called the ***head elements***. These elements have properties and their corresponding compounds that differ from those of their group members. This is due to the resemblance of atomic size and electronegativity, diagonally with the second element in the next group. For example, lithium has properties that resemble those of magnesium more than those of its members in the group.

3.3.1 Anomalous behaviours of lithium

Lithium differs in its chemical behaviours from other alkali metals (group IA), but it shows similarities with the second elements of the alkali earth metals (group IIA). These differences are due to the following reasons:

(a) Atomic and ionic radii of lithium are relatively smaller than of the other elements in the same group.

(b) Lithium ion (Li^+) due to its small size has very high polarising power; hence exhibits covalent character in its compounds.

(c) Lithium does not possess *d*-orbitals in its valence shell, while other group IA elements have *d*-orbitals. Therefore, lithium differs chemically from the other alkali metals (group IA) as explained in the following aspects:

(i) It burns in oxygen to form a normal lithium oxide (Li_2O).

$$4Li(s) + O_2(g) \longrightarrow \underset{\text{lithium oxide}}{2Li_2O(s)}$$

However, the rest of alkali metals form peroxides such as Na_2O_2 or superoxides like KO_2.

$$2Na(s) + O_2(g) \longrightarrow Na_2O_2(s)$$

$$K(s) + O_2(g) \longrightarrow KO_2(s)$$

(ii) It reacts with nitrogen gas to form lithium nitride (Li_3N).

$$6Li(s) + N_2(g) \longrightarrow 2Li_3N(s)$$

Other members in the same group do not reacts with nitrogen gas, for example, Sodium nitride (Na_3N) does exist, but it is highly unstable such that it cannot be formed by direct reaction between sodium and nitrogen gas.

(d) Lithium is harder with higher melting point and boiling point than the rest of the group IA elements because of strong metallic bond caused by small atomic size.

(e) Lithium nitrate, chloride, bromide, and iodide are more soluble in polar organic solvents such as acetone and ethanol than other alkali metal compounds, which are insoluble in polar organic solvents.

(f) Fluoride, carbonate, hydroxide, and phosphate of Li are less soluble in water than those of other alkali metals such as Na and K. This is because Li^+ is very small, highly positive, and hence, its salts do not easily dissociate into ions in water.

(g) Lithium chloride forms hydrated crystals, $LiCl{\cdot}H_2O$, when dissolved in water, but chlorides of other group IA elements do not form hydrates. Lithium chloride is deliquescent, while chlorides of group IA elements are not.

(h) Lithium is the only alkali metal which forms molecular compounds (called organolithium) with hydrocarbon groups from organic halides, which are important reactants in the synthesis of organic compounds. For example, lithium reacts with ethyl bromide to form ethyl lithium (an organolithium compound).

$$2Li(s) + CH_3CH_2Br(g) \longrightarrow CH_3CH_2Li(s) + LiBr(s)$$

(i) The hydroxide and carbonate of lithium decompose on heating.

$$Li_2CO_3(s) \xrightarrow{\text{heat}} Li_2O(s) + CO_2(g)$$

$$2Li(OH)(s) \xrightarrow{\text{heat}} Li_2O(s) + H_2O(g)$$

The other hydroxides and carbonates of other elements in the group do not decompose on heating.

(j) On heating, lithium nitrate evolves nitrogen dioxide and oxygen.

$$4LiNO_3(s) \xrightarrow{\text{heat}} 2Li_2O(s) + 4NO_2(g) + O_2(g)$$

Nitrates of other elements below lithium evolve oxygen gas only on heating.

$$2NaNO_3(s) \xrightarrow{\text{heat}} 2NaNO_2(s) + O_2(g)$$

3.3.2 Diagonal relationships between lithium and magnesium

Lithium and magnesium are diagonally related because they have similar chemical properties such as equal electronegativity and polarising power values. The following are other factors that account for the diagonal relationships between Li and Mg:

(a) On combustion, both Li and Mg form normal oxides.

$$4Li(s) + O_2(g) \longrightarrow 2Li_2O(s)$$

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

(b) Both Li and Mg combine directly with nitrogen gas to form nitrides.

$$6Li(s) + N_2(g) \longrightarrow 2Li_3N(s)$$

$$3Mg(s) + N_2(g) \longrightarrow Mg_3N_2(s)$$

(c) Hydroxides, carbonates, and nitrates of both Li and Mg decompose easily on heating to form oxides.

$$4LiNO_3(s) \xrightarrow{\text{heat}} 2Li_2O(s) + 4NO_2(g) + O_2(g)$$

$$2Mg(NO_3)_2(s) \xrightarrow{\text{heat}} 2MgO(s) + 4NO_2(g) + O_2(g)$$

$$Li_2CO_3(s) \xrightarrow{\text{heat}} Li_2O(s) + CO_2(g)$$

$$MgCO_3(s) \xrightarrow{\text{heat}} MgO(s) + CO_2(g)$$

(d) Carbonates, phosphates, and fluorides of both Li and Mg are sparingly soluble in water. The corresponding group IIA salts are insoluble, and those of group IA elements are soluble in water.

(e) Both halides of Li and Mg are partially covalent in character, hence can dissolve in many organic solvents. However the corresponding halides of groups IA and IIA metals are ionic.

3.3.3 Anomalous behaviours of beryllium

Beryllium in period 2 markedly shows different behaviours from the rest of the alkaline earth metals (group IIA elements). The anomalous behaviours of Be are caused by its extreme small size and high electronegativity. The main chemical differences between beryllium and other group IIA elements are:

(a) Beryllium does not react with water even in hot water, but other alkaline earth metals react with water to form hydroxide and hydrogen gas.

$$Be(s) + H_2O(l) \longrightarrow \text{No reaction}$$

$$Ca(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + H_2(g)$$

(b) The compounds of beryllium with oxygen, nitrogen, sulfur, and chlorine are covalent in nature unlike the corresponding compounds of group IIA elements. In fact, all Be compounds exhibit covalent bonding.

(c) Beryllium dissolves in strong alkalis to form beryllate, while other alkali earth metals do not react with alkalis.

$$\mathrm{Be}(s) + 2\mathrm{NaOH}(aq) \longrightarrow \underset{\text{sodium beryllate}}{\mathrm{Na_2BeO_2}(aq)} + \mathrm{H_2}(g)$$

(d) The oxide and hydroxide of Be are amphoteric and dissolve in acids to form salts, while those of other alkaline earth metals are basic in characters. BeO is insoluble in water unlike the oxides of other alkaline earth metals.

(e) Beryllium forms volatile nitride with nitrogen gas, while other alkaline earth metals form non-volatile nitrides with nitrogen gas.

(f) The sulfate of beryllium is soluble in water, while the sulfates of other alkaline earth metals are sparingly soluble or insoluble in water.

(g) Beryllium shows a maximum coordination number of four, unlike other alkaline earth metals, which have a maximum of six coordination numbers due to the presence of *d*-orbitals.

(h) Beryllium does not liberate hydrogen when reacts with dilute acids, but the corresponding elements in the group react with acids to liberate hydrogen gas. For example, magnesium reacts with dilute hydrochloric acid to liberate hydrogen gas.

$$\mathrm{Mg}(s) + 2\mathrm{HCl}(aq) \longrightarrow \mathrm{MgCl_2}(aq) + \mathrm{H_2}(g)$$

3.3.4 Diagonal relationships between beryllium and aluminium

Beryllium and aluminium are diagonally related because they have similar chemical properties such as polarising power. The following are diagonal relationships between Be and Al:

(a) Both Be and Al do not easily react with acids and water because these elements react with oxygen to form a thin oxide layer which is inert.This makes Be and Al elements impervious to further attack. However their corresponding elements of group IIA and group IIIA metals react with acids and water as follows:

$$\mathrm{Mg}(s) + 2\mathrm{HCl}(aq) \longrightarrow \mathrm{MgCl_2}(aq) + \mathrm{H_2}(g)$$

$$2\mathrm{Ga}(s) + 6\mathrm{HCl}(aq) \longrightarrow 2\mathrm{GaCl_3}(aq) + 3\mathrm{H_2}(g)$$

$$\mathrm{Mg}(s) + 2\mathrm{H_2O}(l) \longrightarrow \mathrm{Mg(OH)_2}(aq) + \mathrm{H_2}(g)$$

(b) Both Be and Al dissolve in excess alkalis to give beryllate and aluminate ions, respectively and liberate hydrogen gas as follows:

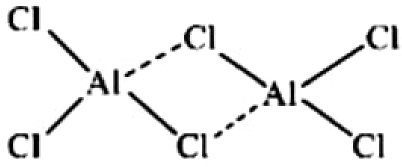
$$Be(s) + 2NaOH(aq) \longrightarrow \underset{\text{sodium beryllate}}{Na_2BeO_2(aq)} + H_2(g)$$

$$2Al(s) + 2NaOH(aq) + 2H_2O(l) \longrightarrow \underset{\text{sodium aluminate}}{2NaAlO_2(aq)} + 3H_2(g)$$

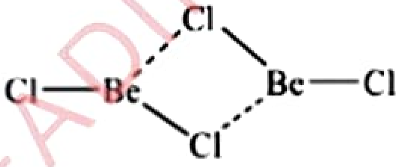
Other elements of group IIA and IIIA do not react with alkalis.

(c) Both Be and Al possess strong tendencies of forming covalent compounds, while other elements in groups IIA and IIIA form ionic compounds.

(d) The chlorides of beryllium (Be_2Cl_4) and aluminium (Al_2Cl_6) are covalent and have bridged polymeric structures.



Al_2Cl_6



Be_2Cl_4

(e) Both Be^{2+} and Al^{3+} ions have strong tendencies of forming complexes due to their similar charge to radius ratios. The following are examples of complexes of Be and Al:

(i) $BeF_4^{2-}(aq)$ (ii) $[Be(C_2O_4)_2]^{2-}(aq)$

(iii) $AlF_6^{3-}(aq)$ (iv) $[Al(C_2O_4)_3]^{3-}(aq)$

But other elements of groups IIA and IIIA do not have a strong tendency of forming complexes.

(f) Both salts of Be and Al hydrolyse in water and precipitate when boiled in hydroxides. The hydroxides and oxides of both Be and Al are amphoteric.

(i) BeO as a base, forms Be^{2+} and $H_2O(l)$.

$$BeO(s) + 2H^+(aq) \rightleftharpoons Be^{2+}(aq) + H_2O(l)$$

(ii) BeO as an acid, forms beryllate ion.

$$BeO(s) + 3H_2O(l) \rightleftharpoons [Be(OH)_4]^{2-}(aq) + H_2(g)$$

(iii) Al_2O_3 as a base, neutralises the HCl to form salt and water.

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

(iv) Al_2O_3 as an acid, reacts with strong alkalis to form aluminate.

$$Al_2O_3(s) + 2NaOH(aq) \longrightarrow 2NaAlO_2(aq) + H_2O(l)$$

Revision exercise 3

1. Fluorine has lower electron affinity than chlorine. Explain.
2. Lithium differs in chemical properties from the rest of the group members. Explain.
3. (a) Which element has the largest electron affinity; Se, Cl or Br?
   (b) Which species has the largest radius; O^{2-}, F, or F^- ?
4. Which of the following series of elements is arranged correctly in the order of increasing ionisation energy? For the incorrect arrangement, show the corrections.
   (a) $C < Si < Li < Ne$
   (b) $Ne < Si < C < Li$
   (c) $Li < Si < C < Ne$
   (d) $Ne < C < Si < Li$
5. Place the following species in the order of decreasing sizes. Give reasons for the arrangements: Ar, K^+, Cl^-, S^{2-}, and Ca^{2+}.
6. How is the electronic structure of an element related to each of the following?
   (a) Position in the periodic table.
   (b) Its valence.
7. How is it possible to predict many of the properties of an element from the knowledge of its atomic number?

8. Consider the elements B, Al, C, and Si. Specify the element that has the;

   (a) most metallic character.

   (b) largest atomic radius.

   (c) largest electron affinity.

9. Explain the following facts:

   (a) Group IA elements have lower melting and boiling points than group IIA elements.

   (b) Group IIA elements have higher densities than group IA elements.

   (c) The melting and boiling points of group VIIA elements increase down the group, while those of group IA and group IIA decrease down the group.

10. Using balanced chemical equations, illustrate why carbonates of lithium and magnesium readily decompose on heating, while the carbonates of other elements below lithium and magnesium in their groups are stable on heating.

11. Explain the following observations:

    (a) Both Be and Al do not easily react with mineral acids and water.

    (b) Both Be and Al have strong tendencies to form complex compounds.

    (c) The chlorides of beryllium (Be_2Cl_4) and aluminium (Al_2Cl_6) have bridged polymeric structures.

