स्वाध्याय स्वमन्थन स्वावलम्बन

UTTAR PRADESH RAJARSHI TANDON OPEN UNIVERSITY

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Indira Gandhi National Open University

UP Rajarshi Tandon Open University

UGCHE-01
Atoms and Molecules

FIRST BLOCK : Structure of Matter-I

SECOND BLOCK : Structure of Matter-II

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UTTAR PRADESH
RAJARSHI TANDON OPEN UNIVERSITY

UGCHE - 01
Atoms and Molecules

Block

1

STRUCTURE OF MATTER – I

UNIT 1

UNIT 2

UNIT 3

UNIT 4

UNIT 5

ATOMS AND MOLECULES

This course, Atoms and Molecules, is one of the elective courses for the students of the Bachelor's Degree Programme in Science. It is a pre-requisite for other elective courses in chemistry.

Chemistry is concerned with composition, characterisation and transformation of matter. In the Foundation Course in Science and Technology, we have discussed the historical aspects of the development of chemistry and other sciences in detail. The multi-dimensional development of modern chemistry began in the late eighteenth century. This was largely due to the contributions of Lavoisier in quantitative experimentation. The stupendous growth of chemical facts has led to the emergence of five distinct branches of chemistry. You must be familiar with the following branches of chemistry from your study of the subject so far.

i) **Physical chemistry** : The study of the physical principles governing the structure of the matter and its chemical transformations.

ii) **Inorganic chemistry** : The chemistry of all the elements and of all their compounds except the hydrocarbons and their derivatives.

iii) **Organic chemistry** : The chemistry of hydrocarbons and their derivatives.

iv) **Biochemistry** : The chemistry of living systems, both plant and animal.

v) **Analytical chemistry** : The study of the qualitative and the quantitative identification of substances.

The frontiers of these branches are not well-defined. Chemistry is, even today, undergoing further "cell divisions". New branches, such as pharmaceutical chemistry agricultural chemistry and textile chemistry are emerging as a result of explosive growth of various aspects of the discipline. These different branches of chemistry deal with the macroscopic nature of matter. But, in this course, we will describe the characteristics of matter at the microscopic level. This knowledge will help you to see the connecting link between the different branches of chemistry.

Before unfolding the main features of this course, let us see what atoms and molecules are. An atom has been defined as the smallest particle of an element that can take part in a chemical reaction. Atoms combine to form molecules. While molecules can exist independently, atoms cannot, in general.

In Block 1 of this course, we discuss the fundamental concepts regarding atomic and molecular structure. We start with the historical ideas about the atom, and build the story upto the modern times. We explain the basic concepts of modern atomic theory, and extend them to show how atoms combine to form molecules. In Block 2 you will study the structural features of the molecules, using physical methods such as dipole moment, magnetic susceptibility and optical rotation. We also discuss some of the main branches of spectroscopy and their use in structure determination. In eight units of this course, we discuss the electronic arrangement of the atoms and molecules with respect to their structure and characteristics. Finally, in the last unit, we talk about the composition and characteristics of atomic nuclei.

Broad Objectives

After studying this course, you should be able to:

- discuss the relationship of this course with other branches of chemistry,
- explain the fundamental concepts of atomic and molecular structure and the contribution of various scientists in the development of these concepts,
- explain the importance of physical methods in identifying the structure of simple molecules, and
- explain the salient features regarding the constitution of atomic nuclei and radioactivity.

BLOCK 1 STRUCTURE OF MATTER-I

Modern chemistry is built upon the atomic theory as the foundation. Knowledge of the structure of atom is essential for an understanding of the formation of molecules. In Unit 1 we discuss the evolution of atomic theory upto the early twentieth century and its application to atomic spectra. In Unit 2 we take up the wave mechanical theory of atom and the arrangement of the electrons around the nucleus of the atom.

The stage is now set to study the linkage of atoms in the formation of molecules. In Unit 3 we deal with the theories of Kossel and Lewis in explaining the ionic and the covalent linkages. We describe the VSEPR theory and use it in explaining the shapes of molecules. In Unit 4 we discuss the valence bond theory in detail to explain the covalent linkages in molecules. We also discuss the main features of resonance and hybridisation in the light of molecular parameters such as bond length and bond angle. In Unit 5 we deal with the molecular orbital theory as another profile of covalent linkage. The materials in the last two units would be particularly helpful in understanding the structure and reactivity pattern discussed in inorganic and organic chemistry courses.

Objectives

After reading this block, you should be able to:

- state various theories regarding the arrangement of electrons, protons, and neutrons inside the atom,
- explain the importance of Schrödinger equation in predicting the shapes of atomic orbitals,
- write the electron configuration of elements using Pauli's principle and Hund's rule,
- discuss the salient features of ionic and covalent linkages,
- describe the main aspects of resonance and hybridisation, and
- explain bonding in simple molecules using molecular orbital theory.

Study Guide

We have tried to present this course in a qualitative way. To the extent possible, the sharp mathematical bends have been flattened and kept at a low-key to enable you to understand this topic, which though difficult, is pivotal to the understanding of chemistry. It assumes, an elementary knowledge of algebra, trigonometry and calculus which you may have studied at the school level. Try the derivations and numericals when you come across them. The SI units have been used for various physical quantities. Before trying to work out a numerical, substitute the SI units for the physical quantities in the equation and check whether the two sides of the equation match. As an aid, the table of SI units of various physical quantities, the table of physical constants and the logarithmic tables are included at the end of this block along with Greek alphabets.

This block may require 22 hours of study time and 2 hours for doing the assignments. On an average, each of the five units may need 4 to 5 hours. You need not worry if you take more time, since this time-frame is not quite rigid and depends on your own pace of learning. To facilitate learning, many figures, diagrams and marginal remarks have been given in all these units. Many solved problems are also included in the text. We advise you to study them carefully. We have given many self-assessment questions (SAQs) and terminal questions in each unit. After each major concept, SAQs have been placed within the text along with space for writing the answer; the terminal questions are given at the end of the unit. Although the outlines of the answers are given for each question at the end of the unit, it is worth solving the questions yourself rather than looking for the answers straight away. The pleasure, you get in solving the SAQs and the terminal questions yourself, is the reward for the pains taken in studying a unit.

For your benefit, some of the abbreviations used in this block are given below:

Fig. X.Y — Figure number Y of Unit X

Sec. X.Y — Section number Y of Unit X

Eq. X.Y — Equation number Y of Unit X

If you wish to go deeper into some aspects, you may refer to the books listed for further reading at the end of this block.

UNIT 1 OLD QUANTUM THEORY

Structure

1.1 INTRODUCTION

The ideas of classical mechanics developed by Galileo, Kepler and Newton, when applied to atomic and molecular systems were found to be inadequate. Need was felt for a theory to describe, correlate and predict the behaviour of the sub-atomic particles. The quantum theory, proposed by Max Planck and applied by Einstein and Bohr to explain different aspects of behaviour of matter, is an important milestone in the formulation of the modern concept of atom.

In this unit, we will study how black body radiation, heat capacity variation, photoelectric effect and atomic spectra of hydrogen can be explained on the basis of theories proposed by Max Planck, Einstein and Bohr. They based their theories on the postulate that all interactions between matter and radiation occur in terms of definite packets of energy, known as **quanta**. Their ideas, when extended further, led to the evolution of wave mechanics, which shows the dual nature of matter and energy.

Objectives

After studying this unit, you should be able to :

- describe the discovery of electron, proton and neutron,
- explain the atom models of Thomson and Rutherford,
- list the wave parameters of light,
- describe the shortcomings of classical physics,
- state Planck's theory and explain its application to black body radiation and heat capacity variation,
- define photoelectric effect and explain it in the light of Einstein's theory,
- list Bohr's postulates and derive an expression useful in calculating the radius of the hydrogen atom,
- explain the atomic spectra of hydrogen in the light of Bohr's theory,
- analyse critically the advantages and limitations of Bohr's theory, and
- state the refinements in the atomic spectra theory.

1.2 DISCOVERY OF SUB-ATOMIC PARTICLES

The atomic theory of the Greek philosophers, Leucippus and Democretus (400 B.C.) held that continued subdivision of matter would ultimately yield atoms which would not be further divided. The word **'atom'** is derived from the Greek word, *atomos*, which means "uncut" or indivisible. Dalton (1808) based his atomic theory on the ideas of Democretus and was able to explain the laws of chemical combination. Toward the end of nineteenth century, it began to appear that the atom itself might be composed of even smaller particles. This discovery was brought about by experiments with electricity.

Cathode rays are a stream of negatively charged particles, known as electrons.

Mass of the electron = 9.109×10^{-31} kg

Charge of the electron = -1.602×10^{-19} C

The unit for charge of the electron is coulomb, C.

Attempts to pass a high voltage electric current through gases under reduced pressure led to Julius Plucker's discovery (1859) of **cathode rays**, Fig. 1.1. The cathode rays stream from the negative electrode, which is called the **cathode.** These rays consist of negatively charged particles which travel in straight lines. The cathode rays give off flashes of light, when they strike a screen coated with substances like zinc sulphide. The picture tubes in television sets and computer monitors, function on this principle.

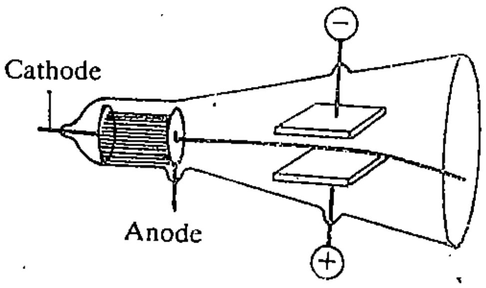

Fig. 1.1: Deflection of cathode rays towards a positive plate in an electrostatic field proving their negative charge.

The particles in cathode rays were later called electrons, as suggested by Stoney. The determination of charge to mass ratio of electrons by Thomson (1897) confirmed the fact that the electrons, which originate from the metal of which the cathode is constituted, are the same no matter what metal is employed as the cathode. In other words, **electrons are fundamental particles of all types of matter.**

If one or more electrons are removed from a neutral atom or molecule; the residual entity is positively charged. During the formation of cathode rays in an electric discharge tube. one or more electrons are removed from each of the atoms, and the positive particles so produced, move toward the negative electrode. If this electrode has holes in it, the positve ions pass through them, as shown in Fig. 1.2.

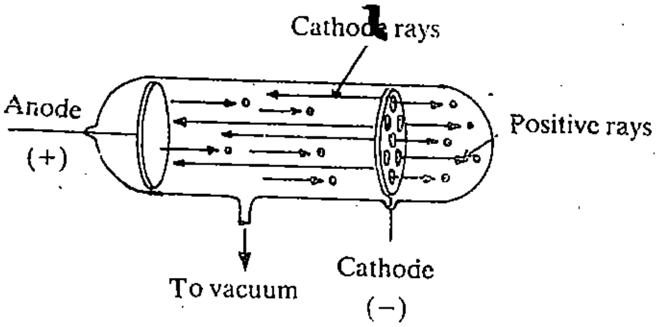

Fig. 1.2: Positive rays.

Charge of the proton is equal in magnitude but opposite in sign to that of the electron.

These streams of positive ions, called positive rays, were first observed by Goldstein (1886). The charge to mass ratios of positive ions depend on the nature of gases taken in the discharge tube. For example, charge to mass ratios for the positive rays obtained from hydrogen and neon are not the same. You can compare this fact with the earlier statement that the charge to mass ratio value of electrons is the same irrespective of the nature of gases kept in the discharge tube.

The positive particles produced, when hydrogen is taken in the discharge tube, are called protons in accordance with the suggestion of Rutherford (1920). In Greek *'protes'* means first. The protons, like electrons are assumed to be constituents of all atoms. The proton has positive charge, although equal in magnitude to that of the electron.

In the same year, Rutherford suggested that there might exist particles which he called neutrons, having a mass equivalent to a proton but without charge. Chadwick (1932) discovered neutrons during his experiments on the bombardment of beryllium by α – particles. The properties of electron, proton and neutron are summarised in Table 1.1. Although other sub-atomic particles have also been identified, atomic structure is adequately explained on the basis of the number of electrons, protons and neutrons in an atom.

α – particles are helium nuclei or helium atoms which have lost their electrons.

Table 1.1: Sub-atomic Particles

Particle	Mass/kg	Charge/C
Electron	9.109×10^{-31}	-1.602×10^{-19}
Proton	1.673×10^{-27}	$+1.602 \times 10^{-19}$
Neutron	1.675×10^{-27}	—

Along with discoveries of sub-atomic particles, various theories were put forward to explain the structure of the atom.

1.3 EARLIER ATOM MODELS

As mentioned in the last section, Dalton proposed a theory that atom is indivisible. But the discovery of sub-atomic particles like electron, led to a revision of this theory. Thomson (1904) proposed a model for the atomic structure, known as "plum pudding" model, which is pictorially described in Fig. 1.3. He considered an atom to be a uniform sphere of positive electricity of about 10^{-8} cm radius, with the electrons embedded in such a way as to give the most stable electrostatic arrangement.

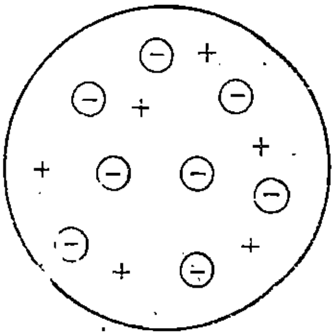

Fig. 1.3: Thomson's "plum pudding" model for the atom.

This model was not able to explain the observation of Geiger and Marsden (1909) regarding the scattering of the α-particles directed towards thin gold foil. Some were deflected from their straight-line path and a few recoiled back toward their source (Fig. 1.4). A uniform sphere of positive charge, would mean only a gradual deflection of the α-particle, but not scattering as it progressed through the foil.

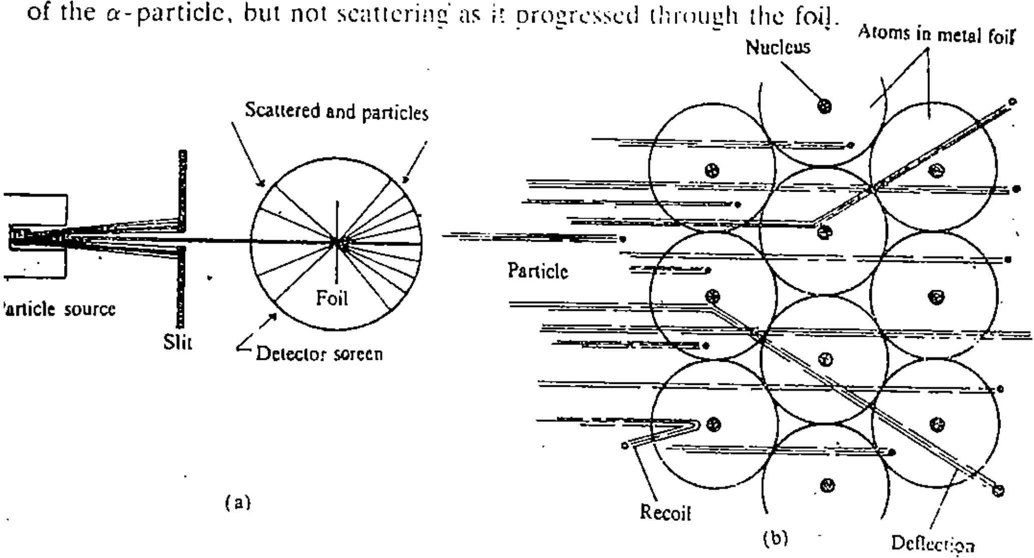

Fig. 1.4: (a) Geiger and Marsden's α - particle experiment;
(b) Deflection of α - particles by nuclei of metal foil. Red lines show the path of α-rays deflected, while black lines indicate the path of those not deflected.

Thomson compared atom to a pudding with partially dried grapes in it.

Rutherford, on observing the recoil of some α – particles from thin gold foil, exclaimed "It was quite the most incredible event that has ever happened to me in my life. It was almost as if you fired a 15 inch shell into a piece of tissue paper and it came back and hit you".

If a nucleus of an atom were the size of a tennis ball, the atom would have a diameter of over one mile.

Rutherford (1911), on the basis of the α-ray scattering experiment, suggested that positive charge and mass of the atom are concentrated in a space which is very much smaller than that occupied by the atom as a whole. He suggested an atomic model, known as nuclear model which consisted of a nucleus at the centre and negative particles surrounding it. The nucleus accounted for mass and positive charge. To support the fact that the electrons did not fall into a nucleus as a result of electrostatic attraction, Rutherford found it necessary to postulate rapid rotation of the electrons about the nucleus just as planets go round the sun. This analogy is misleading, since according to classical electromagnetic theory, an electron in orbit is subject to continual acceleration towards the centre and the accelerated electric charge must emit radiation. The consequent loss of energy, should bring the electron down in a spiral path to the nucleus – that is the collapse of the atom.

Ernest Rutherford
1871-1937

Within two years, Niels Bohr suggested a better theory of the atom. Before studying Bohr's theory, let us analyse the wave properties of light and the reason for the failure of classical physics in describing the properties of sub-atomic particles like electrons.

SAQ 1

What is the essential difference between the atomic models proposed by Thomson and Rutherford?

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....

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1.4 LIGHT AS ELECTROMAGNETIC WAVE

A wave is a travelling disturbance that transports energy.

A beam of light has oscillating electric and magnetic fields associated with it. It is characterised by the properties such as frequency, wavelength and wave number. We can understand all these properties by considering, in general, a wave propagating in one dimension only (Fig. 1.5) along ABCDEFGHI.....

Electromagnetic theory of light depicts propagation of light through space, as oscillating electric and magnetic fields; these fields are mutually perpendicular and also perpendicular to the direction of propagation of light. Further, the energy of a wave depends on the square of its amplitude.