    (d) Beryllium shows a maximum coordination number of four, while aluminium has a maximum of six coordination number.

    (e) Nitric acid can be stored and transported in aluminium containers, while concentrated sulfuric acid can not.

12. $MgCl_2$ can not be prepared by heating of $MgCl_2.6H_2O$. Explain.

13. With reasons, arrange the following structures of oxo-acids of period 3 elements in order of increasing acidity:
    (a) $HClO_4$, H_3PO_4, and H_2SO_4,
    (b) $HClO_2$, $HClO_3$, and H_2SO_4

14. With the aid of chemical equations, explain how Cl_2 and Br_2 react with each of the following:
    (a) Dilute sodium hydroxide solution.
    (b) Hot concentrated sodium hydroxide solution.

Chapter Four

Transition elements

Introduction

In this chapter, you will learn the physical and chemical properties of transitional elements, complex compounds and their formation, and reactions of complex compounds. You will also analyse the uses of transitional elements and complex compounds in industries. The competencies developed will enable you to understand how the unique properties of transition elements are used in various industries such as alloy production, electrical conduction, water purification, dye production, catalysts, and biological processes.

Think

World without transition elements

4.1 The concept of transition elements

Chemical elements in the periodic table are classified according to their groups or periods. Based on electronic configurations, the periodic table can be divided into blocks, denoting which sublevel is in the process of being filled. If the electrons are filled in an *s*-orbital, the elements belong to the *s*-block. If the last electrons are filled in *p*, *d* or *f*-orbitals, the elements belong to the *p*, *d* or *f*-blocks, respectively. The *s*-block is comprised of groups 1 and 2. The *p*-block includes groups 13 to 18, except helium. The *d*-block and *f*-block are situated between the *s*-block and *p*-block. These elements are called transition elements, which can be further classified into four series as follows:

(a) The first series consists of elements from scandium, Sc (Z = 21) to zinc, Zn (Z = 30) where Z is the atomic number. These elements lie in the fourth period of the periodic table.

(b) The second series consists of elements from yttrium Y (Z = 39) to cadmium, Cd (Z = 48). These elements lie in the fifth period of the periodic table.

(c) The third series consists of elements from lanthanum, La (Z = 57) to lutetium, Lu (Z = 71) and from hafnium, Hf (Z = 72) to mercury, Hg (Z = 80). These elements lie in the sixth period of the periodic table.

(d) The fourth series consists of elements from actinium, Ac (Z = 89) and those beyond rutherfordium, Rf (Z = 104). These elements lie in the seventh period of the periodic table.

The *f*-block includes the lanthanides (Z = 57 to 71) and the actinides (Z = 89 to 103). These are the inner transition metals.

The *d*-block elements are called ***inner transition elements,*** They exhibit transition behaviours between the highly reactive ionic-compounds forming *s*-block elements (electropositive elements) on one side and *p*-block elements (electronegative elements) on the other side. For an element to be considered as a transition element, it must have at least one electron in the *d*-orbital or forms at least one ion, which has 1 to 9 electrons in the *d*-orbitals (partially filled *d*-orbitals). The *d*-block elements contain two electrons in their *ns*-orbitals, while the differentiating electron enters an available (*n*-1) *d* orbital. Copper and chromium show exceptions by having one electron in the *ns*-orbital.

This chapter considers only the first series of the transition elements, which include scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, and zinc. Zinc does not qualify to be a transition element because it has full-filled *d*-orbitals. It also forms compounds in which the *d*-orbitals are full-filled. However, since zinc is the last element of the first row of transition elements, its chemistry is discussed along with that of the first row transition elements for comparison purposes. Table 4.1 shows the electronic configurations of the first transition series for the atoms and ions.

Table 4.1: *Electronic configuration of atoms and corresponding ions of the first series of transition elements*

Element symbol	Atomic number	Electronic configuration of atoms	Electronic configuration of ions (M^{2+})	Electronic configuration of ions (M^{3+})	Number of unpaired *d*-electrons in M
Sc	21	$[Ar]3d^{1}4s^{2}$	$[Ar]3d^{1}$	[Ar]	1
Ti	22	$[Ar]3d^{2}4s^{2}$	$[Ar]3d^{2}$	$[Ar]3d^{1}$	2

Element symbol	Atomic number	Electronic configuration of atoms	Electronic configuration of ions (M^{2+})	Electronic configuration of ions (M^{3+})	Number of unpaired *d*-electrons in M
V	23	$[Ar]3d^3 4s^2$	$[Ar]3d^3$	$[Ar]3d^2$	3
Cr	24	$[Ar]3d^5 4s^1$	$[Ar]3d^4$	$[Ar]3d^3$	5
Mn	25	$[Ar]3d^5 4s^2$	$[Ar]3d^5$	$[Ar]3d^4$	5
Fe	26	$[Ar]3d^6 4s^2$	$[Ar]3d^6$	$[Ar]3d^5$	4
Co	27	$[Ar]3d^7 4s^2$	$[Ar]3d^7$	$[Ar]3d^6$	3
Ni	28	$[Ar]3d^8 4s^2$	$[Ar]3d^8$	$[Ar]3d^7$	2
Cu	29	$[Ar]3d^{10} 4s^1$	$[Ar]3d^9$	$[Ar]3d^8$	0
Zn	30	$[Ar]3d^{10} 4s^2$	$[Ar]3d^{10}$	$[Ar]3d^9$	0

The unexpected electronic configurations of chromium and copper are the results of the extra stability acquired from their half-filled or full-filled sub-shells. For chromium, the expected configuration $[Ar]3d^4 4s^2$ is less stable than chromium with a configuration $[Ar]3d^5 4s^1$ (half-filled structure). The $[Ar]3d^5$ is slightly stable compare to the $[Ar]3d^4$. Conversely, copper has a stable electronic configuration of $3d^{10}4s^1$ instead of $3d^9 4s^2$. A full-filled $3d^{10}$ results into a more stable structure than the partially filled $3d^9$.

Example 4.1

Although zinc and scandium belong to the *d*-block elements of the periodic table, they are not transition elements. Justify this statement with reference to the properties of transition elements.

Solution

A transition element is the one which forms at least one compound whose *d*-orbitals are partially filled. Zinc forms compounds in which it exhibits only one oxidation state of +2 (Zn^{2+}, $[Ar]\ 3d^{10}4s^0 4p^0$), and scandium forms compounds in which it exhibits only one oxidation state of +3 (Sc^{3+}, $[Ar]\ 3d^0 4s^0 4p^0$). Looking at the electronic configurations of Zn^{2+} and Sc^{3+}, it is clear that the *d*-orbitals in Zn^{2+} are full-filled, while the *d*-orbitals in Sc^{3+} are empty. Hence, based on the definition of the transition elements, zinc and scandium do not qualify as transition elements.

4.2 Characteristics of transition elements

Transition elements display a variety of unique characteristics, many of which are connected to their partially filled *d*-orbitals. These characteristics are divided into two categories named chemical and physical characteristics.

4.2.1 Physical properties of transition elements

Task 4.1

Use internet sources to explore the physical properties of transition elements and relate them with their uses in daily activities and industrial production. Prepare a report and present the findings to classmates.

Transition elements are metals with good mechanical properties, which make them useful for many industrial applications. The following are some of the physical properties of the transition elements:

(a) They have high tensile strengths; that is, they can withstand high stresses and loads without fracturing, hence, they can be used in construction.

(b) They are ductile, thus, they can be drawn into wires.

(c) They are malleable, therefore, they can be pressed to form sheets.

(d) They have high melting and boiling points; consequently, they can withstand high temperatures.

(e) They are good conductors of heat and electricity; therefore, they are used for to make electric cables.

Other physical properties of the first–row *d*-block elements are summarised in Table 4.2.

Table 4.2: *Selected properties of the first- row d-block elements*

Element symbol	Atomic number	Atomic radius, Å	Ionic radius, Å	Boiling point, °C	Melting point, °C	Density, g cm^{-3}
Sc	21	1.44	0.81	2830	1539	2.99
Ti	22	1.32	0.76	3260	1680	4.49
V	23	1.22	0.74	3450	1710	5.96
Cr	24	1.17	0.69	2642	1890	7.20
Mn	25	1.17	0.66	2100	1247	7.43
Fe	26	1.16	0.64	3000	1528	7.86
Co	27	1.16	0.63	2900	1490	8.90
Ni	28	1.15	0.63	2730	1452	8.90
Cu	29	1.17	0.73	2600	1083	8.92
Zn	30	1.24	0.74	906	419	7.14

4.2.2 Chemical properties of transition elements

Task 4.2

Use online platforms to explore the features which enable transition elements to dominate in engineering activities.

Transition elements exhibit peculiar chemical properties, which are not shown by other elements. The properties of these elements are attributed to the splitting of the *d*-orbitals (d_{z^2}, $d_{x^2-y^2}$, d_{yz}, d_{xz}, and d_{xy}) into the upper and lower sets with slightly different energies. The upper set is known as e_g set, while the lower is called t_{2g} set. The e_g set is slightly higher in energy than the t_{2g} set (Figure 4.1).

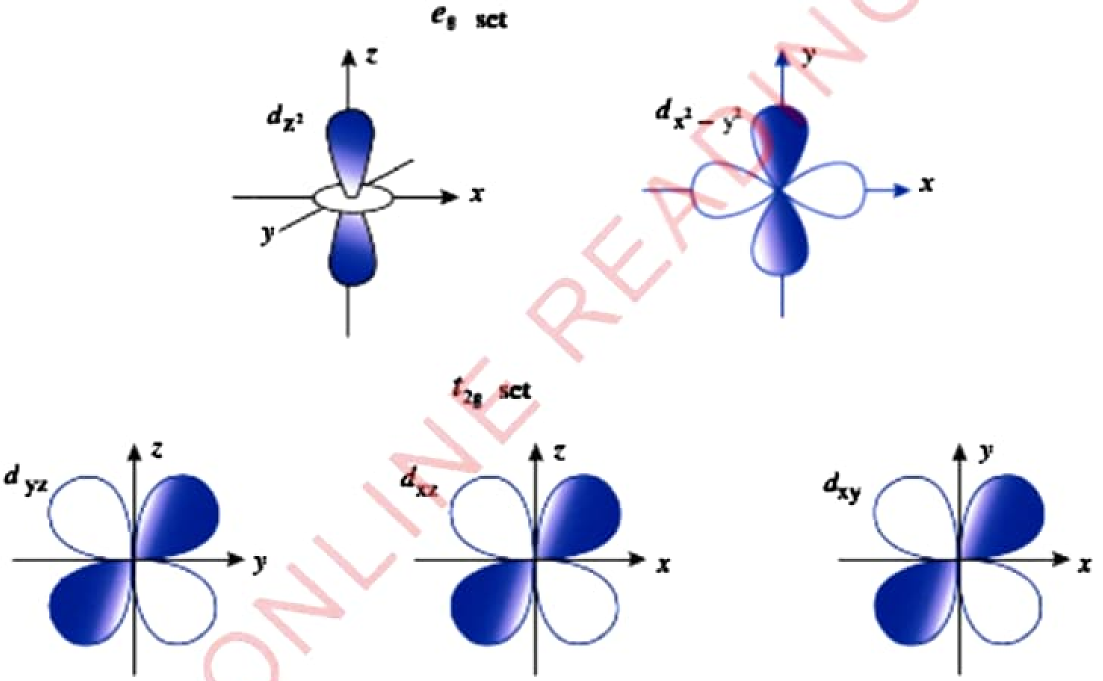


Figure 4.1: *d-orbitals in e_g set and t_{2g} set*

Variable oxidation states

The *d*-block elements show a wide range of oxidation states. Usually, the highest oxidation state of a metal corresponds to its group number in the periodic table. The variable valences are due to the ability of the transition elements to lose electrons from both the outer *quantum shell* and the *penultimate shell* to form ions. The

4*s* and 3*d* orbitals have very little energy differences and hence, can be used for valence purposes. Table 4.3 shows the most common oxidation states of the first series of the transition elements.

Table 4.3: *Common oxidation states shown by the transition elements of the first series*

Element symbol	Common oxidation states				
Sc	+3				
Ti	+2	+4			
V	+2	+3	+4	+5	
Cr	+2	+3	+6		
Mn	+2	+3	+4	+6	+7
Fe	+2	+3			
Co	+2	+3			
Ni	+2				
Cu	+1	+2			
Zn		+2			

As indicated in Table 4.3, the most common oxidation state is +2, which is acquired by losing two electrons. Oxidation states higher than +2 can be obtained upon subsequent removal of electrons from the 3*d*-orbital. Manganese has the greatest number of oxidation states compared with the other first-row transition elements.