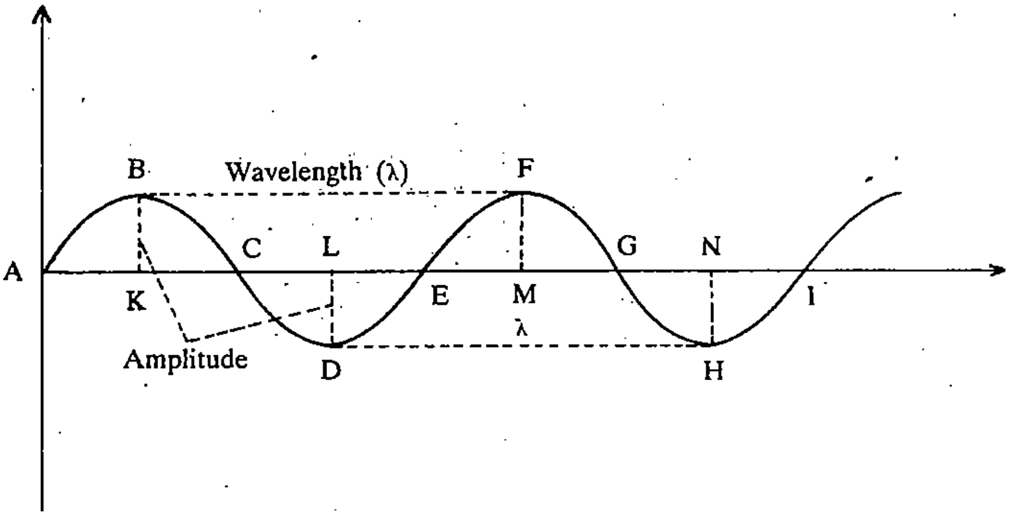


Fig. 1.5: Wave propagation.

Wavelength λ (Greek: *lambda*) is the distance between two successive crests or troughs. The length BF or DH in Fig 1.5 is equal to the wavelength and it is expressed in the unit, metre (m). The **frequency** is the number of waves per second. It is represented by the Greek letter ν (*nu*). Its unit is hertz (Hz). In fact, one hertz is equal to second^{-1} (s^{-1}). Wavelength and frequency are related by the expression (1.1) where c is the velocity of the light wave in the medium.

$$\lambda = \frac{c}{\nu} \qquad \text{....(1.1)}$$

In vacuum, $c = 2.998 \times 10^8$ m s^{-1}, and we use this value for c in our calculations. From the above expression, we understand that wavelength is inversely proportional to frequency.

$\bar{\nu}$ is pronounced as "nu bar". $1\ \text{m}^{-1} = 10^{-2}\ \text{cm}^{-1}$

The reciprocal of frequency is the period of oscillation, $T = \frac{1}{\nu}$. It indicates the time for one oscillation. Similarly the reciprocal of wavelength is the **wave number** ($\tilde{\nu}$: nu tilde). Wave number is related to frequency and wavelength as per Eq. 1.2.

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} \qquad \text{....(1.2)}$$

The maximum displacement of a medium from its equilibrium position is the amplitude of the wave.

The SI unit of $\tilde{\nu}$ is m^{-1} although most of the literature values are in cm^{-1}. The peak height (KB or MF) or trough depth (LD or NH) is called the **amplitude** of the wave. In section 1.6, we shall see how energy of a light wave is related to its frequency and wavelength. The electromagnetic spectrum describes the range of values of frequency and wavelength in the electromagnetic radiation. The characteristics of electromagnetic spectrum are given in Table 1.2.

Table 1.2: Characteristics of Electromagnetic Spectrum

Description	Wavelength Range	Wave Number cm^{-1}	Frequency Hz	Energy kJ mol^{-1}
	3×10^3 m	3.33×10^{-6}	10^5	3.98×10^{-8}
Radio waves				
	0.30 m	0.0333	10^9	3.98×10^{-4}
Microwave				
	0.0006 m (600 μm)	16.6	4.98×10^{11}	0.191
Far infrared				
	30 μm	333	10^{13}	3.98
Near infrared				
	0.8 μm (800 nm)	1.25×10^4	3.75×10^{14}	149.8
Visible				
	400 nm	2.5×10^4	7.5×10^{14}	299.2
Ultraviolet				
	150 nm	6.66×10^4	19.98×10^{14}	795
Vacuum ultraviolet				
	5 nm	2×10^6	6×10^{16}	2.39×10^4
X-rays and gamma-rays				
	10^{-4} nm	10^{11}	3×10^{21}	1.19×10^9

1 millimetre
= 1 mm = 10^{-3} m
1 micrometre
= 1 μm = 10^{-6} m
1 nanometre
= 1 nm = 10^{-9} m
1 picometre
= 1 pm = 10^{-12} m
1 Angstrom unit
= 1 Å = 10^{-10}m

At one end of the spectrum, there are X-rays and gamma-rays with low wavelength and high frequency; at the other end, we find radio waves and microwaves with high wavelength and low frequency. In Table 1.3 you can find the wavelength values of ultraviolet and visible light of different colours.

Table 1.3: Expanded Ultraviolet—Visible Region

Colour	Wavelength/nm
Ultraviolet	200
Violet	410
Indigo	430
Blue	470
Green	520
Yellow	570
Orange	620
Red	710

It is seen that violet light has lower wavelength than the light of the red colour.

Let us calculate λ and $\bar{\nu}$ values for a light having ν, 10^{15} Hz. According to the Eq. 1.1, $\lambda = \frac{c}{\nu}$.

$$= \frac{2.998 \times 10^8}{10^{15}} = 2.998 \times 10^{-7} \text{ m}$$
$$= 299.8 \text{ nm.}$$

using Eq. 1.2, $\bar{\nu} = \frac{\nu}{c}$

$$= \frac{10^{15}}{2.998 \times 10^8}$$
$$= 3.336 \times 10^6 \text{ m}^{-1}$$
$$= 3.336 \times 10^4 \text{ cm}^{-1}.$$

You can verify Eqs. 1.1 and 1.2 by substituting λ, ν and $\bar{\nu}$ values for various regions, given in Table 1.2.

Using the above ideas, attempt the following SAQ.

SAQ 2

a) Calculate the frequency of yellow light, λ = 560 nm.

....

b) In VIBGYOR, relate the frequency of different colours.

....

....

1.5 FAILURES OF CLASSICAL PHYSICS

The laws of motion put forward by Newton are the pillars of classical mechanics. Till 1900, it was thought that these classical concepts and laws hold good both for celestial bodies like planets and sub-atomic entities like electrons. Is this assumption quite acceptable? **Is it advisable to use a lorry weigh-bridge to find the weight of a safety pin?** Before trying to see whether classical mechanics is applicable to sub-atomic system, we have to be familiar with important assumptions of classical mechanics, viz.,

i) No restriction on the value that a dynamic variable (e.g. energy, momentum etc.) can have.

ii) No limit to the accuracy with which one or more of the dynamic variables of a system can be measured except the limit imposed by the precision of the measuring instruments.

iii) No restriction on the number of dynamic variables that can be accurately measured at the same time.

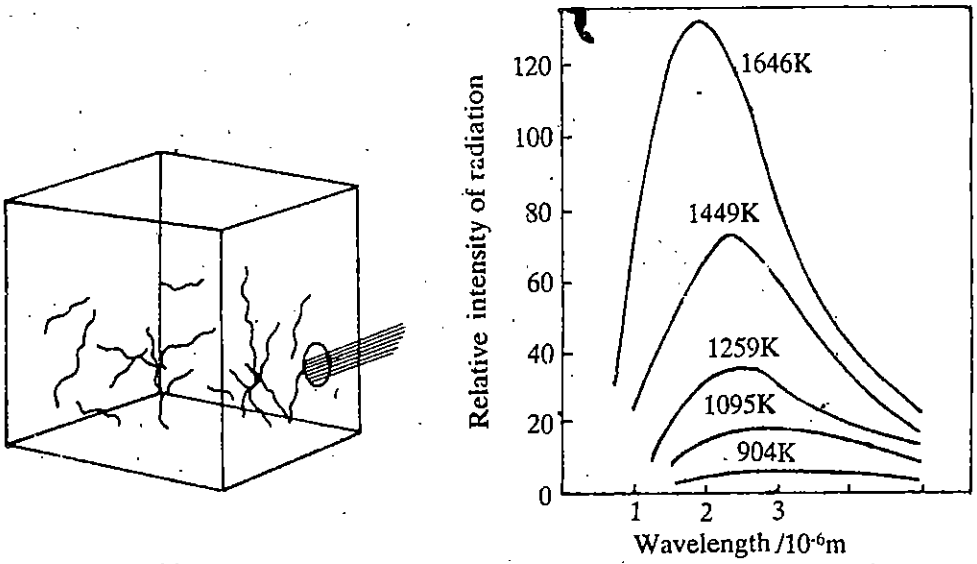
Added to classical mechanics, other tools in the bag of classical physics were thermodynamics, optics and electromagnetic theory. A number of experiments done in the latter half of nineteenth century and the first two decades of the present century gave results totally at variance with the predictions of classical physics. Let us now consider four specific cases given below, which indicated the inadequacy of classical physics:

i) black body radiation	ii) heat capacity variation
iii) photoelectric effect	iv) atomic spectra

As a first case, we shall take up black body radiation.

1.5.1 Black Body Radiation

Black body radiation is the radiation emitted by a non-reflecting solid body. **A perfect black body is one which absorbs all the radiation falling on it.** Experimentally, a hollow body, blackened on the inside and with a small opening, is considered a typical black body. Any radiation that enters through the small opening is reflected repeatedly from the walls until all of the energy eventually becomes absorbed (Fig. 1.6a). **A black body is both a good absorber and radiator of energy.** Of the various types of bodies heated to particular temperature, only black body, radiates the maximum amount of energy. It radiates the same amount of energy as it absorbs.



(a) (b)

Fig. 1.6: (a) Black body radiation. The walls reflect and absorb light, entering the cavity; (b) Distribution of energy in black body radiation.

The main aspects of black body radiation which emerge from experimental observations, are:

i) At shorter wavelength region, that is at higher frequency region, intensity of radiation is low.

ii) At every temperature, there is a wavelength at which energy radiated is maximum. This wavelength is called λ_{max} value of that temperature.

iii) At higher temperatures, there is increased intensity of radiation in the shorter wavelength region.

These facts are pictorially represented in Fig. 1.6 (b).

A piece of iron, say at 375 K, is hot for the hand to touch but no visible radiation, i.e., shorter wavelength radiation, is emitted by the metal. However, with increase of temperature, it becomes progressively dull red, bright red, orange, yellow and white hot. In general, as temperature is increased, the radiation emitted, contains more of shorter wavelength region, whether it is from black body or an iron piece.

In contrast to the above experimental fact, the classical theory predicts that the black body ought to radiate over the whole wavelength region including visible region even at room temperature. As temperature is increased, the radiation emitted should get uniformly more intense. In other words, an iron piece even at room temperature, should radiate a little in the visible range.

When the evidence of eyes and fingers does not fit the predictions of the classical theory, it is time for this theory to be modified. In section 1.6, we shall see how quantum theory successfully explains the experimental facts regarding black body radiation.

1.5.2 Heat Capacity Variation

The second drawback of classical physics is its inadequacy in explaining heat capacity variation with temperature. Dulong and Petit, based on experimental evidence then available, proposed that the molar heat capacity at constant volume for metals must be equal to 24.93 J mol^{-1} K^{-1} irrespective of temperature. Molar heat capacity is the quantity of heat required to raise the temperature of one mole of a substance through one degree kelvin. Anyhow, the experiments performed at low temperatures reveal significant deviation from Dulong and Petit law. All metals are found to have molar heat capacities lower than 24.93 J mol^{-1} K^{-1} at low temperatures and the values appear to approach zero as temperature chosen is near absolute zero. In Section 1.6, we shall see how quantum theory explains heat capacity variation with temperature.

Atomic weight of elements was corrected using Dulong and Petit law.

1.5.3 Photoelectric Effect

Let us now take up the third major setback to classical theory. The emission of electrons when metals are irradiated with ultraviolet light is known as photoelectric effect. This was observed by Hertz in 1887. The electrons, so emitted, are known as photoelectrons, to differentiate them from the electrons remaining inside the metal atoms. The main feature of this phenomenon is that a minimum frequency of light, known as **threshold frequency** (ν_0), is required to emit photoelectrons. If the frequency of the incident light is less than this value, then photoelectrons are not emitted. The value of ν_0 is a characteristic of the metallic surface used. Increasing the frequency of the light beyond threshold frequency value, only increases the velocity of the photoelectrons. These observations could not be explained by the nineteenth century view of light as wave phenomenon. In section 1.7, we shall see how Einstein's theory explains the experimental facts concerning photoelectric effect.

1.5.4 Atomic Spectra

The fourth front, where again classical theory failed, is the atomic spectra. Let us first understand what atomic spectrum is. When gases or vapours of a chemical substance are heated in an electric arc or bunsen flame, light is emitted. If a ray of this light is passed through a prism, a **line spectrum** is produced (Fig. 1.7).

Atomic absorption spectroscopy is used for identification of elements in trace quantities in substance.

This spectrum consists of a limited number of coloured lines, each of which corresponds to different wavelength of light. The line spectrum of each element is

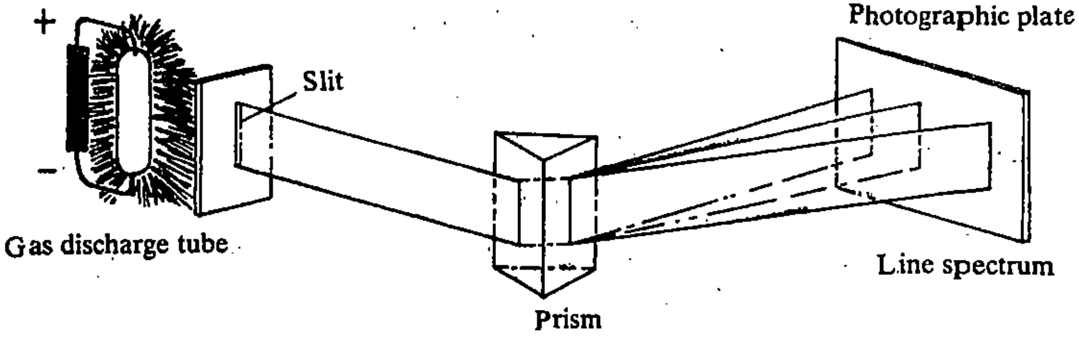
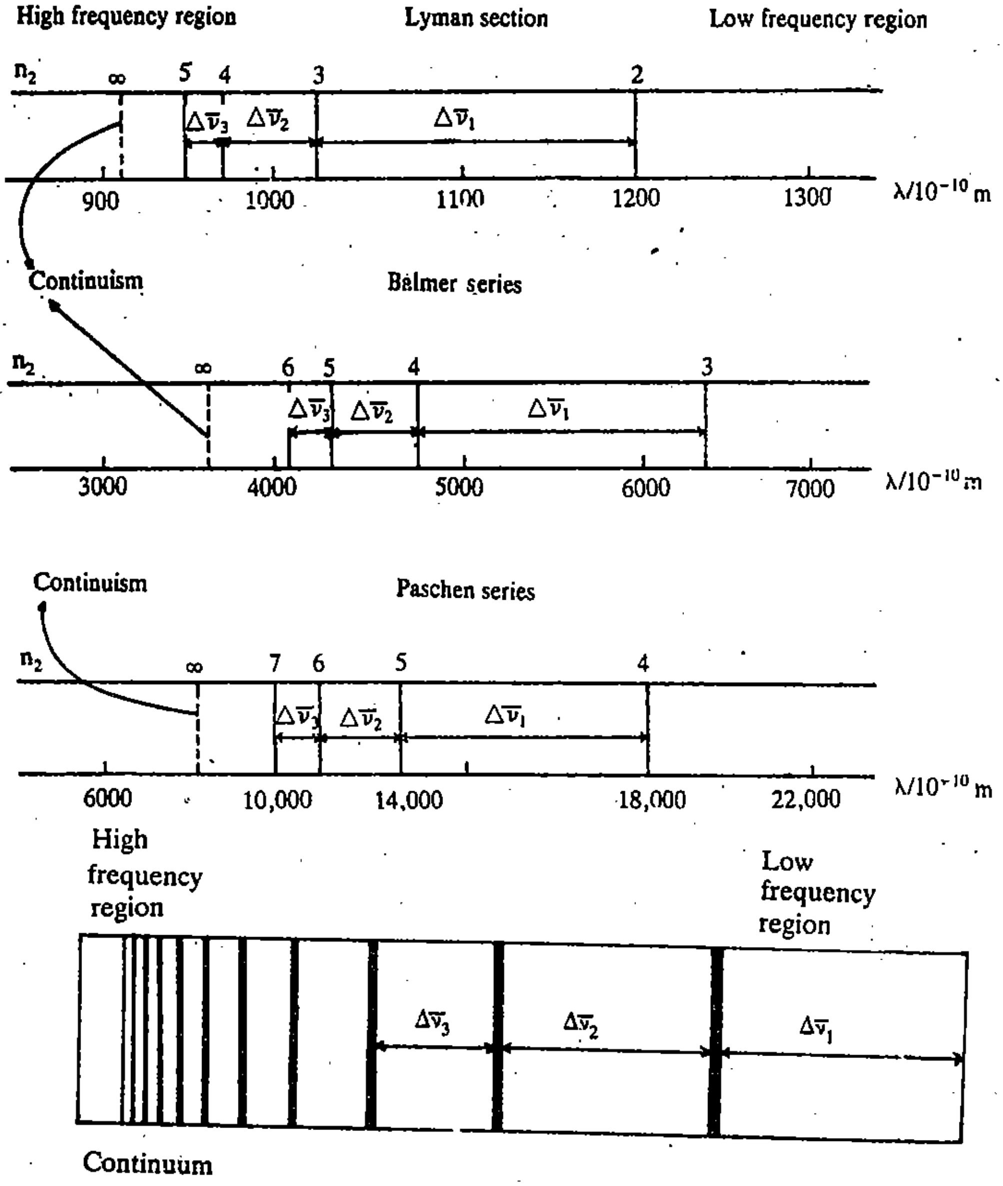


Fig. 1.7: Apparatus for atomic spectra.

unique. On careful examination, it was found that in the atomic spectra of elements, spectral lines occur discretely at lower frequencies followed by a continuous spectrum at very high frequencies. An examination of a part of the spectrum of hydrogen as in Fig. 1.8a, indicates the presence of three groups of lines. One of them is in the visible region, and it was discovered by Balmer in 1885 (Fig. 1.8b). This series, known as Balmer series, has a mathematical relationship as shown by Eq. 1.3.

In the case of atoms, only electronic transitions are possible and therefore, the spectrum is very simple consisting of electronic spectral lines. In the case of molecules, on the other hand, besides electronic transitions, transitions between rotational and vibrational energy levels are also possible and therefore molecular spectrum is relatively complex and has a large number of closely spaced lines and looks like a band (called band spectra).



(b)

Fig. 1.8: (a) Atomic spectra of hydrogen. Only a few discrete lines followed by a continuum in the three series shown. Note the spacing $\Delta\nu$ decreases as frequency increases in each series; that is, in each series, $\Delta\bar{\nu}_1 > \Delta\bar{\nu}_2 > \Delta\bar{\nu}_3$.
(b) Discrete lines followed by a continuum in Balmer series. Reproduced from the actual spectrum.

$$\bar{\nu} = \frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \qquad ....(1.3)$$

In this equation, R is a constant, now known as Rydberg constant, having a value of $1.097 \times 10^7 \text{ m}^{-1}$ and n is a whole number having values 3, 4 etc.