Example 4.2

Calculate the oxidation states of manganese in MnO_4^-, MnO_2, and $MnCl_2$ and account for the observed differences.

Solution

Use the knowledge obtained elsewhere to calculate the oxidation state of different species. The oxidation state of manganese in MnO_4^- is +7, in MnO_2 is + 4, and in $MnCl_2$ is +2. It is therefore, concluded that manganese exhibits a property of variable oxidation states. This property is attributed to its ability to lose electrons from both the outer quantum shell and the penultimate shell.

Catalytic properties

Most of the transition elements and their compounds, particularly oxides, have good catalytic properties. The catalytic properties of the transition elements and their compounds are associated with the presence of vacant *d*-orbitals, the tendency to exhibit variable oxidation states, the tendency to form reaction intermediates with reactants, and the presence of defects (irregular arrangements of atoms) in their crystal lattices. Moreover, the catalytic properties of the transition elements are associated with their ability to provide surfaces where reacting molecules can temporarily attach to allow rearrangement of atoms. Commonly used catalysts in various industries are nickel, iron, vanadium, manganese, and platinum. Nickel or platinum are used in catalytic hydrogenation, iron is used in the Haber process, and vanadium pentoxide is used in the Contact process. Examples of the reactions in which the transition elements exhibit catalytic properties are presented as follows:

(a) Iron and nickel play the roles of catalysts in the Haber process and in the hydrogenation reaction, respectively, by providing contact surface areas to facilitate the reactions.

(i) $N_2(g) + 3H_2(g) \xrightleftharpoons{Fe} 2NH_3(g)$

(ii) $H_2C{=}CH_2(g) - 2H_2(g) \xrightarrow{Ni} CH_3CH_3(g)$

In reactions (i) and (ii), Fe and Ni possess vacant low-lying 3*d*-orbitals, which act as electron acceptors to form temporary bonds between the catalyst and reactant. This process brings the reactant particles closer enough to result into successful reaction.

(b) V_2O_5 and Fe^{3+} exhibit catalytic properties by varying their oxidation states to alter the rates of chemical reactions. When gaseous sulfur dioxide is passed together with air over a solid vanadium pentoxide catalyst, V_2O_5, the catalyst oxidises SO_2 to SO_3, and itself gets reduced to V_2O_4 as shown in the first chemical equation (i) below. The V_2O_4 is then oxidised by oxygen to V_2O_5 as shown in the second chemical equation (ii). The net reaction equation can be represented as:

$$2SO_2(g) - O_2(g) \xrightleftharpoons{V_2O_5} 2SO_3(g)$$

with catalytic steps:

(i) $2SO_2(g) + 2V_2O_5(s) \rightleftharpoons 2SO_3(g) + 2V_2O_4(s)$

(ii) $2V_2O_4(s) + O_2(g) \longrightarrow 2V_2O_5(s)$

(c) Similarly, in the reaction between I^- and $S_2O_8^{2-}$, Fe^{3+} ions catalyse the reaction by changing its oxidation state. The net reaction equation is,

$$2I^-(aq) + S_2O_8^{2-}(aq) \xrightleftharpoons{Fe^{3+}} I_2(aq) + 2SO_4^{2-}(aq)$$

with catalytic steps:

(i) $2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(g)$

Then, the produced Fe^{2+} reacts with $S_2O_8^{2-}$ according to the following reaction:

(ii) $2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \longrightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq)$

In the given catalytic steps (i) and (ii), the transition elements vanadium in V_2O_5 and iron in Fe^{3+} allow electron transfer between the reactants and the products. This happens by means of the catalytic interchange between the two oxidation states, thus facilitating a redox cycle.

Activity 4.1

Aim: To investigate the catalytic effects of transition elements on the decomposition of H_2O_2

Requirements: Copper turnings, MnO_2, V_2O_5, hydrogen peroxide, water, magnesium ribbon, flat-bottomed flask, stopper, delivery tube, gas jar, trough, beehive shelf and thistle funnel

Procedure

1. Set the apparatus for the preparation of oxygen using hydrogen peroxide.
2. Place about 1 g of MnO_2 into a flat-bottomed flask.

3. Put hydrogen peroxide solution into a thistle funnel.
4. Allow the hydrogen peroxide solution to mix with MnO_2 dropwise and observe the changes in terms of the evolution of gas.
5. Repeat steps 1 to 4 using copper turnings, V_2O_5, and magnesium ribbon in place of MnO_2 and observe the changes in the evolution of gas.

Questions

1. Which observations were made on the rates of evolution of gas when copper turning, MnO_2, magnesium ribbon, and V_2O_5 were separately used in the experiment?
2. How did the V_2O_5, magnesium ribbon, copper turnings and MnO_2 play their roles in this experiment in relation to the electronic configurations of their respective metals/metal ions.
3. What is the relevance of the performed activity in the manufacturing industry of your choice?

Formation of coloured compounds

Generally, the compounds of the transition elements are coloured. For example, hydrated copper(II) sulfate is blue, potassium permanganate is purple, and hydrated iron(II) sulfate is light green. The colours are characteristics of their hydrated salts or solutions. The cations of the transition elements become coloured only when they interact with other chemical species such as ions or molecules. The colours of the compounds depend on the type of the chemical species (ligands), which the transition metal cations interact with. The concept of colour formation in transition metals is explained by the Crystal Field Theory (CFT).

In the crystal field theory, the transition metals form colour as a result of the splitting of the degenerate *d*-orbitals. The splitting of the *d*-orbitals of the central metal is a result of the electrostatic attraction between the ion pair electrons of the ligand and the nucleus of the central metal. Besides the electrostatic attraction between the ligand and the nucleus of the central metal, repulsion occurs between the ion pair electrons and the electrons of the central metal. This results into the splitting of the degenerate *d*-orbitals into the two sets. The splitting raises two of the *d*-orbitals d_{z^2} and $d_{x^2-y^2}$ to a higher energy level (the e_g set), while the remaining orbitals d_{xy}, d_{xz}, and d_{yz} occupy a lower energy level (the t_{2g} set) as shown in Figure 4.2.

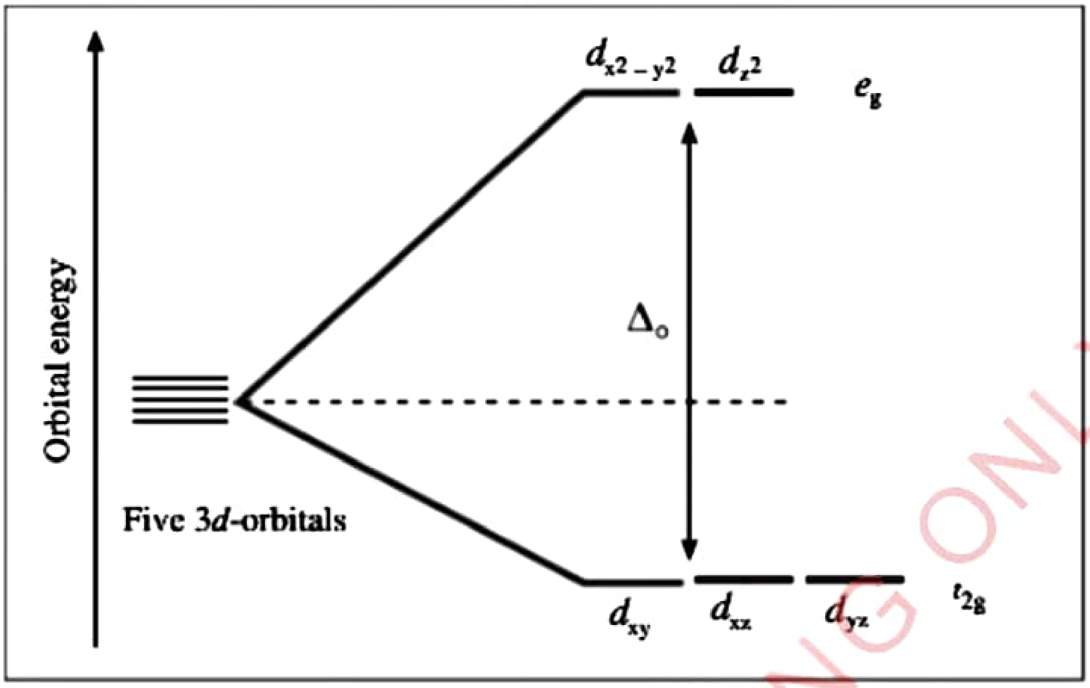


Figure 4.2: *Splitting of d-orbitals in octahedral complex*

The extent to which the orbitals are separated depends on the nature of the ligand. The stronger the ligand, the bigger the splitting effect and vice versa. The energy difference between the e_g and t_{2g} is known as the *Crystal Field Stabilisation Energy* (CFSE). It is a characteristic physical quantity that depends on the strength of the ligand.

The spatial distribution of the degenerate orbitals depends on the geometry of the complex formed between the central metal and the ligand. Stronger splitting results into a greater energy difference (Δ_o) between the e_g and the t_{2g} sets. If the energy difference is large, the electrons absorb more energy and transmit radiations of higher wavelength and lower frequency (colours of visible light are given in terms of wavelengths or frequencies). The electron movements between the two groups of the *d*-orbitals absorb energy and transmit radiations of specific wavelengths corresponding to the specific colours that are observed.

Compounds of some of the 1st series of the *d*-block elements are colourless when no electrons are present in the *d*-orbitals as for Sc^{3+} or when all the *d*-orbitals are filled, as for Cu^+ and Zn^{2+}. Only complexes of the transition elements having partially filled *d*-orbitals form coloured compounds. Examples of ionic complexes of the transition elements which form colours are given in Table 4.4.

Table 4.4: *Coloured complexes of some transition elements*

Ionic complex	Colour
$[Co(H_2O)_6]^{2+}$	Pinkish-red
$[Fe(CN)_6]^{4-}$	Greenish-yellow
$[Fe(H_2O)_6]^{2+}$	Pale-green
$[Fe(H_2O)_6]^{3+}$	Brownish-yellow
$[Cu(NH_3)_4]^{2+}$	Deep-blue
$[Cu(H_2O)_4]^{2+}$	Pale-blue

Consider the different colours of the complexes of cobalt in which H_2O, NH_3, and CN^- are ligands. The complex $[Co(H_2O)_6]^{3-}$ is blue, $[Co(NH_3)_6]^{3+}$ is orange, and $[Co(CN)_6]^{3-}$ is yellow. The effects of the different ligands on the colours of the cobalt complexes can be explained as follows: The aqua ligand (H_2O) induces a small energy difference in Co^{3+}, and low energy photons are absorbed; thus $[Co(H_2O)_6]^{3+}$ appears blue. The ammine ligand (NH_3) induces a larger energy difference, and high energy photons are absorbed; thus $[Co(NH_3)_6]^{3+}$ appears orange. The cyano ligand (CN^-) induces the largest energy difference, and highest energy photons are absorbed; thus, $[Co(CN)_6]^{3-}$ appears yellow. Table 4.5 gives the summary of the effects produced by different ligands on the colours of the cobalt complexes.

Table 4.5: *Effects of different ligands on the colours of the cobalt complexes*

Ion	$[Co(CN)_6]^{3-}$	$[Co(NH_3)_6]^{3+}$	$[Co(H_2O)_6]^{3+}$
Colour of ion	Yellow	Orange	Blue
Colour absorbed	Violet	Blue	Orange
Energy difference	Largest	Intermediate	Smallest
Ligand involved	Cyano, CN^-	Ammine, NH_3	Aqua, H_2O
Splitting ability of the ligands	Strongest	Intermediate	Weakest

Magnetic properties

Magnetic properties explain how a material behaves when placed in magnetic field. The magnetic properties of an element or ion are due to the presence of unpaired electrons in the *d*-orbitals. If the unpaired electrons are many, the material is more strongly attracted by a magnet and is classified as *ferromagnetic material*. If unpaired electrons are present in the *d*-orbital of an atom, ion or molecule, the material is weakly attracted by a magnet and is classified as a *paramagnetic material*. If an atom does not contain unpaired electrons, the material can not respond to magnetism, and it is classified as a *diamagnetic material*.

Unpaired electrons spin about their own axis, and in so doing, create a small magnet (movement of charge creates magnetism). The small magnets of spinning electrons have north and south poles. If an external magnet is introduced, these small magnets are attracted and the material shows magnetic properties. Paired electrons spin in opposite directions and their small magnets have opposite orientations, thus cancelling each other. Materials with paired electrons do not respond to external magnetism. Table 4.6 shows box electronic configurations of the first transition metal series.