You can see in Fig. 1.8b that the Balmer series consists of a series of spectral lines in which the distance of separation or spacing between the lines decreases, as the frequency increases. At very high frequencies, the spectral lines, converge to give a continuous spectrum or **continuum.** The other two series known as Lyman and Paschen series, with a similar pattern, occur in the far ultraviolet and infrared regions, respectively.

Further work by Rydberg showed that the lines in the atomic spectra of the alkali metals could be classified into a number of spectral series, each of which could be described by a relationship of the following type:

$$\bar{\nu} = \bar{\nu}_\infty - \frac{R}{(n-d)^2} \qquad ....(1.4)$$

In this relation, n is an integer and d is a constant. The **Rydberg constant**, R, was shown to have the same value as mentioned above for all the elements and for the first time indicated a common link between the spectra of different elements.

Ritz (1908) showed experimentally that in any spectrum, it was possible to set up charts of quantities called terms, having dimensions of cm^{-1}, such that the wave numbers of the observed spectral lines could be written as the difference of two terms. This is known as Ritz combination principle and in case of hydrogen, new spectral series were predicted for which the frequencies were given by:

$$\bar{\nu} = R\left(\frac{1}{m^2} - \frac{1}{n^2}\right) \qquad ....(1.5)$$

Here m and n are integers and m is constant for a given series. This principle applies to two other series as well, namely, Lyman series and Paschen series.

Classical physics failed in its attempts to account for the appearance of various spectral series, each of which has discrete spectral lines at lower frequencies and a continuous spectra at higher frequencies. On the basis of classical physics, the atomic spectra was assumed to be consisting of a continuous band throughout. We shall see in section 1.11 as to how Bohr was partly successful in explaining the above observations.

1.5 PLANCK'S QUANTUM THEORY, BLACK BODY RADIATION AND HEAT CAPACITY VARIATION

The Quantum Theory, proposed by Max Planck in 1900, is the result of the realisation that the failure of classical physics is due to the wrong assumption that the energy of the system may take any arbitrary value. He suggested a detailed model for the processes taking place at the cavity walls. He considered the black body to consist of oscillators of molecular dimensions, each with a fundamental vibration frequency ν, and that each oscillator could emit energy only by a specified amount, known as **quanta**, but not continuously. His assumptions are given below:

i) An oscillator cannot have any energy, but only energies given by Eq. 1.6.

$$E = nh\nu = n\epsilon \qquad ....(1.6)$$

In this expression, ν is the frequency of emitted radiation, while h is a constant and n is an integer. Presently h is called Planck's constant and n is known as **quantum number**. One quantum of energy, ϵ, is equal to the product $h\nu$. Planck evaluated the value of the constant h as 6.626×10^{-34} J s. So Eq. 1.6 asserts that the oscillator energy is **quantised**. It is interesting to know that h is related to angular momentum, which is equal to linear momentum (mass × velocity) multiplied by length.

ii) The oscillators do not radiate energy continuously but only in quanta. These quanta of energy are emitted when an oscillator changes from one quantised energy state to another. Thus, if the oscillator goes from the level $n+1$ to n, we get from Eq. 1.6, the amount of energy radiated as,

$$\Delta E = E_2 - E_1 = (n+1)h\nu - nh\nu = h\nu \qquad ....(1.7)$$

ϵ, *epsilon*, stands for one quantum of energy, $h\nu$.

Unit of h = J s
= $\text{kg m}^2 \text{ s}^{-2}$. s
= $\text{kg m}^2 \text{ s}^{-1}$ = (kg m s^{-1}) m
= (Unit of mass × unit of velocity) × unit of length
= (Unit of linear momentum) × unit of length
= Unit of angular momentum

h is also known as **action constant;** later in Unit 2, we shall see how h relates wave and particle aspects of sub-atomic particles.

Also an oscillator neither absorbs nor emits energy as long as it remains in the same quantised state.

Let us now see in a qualitative way how Planck's theory is useful in explaining black body radiation. The number of oscillators possessing sufficient energy ϵ, otherwise known as oscillator population at that energy level, is proportional to the exponential term, $e^{-\epsilon/kT}$, known as Boltzmann factor. Here T is the temperature and k, the Boltzmann constant. The intensity of radiation is proportional to the oscillator population at a particular energy level. Hence the intensity of radiation is proportional to $e^{-\epsilon/kT}$ Using Eq. 1.6, we can say that the intensity of radiation is proportional to the quantity, $e^{-h\nu/kT}$. The term $e^{-h\nu/kT}$ is in fact equal to $\frac{1}{e^{h\nu/kT}}$ and hence is a fraction. As ν increases, the value of the fraction $e^{-h\nu/kT}$ and also the population of the oscillators decrease. It is something like decreasing the percentage of successful students at an examination by increasing the minimum pass marks! This means, the intensity of radiation of higher frequency region or shorter wavelength region is low (Fig. 1.6b).

The intensity of radiation is increased, once the temperature is increased. Since T is in the denominator of the exponential term, when T increases, $e^{h\nu/kT}$ decreases. Hence, increase of temperature increases the value of $1/e^{h\nu/kT}$ and the intensity of radiation. That is, more radiation of even shorter wavelengths will be emitted at higher temperatures (Fig. 1.6b). Planck, using a mathematical approach, was able to explain the λ_{max} value at each temperature.

Apart from explaining the black body radiation, Planck's theory is useful in calculating the energy of oscillators from the frequency values. The values of energy are given in Table 1.2 in kJ mol^{-1} as per Eq. 1.6 for each constituent of electromagnetic radiation, assuming that n is numerically equal to Avogadro number.

A ray of light having frequency ν can be considered as a stream of particles, each one having energy $h\nu$. These particles are now known as *photons*. This means that if a ray carries an energy E into some region, then the number of photons n, arriving is $E/h\nu$.

$$\text{i.e.} \quad n = \frac{E}{h\nu}$$

Planck's theory was extended by Einstein to explain heat capacity variation with temperature. Energy was considered to be taken up by the vibrations of particles. Einstein assumed that each atom could vibrate about its equilibrium position with a single frequency ν. He derived an expression to calculate the heat capacity and used it successfully to explain the decrease of heat capacity at low temperatures. The physical reason for this success is that at low temperatures only a few oscillators possess enough energy to begin oscillating. At higher temperatures, energy is available for all the oscillators to become active and the heat capacity approaches its classical value as predicted by Dulong and Petit law. The essence of Einstein's theory of heat capacities is that quantisation must be introduced in order to explain thermal properties of matter.

Using the above ideas, try the following SAQ.

SAQ 3

A yellow bulb generates 2.80×10^{20} photons with $\lambda = 560$ nm. Calculate the total energy generated.

....

....

1.7 EINSTEIN'S THEORY OF PHOTOELECTRIC EFFECT

Applying the photon concept to the photoelectric effect, Einstein proposed that an electron at the surface of the metal gains an energy $h\nu$ by the absorption of a photon from the electromagnetic radiation. If the frequency ν of the photon is greater than the minimum v ν_0. called threshold frequency which is characteristic of a particular metal, then the emission of photoelectron occurs. The difference, $h\nu - h\nu_0$, is transformed as the kinetic energy of the photoelectron which is equal to $mv^2/2$. In conformity with the principle of conservation of energy, Einstein's theory can be stated as:

$$h\nu - h\nu_0 = mv^2/2 \quad \text{....(1.8)}$$

In this expression, ν and ν_0 are the photon and threshold frequencies, respectively while m and v are the mass and velocity of the photoelectron. If $\nu < \nu_0$, then $mv^2/2$ is negative which is meaningless. That is, **photoelectron emission does not take place when ν is less than ν_0**. Using Eq. 1.8, you try the following SAQ.

SAQ 4

Calculate the frequency of the radiation required to eject photoelectrons at a velocity of 9×10^5 m s^{-1} from sodium metal surface, having a threshold frequency of 4.61×10^{14} Hz (mass of the photoelectron = 9.109×10^{-31} kg).

....

....

....

1.8 BOHR ATOM MODEL

The quantum theory was applied by the Danish physicist, Niels Bohr (1913) to explain the spectrum of hydrogen atom. He suggested an atom model which is an improvement over Rutherford model described in section 1.3.

Niels Bohr
1885-1962

Bohr based his theory on the following postulates:

i) An electron can exist only in orbits of definite angular momentum and energy. Each orbit is known as a **stationary state**.

ii) The electron does not radiate energy when it is in an allowed orbit.

iii) While in an orbit, the angular momentum of the electron, mvr, is an integral multiple of $h/2\pi$ units.

$$mvr = \frac{nh}{2\pi} \quad \text{....(1.9)}$$

Where m and v stand for the mass and velocity of the electron, r is the orbit radius and **n is an integer called principal quantum number**. The orbits are called K, L, M, N, ... depending on the values of n, viz., 1, 2, 3, 4, ... At the time this view was proposed, there was no reason for the quantisation of angular momentum. Anyhow, in section 1.6 you saw, how h has the units of angular momentum.

iv) Each spectral line is produced by a single electron. When an electron jumps from one orbit to another, radiation of a definite frequency is emitted or absorbed giving rise to a definite spectral line. The frequency of the spectral line is related to the difference in energy, ΔE, between initial and final levels, as per the equation:

$$\Delta E = h\nu = hc\bar{\nu} \quad \text{....(1.10)}$$

Using the above postulates, he was able to calculate the radius of different orbits in hydrogen atom, the energy of the electron in its orbits and the frequency of the spectral lines.

1.9 CALCULATION OF RADIUS OF ORBITS

Bohr atom model considers an electron of charge $-e$ and mass m revolving round the nucleus of charge $+Ze$ with velocity v in a stationary orbit of radius r (Fig. 1.9). The nuclear charge is taken as $+Ze$ since the nucleus is assumed to contain Z protons and each proton has charge $+e$.

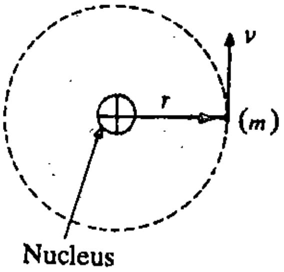


Fig. 1.9 : Bohr model for the hydrogen atom. An electron of mass m moves with the velocity v in an orbit with radius r from the nucleus.

For attaining mechanical stability, the electrostatic force of attraction, f_a, between the electron and the nucleus must be equal to the centrifugal force, f_c, which is operating in the opposite direction.

$$\text{i.e.,} \quad f_a = -f_c \quad \text{....(1.11)}$$

Note the negative sign in Eq. 1.11 which indicates that one type of force opposes the other. The electrical force of attraction, f_a, is proportional directly to the product of charges, $-e$ and Ze, and inversely to the square of the distance of separation, r^2, between the nucleus and the electron.

$$f_a \alpha \frac{(-e)(+Ze)}{r^2}$$

$$\text{i.e. } f_a = \frac{-Ze^2}{(4\pi\epsilon_0)r^2} \qquad \text{....(1.12)}$$

ϵ_0 is pronounced as "epsilon zero".

Here $(4\pi\epsilon_0)^{-1}$ is a proportionality constant in SI units. The term, ϵ_0, is the **permittivity in vacuum,** and it is equal to $8.854 \times 10^{-12} C^2 N^{-1} m^{-2}$. The terms e and r have coulomb (C) and metre (m) units, respectively while Z is unitless.

$$\text{The centrifugal force, } f_c = \frac{mv^2}{r} \qquad \text{....(1.13)}$$

Substituting Eq. 1.12 and Eq. 1.13 in Eq. 1.11.

Unit of : f_a = Unit of $\frac{-Ze^2}{4\pi\epsilon_0 r^2}$; π and Z are unitless.
Unit of f_a = $\frac{C^2}{C^2 N^{-1} m^{-2} m^2} = N$

$$\frac{-Ze^2}{4\pi\epsilon_0 r^2} = \frac{-mv^2}{r}$$

$$mv^2 = \frac{Ze^2}{4\pi\epsilon_0 r} \qquad \text{....(1.14)}$$

Rearranging Eq. 1.9, we can write, $v = \frac{nh}{2\pi mr}$

Squaring both sides, $v^2 = \frac{n^2h^2}{4\pi^2m^2r^2}$

Multiplying both sides by m,

$$mv^2 = \frac{n^2h^2}{4\pi^2mr^2} \qquad \text{....(1.15)}$$

Substituting Eq. 1.14 in Eq. 1.15 we get,

$$\frac{Ze^2}{4\pi\epsilon_0 r} = \frac{n^2h^2}{4\pi^2mr^2}$$

$$r = \frac{n^2\epsilon_0 h^2}{\pi mZe^2} \qquad \text{....(1.16)}$$

The radius of the first orbit in hydrogen atom is called Bohr radius, a_0.

Eq. 1.16 is useful in calculating the radius of the orbits with different n values. As an illustration, we calculate the radius of the first Bohr orbit (r_1) for hydrogen atom (n=1, Z=1).

$$r_1 = \frac{1^2 \times 8.854 \times 10^{-12} \times (6.626 \times 10^{-34})^2}{3.142 \times 9.109 \times 10^{-31} \times 1 \times (1.602 \times 10^{-19})^2}$$

$$= 53 \times 10^{-12} \text{ m} = 53 \text{ pm (rounded to whole number)}$$

Using this value in Eq. 1.16, a general expression for the radius of the different orbits of hydrogen atom is given below:

$$r = 53\,n^2 \text{ pm} \qquad \text{....(1.17)}$$

From Eq. 1.17, you can infer that **radius of a particular orbit in hydrogen atom is proportional to the square of its principal quantum number** value. This is illustrated in Fig. 1.10.

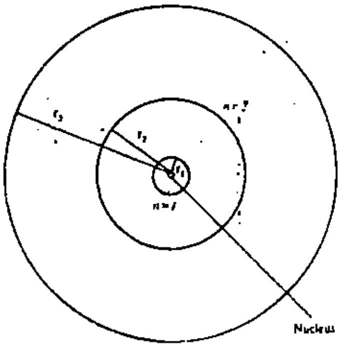


Fig. 1.10 : The radius of the orbits in hydrogen atom is proportional to n^2 values. First three orbits only shown; $r_1 : r_2 : r_3 = 1:4:9$.

The unit, picometre (pm), is quite convenient in describing the radius of the orbits in atoms.

SAQ 5

Calculate the radius of the second orbit in hydrogen atom.

....

....

....

1.10 ENERGY OF AN ELECTRON IN AN ORBIT

The total energy, E_n, of an electron in nth orbit, is given by the sum of its potential energy (P.E.) and kinetic energy (K.E.), i.e.,

$$E_n = \text{P.E.} + \text{K.E.} \qquad \ldots(1.18)$$

The potential energy of the electron is defined as the work necessary to take the electron to infinity from its equilibrium distance r, with respect to the nucleus. Since the coulmbic force (f_a) between the electron and nucleus is $-Ze^2/4\pi\epsilon_0 r^2$ as per Eq. 1.12, potential energy is calculated as follows:

$$\text{P.E.} = \int_r^\infty f_a \cdot dr$$

$$= \int_r^\infty \frac{-Ze^2}{4\pi\epsilon_0 r^2} \cdot dr$$

$$= \frac{-Ze^2}{4\pi\epsilon_0} \int_r^\infty \frac{dr}{r^2}$$

$$= \frac{-Ze^2}{4\pi\epsilon_0} \left[-\frac{1}{r} \right]_r^\infty$$

$$\text{P.E.} = \frac{-Ze^2}{4\pi\epsilon_0 r} \text{ ; also, K.E.} = \frac{mv^2}{2}$$

The negative sign indicates that work must be done on the electron to remove it to infinity.

So substituting the values of P.E. and K.E. in Eq. 1.18, we get,

$$E_n = \frac{mv^2}{2} - \frac{Ze^2}{4\pi\epsilon_0 r} \qquad \ldots.(1.19)$$

From Eq. 1.14, $\frac{mv^2}{2} = \frac{Ze^2}{8\pi\epsilon_0 r}$ ....(1.20)

Substituting Eq. 1.20 in Eq. 1.19,

$$E_n = \frac{Ze^2}{8\pi\epsilon_0 r} - \frac{Ze^2}{4\pi\epsilon_0 r}$$

$$= \frac{-Ze^2}{8\pi\epsilon_0 r} \qquad \ldots.(1.21)$$

Substituting for r from Eq. 1.16,

$$E_n = \frac{-Ze^2}{8\pi\epsilon_0} \cdot \frac{\pi m Z e^2}{n^2 \epsilon_0 h^2}$$

$$= \frac{-Z^2 e^4 m}{8\epsilon_0^2 h^2 n^2} \qquad \ldots.(1.22)$$

The negative sign in this expression denotes the fact that there is attraction between the nucleus and the electron; so work must be done to move it to a distance greater than the equilibrium distance r from the nucleus.

Substituting the values of e, m, ϵ_0 and h in Eq. 1.22, the energy of the electron in the nth orbit of hydrogen atom is obtained as,

$$E_n = \frac{-1^2 \times (1.602 \times 10^{-19})^4 \times 9.109 \times 10^{-31}}{8 \times (8.854 \times 10^{-12})^2 \times (6.626 \times 10^{-34})^2 \times n^2} \text{ J}$$

$$E_n = \frac{-2.178 \times 10^{-18}}{n^2} \text{ J} \qquad \text{....(1.23)}$$

You must remember that $Z = 1$ for hydrogen atom. In the first orbit, $n = 1$, the energy of the electron, is equal to -2.178×10^{-18} J. Since E_n is related to n^2 in Eq. 1.22, the increase in energy with the value of n is, as shown, in Table 1.4.

Table 1.4: Energy variation with n values

n	$\frac{E_n}{\text{J}} = \frac{-2.178 \times 10^{-18}}{n^2}$	$\frac{E_n - E_{n-1}}{\text{J}}$
1	-2.178×10^{-18}	–
2	-5.445×10^{-19}	1.634×10^{-18}
3	-2.42×10^{-19}	3.025×10^{-19}
4	-1.361×10^{-19}	1.059×10^{-19}
5	-8.712×10^{-20}	4.898×10^{-20}

The successive differences in energy values in Table 1.4 are obtained to show how successive energy levels become closer. So energy levels are distinctly discrete at lower n values. As n becomes sufficiently large, the energy levels differ only slightly. This is called convergence of the energy levels. This principle will be helpful to you in understanding the atomic spectra of hydrogen described in the next section. But before proceeding to the next section, why don't you try the following SAQ?

SAQ 6

What is the energy value of an electron if $n = \infty$?

....

....

....

1.11 ATOMIC SPECTRA AND BOHR'S THEORY

Bohr's theory is useful in calculating the frequencies of spectral lines in the atomic spectra of hydrogen. Let us assume that E_1 and E_2 represent the energies at the inner and outer quantum number values n_1 and n_2, respectively. Using Eq. 1.22 we can write,

$$E_1 = \frac{-Z^2 e^4 m}{8\epsilon_0^2 h^2} \cdot \frac{1}{n_1^2} \qquad \text{....(1.24)}$$

$$E_2 = \frac{-Z^2 e^4 m}{8\epsilon_0^2 h^2} \cdot \frac{1}{n_2^2} \qquad \text{....(1.25)}$$

The amount of energy emitted when an electron jumps from an outer level n_2 to an inner level n_1 is given by,

$$E_2 - E_1 = \frac{-Z^2 e^4 m}{8\epsilon_0^2 h^2} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right)$$

Representing this quantity as ΔE,

$$\Delta E = \frac{Z^2 e^4 m}{8\epsilon_0^2 h^2} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \text{....(1.26)}$$

Substituting Eq. 1.10 in Eq. 1.26, it is possible to get the wave numbers of spectral lines as given by the expression,

$$\bar{\nu} = \frac{\Delta E}{hc} = \frac{Z^2 e^4 m}{8\epsilon_0^2 h^3 c} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \text{....(1.27)}$$

The term $\frac{Z^2e^4m}{8\epsilon_0^2h^3c}$ *is called* **Rydberg constant** for hydrogen atom. It is equal to $1.097 \times 10^7 \mathrm{m}^{-1}$ and is denoted by the symbol R_H. Equation for hydrogen atom can be written as

$$\bar{\nu} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \qquad \ldots(1.28)$$

You can see that Eq. 1.28 is similar in form to Eqs. 1.3, 1.4 or 1.5 given in section 1.5.4. In the above derivation, it has been assumed that the nucleus is fixed at the centre of the orbits. In fact, nucleus and the electrons are both rotating about the common centre of mass. Anyhow, by using Eq. 1.28, we can calculate the frequencies of the spectral lines in Lyman, Balmer, Paschen, Brackett and Pfund series although at the time Bohr formulated his theory, only Balmer and Paschen series were known. For these five series in the atomic hydrogen spectra, the values of n_1 and n_2 are given in Table 1.5.

Table 1.5: Atomic Hydrogen Spectral Series

Name of the series	n_1	n_2	Region
Lyman	1	2,3,4,..	Ultraviolet
Balmer	2	3,4,5,..	Visible
Paschen	3	4,5,6,..	Infrared
Brackett	4	5,6,7,..	Infrared
Pfund	5	6,7,8,..	Infrared

A diagrammatic representation of spectral transitions among the different energy levels is given in Fig. 1.11.

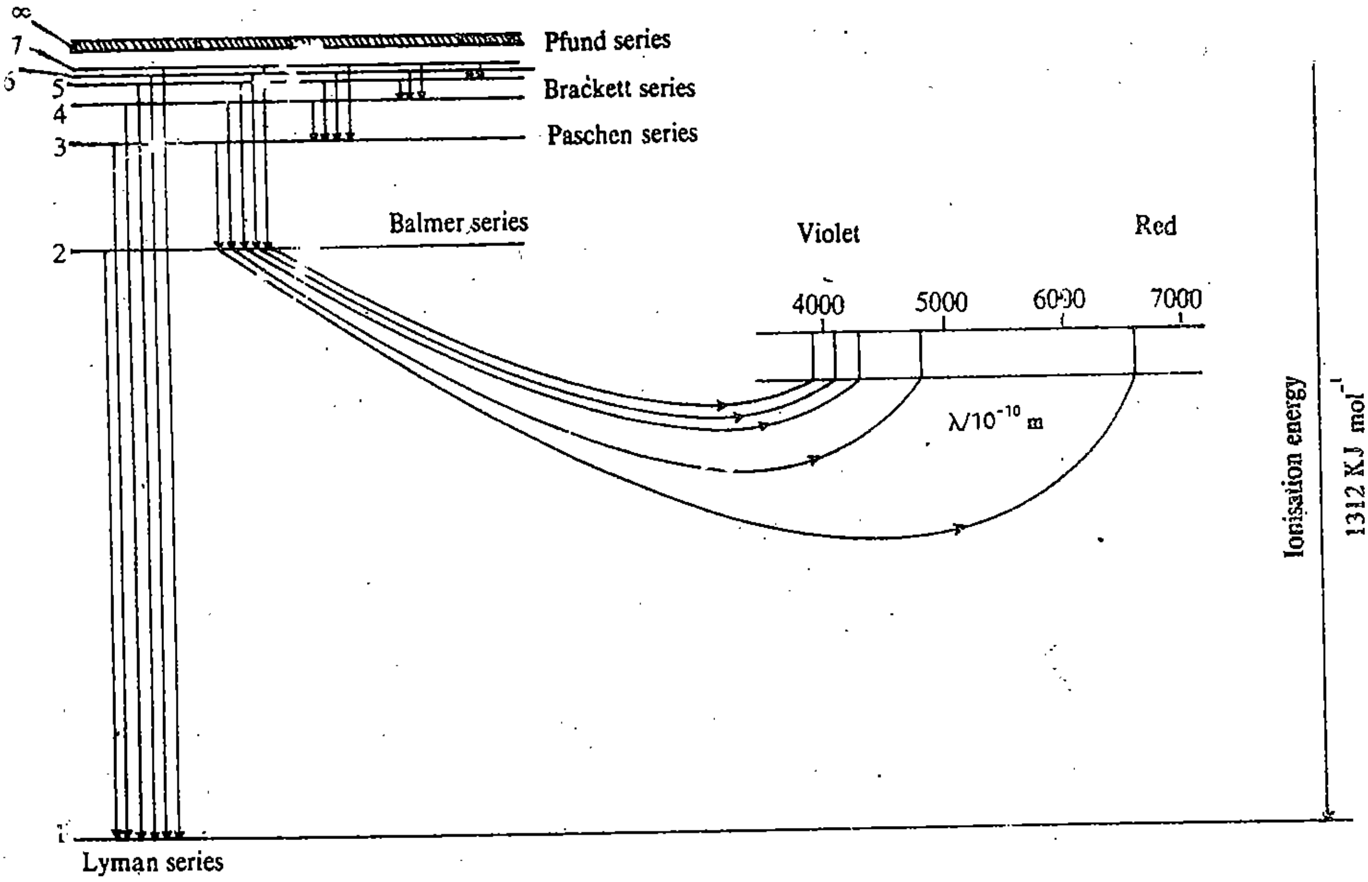


Fig. 1.11: Spectral transitions among different energy levels. Note, for Balmer series, the corresponding spectral lines are shown.

Note that the spacing between two successive levels becomes smaller, as n increases. We have mentioned about the converging nature of energy levels in section 1.10 also. Experimentally it has been found that within a particular series, for example, Lyman series, the lines in the spectrum of atomic hydrogen are discrete at lower frequencies and they converge as the frequency increases. Each successive line becomes closer to the previous one. This is quite evident from the spacings of the first four lines in Lyman series, as entered in the last column of Table 1.6.

Table 1.6: Wave Number Values in Lyman Series

Number of the spectral line (n)	n_1	n_2	$\frac{\tilde{\nu}_n}{m^{-1}} = 1.097 \times 10^7 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$	Spacing $(\tilde{\nu}_n - \tilde{\nu}_{n-1})/m^{-1}$
1	1	2	8.228×10^6	–
2	1	3	9.751×10^6	1.523×10^6
3	1	4	1.028×10^7	5.29×10^5
4	1	5	1.053×10^7	2.5×10^5

As Eq. 1.26 predicts, each series of lines converges towards a limit beyond which the spectrum is continuous. At this point, electron responsible for the spectral line has been excited into an orbit of such high energy ($n_2 = \infty$) that it has effectively escaped from the influence of the nucleus. In other words, the atom has lost its electron and formed a positive ion:

$$H(g) \longrightarrow H^+(g) + e^-$$

The energy difference between the ground state of the atom, and the excited state that corresponds to convergence limit of the spectral lines, $n_2 = \infty$, is called the **ionisation energy of the atom.** Note that ionisation energies refer to the removal of an electron in the gas phase. We will study more about ionisation energies in section 1.12 and in Unit 3.

Thus, Bohr's theory can explain the appearance of discrete spectral lines at lower frequencies and a continuous spectra at higher frequencies in the atomic spectra of hydrogen. In the light of what you have studied above, answer the following SAQ.

SAQ 7

What is the reason for the increase in the spectral frequency as n_2 increases?

....

....

....

1.12 CRITICAL ANALYSIS OF BOHR'S THEORY

Let us examine how the theoretical model of Bohr is able to explain some of the features given below:

- atomic spectra of hydrogen
- Rydberg constant value
- ionisation energy of hydrogen
- prediction of new elements

Bohr's theory is successful as an atom model to the extent that its findings are consistent with atomic spectra of hydrogen. The agreement between the theoretical and experimental values of spectral frequencies is a testimony to the validity of this theory. Again, the value of Rydberg constant, calculated according to Bohr's theory, is in agreement with the experimental value. **Ionisation energy,** which is defined as **the energy necessary to remove an electron from a gaseous atom in its outermost level to infinite distance ($n_2 = \infty$),** can be calculated using Eq. 1.28. For hydrogen atom, $n_1 = 1$ and hence its ionisation energy in wave number unit is,

$$\tilde{\nu} = R_H \left(\frac{1}{1^2} - \frac{1}{\infty^2}\right) = R_H = 1.097 \times 10^7 \ m^{-1}$$

For the purposes of chemical calculations, ionisation energy is defined as the energy required to remove one mole of electrons, i.e., 6.022×10^{23} electrons, from one mole atoms of hydrogen in the ground state. Hence, ionisation energy

$$= 6.022 \times 10^{23}\, h\, c\, \bar{\nu}\ \text{J mol}^{-1}$$
$$= 6.022 \times 10^{23} \times 6.626 \times 10^{-34} \times 2.998 \times 10^{8} \times 1.097 \times 10^{7}\ \text{J mol}^{-1}$$
$$= 1.312 \times 10^{6}\ \text{J mol}^{-1}$$
$$= 1312 \times 10^{3}\ \text{J mol}^{-1}$$
$$= 1312\ \text{kJ mol}^{-1}.$$

Thus Bohr's theory offers a method of calculating ionisation energy of hydrogen and this principle has been extended to other elements in calculating their ionisation energies.

From spectral studies, Bohr constructed a theoretical periodic chart which agreed with Mendeleev's chart. On the basis of atomic spectra, Bohr was able to predict that the element with $Z = 72$, has properties similar to titanium ($Z = 22$), and zirconium ($Z = 40$), and this element was later discovered and named hafnium.

Limitations of Bohr's Theory

According to Bohr's theory, angular momentum of this electron can never be zero. However, later on, wave mechanics (Unit 2) shows that in this $n = 1$ state, electron has zero angular momentum.

The hyperfine structure in the atomic spectra of hydrogen is not well explained by Bohr's theory. Also, Bohr's theory is not able to explain the spectra of multi-electron atoms. Further this theory does not explain how molecules are formed from atoms. It does not recognise the wave properties of electrons. Just like electromagnetic radiation, the electron also has both particle and wave aspects. Using the crystal spacings in a nickel crystal as a diffraction grating, it is possible to obtain diffraction patterns that could be understood in terms of wave motion of the electron. But Bohr's theory has not provided any explanation for this phenomenon. According to Bohr's theory, electron moves in orbits known as stationary states. The path of this orbit (or its trajectory) can be known only if we know simultaneously both the position and the velocity of electron. It, therefore, assumes the accurate and simultaneous determination of both position and velocity of the electron. But this assumption is not in conformity with the wave nature of electron. In the next unit, we shall see, how theories were developed by Heisenberg and Schrödinger, to explain the wave characteristics of electrons.

The splitting of spectral lines in the atomic spectra is called hyperfine structure. It is caused by the spin angular momentum of the electrons and the coupling of the spin to the orbital angular momentum.

1.13 REFINEMENTS IN THE ATOMIC SPECTRA THEORY

Sommerfeld (1916) modified Bohr's theory and tried to interpret the fine structure in the atomic spectra of hydrogen as due to elliptical path of the electron. He introduced another quantum number, known as **azimuthal quantum number**, which was by later modifications represented as 'l' and shown to have values $0, 1, \ldots, (n-1)$ where n is the principal quantum number. Thus if $n = 2$, then l can have values 0 and 1.

The splitting of spectral lines when atoms are placed in a strong magnetic field, known as **Zeeman effect**, could also be partially explained by introducing **magnetic quantum number** (m_l) describing the allowed orientations of electron orbits in space. It was shown that for each value of l, m_l can have $(2l + 1)$ values namely from $+l$ to $-l$. Hence if $l = 1$, m_l can have three values, $+1$, 0 and -1. You will see in the next unit, an alternate way of arriving at the quantum numbers n, l and m_l.

SAQ 8

a) If $n = 3$, what are the possible values of l?

....

....

b) If $l = 2$, what are the values of m_l?

....

....

1.14 SUMMARY

In this unit, we have focused our attention on the developments leading to Bohr atom model. The instances and reasons for the failure of classical physics are given. Using quantum theory, Planck, Einstein and Bohr explained black body radiation, heat capacity variation, photoelectric effect and atomic spectra of hydrogen. But each of the above theories had limited success. No doubt these theories rejected the classical concept of the arbitrary energy values for an atomic system. But with regard to other major cracks in the classical theory, namely simultaneous and precise determination of position and momentum, no remedy has been suggested. This loophole was plugged by de Broglie, Heisenberg and Schrödinger and we shall study in the next unit about their concepts, collectively known as **Wave Mechanics**. Since wave mechanics is based on new quantum postulates, the theories proposed by Planck, Einstein and Bohr are collectively called **Old Quantum Theory**.

1.15 TERMINAL QUESTIONS

1) Explain the significance of α-ray scattering experiment.

2) In what way is the analogy between an atom and solar system contradicting classical electromagnetic theory?

3) For a light of wavelength 300 nm, calculate frequency, wave number, energy per quantum and energy per mole.

4) Specify three major theoretical routes used for explaining atomic structure.

5) For the following statements, mark T for correct statements and F for false ones.
   a) The cathode rays carry positive charge.
   b) Neutrons were discovered when beryllium was bombarded by α-particles.
   c) The frequency of X-rays is less than that of microwaves.
   d) The unit for wave number is m^{-1}.
   e) The threshold frequency is the same for all the metals.

6) Explain the two main reasons for the failure of classical mechanics.

7) a) Explain the salient features of black body radiation.
   b) In what way, classical theory is inadequate in explaining black body radiation?

8) a) Define photoelectric effect.
   b) State the mathematical form of Einstein's theory of photoelectric effect.

9) Calculate the wavelength of the light required to eject a photoelectron from caesium metal with a kinetic energy of 2.0×10^{-19} J (ν_0 for caesium is 4.55×10^{14} Hz).

10) State Ritz combination principle.

11) What do you think is the most novel idea among Bohr's postulates?

12) Derive an expression relating radius of the atom to the mass, charge and orbit number of the electron.

13) Calculate the radius of the third orbit in hydrogen atom, using Bohr's theory.

14) Derive an expression useful in calculating the energy of an electron in nth orbit of hydrogen atom.

15) What are the energy values of the electron in the third and fourth orbits of hydrogen atom?

16) a) From the expression, $R_H = \dfrac{Z^2 e^4 m}{8\epsilon_0^2 h^3 c}$, find the value of R_H.
    b) What is the value of R_H in cm^{-1}?

17) Calculate the wave numbers of the first two lines in Balmer series.

18) Explain the limitations of Bohr's theory.

1.16 ANSWERS

SAQs

1) Thomson proposed that electrons are distributed within a sphere of positive electricity whereas Rutherford thought that the electrons move around a central positively charged nucleus.

2) a) $\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8}{560 \times 10^{-9}}$ Hz $= 5.35 \times 10^{14}$ Hz.

   b) $\nu_R < \nu_O < \nu_Y < \nu_G < \nu_B < \nu_I < \nu_V$.

While working out [illegible] must be converted [illegible]

3) $E = nh\nu = \frac{nhc}{\lambda}$

$$= \frac{2.80 \times 10^{20} \times 6.626 \times 10^{-34} \times 2.998 \times 10^8}{560 \times 10^{-9}} \text{ J} = 99.3 \text{ J}.$$

4) $\nu = \frac{(h\nu_0 + mv^2/2)}{h}$

$$= \frac{(6.626 \times 10^{-34} \times 4.61 \times 10^{14}) + (\frac{1}{2} \times 9.109 \times 10^{-31} \times (9 \times 10^5)^2)}{6.626 \times 10^{-34}} \text{ Hz}$$

$= 1.02 \times 10^{15}$ Hz.

5) $r_2 = 53\,n^2$ pm $= 53 \times 2^2$ pm $= 212$ pm.

6) $E_\infty = 0$.

7) The electron in an outer orbit has higher energy than while in an inner orbit, i.e., as n_2 increases, E_2 also increases. Since E_1 remains constant, the spectral frequency increases with increase of n_2.

8) a) $l = 0, 1$ and 2,

   b) $m_l = +2, +1, 0, -1, -2$.

Terminal Questions

1) This experiment was utilised by Rutherford to formulate nuclear atom model.

2) According to classical theory, an electron being a charged particle, as it moves, must gradually lose its energy and fall into the nucleus.

3) $\nu = 9.993 \times 10^{14}$ Hz; $\bar{\nu} = 3.333 \times 10^6$ m^{-1};
   $\epsilon = 6.621 \times 10^{-19}$ J; $E = 398.8$ kJ mol^{-1}.

4) Classical mechanics, old quantum theory and wave mechanics.

5) a) F b) T c) F d) T e) F.

6) i) Energy can have any arbitrary value,
   ii) Simultaneous fixation of position and momentum is possible.

7) a) i) At shorter wavelength region, intensity of radiation is low,
      ii) As temperature increases, the intensity of radiation in the shorter wavelength region also increases.
   b) Classical theory suggested that black body must radiate over the whole wavelength region.

8) a) Emission of photoelectrons when a metal is irradiated with ultraviolet light.
   b) $h\nu - h\nu_0 = mv^2/2$.

9) $\frac{hc}{\lambda} = h\nu_0 + mv^2/2$

$= [(6.626 \times 10^{-34} \times 4.55 \times 10^{14}) + 2.0 \times 10^{-19}]$ J

$\lambda = 396.1$ nm.

10) The wavelength of each spectral line could be written as difference between two terms.