Table 4.6: *Arrangement of valence shell electrons of the first transition metal series*

Element symbol	Electronic configuration						
		3*d*					4*s*
Sc	[Ar]	↑					↑↓
Ti	[Ar]	↑	↑				↑↓
V	[Ar]	↑	↑	↑			↑↓
Cr	[Ar]	↑	↑	↑	↑	↑	↑
Mn	[Ar]	↑	↑	↑	↑	↑	↑↓
Fe	[Ar]	↑↓	↑	↑	↑	↑	↑↓
Co	[Ar]	↑↓	↑↓	↑	↑	↑	↑↓
Ni	[Ar]	↑↓	↑↓	↑↓	↑	↑	↑↓
Cu	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Zn	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

The number of unpaired electrons determines the strength of the magnetic moment. The higher the number of unpaired electrons, the higher the magnetic moment and the greater the magnetic behaviour of the substance. Furthermore, the magnetic properties of the compounds are affected by the types of ligands surrounding the central atom in a complex compound. This is because, when the ligands approach the central atom, they cause repulsion of the *d*-electrons of the central atom; thus, the orbitals split into sublevels. The extent to which the *d*-orbitals split depends on the strength of the external electric field of the ligands.

Taking the complexes of Fe^{2+} as examples, when the ligands approach the cation (Fe^{2+}) along its six axes, the energy of d_{z^2} and $d_{x^2-y^2}$ is raised above that of d_{xy}, d_{xz}, and d_{yz}. Ligands such as NH_3, H_2O, F^-, Cl^-, Br^-, and I^- have low external electric fields. The split caused by these ligands is always small, and therefore, electrons are distributed according to the Hund's Rule of maximum multiplicity. Therefore, since Fe^{2+} has six electrons in the five *d*-orbitals, the spread is as shown in Figure 4.3. Each of the unpaired electrons in the split *d*-orbital exhibits a magnetic moment. This compound strongly paramagnetic, and it is said to be of high spin.

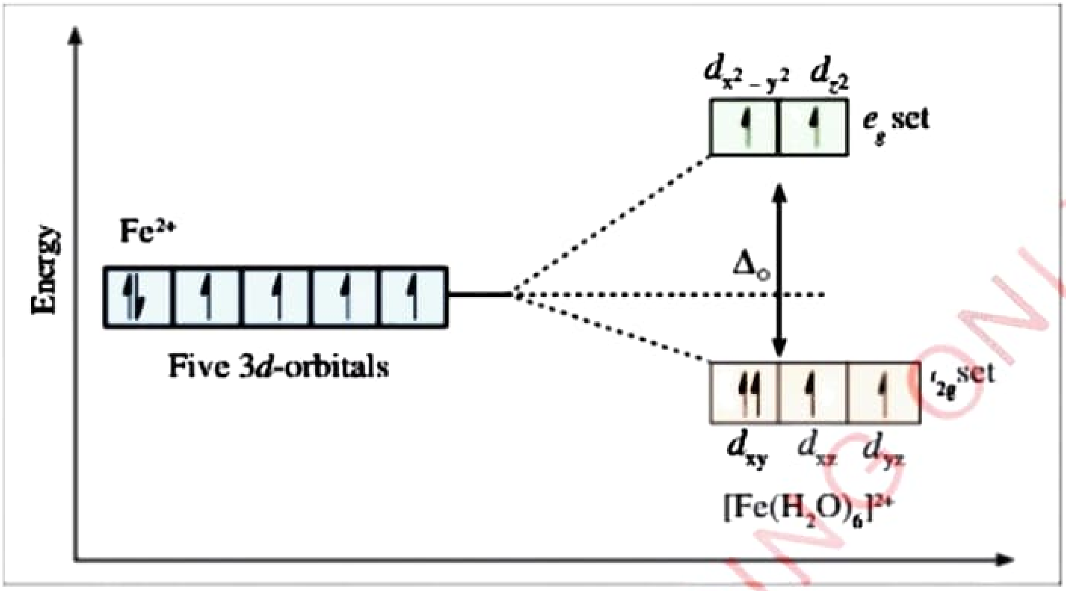


Figure 4.3: *Splitting of d-orbitals of Fe^{2+} caused by weak field ligands*

Conversely, when the Fe^{2+} is coordinated by ligands having a high external electric field such as CN^- and ethylenediamine (en), the split is so large that the electrons are forced to form pairs in the lower t_{2g} orbitals as shown in Figure 4.4. Pairing of electrons results into disappearance of the paramagnetic property, thus, $[Fe(CN)_6]^{4-}$ is a diamagnetic low spin complex.

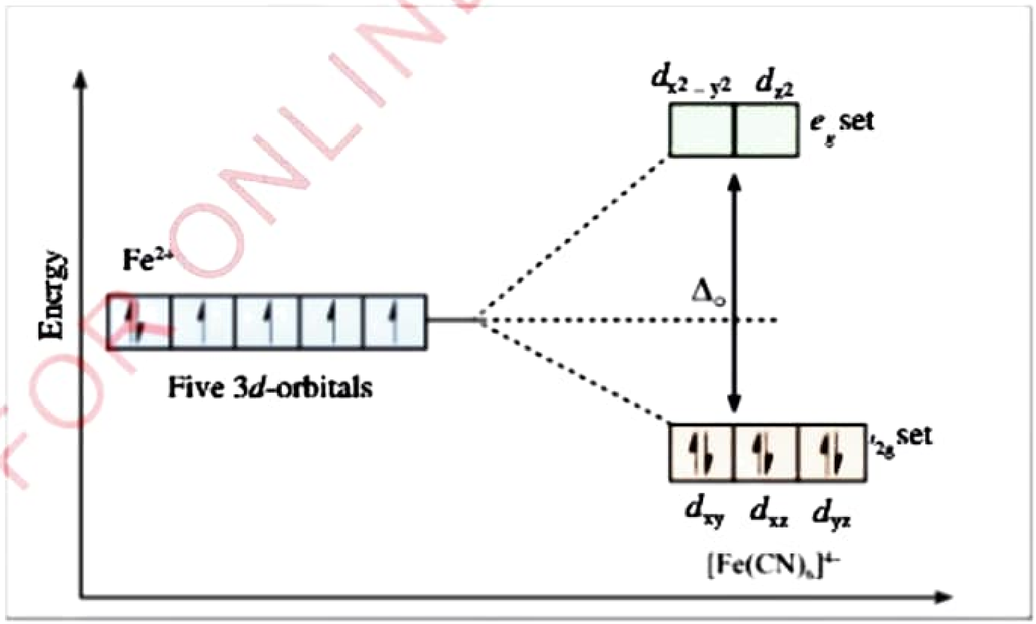


Figure 4.4: *Splitting of d-orbitals of Fe^{2+} caused by strong field ligands*

Activity 4.2

Aim: To investigate the magnetic properties of transition elements and their compounds

Requirements: Magnet, iron fillings, copper turnings, zinc granules, chromium, $CaCO_3$, $NaCl$, $K_2Cr_2O_7$, K_2CrO_4, $KMnO_4$, $K_4[Fe(CN)_6]$, $K_3[Fe(CN)_6]$, manila paper

Procedure

1. Place iron fillings on a piece of manila paper.
2. Pass the magnet over the paper and observe the ability of the magnet to attract the fillings.
3. Repeat steps 1 and 2 using copper turnings, zinc granules, chromium, $CaCO_3$, $NaCl$, $K_2Cr_2O_7$, K_2CrO_4, $KMnO_4$, $K_4[Fe(CN)_6]$, and $K_3[Fe(CN)_6]$ in place of iron fillings.

Questions

1. How did each type of the material behave when the magnet was passing over it?
2. What classification can you make in question 1 based on the electronic configuration of each metallic species in relation to the magnetic ability exhibited?

Example 4.3

Account for the fact that $[Fe(CN)_6]^{4-}$ is diamagnetic, whereas $[FeCl_4]^{2-}$ is paramagnetic.

Solution

In both complexes, the central metal oxidation state is +2 (Fe^{2+}) with the valence shell electronic configuration of $3d^6 4s^0 4p^0$, and the electrons are arranged as follows:

When chloride ligands approach Fe^{2+}, they cause splitting of the *d*-orbitals but to a lesser extent as they are weak field ligands. As a result, the arrangements of the electrons in the *d*-orbitals remain unchanged in e_g and t_{2g} sets as shown in Figure 4.5.

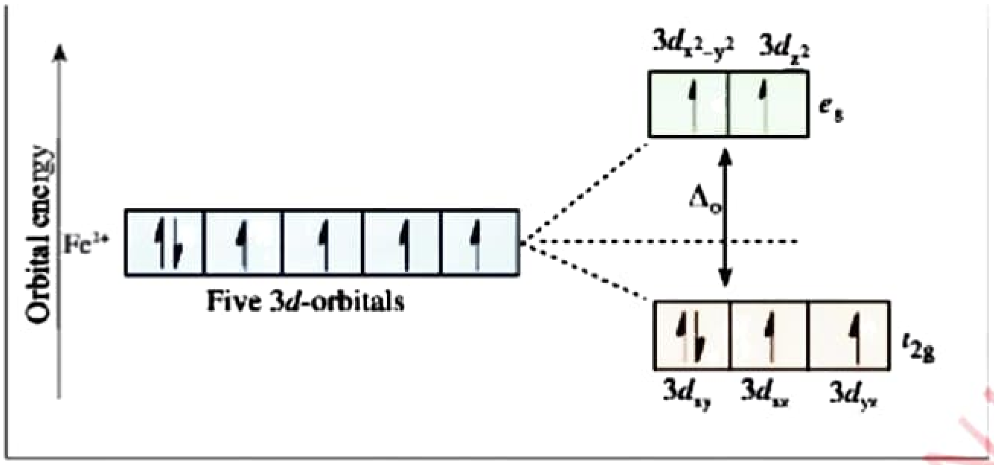


Figure 4.5: *Splitting of d-orbital of Fe^{2+} caused by weak field ligands leading to paramagnetism*

Conversely, CN^- ligands which are strong field ligands cause large splitting of *d*-orbitals. The large energy gap between the e_g and t_{2g} sets prevents electrons from being distributed to the higher energy level, and they fall back from e_g to t_{2g} as shown in Figure 4.6.

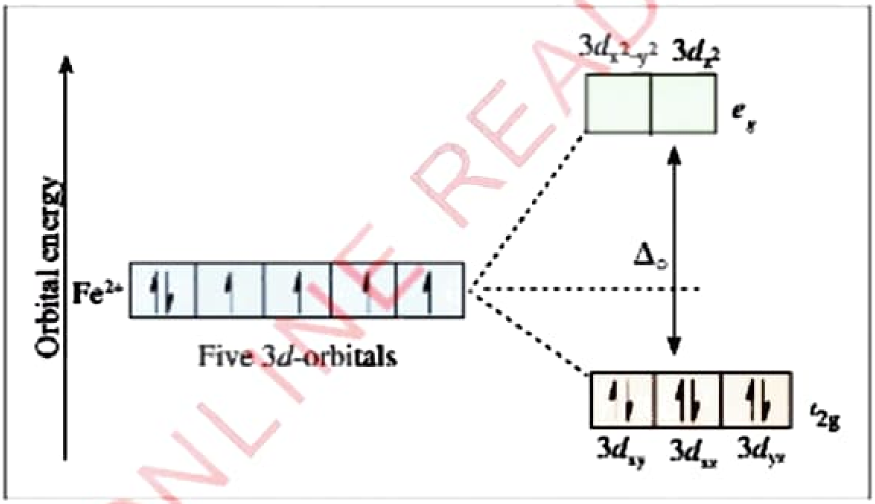


Figure 4.6: *Splitting of d-orbital of Fe^{2+} caused by strong field ligands leading to diamagnetism*

The electron pairing leads to the loss of the paramagnetic property of the material, and hence, $[Fe(CN)_6]^{4-}$ is diamagnetic, whereas $[FeCl_4]^{2-}$ is paramagnetic.

Alloy formation

When transition metals are fused with other metals, they form alloys. An *alloy* is a solid mixture obtained by fusing a metal with another metal(s) or non-metal. Transition elements form alloys with other metals which are not transition metals or with other transition metals. For example, steels are alloys of iron with metals such as chromium, vanadium, molybdenum, tungsten, and manganese or with other elements such as carbon. Alloys of transition elements have desired properties compared to the pure elements. Looking at the atomic radii of the first series of the transition elements (Table 4.2), it can be noted that they are not much different from each other. Because of this property, they can very easily replace each other in the lattice and form solid mixtures over an appreciable composition range. This is attributed to their ability to form alloys.

Exercise 4.1

1. Explain the attributes of the transition elements which are responsible for their catalytic activity.
2. Which is a stronger oxidising agent in aqueous solution, Mn^{3+} or Cr^{3+}? Explain your choice in terms of electronic configuration.
3. Examine the significance and potential hazards of transition elements and their compounds.
4. Explain the easiest method for testing the purity of an earth rod from pure copper metal.