11) Quantisation of angular momentum.

12) By balancing the force of attraction with centrifugal force, the equation can be derived. The final expression is,

$$r = \frac{n^2 \epsilon_0 h^2}{\pi m Z e^2}.$$

13) $r_3 = 9r_1 = 477$ pm.

14) Total energy of the electron is calculated by adding its kinetic energy and potential energy terms. The final expression is

$$E_n = \frac{-Z^2 e^4 m}{8\epsilon_0^2 n^2 h^2}.$$

15) -2.42×10^{-19} J; -1.361×10^{-19} J.

16) a) substitution of the values of the various parameters gives $R_H = 1.097 \times 10^7 \text{ m}^{-1}$,

b) $1.097 \times 10^5 \text{ cm}^{-1}$.

17) $1.524 \times 10^6 \text{ m}^{-1}$; $2.057 \times 10^6 \text{ m}^{-1}$.

18) Bohr's theory cannot explain the hyperfine structure in the atomic spectra of hydrogen or the atomic spectra of multi-electron elements. It cannot explain the formation of molecules from atoms. It does not take into account the wave property of electron.

UNIT 2 WAVE MECHANICS

Structure

2.1 INTRODUCTION

In Unit 1, you have studied about the Bohr model of atom. Bohr model was successful in explaining the atomic spectra of one-electron atom, namely, hydrogen. But it failed in case of multi-electron atoms, even for the simplest case of helium atom. Even in the case of hydrogen atom, Bohr's theory could not explain the finer details of the atomic spectrum such as the intensities of spectral lines and the spectra that arise when magnetic field is applied to the system. In this unit we will study how the Bohr's theory was modified on the suggestion of de Broglie (1924) who said that if light, although usually regarded as a wave, sometimes could act like a particle, then electrons, although usually regarded as particles, sometimes could act like waves. Shortly after de Broglie's suggestion of dual behaviour of matter, quantum mechanics was founded simultaneously and independently by Schrödinger and Heisenberg. Schrödinger (1926), reasoning that electronic motions could be treated as waves, developed **Wave Mechanics** and the principal mathematical formulation of Schrödinger is a partial differential equation known as Schrödinger equation. Heisenberg (1925) independently used the properties of matrices to get the same results as Schrödinger obtained and his formulation is known as **Matrix Mechanics.** In this unit we shall be dealing mainly with the Schrödinger's formulation.

You will also learn the applications of Schrödinger equation to simple systems including hydrogen-like atoms and study the shapes of various orbitals and the electron configuration of simple systems, i.e., the filling of electrons in the various available orbitals according to certain principles, namely Pauli's exclusion principle and Hund's rule etc.

Objectives

After studying this unit, you should be able to :

- explain the dual nature of radiation and matter,
- compute de Broglie wavelength of a given system,
- state Heisenberg uncertainty principle,
- explain the terms used in Schrödinger equation,
- define the terms, eigenfunction and eigenvalues,
- describe the meaning of ψ and ψ^2,
- rewrite Schrödinger equation for simple systems like particle in a one-dimensional box and particle in a three-dimensional box,
- apply Schrödinger equation to hydrogen atom and describe various atomic energy levels,
- summarise quantum numbers and shapes of orbitals, and
- predict the electron configuration of multi-electron atoms with the help of various principles.

2.2 THE NATURE OF RADIATION AND MATTER

Louis de Broglie

It had been assumed that matter is composed of particles like atoms and molecules or more correctly, electrons and nuclei; and it is distinct from radiation which is the transmission of energy by wave motion. However, the experiments conducted during the years 1887-1927 demonstrated that the boundary between matter with its particle-like behaviour and radiation with its wave-like behaviour, is not as rigid as it was supposed to be. These observations implied that matter and radiation can possess both particle and wave aspects; the behaviour depends upon the nature of the experiment. For example, the phenomenon of diffraction and interference can be understood if the wave nature of radiation is assumed. However, the photoelectric effect is explainable only in terms of the particle nature of radiation. Thus, it was concluded that radiation has dual nature. In 1924, de Broglie reasoned that a similar relation should hold for material particles also. Thus, every particle is associated with a wave whose wavelength, λ, is given by the equation

$$\lambda = \frac{h}{p} \qquad \text{....(2.1)}$$

where h is Planck's constant and p is the momentum of the particle.

For a particle of mass m, and velocity v, momentum p can be expressed as

$$p = mv \qquad \text{....(2.2)}$$

Substituting the value of p from Eq. 2.2 into Eq. 2.1, we get

$$\lambda = \frac{h}{mv} \qquad \text{....(2.3)}$$

Waves, which are associated with material particles and which obey Eq. 2.3, are called **matter waves**. Since, electron is also a material particle, let us apply the above ideas to electron. When an electron moves in a circular orbit round the nucleus, the circumference of the orbit is given by $2\pi r$. Now, if the wave associated with it is extended round the circle as shown in Fig. 2.1, it can be continually **in phase** only when the circumference of the circle is equal to integral multiple of the wavelength,

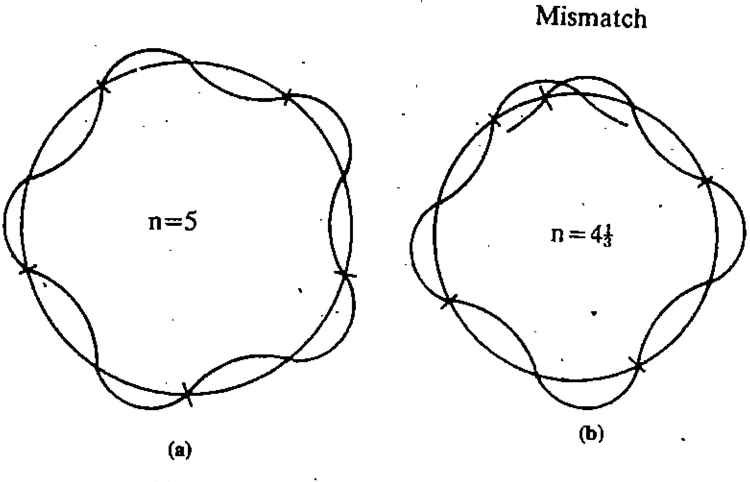


Fig. 2.1 : (a) In phase and (b) out of phase waves.

i.e., $n\lambda = 2\pi r$ where $n = 1,2,3,....$ ....(2.4)

Substituting the value of λ from Eq. 2.3 into Eq. 2.4, we obtain

$$\frac{n \cdot h}{mv} = 2\pi r \qquad \text{....(2.5)}$$

After rearranging Eq. 2.5, we get,

$$\frac{nh}{2\pi} = mvr \qquad \text{....(2.6)}$$

Since mvr is the angular momentum, it can be concluded that only those circular orbits are permitted for which the angular momentum is an integral multiple of $h/2\pi$

units. This is the same idea which Bohr postulated earlier intuitively (Unit 1, section 1.8). The de Broglie's idea was experimentally verified by Davisson and Germer in 1927 who observed the reflection of an electron beam from the metal surface, supporting its wave nature. Similar support was provided by Thomson and Reid in 1928 who photographed the diffraction rings produced when the electrons passed through a very thin metal foil (Fig. 2.2).

Electron microscope operates on the principle of electron diffraction; using this instrument particles of molecular size can be observed.

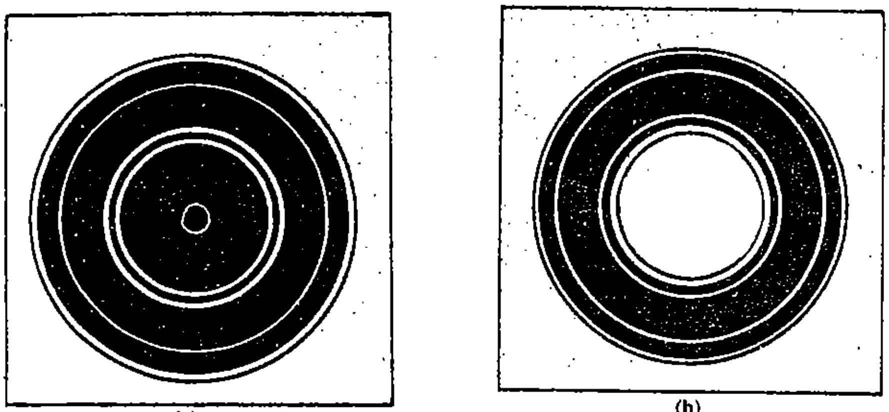

(a) (b)

Fig. 2.2 : Diffraction of waves by aluminium foil (a) X-rays of wavelength 71 pm and (b) Electrons of wavelength 50 pm. The similarity of these two patterns is a strong evidence for the wave properties of particles.

In both the cases, the experimental results fitted well with Eq. 2.1. Having understood that the electron can behave as a wave, let us now calculate the de Broglie wavelength associated with an electron having a velocity of 2.19 × 10^6 m s^{-1}, using Eq. 2.3.

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

$$= \frac{6.626 \times 10^{-34}\ \text{J s}}{(9.109 \times 10^{-31}\ \text{kg})\ (2.19 \times 10^{6}\ \text{m s}^{-1})} = 3.32 \times 10^{-10}\ \text{m}.$$

Now, let us calculate the de Broglie wavelength associated with a bullet of mass 2.2×10^{-3} kg moving with a velocity of 30 m s^{-1}.

$$\lambda = \frac{h}{mv} = \frac{6.626 \times 10^{-34}\ \text{J s}}{(2.2 \times 10^{-3}\ \text{kg})\ (30\ \text{m s}^{-1})} = 1 \times 10^{-32}\ \text{m}.$$

You can compare the two wavelengths and see how the mass of the system affects the de Broglie wavelength associated with it.

You can also conclude from Eq. 2.3 that de Broglie wavelength at a given velocity is inversely related to its mass. That is, for particles of larger mass, λ becomes smaller and hence, macroscopic bodies of large m have too small a λ to be measured.

Experimentally, λ can be measured using diffraction phenomenon.

SAQ 1
Why is not the wave nature of matter apparent in our daily observations?

....

....

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2.3 HEISENBERG UNCERTAINTY PRINCIPLE

In the last section, you have studied about the dual nature of electrons. Let us now see if we can say something on the location of an electron. We define the location of any particle of macroscopic size, by the terms **position** and **velocity**. When we try to determine the position of a moving electron by focusing light on it or perturbing it with photons, this will result in a change in its momentum. Thus, **increasing** certainty in its position would **decrease** the certainty in its momentum. Heisenberg, thus, stated that it is impossible to make, simultaneously, the determination of the exact position of a particle and its momentum. The uncertainties in the determination of these two quantities vary inversely, so that if one is determined fairly accurately, the other must be correspondingly less accurate. In the case of an electron, the product of the uncertainty of position and the uncertainty of momentum is equal to h, i.e., the Planck's constant. Thus,

$$\Delta P_x \cdot \Delta x = h \qquad \text{....(2.7)}$$

It needs to be noted that in the above equation, both momentum and position are along the same axis and not along different axes. It means that it is impossible to measure simultaneously both the momentum p_x and position x along x-axis, although one can always measure p_y (momentum along y-axis) and x (position along x-axis), simultaneously and accurately.

This limitation applies equally well to other combinations of variables like velocity, energy, time, angular momentum etc. Thus, we can also say that

$$\Delta E \cdot \Delta t = h \qquad \text{...(2.8)}$$

It is interesting to note that for each pair of variables to which Heisenberg uncertainty principle applies, the product has the same dimensions as Planck's constant.

Thus, in view of the uncertainty principle, Bohr's model having **definite orbits** needs some modification because we are not able to locate the electron precisely. The best we can do is that only the probability of finding an electron in a particular region of space can be predicted at a given time.

The difficulties of explaining certain facts with the help of classical mechanics as studied in Unit 1 led Schrödinger to develop a new approach towards the atomic structure which is known as **wave mechanics**. You will now study this approach in detail.

2.4 THE SCHRÖDINGER EQUATION

Schrödinger argued that if an electron (or any other particle) has wave-like properties, then it must be described by a **wave function**. This wave function is represented by the Greek letter, ψ (psi) and it denotes the amplitude of the wave at a given point. Schrödinger expressed the wave properties of an electron in the form of an equation which is known as Schrödinger equation. Schrödinger equation is the fundamental equation of wave mechanics and it may be obtained in the following way.

Consider the equation of wave motion in one direction, say x-direction only, which can be written as

$$\frac{\partial^2 \psi}{\partial x^2} = \frac{-4\pi^2 \psi}{\lambda^2} \quad \text{or} \quad \frac{\partial^2 \psi}{\partial x^2} + \frac{4\pi^2 \psi}{\lambda^2} = 0 \qquad \text{....(2.9)}$$

In Eq. 2.9, the term $\frac{\partial^2 \psi}{\partial x^2}$ represents the second order partial derivative of ψ with respect to x.

This equation is applicable to all particles including electrons and protons.

Total energy E of a moving particle may be considered as a sum of its potential energy, V and its kinetic energy. Thus,

$$E = \text{P.E.} + \text{K.E.} \quad \text{or K.E.} = E - \text{P.E.} = E - V \qquad \text{....(2.10)}$$

The kinetic energy of a particle of mass m moving with momentum p is given by

$$\text{K.E.} = \frac{p^2}{2m} \qquad \text{....(2.11)}$$

$p = mv$

$p^2 = m^2v^2$

$\frac{p^2}{2m} = \frac{m^2v^2}{2m}$

$= \frac{1}{2}mv^2$

$=$ K.E.

From Eq. 2.1, p can be written as $p = h/\lambda$; hence Eq. 2.11 can be written as

$$\text{K.E.} = \frac{h^2}{\lambda^2(2m)} = E - V$$

$$\text{or } \lambda^2 = \frac{h^2}{2m(E-V)} \qquad \text{....(2.12)}$$

Substituting the above value of λ^2 in Eq. 2.9, one gets

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{4\pi^2 2m}{h^2}(E-V)\psi = 0$$

or

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \quad \text{....(2.13)}$$

Eq. 2.13 is the well-known Schrödinger equation in one dimension. In three dimensions, it may be written in the following way

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \quad \text{....(2.14)}$$

Alternatively, it can also be written as

$$\nabla^2 \psi + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0 \quad \text{....(2.15)}$$

where ∇^2 is $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ and is known as **Laplacian operator.**

An operator is a mathematical command that tells one to do something on what follows the command. Thus in the expression $\sqrt{2}$, the $\sqrt{\ }$ is an operator telling one to take the square root of what follows, in this case 2. Likewise, in the expression $\frac{d(x^2+5x)}{dx}$, d/dx is an operator telling one to take the derivative with respect to x of what follows, that is $x^2 + 5x$.

Eq. 2.15 is customarily written in the following form

$$\left[\frac{-h^2}{8\pi^2 m}\nabla^2 + V\right]\psi = E\psi \quad \text{....(2.16)}$$

Defining the Hamiltonian operator H as,

$$H = \frac{-h^2}{8\pi^2 m}\nabla^2 + V \quad \text{....(2.17)}$$

Eq. 2.16 becomes

$$H\psi = E\psi \quad \text{....(2.18)}$$

which is the abbreviated form of Schrödinger equation.

2.4.1 Nature and Physical Significance of ψ and ψ^2

The wave function ψ can be regarded as an amplitude function for a wave. Similar to the amplitude, the wave function can take positive values in some region of space and negative values in the other regions. You will see later in Unit 5 how the nature of ψ affects the formation of a bond between the atoms, e.g., only the wave functions of same phase will lead to the bonding combination.

The Schrödinger equation can be solved using various trial wave functions. The particular values of ψ which yield satisfactory solutions of the above equation are called **eigenfunctions** and the corresponding energy values are called **eigenvalues**, for the system under consideration. For any particular physical situation under consideration, ψ must be **finite, single-valued** and **continuous;** then only the wave function is said to be **well behaved,** for example, in Fig. 2.3(a), the wave function shown is *not* well behaved because it is not finite. Similarly, the wave function shown in Fig. 2.3(b) is *not* single-valued for a particular value of x. It has three values of ψ at points p, q and r. Again, the wave function shown in Fig. 2.3(c) is *not* well behaved because it is not continuous. Now, you compare the above wave functions with the one shown in Fig. 2.3(d). You can see that this wave function is single-valued, continuous and finite. So it is a well behaved wave function.

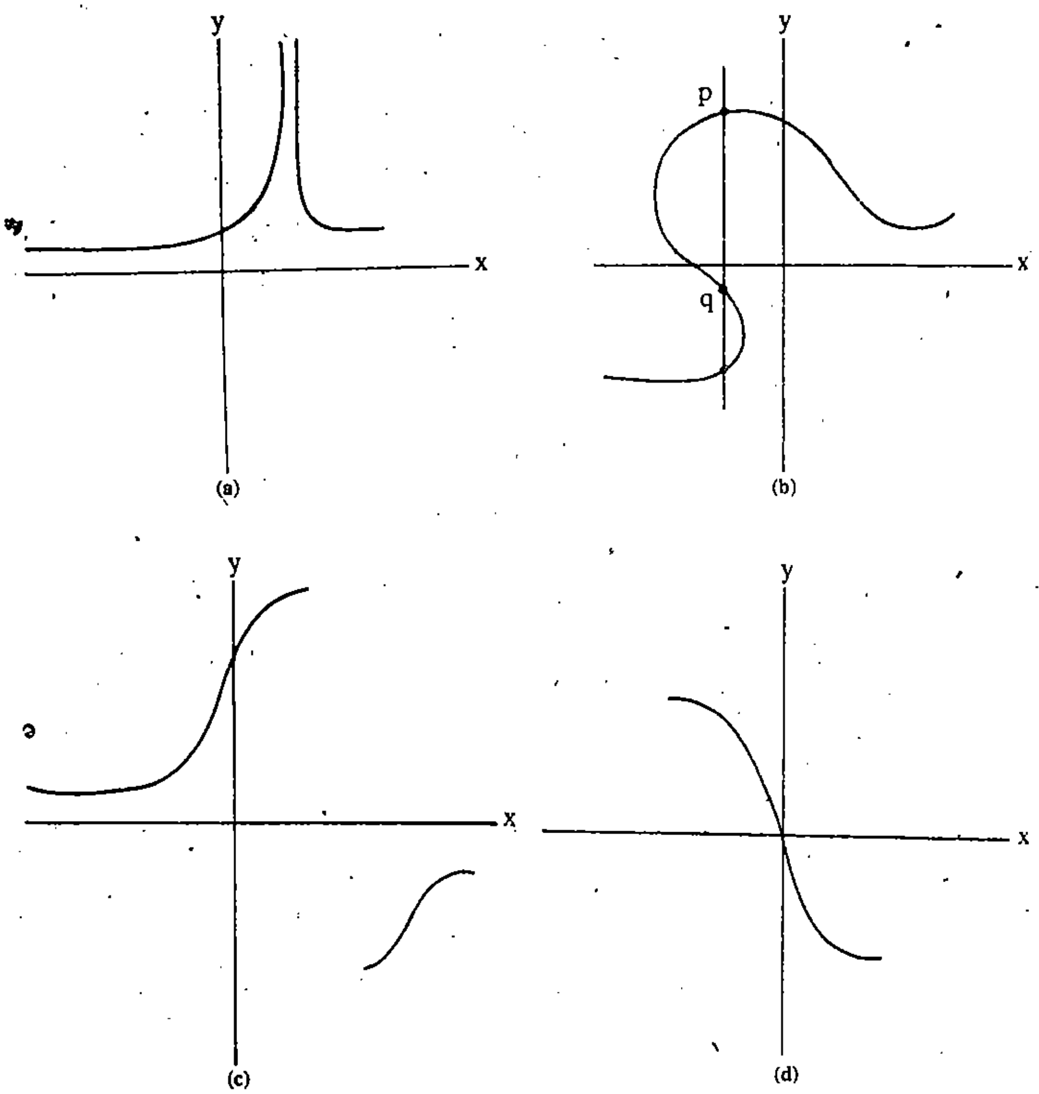

Fig. 2.3 : Pictorial representation of wave functions; the curves (a), (b) and (c) correspond to functions which are not well behaved. The curve (d) represents a well behaved function which is single-valued, continuous and finite.