4.3 Ligands and formation of complexes

One of the most important chemical properties of the *d*-block elements is their ability to form complexes. A complex *is a molecule or ion composed of a central metal atom or ion surrounded by negative, positive, or neutral ligands*. Ligands *are ions or molecules which bind to the central atom in a complex*. They are either polar molecules such as H_2O and NH_3, or anions such as Cl^- and CN^-, which have at least one lone pair of electrons to be shared with a central metal atom or ion.

Complexes are formed by dative (or coordinate) bonding. For a complex compound, the central atom/ion should have vacant (empty) orbitals of appropriate energy, and the ligand should have at least one lone pair of valence electrons. The most stable complexes are formed by the central ion with a high positive charge and a small ionic radius. Transition elements qualify in complex formation since they can utilise some of the vacant *d*-orbitals of their penultimate quantum shell for bonding purposes.

For example, when a solution of chromium(III) chloride is mixed with ammonia, a chromium complex is formed.

$$CrCl_3(aq) + 4NH_4(aq) \longrightarrow [Cr(NH_3)_4Cl_2]^+(aq) + Cl^-(aq)$$

In this reaction, the vacant orbital in the chromium ion (central ion) can coordinate with six ligands, making a cationic complex.

Similarly, a copper complex is formed when copper sulfate solution is mixed with water as shown in the following equation:

$$CuSO_4(aq) + 4H_2O(l) \longrightarrow [Cu(H_2O)_4]^{2+}(aq) + SO_4^{2-}(aq)$$

The above reaction shows that four water molecules can be accommodated by a single copper ion to form a complex compound.

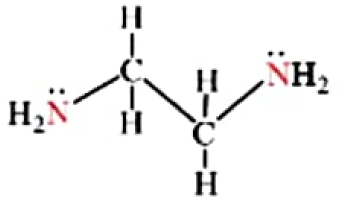
The solubility of complex compounds depends on various factors, including the structure and polarity of the compound as well as the interactions between the compound and water molecules. Thus, some complex compounds may be soluble, while others may be insoluble or only partially soluble in water.

4.3.1 Ligands

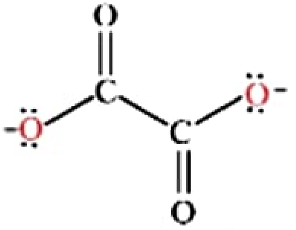
Ligands are attached to the central metal ion by a coordinate bond. The atom in a ligand that is bound directly to the central metal atom or ion is known as the *donor atom*. The number of the donor atoms surrounding the central metal atom or ion in a complex is called the *coordination number*. For example, in $[Cu(NH_3)_4]^{2+}$, the coordination number is four, and the donor atom is nitrogen. Depending on the number of the donor atoms present in the ligand, ligands are classified as monodentate, bidentate or polydentate (Table 4.7).

Monodentate ligands have only one donor atom per ligand. Examples of monodentate ligands are H_2O, NH_3, and Cl^-. H_2O donates electrons through oxygen atom, O; NH_3 donates through the nitrogen atom, N; and Cl^- donates through the electron pairs present on the chlorine atom. *Ambidentate* is a monodentate ligand, which uses one atom at a time to form coordinate bonds with the central metal atom or ion. For example, the nitrite ion (NO_2^-) can bind to the central metal atom/ion at either the nitrogen atom or one of the oxygen atoms. The thiocyanate ion (SCN^-) can bind to the central metal at either the sulfur or the nitrogen, while the CN^- binds to the central metal at either the carbon or nitrogen.

Bidentate ligands have two donor atoms per ligand molecule. Examples of the bidentate ligands are ethylene diamine (en) and exalate ion (oxalato). Atoms in red are donor atoms.



ethylenediamine (en)



oxalate ion (oxalato)

Ligands with more than two donor atoms are referred to as *polydentate ligands*. An example of the polydentate ligands is ethylenediaminetetraacetic acid (EDTA).

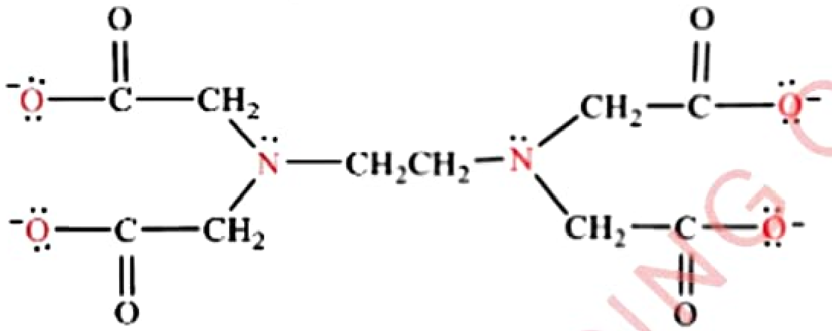
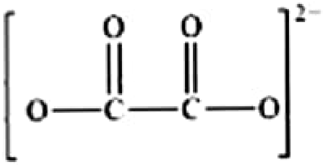
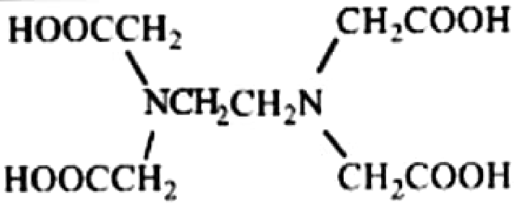


Table 4.7: *Examples of some common ligands*

Ligand name	Ligand formula	Classification
Bromo	Br^-	Monodentate
Iodo	I^-	Monodentate
Chloro	Cl^-	Monodentate
Thiocyanato	SCN^-	Monodentate
Aqua	H_2O	Monodentate
Nitro	ONO^-	Monodentate
Fluoro	F^-	Monodentate
Ammine	NH_3	Monodentate
Hydroxo	OH^-	Monodentate
Cyano	CN^-	Monodentate
Carbonyl	CO	Monodentate
Nitrosyl	NO	Monodentate
Methylamine	CH_3NH_2	Monodentate
Ethylenediamine (en)	$H_2NCH_2CH_2NH_2$	Bidentate

Ligand name	Ligand formula	Classification
Oxalato	 $\left[\mathrm{O{-}\overset{O}{\overset{\Vert}{C}}{-}\overset{O}{\overset{\Vert}{C}}{-}O}\right]^{2-}$	Bidentate
Diethylenetriamine	$H_2N(CH_2)_2NH(CH_2)_2NH_2$	Polydentate
Ethylenediaminetetraacetic acid (EDTA)		Polydentate

4.3.2 Formation of complexes

The transition elements differ in their ability to form complex compounds. This is attributed to the sizes of the cations and the presence of empty or vacant *d*-orbitals.

Ionic radii

The term ionic radius *refers to half the distance between two bonded ions*. It indicates the distance from the nucleus of an ion to a point where it has an influence on its electron cloud. Ionic radius is important in determining the polarising power of a cation or the polarisability of anions. It is a measure of charge density of the ion which is given by the ratio of the ionic charge to the ionic radius. The ionic radii for the *d*-block transition metals are shown in Table 4.2.

The effect of ionic size on complex compound formation is explained in terms of the polarising power of the central metal ion. *Polarising power* refers to the ability of a central metal ion to deform a ligand. The smaller the size of a central metal ion, the higher the polarising power. The more a central metal ion polarises a ligand, the higher the chance for complex compound formation.

Vacant *d*-orbitals

The atom with vacant *d*-orbitals acts as an electron pair acceptor; therefore, it is a Lewis acid. The central metal atom or ion together with all the coordinated ligands form the *coordination sphere*. Looking at the coordination sphere of a complex compound or ion, it becomes possible to classify complexes into neutral, anionic, and cationic. Negatively charged complexes such as $[Fe(CN)_6]^{3-}$, $[CoCl_4]^{2-}$ and $[Al(H_2O)_2(OH)_4]^-$ are called *anionic complexes*. They have a net negative charge outside the coordination sphere. On the other hand, complexes that carry a net positive charge outside the coordination sphere such as $[Cu(H_2O)_6]^{2+}$ and $[Co(NH_3)_6]^{3+}$ are called *cationic complexes*. Complexes whose coordination spheres have no charge outside their coordination spheres are called *neutral complexes*. Therefore, $[Ni(CO)_4]$ and $[Pt(NH_3)_2Cl_4]$ are neutral complexes.

Example 4.4

Choose one complex cation of cobalt and one complex anion of nickel and complete the following table by showing the formula of the complex ion, type of ligand(s), and oxidation state of the central metal.

Element	Formula of the selected complex	Ligand(s)	Type of ligand	Oxidation state
Cobalt				
Nickel				

Solution

Element	Formula of the selected complex	Ligand (s)	Type of ligand	Oxidation state
Cobalt	$[Co(en)_2(H_2O)CN]^{2+}$	en	Bidentate	+3
		H_2O	Monodentate	
		CN^-	Monodentate	
Nickel	$[Ni(CN)_4]^{2-}$	CN^-	Monodentate	+2

Task 4.3

Use any source to establish the chemical structures of different complex compounds. Finally, use these structures to simulate their formation processes. Present the results to classmates and subject teachers for evaluation.

Exercise 4.2

1. (a) Explain the following terms:
    - (i) Coordination number
    - (ii) Central metal ion
    - (iii) Ligand

(b) Consider the following complex: $[Co(en)_2(H_2O)CN]^{2+}$
   (i) What does "en" entail in the compound?
   (ii) Calculate the oxidation state of Co.
   (iii) What is the coordination number of Co?
   (iv) Explain the ability of each ligand to bond with the central metal ion.

2. Account for the following observations:
   (a) Hydrated copper(II) salts are coloured, but the anhydrous salts are colourless or white.
   (b) Chromium is less reactive than its standard reduction potential.
   (c) $[FeF_6]^{3-}$ has stronger magnetic field than $[Fe(CN)_6]^{3-}$.
   (d) A concentrated aqueous copper(II) chloride solution is bright green in colour. When diluted with water, the solution becomes light blue.

3. (a) Explain how the following features affect the ability of transition elements to form complex compounds:
   (i) Ionic size
   (ii) Vacant d-orbitals
   (b) Write the catalytic reaction steps involved in the following chemical equations:
   (i) $2SO_2(g) + O_2(g) \overset{V_2O_5}{\rightleftharpoons} 2SO_3(g)$
   (ii) $2I^-(aq) + S_2O_8^{2-}(aq) \overset{Fe^{3+}}{\rightleftharpoons} I_2(aq) + 2SO_4^{2-}(aq)$

4. How ligands are significant in the real-world applications?

Coordination number and geometries of complexes

Complex compounds are formed by a central metal atom or ion directly coordinated to the ligands. The ligands donate an electron pair to the empty d-orbitals of the central metal. The number of ligands which is directly coordinated to the central metal ion is the coordination number of that atom in the complex. The most frequent coordination numbers for the complexes of the first transition metal series are 6, 5, and 4. The coordination numbers depend on the relative sizes of the central metal atoms or ions, the ligands surrounding, and the charges of the ligands. Large ligands favour low coordination numbers, while small ligands favour high coordination numbers. Neutral ligands favour high coordination numbers, while anionic ligands favour low coordination numbers. For example, on complexing with iron(II) ion, the chloride ion (a large ion) forms $[FeCl_4]^{2-}$, while the fluoride ion (a small ion) forms $[FeF_6]^{4-}$. On complexing with nickel(II), ammonia (neutral ligand) forms $[Ni(NH_3)_6]^{2+}$, while the chloride ion (an anionic ligand) forms $[NiCl_4]^{2-}$ ion.

The coordination number is usually associated with the geometry of the complex. Considering the most common coordination numbers 4 and 6, the coordination number of 4 forms two types of geometries, namely a *square planar* and a *tetrahedral,* while coordination number 6 has an *octahedral geometry*. The illustration is given by the Valence bond theory, which predicts the use of unoccupied orbitals.

Square planar complexes such as $[Ni(CN)_4]^{2-}$ and $[Pt(NH_3)_4]^{2+}$ have central metal atoms or ions surrounded by four ligands at the four corners of the square, making an angle of 90°. The square planar geometry is commonly formed when the ions with electronic configuration of $(n\text{-}1)d^8$ form dsp^2 hybridised orbitals. This is illustrated by the formation of $[Ni(CN)_4]^{2-}$ in Figure 4.6.