Similar to the wave theory of light in which the square of the amplitude represents the intensity of light, the square of the wave function ψ, i.e., ψ^2 is proportional to the probability of finding an electron in the given region of space.

Since we presume that ψ^2 is **proportional** to the probability of finding an electron in a given region of space and **not equal** to the probability; the wave function ψ has to be multiplied by a constant N so that its square becomes,

$$(N\psi)^2 = N^2\psi^2 \qquad \text{....(2.19)}$$

When an electron is confined in a particular region of space $d\tau$, the probability of locating the electron in this region can be obtained by integration, as shown in the following expression. This integral quantity has to be equal to unity. Hence,

$$\int N^2\psi^2 d\tau = N^2\int \psi^2 d\tau = 1 \qquad \text{....(2.20)}$$

Now this probability indicates the certainty of finding the electron in the given region. Here, N is called the **normalisation constant** and it ensures that the probability of finding the electron is equal to unity and not just proportional to it. Here onwards we will deal with normalised functions only.

Concept of ψ^*

Sometimes ψ is a complex function. Since the probability of finding the particle has to be a real quantity, in such cases, the above normalisation condition represented by

$N^2\int \psi \cdot \psi \, d\tau = 1$, does not yield real values. In these cases, normalisation condition

is given by $N^2\int \psi \cdot \psi^* \, d\tau = 1$ where ψ^* is the complex conjugate of ψ and is obtained by replacing i (square root of -1) in ψ by $-i$. This ensures that $\psi\psi^*$ is a real number.

For example if

$\psi = e^{ix}$, then

$\psi\psi = e^{ix} \cdot e^{ix} = e^{2ix}$ ....(2.21)

which is a complex quantity. But

$\psi\psi^* = e^{ix} \cdot e^{-ix} = e^0 = 1$ ....(2.22)

which is a real quantity

SAQ 2

Explain the meaning of ψ^2.

....

....

....

2.5 APPLICATIONS OF SCHRÖDINGER EQUATION

You are now familiar with Schrödinger equation. Let us now apply Schrödinger equation to some simple systems and see what information can be derived from its solution. In all the cases the following steps are involved:

a) Since the Hamiltonian operator is H for the system, the corresponding Schrödinger equation is

   $H\psi = E\psi$

b) The Schrödinger equation is solved for the system. Its solution gives wave functions. As already mentioned, only those wave functions are acceptable which are well behaved, i.e., which are single-valued, continuous and finite. Such solutions are called eigenfunctions and the corresponding energy values are called eigenvalues.

c) According to quantum mechanics, all the information about the system is contained in its wave function ψ and it provides a recipe for calculating the values of dynamic variables (position, momentum, energy etc.) of a particle.

   In this section we shall study the applications of Schrödinger equation to simple systems like particle in a one-dimensional box and particle in a three-dimensional box.

2.5.1 The Particle in a One-Dimensional Box

Let us consider a particle (say an electron) of mass m, moving only in one direction (say x-axis) and assume that its movement is restricted between the walls of the box, i.e., from $x = 0$ and $x = a$. This distance, a, can be taken as the length of the box. This restriction can be met if we say that the potential energy inside the box is zero. But outside the box and at walls of the box, the potential energy increases to infinity, (Fig. 2.4).

Particle in one-dimensional box is a figurative way of applying quantum restriction to its energy values.

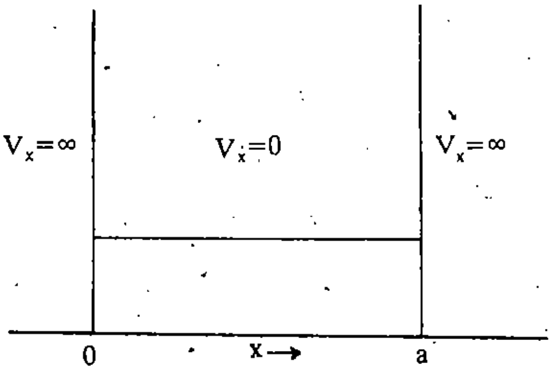

Fig. 2.4 : Particle in one-dimensional box

Let us now see what happens when the particle travels the distance, a. Since the potential energy outside the box is infinity, it cannot go out of the box and hence it bounces back after striking the wall. This situation is similar to the vibration of a guitar string fixed at the two ends, (Fig. 2.5).

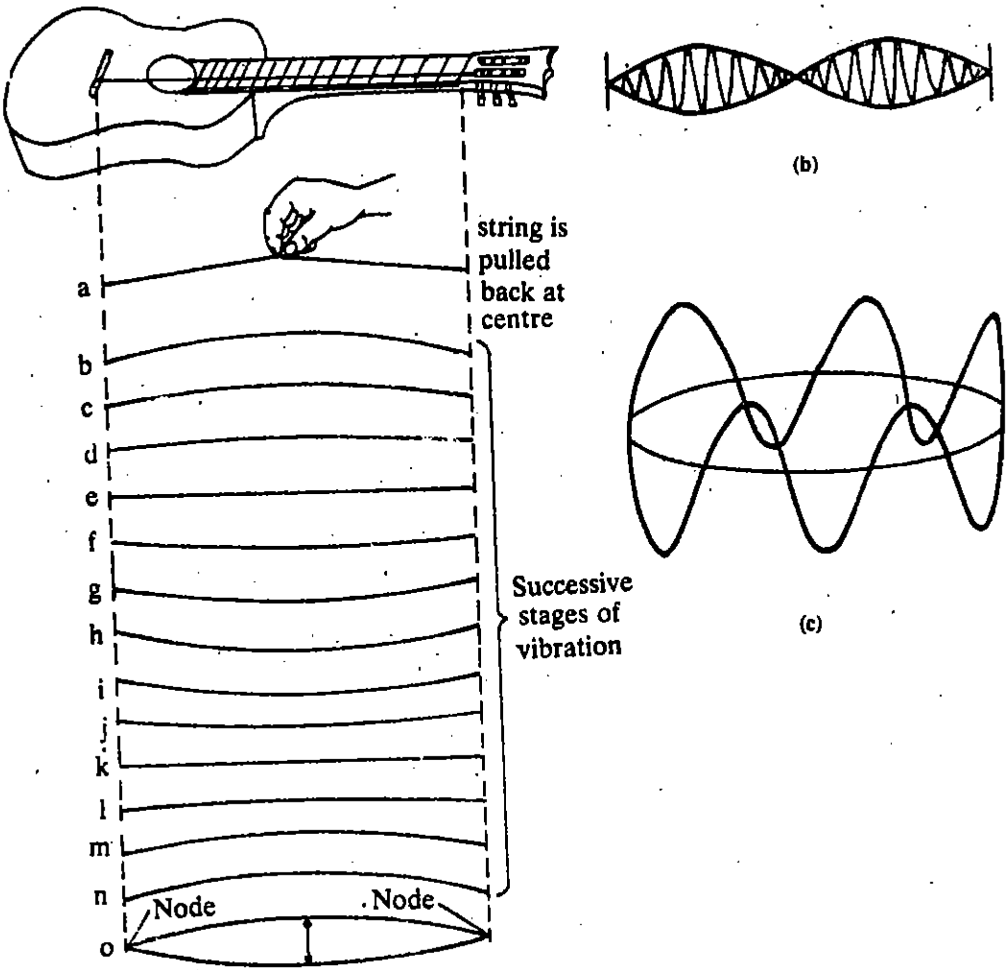

Fig. 2.5 : (a) A standing wave in a guitar string, (b) First overtone (excited state) of a guitar string and (c) Circular standing wave on a closed loop, the fifth overtone, with ten nodes.

Let us now write the Schrödinger equation for such a system. Eq. 2.13 now becomes,

$$\frac{\partial^2 \psi_x}{\partial x^2} + \frac{8\pi^2 m E \psi_x}{h^2} = 0 \qquad \ldots.(2.23)$$

since potential energy inside the box is zero.

Eq. 2.23 can be simplified to

$$\frac{\partial^2 \psi_x}{\partial x^2} + \alpha^2 \psi_x = 0 \qquad \ldots.(2.24)$$

where, $\alpha^2 = \frac{8\pi^2 m}{h^2} E$

The general solution of Eq. 2.24 is

$$\psi_x = A \sin \alpha x + B \cos \alpha x \qquad \ldots.(2.25)$$

Let us analyse the solution given by Eq. 2.24 in the light of restrictions we imposed in the beginning. We mentioned that outside the box the potential energy is infinitely high and hence there is a zero probability of finding the particle outside the box. It follows that ψ^2 must be zero for $x < 0$ and $x > a$; so also must be the ψ. To avoid discontinuity, we take $\psi = 0$ at walls also. Mathematically, it can be stated that $\psi = 0$, if $x \leq 0$ and $x \geq a$. Substituting these values in Eq. 2.25, we get, When $x = 0$

$$0 = A \sin \alpha 0 + B \cos \alpha 0 \qquad \text{....(2.26)}$$

$$0 = A\,(0) + B\,(1) \; \{\text{because } \cos 0 = 1\}$$

or $B = 0$

Putting $B = 0$ in Eq. 2.25, we get,

$$\psi_x = A \sin \alpha x \qquad \text{....(2.27)}$$

When $x = a$, we can write

$$0 = A \sin \alpha a \qquad \text{....(2.28)}$$

The right hand side of Eq. 2.28 can be zero only when either $A = 0$ or $\sin \alpha a = 0$. If A is zero, then ψ will be zero at all points in the box which is impossible because particle has to be somewhere in the box. The second possibility that $\sin \alpha a$ is zero, is valid only when αa is any integral multiple of π, i.e.,

$$\alpha a = n\pi \qquad \text{....(2.29)}$$

then $\alpha = \frac{n\pi}{a}$ ....(2.30)

Substituting the value of α from Eq. 2.30 into Eq. 2.27, we get,

$$\psi_x = A \sin \frac{n\pi x}{a} \qquad \text{....(2.31)}$$

The value of the constant A was determined to be $\sqrt{2/a}$. (See Appendix for the derivation of $A = \sqrt{2/a}$).

Thus, the wave function ψ_x can be written by substituting the value of A in Eq. 2.31 as,

$$\psi_x = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \qquad \text{....(2.32)}$$

Now, to determine the energy of the particle, let us go back to Eq. 2.24 where we assumed,

$$\alpha^2 = \frac{8\pi^2 m}{h^2} E$$

Also, you know from Eq. 2.30 that $\alpha = \frac{n\pi}{a}$. Substituting the value of α from Eq. 2.30 into the above equation, we get,

$$\frac{n^2\pi^2}{a^2} = \frac{8\pi^2 m}{h^2} E \qquad \text{....(2.33)}$$

$$\text{or} \quad E = \frac{n^2 \cancel{\pi^2} h^2}{8\cancel{\pi^2}\, m\, a^2} = \frac{n^2 h^2}{8ma^2} \qquad \text{....(2.34)}$$

You can conclude from Eq. 2.34 that a particle moving between the two points of a given axis can have energy values governed by the value of n, whereas a perfectly free particle can have any value of energy. Thus the particle in one-dimensional box can take up only discrete energy values. In other words, you can say that energy is quantised because n can have only integral values. Here n has the same significance as that of the principal quantum number of Bohr's theory. The energy value E can be determined by substituting n as 1,2,3,.... and the values of other quantities (i.e., h, m and a). You can see that the energy values for various values of n are as given below:

$$n = 1; \quad E_1 = \frac{h^2}{8ma^2} \qquad \text{....(2.35)}$$

$$n = 2; \quad E_2 = \frac{4h^2}{8ma^2} \qquad \text{....(2.36)}$$

$$n = 3; \quad E_3 = \frac{9h^2}{8ma^2} \qquad \ldots(2.37)$$

From Eq. 2.35, one sees that the particle can never have zero energy. The minimum possible energy it can have is $\frac{h^2}{8ma^2}$ (for $n = 1$), which is known as **zero point energy**. Its origin can be explained in two ways. Firstly, the uncertainty principle requires a particle to possess kinetic energy if it is confined to a finite region. Since the location of the particle is not completely indefinite, its momentum cannot be precisely zero. Alternatively, if energy has to be zero, it shall be so, only if $n = 0$ in Eq. 2.35. But for $n = 0$, the wave function ψ_x also becomes equal to zero inside the box (for all values of x). This is impossible since the particle has to be some where inside the box.

Node is a point of zero amplitude.

Greater the number of nodes, smaller the wavelength, higher the frequency and the energy.

Comparing E_1, E_2 and E_3 (Eqs. 2.35 – 2.37), you can judge that the second energy level is four times higher as compared to the first energy level and the third energy level is nine times higher as compared to the first energy level. The wave function ψ and probability densities ψ^2 for $n = 1$, 2 and 3 are shown in Fig. 2.6. The point at which the wave function is equal to zero, is called a **node**. In general, the greater the number of nodes for a given wave function, the higher will be its energy. You can see the probability density pictorially depicted by dots in the right side blocks in Fig. 2.6.

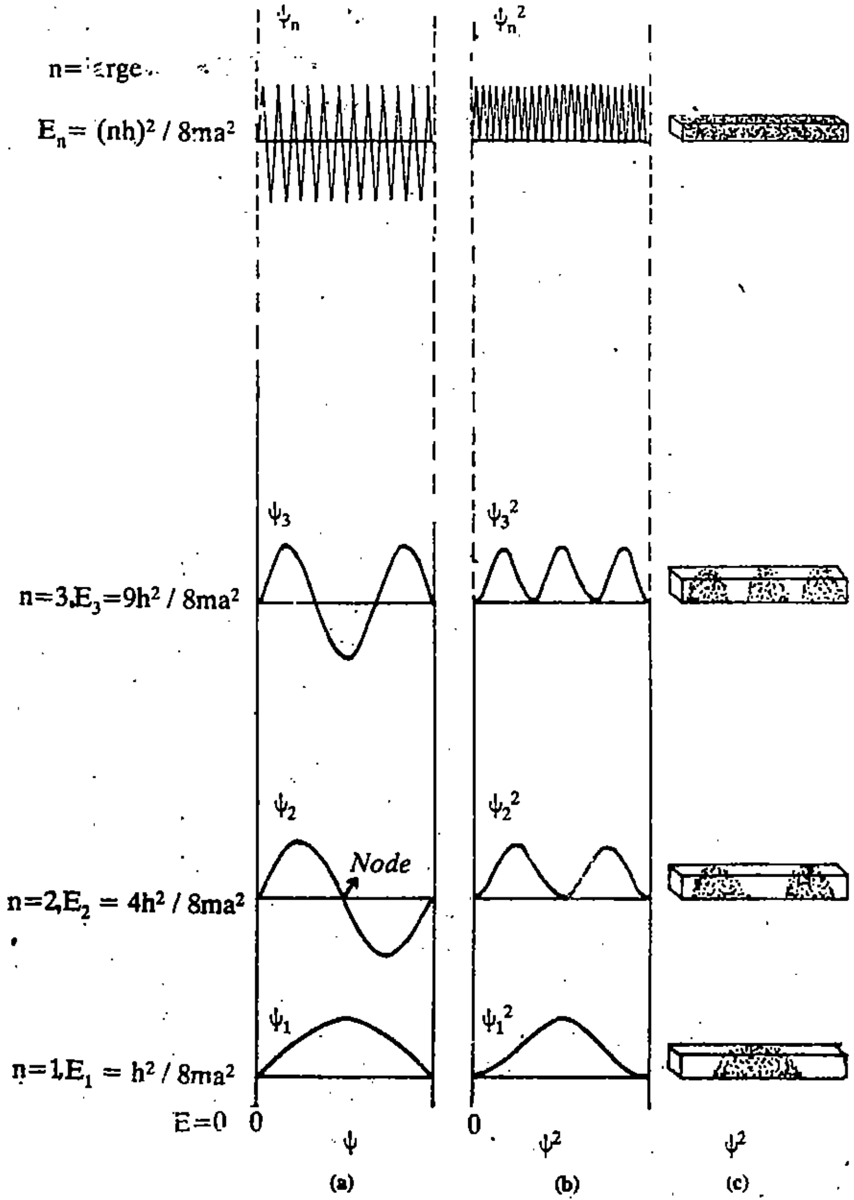

Fig. 2.6 : (a) Variation of ψ with n, (b) Probability density ψ^2 as a function of n and (c) Pictorial representation of probability density.

As shown in Fig. 2.6, the distribution of the particle in a box, as determined by ψ^2, is not uniform. At low quantum numbers, there is an apparent repulsion from the walls of the box with the particle preferring to remain away from the walls. For $n = 1$ state, ψ^2 is maximum at the centre of the box. At higher quantum numbers, the distribution becomes more uniform. This reflects the classical result that a particle bouncing between the walls, stands on an average equal time at all the points. It means that at high value of quantum number, quantum mechanics yields results similar to those obtained by classical mechanics. This is true in general for all systems and is also known as **correspondence principle.**

SAQ 3

Calculate the first three energy levels of an electron confined to a one-dimensional box of length 10^{-9} m.

....

....

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2.5.2 The Particle in a Three-Dimensional Box

Let us now extend the arguments we studied in the last section to a particle confined to a three-dimensional box. Consider a particle in the box shown in Fig. 2.7.

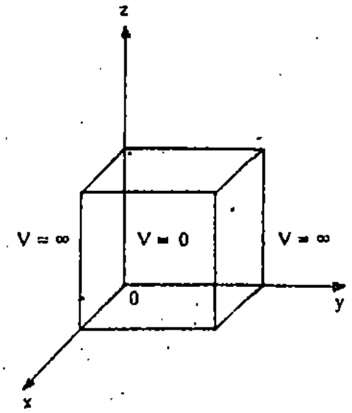


Fig. 2.7 : Three-dimensional box.

The potential energy outside the box is infinite, but it is zero everywhere inside the box. The dimensions of the box are a, b and c in the x, y and z directions, respectively. The Schrödinger equation for this system can be written assuming that the wave function ψ is a function of the three coordinates x, y and z and it can be separated into the respective components as,

$$\psi_{xyz} = \psi_x \psi_y \psi_z \qquad ...(2.38)$$

where ψ_x represents the wave function which depends only on the variable x. Similarly, we can interpret for ψ_y and ψ_z. Thus, the Schrödinger equation is

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) \psi_x\psi_y\psi_z + \frac{8\pi^2 m}{h^2} E\, \psi_x\psi_y\psi_z = 0 \qquad ....(2.39)$$

Rearranging Eq. 2.39, we get,

$$\psi_y\psi_z \frac{\partial^2 \psi_x}{\partial x^2} + \psi_x\psi_z \frac{\partial^2 \psi_y}{\partial y^2} + \psi_x\psi_y \frac{\partial^2 \psi_z}{\partial z^2} + \frac{8\pi^2 m}{h^2} E\, \psi_x\psi_y\psi_z = 0 \qquad ....(2.40)$$

Dividing by $\psi_x\psi_y\psi_z$, we obtain,

$$\frac{1}{\psi_x}\frac{\partial^2 \psi_x}{\partial x^2} + \frac{1}{\psi_y}\frac{\partial^2 \psi_y}{\partial y^2} + \frac{1}{\psi_z}\frac{\partial^2 \psi_z}{\partial z^2} + \frac{8\pi^2 m}{h^2} E = 0 \qquad ....(2.41)$$

Note that each of the first three terms in the above equation is a function of one variable only and E can also be expressed as,

$$E = E_x + E_y + E_z \qquad ....(2.42)$$

where E_x, E_y and E_z are the components of energy in the respective axes. So, we can write,

$$\frac{1}{\psi_x}\frac{\partial^2 \psi_x}{\partial x^2} + \frac{1}{\psi_y}\frac{\partial^2 \psi_y}{\partial y^2} + \frac{1}{\psi_z}\frac{\partial^2 \psi_z}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E_x + E_y + E_z) = 0 \qquad ....(2.43)$$

$$\text{or} \left(\frac{1}{\psi_x}\frac{\partial^2 \psi_x}{\partial x^2} + \frac{8\pi^2 m}{h^2} E_x\right) + \left(\frac{1}{\psi_y}\frac{\partial^2 \psi_y}{\partial y^2} + \frac{8\pi^2 m}{h^2} E_y\right) +$$

$$\left(\frac{1}{\psi_z}\frac{\partial^2 \psi_z}{\partial z^2} + \frac{8\pi^2 m}{h^2} E_z\right) = 0 \qquad ....(2.44)$$

The equality in Eq. 2.44 is valid only when each of the three terms individually is equal to zero. Thus, we can write three equations with the variables separated as,

$$\frac{1}{\psi_x}\frac{\partial^2 \psi_x}{\partial x^2} + \frac{8\pi^2 m}{h^2} E_x = 0 \qquad \text{....(2.45a)}$$

$$\frac{1}{\psi_y}\frac{\partial^2 \psi_y}{\partial y^2} + \frac{8\pi^2 m}{h^2} E_y = 0 \qquad \text{....(2.45b)}$$

$$\frac{1}{\psi_z}\frac{\partial^2 \psi_z}{\partial z^2} + \frac{8\pi^2 m}{h^2} E_z = 0 \qquad \text{....(2.45c)}$$

Each of these equations can be solved separately, similar to Eq. 2.24 to yield solutions of the type shown in Eq. 2.32.

$$\psi_x = \sqrt{\frac{2}{a}} \sin \frac{n_x \pi x}{a} \qquad \text{....(2.46a)}$$

$$\psi_y = \sqrt{\frac{2}{b}} \sin \frac{n_y \pi y}{b} \qquad \text{....(2.46b)}$$

$$\text{and } \psi_z = \sqrt{\frac{2}{c}} \sin \frac{n_z \pi z}{c} \qquad \text{....(2.46c)}$$

Substituting ψ_x, ψ_y, ψ_z from Eq. 2.46(a–c) into Eq. 2.38, we get,

$$\psi_{xyz} = \sqrt{\frac{2}{a}} \sin \frac{n_x \pi x}{a} \cdot \sqrt{\frac{2}{b}} \sin \frac{n_y \pi y}{b} \cdot \sqrt{\frac{2}{c}} \sin \frac{n_z \pi z}{c}$$

$$= \sqrt{\frac{8}{abc}} \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{b} \sin \frac{n_z \pi z}{c} \qquad \text{....(2.47)}$$

Similarly, the values for the energy components can be written as,

$$E_x = \frac{n_x^2 h^2}{8ma^2} \qquad \text{....(2.48a)}$$

$$E_y = \frac{n_y^2 h^2}{8mb^2} \qquad \text{....(2.48b)}$$

$$E_z = \frac{n_z^2 h^2}{8mc^2} \qquad \text{....(2.48c)}$$

Substituting E_x, E_y and E_z from Eq. 2.48(a), (b) and (c) into Eq. 2.42, we get the total energy E as,

$$E = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2} + \frac{n_z^2 h^2}{8mc^2}$$

$$= \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \qquad \text{....(2.49)}$$

When the box is cubic, you can say that $a = b = c$ and,

$$E = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right) \qquad \text{....(2.50)}$$

You can arrive at the lowest energy level when $n_x = n_y = n_z = 1$, i.e., 111. The next higher energy state is 211, 121 or 112 which represents the three states of equal energy. Such equal energy states are called **degenerate levels.**

2.6 HYDROGEN AND HYDROGEN-LIKE ATOMS

In the preceding discussion we described the general principles of wave mechanics and its applications to some problems. Now, we take up the application of wave mechanics for the investigation of the structure of hydrogen and hydrogen-like atoms. By hydrogen-like atoms we mean any species having one electron. For example, He^+, Li^{2+}, Be^{3+} etc. are called hydrogen-like atoms. These species differ from hydrogen atom in their nuclear charge. Also these have an overall charge +1, +2, +3 etc., whereas hydrogen atom itself is neutral. We have seen in the last unit that the success of the old quantum theory of Bohr was due to its ability to explain the structure of hydrogen atom. Schrödinger equation also was applied to hydrogen atom first and its success provided a convincing proof of the theory of wave mechanics.

In the hydrogen-like atoms, we have an electron moving in the force field of the nucleus. There is coulomb attraction between a fixed nucleus of charge Ze and mass M and a moving electron of charge e and mass m. The potential energy of this system is given by

$$V = \frac{-Ze^2}{4\pi\epsilon_0 r} \qquad \text{....(2.51)}$$

In atom, the nucleus is very heavy as compared to an electron. If we have a single electron and a single proton (1836 times heavier than electron) exerting force on each other, then centre of gravity of whole system will move, with uniform velocity in a straight line with each particle rotating about the common centre of gravity. The centre of gravity divides the vector joining nucleus and electron in the ratio of 1:1836 (ratio of mass of electron to proton) so that the nucleus executes only a very slight motion and we can almost treat it as being fixed and the electron as moving about a fixed centre of attraction at the nucleus. This becomes an exact method of handling the problem of electronic rotation, provided we assign to the electron so called 'reduced mass', μ, slightly different from its true mass.

and the reduced mass, μ, of the electron is given by Eq. 2.52

$$\frac{1}{\mu} = \frac{1}{m} + \frac{1}{M} \text{ or } \mu = \frac{mM}{m+M} \qquad \text{....(2.52)}$$

The Schrödinger wave equation for hydrogen atom thus becomes,

$$\nabla^2\psi + \frac{8\pi^2\mu}{h^2}\left(E + \frac{Ze^2}{4\pi\epsilon_0 r}\right)\psi = 0 \qquad \text{....(2.53)}$$

The only successful attempts to find solutions of the wave equation have been those in which position of the electron is given in polar coordinates. The spherical polar coordinates, r, θ and ϕ are associated with rectangular cartesian coordinates x, y, z by the relations (see Fig. 2.8 also):

$$\left.\begin{aligned} x &= r\sin\theta\cos\phi \\ y &= r\sin\theta\sin\phi \\ z &= r\cos\theta \end{aligned}\right\} \qquad \text{....(2.54)}$$

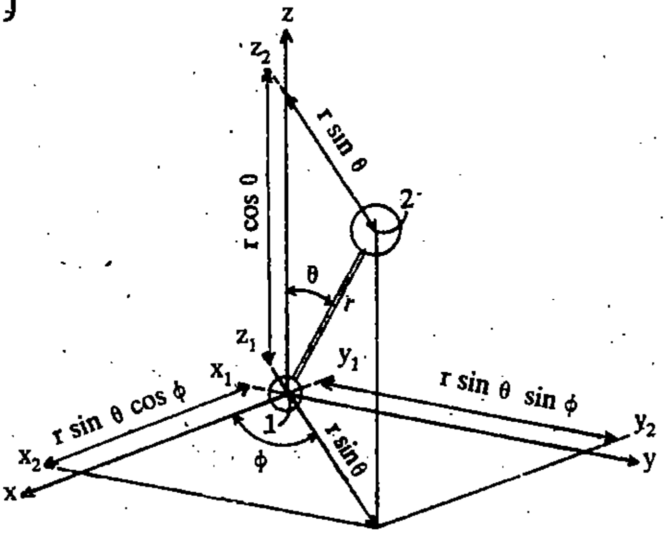


Fig. 2.8 : Transformation of cartesian to spherical polar coordinates.

Schrödinger equation (Eq. 2.53) for hydrogen atom can be expressed in spherical polar coordinates r, θ and ϕ as,

$$\frac{1}{r^2}\cdot\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin^2\theta}\cdot\frac{\partial^2\psi}{\partial\phi^2} + \frac{1}{r^2\sin\theta}\cdot\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)$$
$$+ \frac{8\pi^2\mu}{h^2}\left(E + \frac{Ze^2}{4\pi\epsilon_0 r}\right) = 0 \qquad \text{....(2.55)}$$

Accordingly, the position of the electron in spherical polar coordinates is shown in Fig. 2.9.

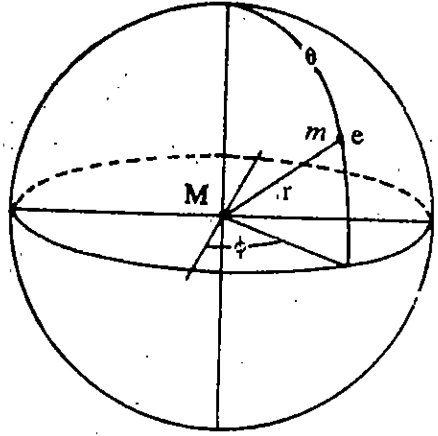


Fig. 2.9 : Position coordinates of the electron

We write the wave function for the Eq. 2.55 as,

$$\psi_{(r,\theta,\phi)} = R_{(r)}\,\Theta_{(\theta)}\,\Phi_{(\phi)} \qquad \ldots(2.56)$$

where $R_{(r)}$ is a function of r only, $\Theta_{(\theta)}$ is a function of θ only and $\Phi_{(\phi)}$ is a function of ϕ only. Then Eq. 2.55 can be separated into three differential equations with the separation of variables r, θ and ϕ. The solutions for these differential equations are characterised by three quantum numbers; n, l and m_l. To be a well behaved function, a function must be continuous, finite and single-valued; these boundary conditions or the restrictions will not be met unless n, l and m_l are integers. Also l is zero or any positive integer less than n whereas m_l can take the values $+l$ to $-l$ through 0. The various values of n, l and m_l are,

$n = 1, 2, 3, 4, \ldots$
$l = 0, 1, 2, \ldots (n-1)$
$m_l = +l \ldots +2, +1, 0, -1, -2, \ldots -l.$

You can realise that n, l and m_l are exactly the same as the principal, azimuthal and magnetic quantum numbers, respectively, mentioned in the last unit. Thus, the wave function, ψ_{nlm_l}, for any electron can be given by substituting the values of the three quantum numbers n, l and m_l. When $n=1$, $l=0$, $m_l=0$, ψ_{nlm_l} becomes ψ_{100}.

Various combinations of l and m_l for values of n upto 4 are given in Table 2.1.

Table 2.1: Possible Values of l and m_l

l has as many possible values as the value of n.

n	l	m_l	orbital representation
1	0 One Value	0	1s
2	0 1 Two Values	0 +1, 0, −1	2s 2p
3	0 1 2 Three Values	0 +1, 0, −1 +2, +1, 0, −1, −2	3s 3p 3d
4	0 1 2 3 Four Values	0 +1, 0, −1 +2, +1, 0, −1, −2 +3, +2, +1, 0, −1, −2, −3	4s 4p 4d 4f

The various values of l are designated by the letters s, p, d, f, g.... as given below:

values of l	0	1	2	3	4
letters	s	p	d	f	g

The letters s,p,d,f denote the initial letters of the words *sharp, principal, diffuse* and *fundamental* which were originally used to describe the lines in spectra. After f, alphabetical order follows.

Thus, we can summarise various energy levels with their notations as,

Value of n	1	2		3			4			
Value of l	0	0	1	0	1	2	0	1	2	3
Notation	$1s$	$2s$	$2p$	$3s$	$3p$	$3d$	$4s$	$4p$	$4d$	$4f$

The notation in the last line denotes the combination of n and l. Thus, we can list the various *quantum numbers* as:

1) The *principal quantum number n*, denotes the major energy level.
2) The *azimuthal quantum number l*, denotes the angular momentum and shape of the orbital. It can also be understood as the sublevel of the major level, n. When $l = 0$, the orbital is an s orbital and is spherical in shape. If $l = 1$, the orbital is designated as p orbital. Similarly, the orbitals having $l = 2$ and $l = 3$ are termed as d and f orbitals, respectively.
3) The *magnetic quantum number*, m_l, determines the possible quantised orientations of the angular momentum and of the orbital, in space.
4) There is a fourth quantum number, known as *spin quantum number*, m_s, which arises from the spectral evidence that any electron moving around the nucleus will spin or rotate about its own axis also. It will then behave like a small magnet. This spinning of the electron affects the angular momentum and hence the energy. The spinning can be clockwise or anticlockwise leading to two values of m_s, i.e., m_s can be $+1/2$ or $-1/2$ depending upon the direction of the spin.

For a hydrogen-like atom, the total wave function is the product of the radial function, namely $R_{(r)}$ and the two angular functions $\Theta_{(\theta)}$ and $\Phi_{(\phi)}$. The expressions for the radial and angular components for $n = 1$ to $n = 3$ are given below in the Table 2.2.

Table 2.2: The Hydrogen-Like Wave Functions

Orbital Designation	n	l	m_l	R	$\Theta\Phi$
$1s$	1	0	0	$2\left(\frac{Z}{a_0}\right)^{3/2} e^{-q}$	$\left(\frac{1}{4\pi}\right)^{1/2}$
$2s$	2	0	0	$\frac{1}{2\sqrt{2}}\left(\frac{Z}{a_0}\right)^{3/2}(2-q)e^{-q/2}$	$\left(\frac{1}{4\pi}\right)^{1/2}$
$2p_z$	2	1	0	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} qe^{-q/2}$	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
$2p_x$	2	1	1	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} qe^{-q/2}$	$\left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\cos\phi$
$2p_y$	2	1	–1	$\frac{1}{2\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2} qe^{-q/2}$	$\left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\sin\phi$
$3s$	3	0	0	$\frac{2}{81\sqrt{3}}\left(\frac{Z}{a_0}\right)^{3/2}(27-18q+2q^2)e^{-q/3}$	$\left(\frac{1}{4\pi}\right)^{1/2}$

Orbital Designation	n	l	m_l	R	ΘΦ
$3p_z$	3	1	0	$\frac{4}{81\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}(6-q)qe^{-q/3}$	$\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$
$3p_x$	3	1	1	$\frac{4}{81\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}(6-q)qe^{-q/3}$	$\left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\cos\phi$
$3p_y$	3	1	-1	$\frac{4}{81\sqrt{6}}\left(\frac{Z}{a_0}\right)^{3/2}(6-q)qe^{-q/3}$	$\left(\frac{3}{4\pi}\right)^{1/2}\sin\theta\sin\phi$
$3d_{z^2}$	3	2	0	$\frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2}q^2e^{-q/3}$	$\left(\frac{5}{16\pi}\right)^{1/2}(3\cos^2\theta-1)$
$3d_{xz}$	3	2	1	$\frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2}q^2e^{-q/3}$	$\left(\frac{15}{4\pi}\right)^{1/2}\sin\theta\cos\theta\cos\phi$
$3d_{yz}$	3	2	-1	$\frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2}q^2e^{-q/3}$	$\left(\frac{15}{4\pi}\right)^{1/2}\sin\theta\cos\theta\sin\phi$
$3d_{x^2-y^2}$	3	2	2	$\frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2}q^2e^{-q/3}$	$\left(\frac{15}{16\pi}\right)^{3/2}\sin^2\theta\cos 2\phi$
$3d_{xy}$	3	2	-2	$\frac{4}{81\sqrt{30}}\left(\frac{Z}{a_0}\right)^{3/2}q^2e^{-q/3}$	$\left(\frac{15}{16\pi}\right)^{3/2}\sin^2\theta\sin 2\phi$

Here Z is nuclear charge and $q = Zr/a_0$; a_0 is Bohr radius and r is the distance of the electron from the nucleus.