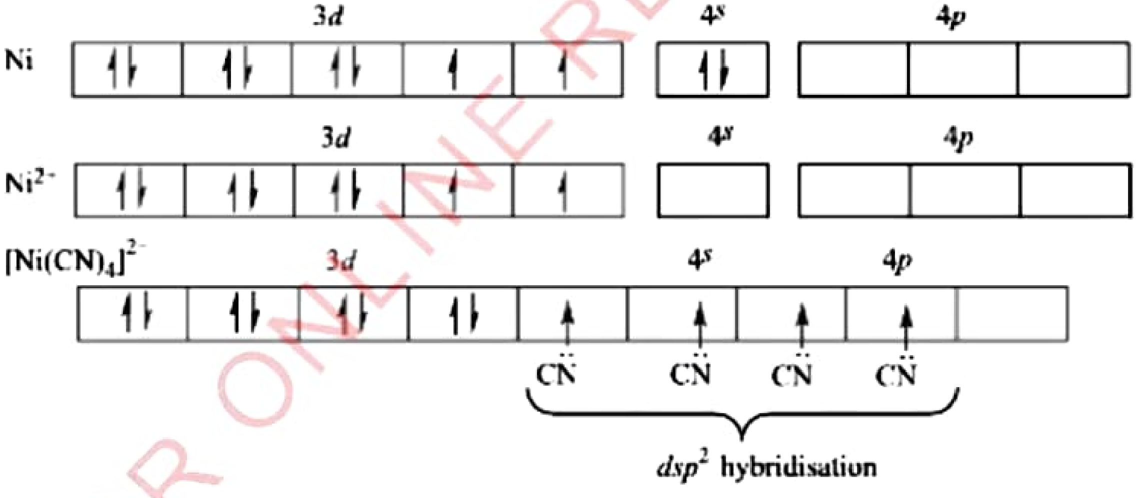


Figure 4.6: *dsp^2 hybridisation in $[Ni(CN)_4]^{2-}$*

The outermost electronic configuration of Ni^{2+} is $3d^8 4s^0 4p^0$. In the formation of $[Ni(CN)_4]^{2-}$, two unpaired $3d$ electrons pair in one orbital, and the vacant $3d$ orbital mixes with the $4s$ and two $4p$-orbitals forming four dsp^2 hybrid orbitals. These lie in the same plane with their four lobes directed to the four corners of the square (Figure 4.7).

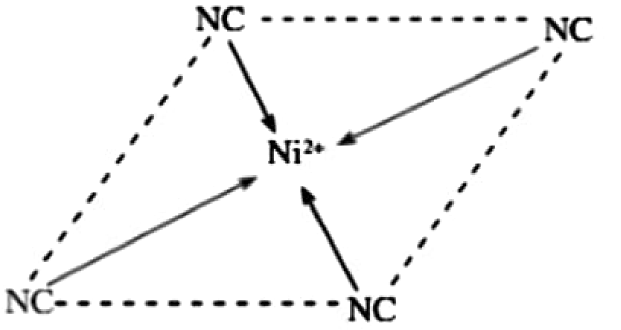


Figure 4.7: *Square planar complex ion of* $[Ni(CN)_4]^{2-}$

Tetrahedral complexes, such as $[CoCl_4]^{2-}$, $[CuCl_4]^{2-}$, and $[Cu(H_2O)_4]^{2+}$, have a central metal atom or ion at the centre of a regular tetrahedron with ligands, making the angle of around 109.5°. The formation of tetrahedral geometry in $[Cu(H_2O)_4]^{2+}$ can be described using the illustration shown in Figure 4.8.

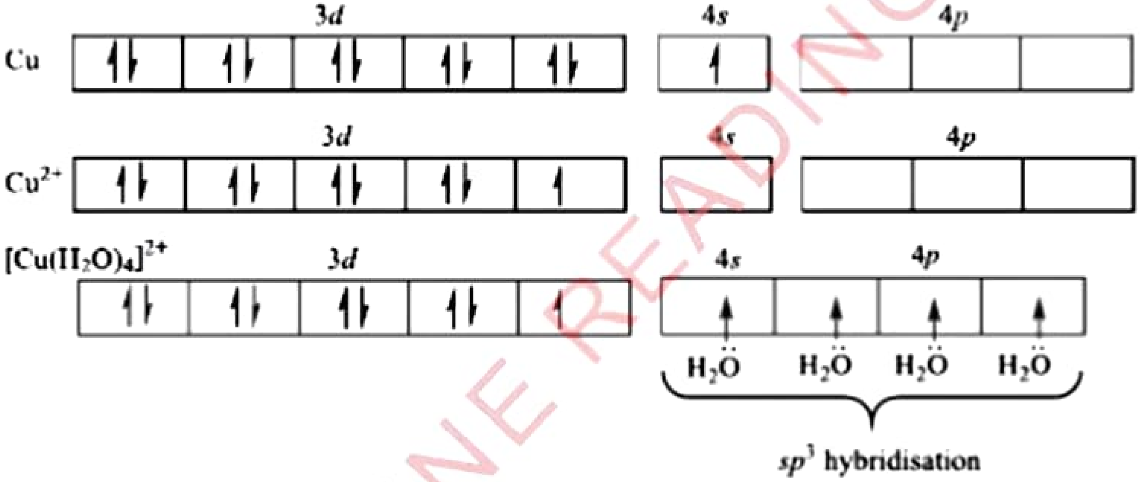


Figure 4.8: sp^3 *hybridisation in* $[Cu(H_2O)_4]^{2+}$

Cu^{2+} has the outermost electronic configuration of $3d^9 4s^0 4p^0$. As ligands (water molecules) approach the central metal atom, the 4*s* mixes with the three 4*p*-orbitals forming four sp^3 hybrid orbitals with their lobes at 109.5° apart, forming the corners of the tetrahedron as shown in Figure 4.9.

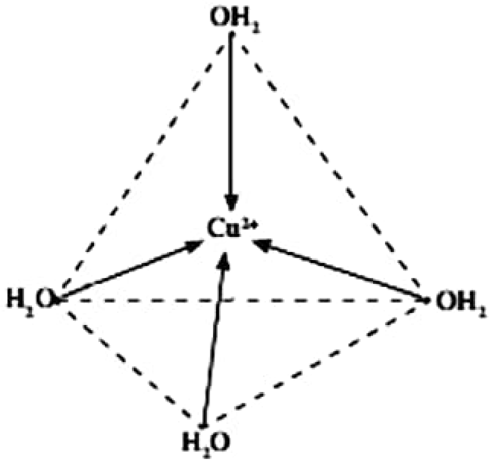


Figure 4.9: *Tetrahedral complex ion of* $[Cu(H_2O)_4]^{2+}$

An octahedral geometry has a central metal atom or ion coordinated to six ligands. The four of the ligands are in one plane with the fifth one above the plane and the sixth below the plane. An example of an octahedral complex is $[Fe(CN)_6]^{4-}$ (Figure 4.10).

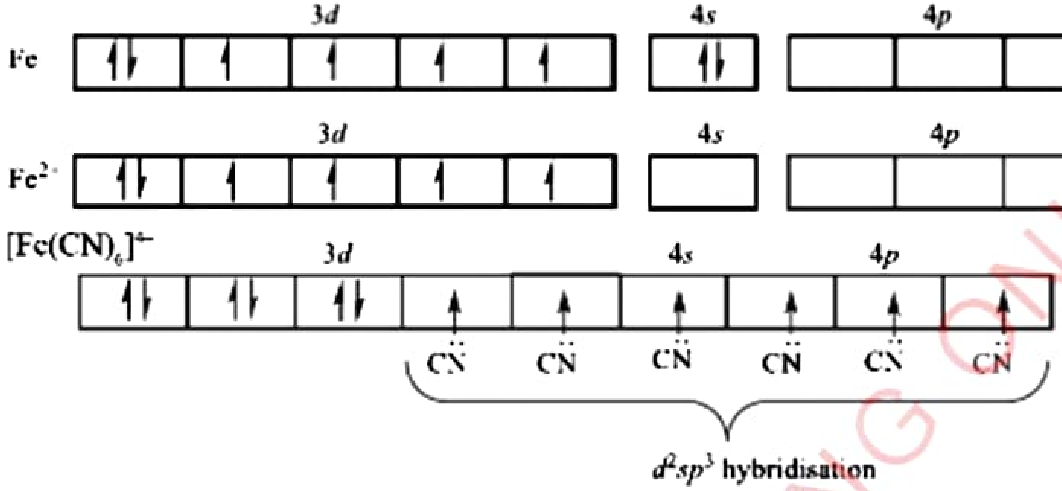


Figure 4.10: *d^2sp^3 hybridisaton in $[Fe(CN)_6]^{4-}$*

Fe^{2+} has the ground state outermost configuration of $3d^6 4s^0 4p^0$. As CN^- ligand (strong field ligand) approaches the Fe^{2+}, the six electrons in the 3*d* orbitals pair off leaving two vacant *d*-orbitals, which hybridise with the 4*s*-orbital and three 4*p*-orbitals forming six d^2sp^3 hybrid orbitals with octahedral geometry (Figure 4.11).

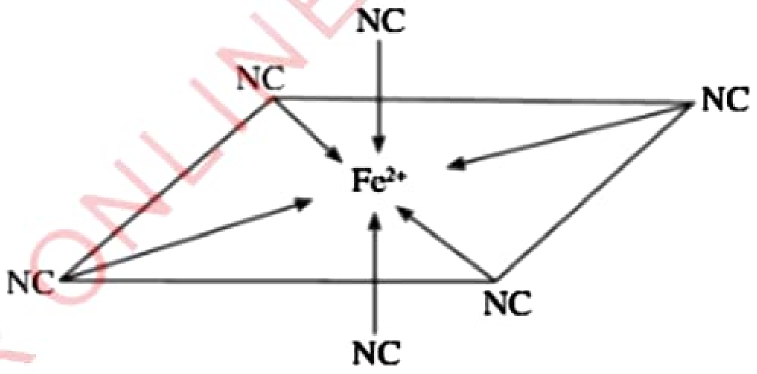


Figure 4.11: *Octahedral complex ion of $[Fe(CN)_6]^{4-}$*

Formation of a geometry depends on the type of hybridisation of the central metal ions or atoms. When the central metal ion or atom is *sp* hybridised, the bond angle is 180°, and the shape of the complex is linear. Table 4.8 summarises the structures of the complexes by giving the mode of hybridisation of the atomic orbitals of the central metal atom, shapes of the complex ions, coordination numbers, bond angles of the complex crystals, and examples of the complexes encountered.

Table 4.8: *Hybridisation of a central metal ion and geometries of complexes*

Hybridisation of a central metal	Coordination number	Bond angles of the complex	Shape of the complex	Example(s)
sp	2	180°	Linear	$[CuCl_2]^-$
sp^2	3	120°	Trigonal planar	$[Cu(CN)_3]^{2-}$
dsp^2	4	90°	Square planar	$[Pt(NH_3)_4]^{2+}$, $[Cu(NH_3)_4]^{2+}$ and $[Ni(CN)_2Br_2]^{2-}$
sp^3	4	109.5°	Tetrahedral	$[Zn(NH_3)_4]^{2+}$ and $[MnCl_4]^{2-}$
dsp^3	5	120° and 90°	Trigonal bipyramidal	$[Fe(CO)_5]$
sp^3*d*^{2} or *d*^{2}*sp*^{3}	6	90°	Octahedral	$[V(CN)_6]^{4-}$, $[Cr(NH_3)_4Cl_2]^+$, $[Mn(H_2O)_6]^{2+}$ and $[FeCl_6]^{3-}$

Example 4.5

Draw one possible structure of $[Co(NH_3)_4(NO_2)_2]^+$.

Solution

The possible structure of $[Co(NH_3)_4(NO_2)_2]^+$ is as shown in Figure 4.12:

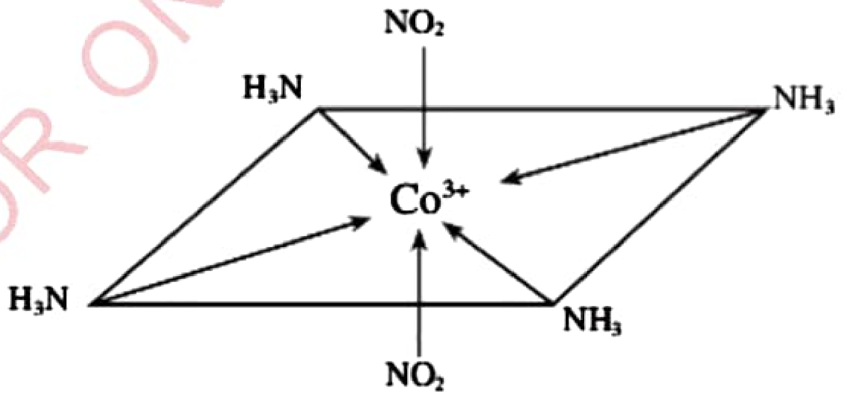


Figure 4.12: *Structure of* $[Co(NH_3)_4(NO_2)_2]^+$

Naming complexes using the IUPAC system

In order to have standard names of the complexes, a universal system of naming them was adopted. Complexes are named by using the International Union of Pure and Applied Chemistry (IUPAC) system. The following are the rules used for naming complexes:

1. The cations are always named before the anions. The oxidation state of the central metal atom or ion is shown in Roman numeral in brackets immediately after its name. For example, the complex $[Fe(H_2O)_6]Cl_3$ is named as hexaaquairon(III) chloride and $[Cu(NH_3)_4]SO_4$ is named as tetraamminecopper(II) sulfate.

2. Within a complex, the ligands are named first followed by the central metal ion. Within each category, if there are more than one type of ligands, they are named in an alphabetical order. For example, the complex $[Co(NH_3)_4Cl_2]^+$ is named tetraamminedichlorocobalt(III) ion, $[Pt(NH_3)_2Cl_4]$ is named diamminetetrachloroplatinum(IV), and $[Cu(NH_3)_4(H_2O)_2]^{2+}$ is named tetraamminediaquacopper(II) ion.

3. The number of the same ligands present must be specified by using the following prefixes: *di* = 2 ligands, *tri* = 3 ligands, *tetra* = 4 ligands, *penta* = 5 ligands, *hexa* = 6 ligands, and so on.

4. The names of the negative ligands end up with the suffix *-o*, as in CN^- (cyano) and Cl^- (chloro). Neutral ligands usually retain their normal names, except for such special cases as H_2O (aqua), NH_3 (ammine), CO (carbonyl), and NO (nitrosyl).

5. Anionic complexes are those which have an overall negative charge outside the square brackets. These end up in the suffix *-ate* often appended to the Latin or English name of the metal. For example, $[Co(CN)_6]^{3-}$ is named hexacyanocobaltate(III) ion, $[CuCl_4]^{2-}$ is named tetrachlorocuprate(II) ion, $[Fe(CN)_6]^{3-}$ is named hexacyanoferrate(III) ion, and $[Fe(CN)_6]^{4-}$ is named hexacyanoferrate(II) ion. The Latin names used for some metal ions are presented in Table 4.9.

6. Cationic complexes are those which have an overall positive charge outside the brackets. These use the English names unchanged for the central metal ion. For example, $[Cr(NH_3)_4Cl_2)]^+$ is named tetraamminedichlorochromium(III) ion and $[Co(NH_3)_4Cl_2]^+$ is named tetraamminedichlorocobalt(III) ion.

7. If a ligand contains a Greek prefix as in ethylenediamine, the prefixes *bis*, *tris*, and *tetrakis* are used for indicating two, three, and four ligands present, respectively. For example, the ligand $H_2NCH_2CH_2NH_2$ (ethylenediamine) already contains *di*, therefore, if two such ligands are present as in $[Pt(en)_2Cl_2]^{2+}$, the name of $(en)_2$ is bis(ethylenediamine).

Table 4.9: *Names used for some metal ions in anionic complexes*

Common name	Symbol	Latin name for metal ions
Iron	Fe	Ferrate
Copper	Cu	Cuprate
Lead	Pb	Plumbate
Silver	Ag	Argentate
Gold	Au	Aurate
Tin	Sn	Stannate

Activity 4.3

Aim: To prepare tetraammineaquacopper(II) sulfate, $[Cu(NH_3)_4(H_2O)]SO_4$.

Requirements: Copper(II) sulfate pentahydrate ($CuSO_4.5H_2O$), funnel, concentrated ammonia solution, deionised water, ethanol, water bath, beakers, droppers, stirring rod, and heat source

Procedure

1. Dissolve copper(II) sulfate pentahydrate ($CuSO_4.5H_2O$) in deionised water in a beaker.
2. Slowly, add a concentrated ammonia solution to the solution and stir the mixture.
3. Add 20.0 mL of ethanol from the dropping funnel to the beaker so that the blue colour is nearly discharged, and the purple-coloured tetraammineaquacopper(II) sulphate separates.
4. Heat the reaction mixture to about 60°C to 70°C in a water bath for 10 to 15 minutes.
5. Stop heating and allow the solution to cool.

Questions

1. What happened at step 2 of the procedure? Write a balanced chemical equation for the process.

2. What is the role of ethanol in the mixture?
3. Why did you heat the mixture?
4. What is the colour and geometrical shape of the resulting product(s) after heating? Draw its structure using an appropriate software.

Example 4.6

1. Give the IUPAC names of the following compounds:
   (a) $K_2[Fe(CN)_2Cl_2(NH_3)_2]$
   (b) $[Co(NH_3)_4(NO_2)_2]Cl$
2. To which class of the complexes do the compounds in (1) belong?

Solution

1. (a) The compound $K_2[Fe(CN)_2Cl_2(NH_3)_2]$ consists of a non-complex cation and a complex anion. The name starts by first naming the cation (potassium), followed by the name of the complex anion, which is obtained by first giving the names of the ligands in alphabetical order. Then, the name of the central atom is followed with the indication of its oxidation state. Thus, its name is potassium diamminedichlorodicyanoferrate(II).

   (b) The compound $[Co(NH_3)_4(NO_2)_2]Cl$ consists of a complex cation and a non-complex anion. The cation is named first followed by the anion. The complex cation is named by first naming the ligands in alphabetical order, followed by the name of the central atom with its oxidation state. Lastly, the name of the non-complex anion follows. Thus, the name of the compound is tetraamminedinitrocobalt(II) chloride.

2. (a) Anionic complex (b) Cationic complex

Effects of complexes formation on the solubility of some compounds

Slightly soluble compounds of metals dissolve when excess ammonia, chloride ion or hydroxide ion is added to their solutions. The following observations serve as illustrative examples:

(a) When sodium hydroxide solution is added to a solution of zinc nitrate, a white precipitate of zinc hydroxide is formed. An addition of excess sodium hydroxide solution results into dissolution of the precipitate. To account for this observation, consider the equilibrium established between the solid zinc hydroxide and its ions (Zn^{2+} and OH^-) which is illustrated in the following chemical reaction:

$$Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^-(aq)$$

According to the Le Châtelier's principle, dissolution of $Zn(OH)_2$ is facilitated by the consumption of Zn^{2+} or OH^- from the equilibrium system. When excess OH^- is added from an extra solution of NaOH, the following chemical reaction takes place:

$$Zn^{2+}(aq) + 4OH^-(aq) \rightleftharpoons [Zn(OH)_4]^{2-}(aq)$$

This drives the equilibrium to the right, hence, facilitates dissolution of $Zn(OH)_2$.

(b) Similarly, when sodium hydroxide solution is added to a solution of copper(II) nitrate, a blue precipitate is formed as represented by the following chemical equation:

$$Cu(NO_3)_2(aq) + 2NaOH(aq) \longrightarrow Cu(OH)_2(s) + 2NaNO_3(aq)$$

The precipitates of copper(II) hydroxide dissolve to form a deep blue solution when ammonia solution is added. To account for this observation, consider the equilibrium, which exists between the solid copper(II) hydroxide and its ions Cu^{2+} and OH^-.

$$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$$

To dissolve $Cu(OH)_2$, Cu^{2+} ions or OH^- ions have to be consumed from the equilibrium system. This can be done by adding ammonia solution, which furnishes NH_3 molecules that react with Cu^{2+} ions.

$$Cu^{2+}(aq) + 4NH_3(aq) \longrightarrow [Cu(NH_3)_4]^{2+}(aq)$$

To offset the effect produced by this reaction, more copper hydroxide dissolves to replace the consumed Cu^{2+} ions from the equilibrium system.

Aqueous solutions containing Ag^+, Pb^{2+}, Cr^{2+}, and Ni^{2+} also show the same behaviour.

Therefore, it can be concluded that, complex formation affects the solubility of slightly soluble compounds of the transition elements.

Task 4.4

Prepare any cobalt complex containing two different ligands.

Example 4.7

Using a chemical equation, show the effect of complex formation on the solubility of a slightly soluble hydroxide of a transition element.

Solution

Nickel(II) hydroxide, for example, is a slightly soluble hydroxide which dissolves in ammonia solution.

$$Ni(OH)_2(s) + 4NH_3(aq) \longrightarrow [Ni(NH_3)_4]^{2+}(aq) + 2OH^-(aq)$$

The formation of the complex $[Ni(NH_3)_4]^{2+}$ causes more $Ni(OH)_2$ to dissolve. It can, therefore, be concluded that, complex formation facilitates the dissolution of slightly soluble hydroxides like $Ni(OH)_2$.

Exercise 4.3

1. **A complex ion, $[Ni(CN)_2Br_2]^{2-}$ has a square planar geometry. Draw the possible geometric structure of this complex.**

2. **(a) Explain the following terms:**
   - **(i) Neutral complex**
   - **(ii) Cationic complex**
   - **(iii) Anionic complex**

   (b) Classify the following complexes as neutral, cationic, or anionic. Give a reason for each classification.
   - **(i) $[Co(NH_3)_2Cl_4]^-$**
   - **(ii) $[Co(NH_3)_3Cl_3]$**

(iii) $[Co(NH_3)_4Cl_2]^+$

(iv) $[Cu_3(OH)_2(CO_3)_2]$

(v) $[Co(NO_2)_6]^{3-}$

(vi) $[Pt(en)_2Cl_2]^{2+}$

3. With the aid of an example, show the effects of complex formation on the solubility of chromium(II) hydroxide in water.
4. Give the IUPAC names of the following compounds:
   (a) $[Co(NH_3)_4Cl_2]SO_4$
   (b) $[Cr(en)_2Cl_2]_3[Co(C_2O_4)_3]$
   (c) $[Cr(H_2O)_4Cl_2]Cl$
   (d) $[Co(en)_3]_2[Ni(CN)_2Br_2]_3$
   (e) $[Co(NH_3)_2Cl_4]^-$
5. Write the formulae of the following compounds:
   (a) Dichlorobis(ethylenediamine)platinum(II) chloride
   (b) Sodium tetrachloronickelate(II)
   (c) Ammonium diaquabis(oxalato)nickelate(II)
   (d) Hexaammineiron(III) hexacyanochromate(III)
   (e) Aquabis(ethylenediamine)cyanocobalt(III)

Revision exercise 4

1. Describe the characteristic features of transition elements, giving example(s) in each case.

2. Write the electronic configurations of the ions Mg^{2+}, Cr^{3+}, Cu^+, S^{2-} and Na^+, and compare their outer electronic configurations. Comment on the differences.

3. Justify the classification of either chromium or iron as transition elements, illustrate your answer with reference to;
   (a) the formation of coloured ions.
   (b) the possession of magnetic properties.
   (c) the catalytic activity.
   (d) the partially filled 3*d*-orbitals.

4. The colours of the transition metal compounds are characteristics of their hydrated ions and not their simple ions. Explain by giving examples.

5. Calculate the oxidation number of the central metals in the following compounds:

   (a) $MnCO_3$ (b) $[Fe(H_2O)_6]Cl_3$

   (c) $[Cr(H_2O)_4(NH_3)_2]Cl_3$ (d) $K_2Cr_2O_7$

6. Explain the following observations:

   (a) $[Fe(CN)_6]^{4-}$ is diamagnetic, while $[Fe(F)_6]^{4-}$ is paramagnetic.

   (b) Cu^{2+} behaves as a transition ion, while Cu^+ does not.

   (c) Chromium and copper atoms show exceptional electronic configuration.

7. Describe the following properties associated with transition elements:

   (a) Application in construction

   (b) Drawing into a wire

   (c) Manufacturing of electric cables

   (d) Withstanding high temperatures

8. Write the electronic configurations of all elements with atomic numbers 21 to 30 and answer the following questions:

   (a) To which level do the electrons add?

   (b) Would you classify Sc and Zn as transition elements?

9. Under what conditions is copper considered a non-transition element?

10. Element M has an atomic number of 26.

    (a) Discuss the physical and chemical characteristics of element M.

    (b) Write the possible oxidation states of element M. Give reasons for each oxidation state.

    (c) Which oxidation state represents the most stable species? Explain.

11. Explain the following terms and give examples in each case:

    (a) Complex compound (b) Ambidentate ligand

    (c) Coordination sphere (d) Octahedral complex

12. The complex compounds of cobalt have different colours. For example, $[Co(CN)_6]^{3-}$ is yellow, $[Co(NH_3)_6]^{3+}$ is orange and $[Co(H_2O)_6]^{3+}$ is blue. Account for these observations.

13. Give the name and the chemical formula of each of the following:
    (a) A neutral complex compound
    (b) A complex compound with mixed ligands
    (c) Two complex anions of chromium

14. Name the following complex compounds:
    (a) $[Pt(NH_3)_3Cl_3]Cl$
    (b) $[Cr(NH_3)_4Cl_2]Cl$
    (c) $K_4[Fe(CN)_6]$

15. Silver nitrate reacts with $[Pt(NH_3)_3Cl_3]Cl$ but not with $[Pt(NH_3)_2Cl_4]$. Explain.

16. Give the chemical structures of the following complexes:
    (a) Hexaamminenickel(II) chloride
    (b) Tetraammineplatinum(II) tetrachloroplatinate(II)
    (c) Pentaaquathiocyanoferrate(II)
    (d) Dichlorobis(ethylenediamine)platinum(IV) nitrate.

17. Water molecules readily coordinate with cations of the transition metals, but hydroxonium ions (H_3O^+) do not. Explain.

18. The addition of excess silver nitrate to an aqueous solution containing 0.01 mol of $CoCl_3 \cdot 6NH_3$ leads to immediate precipitation of 0.03 mol of silver chloride. However, a similar addition to an aqueous solution containing 0.01 mol of $CoCl_3 \cdot 5NH_3$ leads to immediate precipitation of only 0.02 mol of silver chloride. Use this observation to suggest the correct structures of the compounds.

19. (a) A metal ion of an atom of a transition element is described by using d^2sp^3 set of orbitals when forming complexes. What is the coordination number of the metal ion and the shape of the complex formed?

(b) $[Ni(NH_3)_6]^{2+}$ is paramagnetic whereas $[Pt(CN)_4]^{2-}$ is diamagnetic although the central metal ions in both are d^8 species. Show the crystal field splitting diagram for the two complexes and provide explanations.

20. (a) What electronic features must a donor atom of any ligand possess?
    (b) What is the difference between the coordination number and the oxidation number?
    (c) A white gelatinous precipitate of zinc hydroxide dissolves when excess potassium hydroxide solution is added. Explain.

21. Describe the properties which have favoured iron to be used as an important transition element in the human body.

22. How can the transition elements be used in water purification and dye production? Explain with examples.

Project work

Select an area of your interest related to Chemistry, then design and conduct a project .

Answers for Some Questions

Chapter One

Exercise 1.2

2. $\lambda = 333.33$ m, $E = 7.36$ J

4. $n_2 = 4$

6. (a) Absorption (b) Emission

   (c) Emission (d) Absorption

9. 4.86×10^{-7} m, emitted.

Exercise 1.3

4. (a) M = 14, N = 26 (b) M = 7, N = 12

5. (a) (i) p = 5, n = 6, e = 5

   (ii) p = 20, n = 21, e = 20

   (iii) p = 53, n = 78, e = 53

6. ^{28}Si (p = 14, n = 14, e = 14) ^{29}Si (p = 14, n = 15, e = 14) ^{30}Si (p = 14, n = 16, e = 14).

7. ^{10}B = 51.1% and ^{11}B = 48.9%

8. 197.5

9. (a) 6 protons, 6 neutrons (b) 6 protons, 7 neutrons

   (c) 6 protons, 8 neutrons

10. 126.86 a.m.u

Exercise 1.4

3. 1.09×10^{6} m s^{-1}

5. 2.58×10^{-7} m

6. (a) 9.5613×10^{-8} m (b) 2.079×10^{-18} J

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. (a) 1.299×10^{-34} m

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
Alloying	Mixing of a metal with one or more other metals in specified proportions
Alumina	A term used for one of the solid forms of aluminium oxide
Amphoteric substances	Are substances which show both acidic and basic properties
Anhydrous	A term meaning without water
Anion	A negatively charged ion or an atom with extra electrons
Anion analysis	Procedures for detecting anions in a chemical substance
Anionic complexes	Are complexes that have a net negative charge outside the coordination sphere
Atom	The smallest particle of matter that can take part in a chemical reaction
Atomic mass (weight)	The average of the masses of the naturally occurring isotopes of an element weighted according to their abundances
Atomic mass unit	The mass of a carbon–12 atom
Atomic number (Z)	The unique number of protons in the nucleus of each atom of an element (equal to the number of electrons in the neutral atom)
Atomic radius	One-half the distance between nuclei of two covalently bonded atoms
Atomic size	A term referring to the atomic radius, one half the distance of nuclei of an identical bonded atom
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 consists of well-defined number of groups of closely packed lines usually emitted by molecules

Base	Any substance which contains hydroxyl (OH) groups and furnishes hydroxide ions in solution; a molecular or ionic substance capable of combining with a proton to form a new substance.
Boiling point	The temperature at which the vapour pressure of a substance is equal to the atmospheric pressure
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
Catalyst	A chemical substance that alters the rate of a chemical reaction but remains chemically unchanged at the end of the reaction
Cation	A positively charged ion
Cationic complexes	Complexes that carry a net positive charge outside the coordination sphere
Central atom	An atom that is bonded to two or more other atoms
Chemical bonding	An interaction process that results into the association of atoms to form molecules, ions or crystals
Chemical equation	A symbolic representation of a chemical reaction
Chemical formula	Any of various means of concisely displaying information about the chemical composition of a compound or molecule using letters, numbers, and/or symbols
Chemical reaction	A process in which one set of substances (reactants) is transformed into a new set of substances (products)
Complex compound	A molecule or ion composed of a central metal atom which is surrounded by ligands
Compound	Two or more elements combined; a substance having different properties than of the elements used
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

Coordination compound	A complex compound or ion in which a central metal atom or ion is combined by coordinate bonds with a definite number of ligands
Coordination number	The number of ligand atoms bonded to the central metal ion
Coordination sphere	The region around a central atom or ion where linkage to ligands can occur to produce a complex
Covalent bond	A chemical bond which is formed by sharing of electrons between two bonding atoms of non-metals
Crystal field stabilisation energy	The stabilisation energy that occurs when transition metal ions are surrounded by a field of ligands
Crystal Field Theory	A model that explains the colour and magnetism of coordination compounds based on the effects of the ligands on metal ion which result from splitting of *d*-orbital
***d*-block elements**	A group of elements whose valence shells comprise electrons in *d*-orbitals as the highest energy of sub –levels
Degenerate orbitals	Orbitals with the same energy, size, and shape but differ in orientations in space
Diagonal relationship	The resemblance in properties whereby the first element in a particular group has similar properties diagonally with the second element in the next group
Diamagnetic material	A material which does not respond to magnetism, the atoms of this material contain no unpaired electrons
***d*-orbital**	An atomic orbital with $l = 2$
e_g set of orbitals	A set of orbitals that are formed when the energies of metal ion in *d*-orbitals are split by ligand field
Electron affinity	The energy change when one mole of electrons is added to one mole of gaseous atom or ion
Electron pair	Two electrons which occupy the same molecular orbital but have opposite spins
Electron shell	An orbital around the nucleus of an atom which contains a fixed number of electrons (usually two or eight)
Electron	The negatively charged particle of an atom
Electronegativity	The relative ability of an atom to attract the bonding electrons towards itself

Electronic configuration	A designation on how electrons are distributed or arranged among various orbitals in 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
Ferromagnetic material	A material that contains unpaired electrons which is more strongly attracted by a magnet
Frequency	The number of complete oscillations per second
Fusion	A process of joining lighter nuclei to form heavier nuclei
Group in a periodic table	A set of elements which have the same numbers of electrons in their outermost shells and hence, have similar properties
Halogen	Any of the five non-metallic elements of group 17 of the periodic table: fluorine, chlorine, bromine, iodine, and astatine
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 a 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
Inorganic compound	Any chemical compound that does not contain carbon, though there are exceptions
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
Intramolecular hydrogen bond	The type of hydrogen bond that exists between hydrogen atom and a small, highly electronegative atom within the same molecule
Ionic radius	Half the distance between two ions that are barely touching each other

Ionisation energy	The minimum energy required to remove one mole of electrons from a gaseous atom to form a cation
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
Ligand	An ion or molecule that bonds to a central metal atom to form a complex compound
Line spectrum	The type of spectrum which consists 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
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
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	A set of chemical properties that are associated with the elements classified as metals in the periodic table
Momentum	A product of mass and velocity of a moving body
Neutral complexes	Complexes whose coordination spheres have no net charge
Neutron	The sub-atomic particle of an atom that carries no charge
Noble gas	Any of the six non-metallic elements of group 18 of the periodic table: helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn). All of the noble gases have outer electron shells that are completely filled in their naturally occurring states, giving them very low chemical reactivity

Nomenclature	A systematic way of writing chemical names and formulae
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
Oxidation state	The number of electrons gained, shared or lost by an atom during combination with other atoms
p-block elements	A group of elements whose valence shells comprise electrons in *p*-orbitals as the highest energy sub-levels
Penultimate shell	The second to last electron shell of an atom
Period	A horizontal row of the elements in the periodic table
Periodic table	A table of elements arranged in order of increasing atomic numbers
Periodic trend	A regular pattern in the properties of the elements with increasing atomic numbers caused by regular variations in the atomic structures of the elements
Periodicity	A tendency of a particular property of an element to appear every after a certain specific interval in a given arrangement
Polar covalent bond	The covalent bond which is formed between atoms of different electronegativities because of unequal sharing of electrons
Polarising power	The ability of a cation to deform a negatively charged radical in a compound
Polydentate ligand	A ligand that has ability to denote more than a single electron pair in a central metal atom of a complex, from different atoms in ligand and different sites in the geometric structure
Proton	The positively charged particle found in the nucleus of an atom

Quantum numbers	The numbers which are used for describing the properties of electrons in an atom
Quantum shell	The region around an atom's nucleus where electrons are likely to be found
***s*-block elements**	A group of elements whose valence shells comprise electrons in *s*-orbital as the highest energy sub-level
Screening effect	The tendency of the inner most electrons to protect the outer most electrons from the attractive influence of the nucleus
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
t_{2g} set of orbitals	A set of orbitals that are formed when the energies of the metal ions in *d*-orbitals are split by a ligand field
Transition elements	A group of elements which have partially filled *d*-orbitals of their atoms or ions
Valence Shell Electron Pair Repulsion (VSEPR) Theory	The theory that explains the shapes of molecules and ions to be determined by the electron pair repulsions around the central atom
Wavelength	The distance between two successive crests (maxima) or troughs (minima) of a wave

Bibliography

Abdallah, A., McGuire P., Nkunya, M. H., & Schiess, M. (1986). *Chemistry for A- level and 1st-year undergraduate students (Vol. III)* (1st ed.). Tanzania Publishing House.

Chang, R. (2005). *Chemistry* (8th ed.). McGraw-Hill Companies Inc.

Daniel, M., Damian, H. S. (2012). *Physical chemistry with general chemistry* (2nd ed.). APE Network.

Ddungu, M. L., Mihigo, J. B., Mkayula , L. L., Mkwizu A. B., & Schies, M. (1998). *Physical chemistry for A-Level and 1st-year undergraduate students (Vol. I)* (1st ed.). Mzumbe Book Project.

Freemantle, M. (1987). *Chemistry in action* (1st ed.). Macmillan Press Ltd.

Hill, G. C., & Hollmann, J. S. (1987). *Chemistry in Context* (2nd ed.). Thomas Nelson & sons Ltd.

Jain, S. K. (2011). *Conceptual chemistry* (4th ed.). S. Chand & Company.

Liptrot, G. F. (1985). *Modern Inorganic Chemistry* (4th ed.). Denmark House Ltd.

Petrucci, R. H., Herring, G.Y., Madura, J. D., & Bissonnette, C. (2017). *General chemistry, principles and modern applications* (11th ed.). Pearson Canada Inc.

Ramsden, E. N. (2014). *A-Level Chemistry* (4th ed.). Nelson Thornes Publishers Ltd.

Silberberg, S. M. (2003). *Chemistry: The molecular nature of matter and change* (3rd ed.). McGraw-Hill Companies Inc.

Tanzania Institute of Education. (1995). *Advanced level inorganic chemistry part I and II* (1st ed.). Dar es Salaam University Press.

Tanzania Institute of Education. (2019a). *General Chemistry for Advanced Level Secondary Schools* (1st ed.). Tanzania Institute of Education.

Tanzania Institute of Education. (2019b). *Inorganic Chemistry for Advanced Level Secondary Schools* (1st ed.). Tanzania Institute of Education.

Thakur, N. M. (2001). *Fundamental concepts in physical chemistry* (1st ed.). S. Chand & Company Ltd.

Zumdahl, S. S., & Zumdahl, S. A. (2014). *Chemistry* (Lockwood Lisa (ed.); 9th ed.). Cengage Learning.

Appendix

Appendix 1: *Table of elements showing atomic numbers and atomic masses*

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	292	-	-
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
Sulfur	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

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