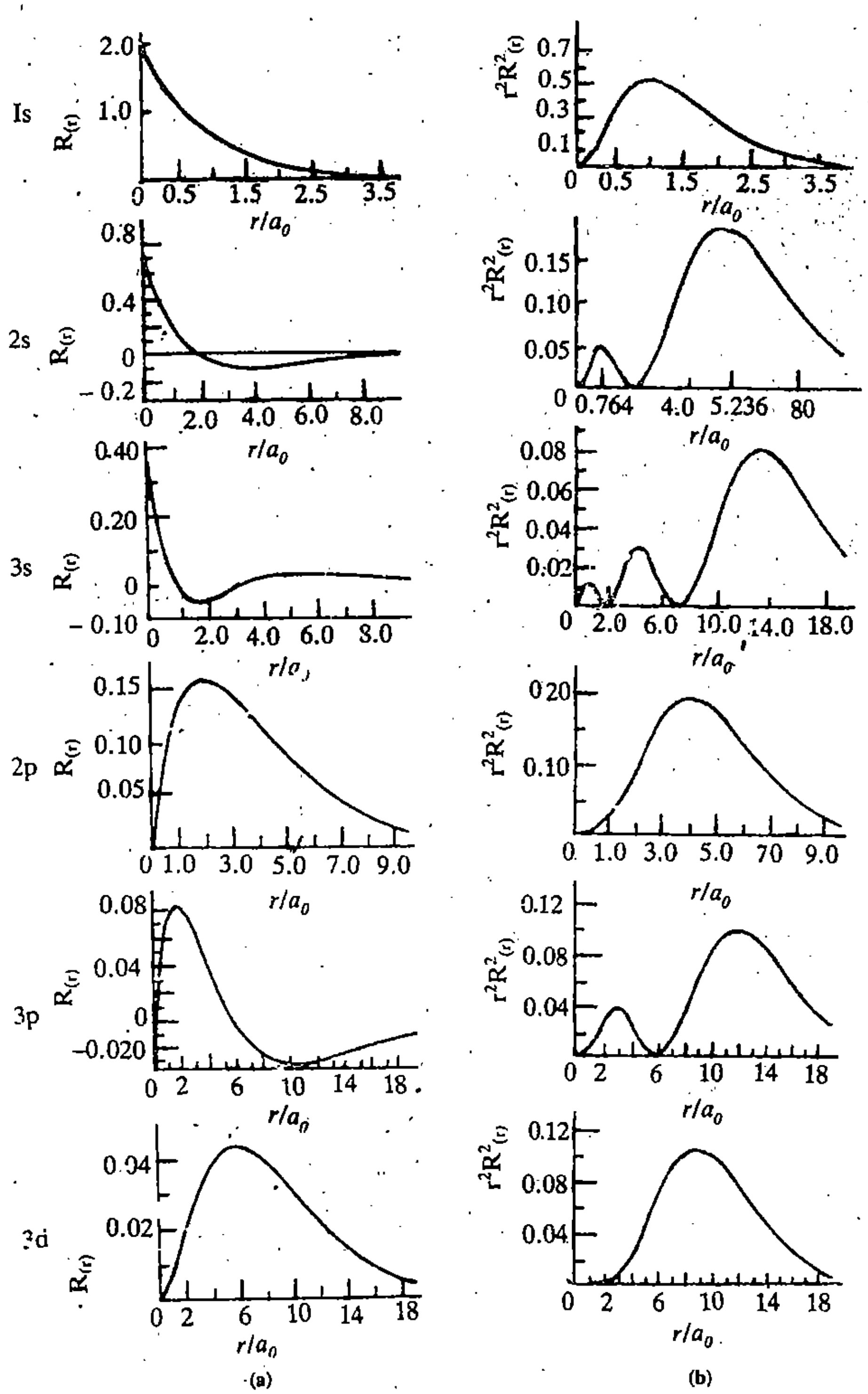
Also, $a_0 = \dfrac{\epsilon_0 h^2}{\pi\mu e^2} = 53$ pm. This is similar to Eq. 1.16 (Unit 1); the only difference is that here m is replaced by μ and $Z = 1$ for hydrogen. The term a_0 was denoted as Bohr radius in Unit 1, Section 1.9.

The term 'radial probability density' is usually applied to the probability divided by 4π times the thickness of the shell.

The radial wave functions $\mathbf{R}_{(r)}$ are plotted in Fig. 2.10(a) for various combinations of n, l and m_l. The radial distribution function $\mathbf{D}_{(r)}$ indicates the electron distribution or the probability of finding an electron in a spherical shell between r and $r + dr$. If r is the distance of the electron from the nucleus, the volume between the two shells is given by $4\pi r^2 dr$ and the probability of finding the electron between this volume element can be given by,

$$\mathbf{D}_{(r)}dr = 4\pi r^2\psi^2 dr \qquad \ldots(2.57)$$

Figure 2.10(b) shows the probability densities for finding an electron for various values of n and l. Note that in case of 1s state, the probability of finding an electron is maximum in the spherical shell which has a radius a_0, which in turn is the same as predicted by Bohr for the first orbit. Similarly you can compare the probability density of the electron in 2s orbital. The maximum now is shifted away from the nucleus i.e., the electron in the 2s orbital will have its probable location farther away from the nucleus as compared to the 1s electron. But you can see that the small hump indicates that although small, there is still finite probability of finding the 2s electron near the nucleus also.



(a)

(b)

Fig. 2.10 : (a) Electronic radial wave function R(*r*) for the hydrogen atom (b) Radial probability density for finding an electron at a distance between *r* and *r* + *dr*.

SAQ 4

Calculate the reduced mass of an electron.

mass of proton, $M = 1.673 \times 10^{-27}$ kg; mass of electron, $m = 9.109 \times 10^{-31}$ kg.

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2.6.1 Angular Dependence of the Wave Function and Shapes of Orbitals

The wave functions for single electron as obtained in the previous section are often termed as **atomic orbitals.** The shapes of these atomic orbitals depend on the angles θ and ϕ, which in other words determine the geometry or the spatial distribution of the orbitals. This angular dependence is represented by spherical polar coordinates

θ and ϕ and is given in the last column of Table 2.2 as $\Theta\Phi$ term. You can see that for 1s orbital it is just $\frac{1}{\sqrt{4\pi}}$; this means that the s orbital is independent of the angles θ and ϕ. Thus, whatever be the values of θ and ϕ, the **angular** portion of the wave function is constant. Hence, it is **spherically** symmetrical (Fig. 2.11). The orientations of the p orbitals can be calculated by considering the magnitudes and signs of the trigonometric functions. Thus for $2p_z$ orbital, as per Table 2.2, the $\Theta\Phi$ term contains cos θ, which according to the relations given in Eq. 2.54 implies that this orbital is directed along the z direction. Similarly according to Eq. 2.54 the wave function for p_y orbital contains sin θ sin ϕ term, and hence will correspond to the orbital having maximum electron density along y direction. The wave function for p_x, containing sin θ cos ϕ term, indicates that the orbital points to the x direction. Similarly we can conclude that 2s and 3s orbitals are spherically symmetrical because they do not involve θ and ϕ terms in their angular functions. Also we can interpret the directional characteristics of 3p and 3d orbitals. In the absence of any electric or magnetic field, the electrons in the three p orbitals will have the same energy, which depends on the value of n. Hence, the three p orbitals are termed as **triply degenerate**. But, when the magnetic field is applied, the electrons in the p orbital in the direction of the field shows different energy and m_l, the magnetic quantum number comes into picture.

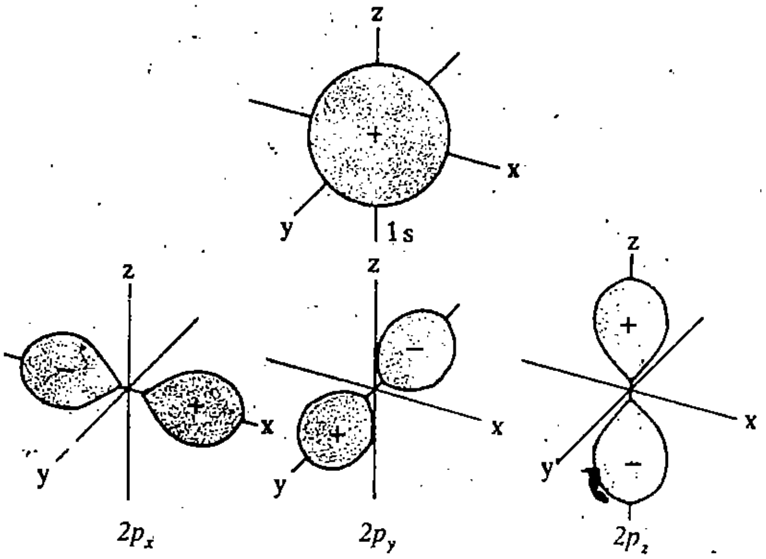

Fig. 2.11 : s and p orbitals

Similarly, the angular dependence of d orbitals can be visualised. There are five d orbitals and these are shown in Fig. 2.12. The + and − signs refer to the symmetry of

If a crest of a wave is assumed to have positive amplitude, its trough can be considered to have negative amplitude. The positive and negative signs for ψ values are inherent in their solution containing trigonometric functions like sin θ, sin ϕ, cos θ and cos ϕ.

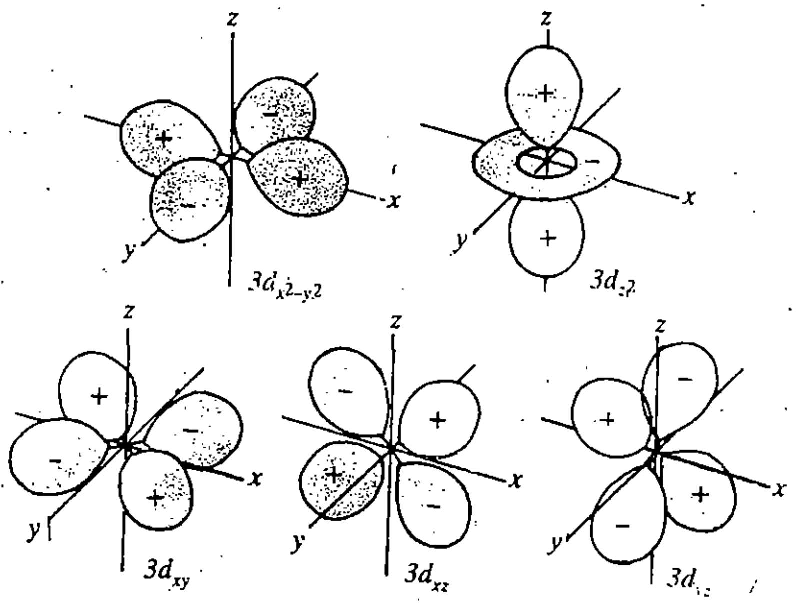

Fig. 2.12 : Five d orbitals. The indicated signs are those of the wave functions. These signs are indicated because they will be of interest later when we discuss molecular orbitals. The probability density is, of course, always positive.

wave function and you should not confuse then with the electrical charges. You will understand the importance of these signs in the bonding of orbitals during the formation of the molecules in sec. 5.2 of Unit 5 on molecular orbital theory.

Similarly, the seven f orbitals can be represented as shown in Fig. 2.13.

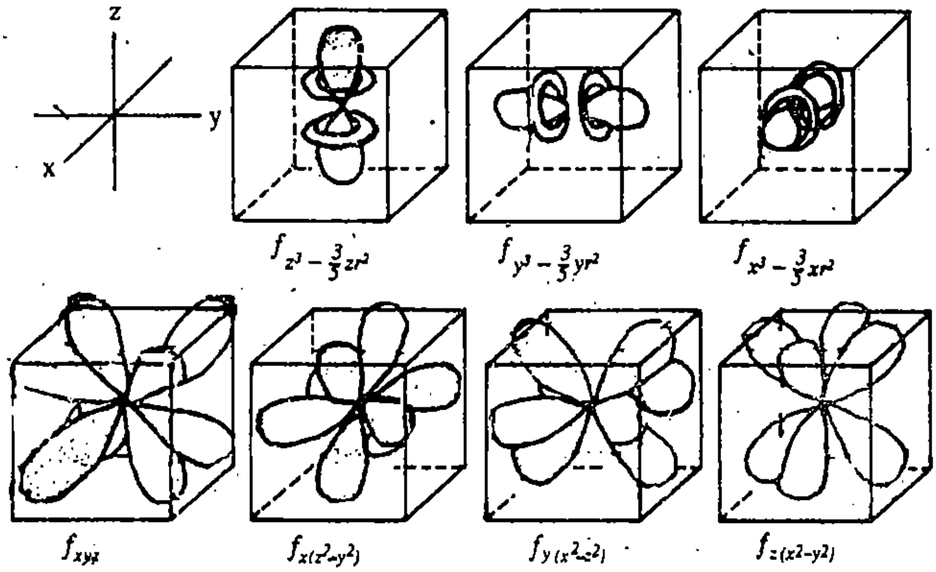

Fig. 2.13 : Shapes of seven f orbitals.

In the light of above discussion, answer the following SAQs.

SAQ 5

State the four quantum numbers and their significance.

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SAQ 6

Define the term degenerate orbitals.

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2.6.2 Energy States of the Hydrogen-like Atoms

The solution of the Schrödinger equation for hydrogen atom, i.e. Eq. 2.53, yields the expression for energy E, as

$$E = \frac{-Z^2 e^4 \mu}{8\epsilon_0 h^2 n^2} \qquad \text{....(2.58)}$$

where $n = 1, 2, 3, ...$

As M, the mass of the nucleus, is very large compared to that of an electron, μ can be replaced by m. Hence the energy expression becomes,

$$E = \frac{-Z^2 e^4 m}{8\epsilon_0^2 h^2 n^2} \qquad \text{....(2.59)}$$

which is identical to the energy expression (Eq. 1.22) obtained from the Bohr's theory. Since this expression does not involve l and m_l, the levels given by a certain value of n are degenerate. The value of n^2 gives the degeneracy of the n^{th} energy level. For example, when $n=1$, there is only one energy level and this corresponds to 1s level. When $n=2$, degeneracy is $n^2=2^2=4$ and hence the 2s and three 2p orbitals are degenerate. Similarly n=3 gives a n^2 value of 9. This corresponds to nine degenerate states which can be represented by 3s, three 3p and five 3d orbitals.

2.7 ELECTRON CONFIGURATION OF MULTI-ELECTRON ATOMS

The multi-electron systems can be considered as the extension of hydrogen atom. But it is not easy to solve the Schrödinger equation for such systems. Hence, various approximations have to be made and the energy values obtained are also not exact. These energy values can be arranged, as shown in Fig. 2.14. You can see that there is degeneracy among the sub-levels of a particular energy level in the case of hydrogen atom. But such degeneracy is lifted in the case of multi-electron atoms.

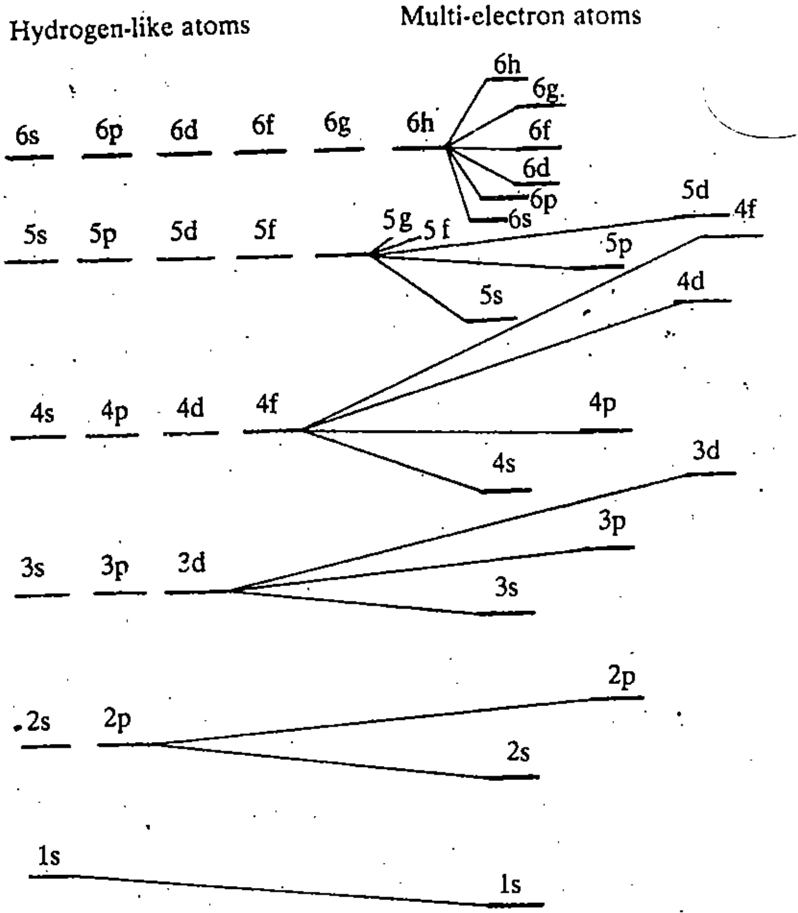


Fig. 2.14 : Splitting of orbital degeneracy in multi-electron atoms.

Thus, the energy levels so obtained can be arranged according to increasing energy as given in the following sequence:

$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d \ldots$

This sequence is obtained on the basis of Bohr-Bury rule according to which the energy of the orbital is determined by $(n + l)$. The orbitals are arranged in the order of increasing $n+l$ values and when $n+l$ is same for some of the orbitals, then the one with smaller n will have lower energy. You can easily understand this by taking the example of 3p and 4s orbitals. Both of them have $n+l = 4$. 3p orbital has $n=3$ and $l=1$ whereas 4s orbital has $n=4$ and $l=0$; hence, due to lower n value 3p orbital will be lower in energy than 4s orbital.

When we try to fill up various orbitals according to the number of available electrons, certain rules are to be followed. Let us first study these rules. Then we will discuss the filling of electrons in the orbitals in the light of the guidelines provided by these rules.

1) **The *aufbau* principle.** In German, the word ***aufbau*** stands for 'building up'. It states that the orbitals will be filled up according to the increasing order of energy, i.e., the electrons will be filled from lower energy orbitals to the higher energy orbitals.

2) **Hund's rule** says that in a given energy level, the number of unpaired electrons is maximum, i.e., the electrons will fill the available orbitals first singly and then the pairing of electrons will start. This is so since there will be repulsion between the two electrons occupying the same orbital. Hence, if orbitals of equivalent energy are available, the electrons prefer occupying the orbitals singly. If two electrons share the same orbital, for example 1*s* level, their spins remain antiparallel.

3) **Pauli's exclusion principle.** You have studied earlier that each electron can be defined by a set of four quantum numbers: n, l, m_l and m_s. Pauli's exclusion principle states that no two electrons in an atom can have the same set of four quantum numbers. Since n, l and m_l are the same for a particular orbital, two electrons occupying it must have different spin quantum numbers. In other words, the two electrons should have opposite spins, if they are to occupy the same orbital. So, you can calculate the maximum number of electrons whch occupy the various orbitals with the help of the Pauli's exclusion principle.

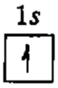
Wolfgang Pauli

n	l	m_l	m_s	No. of electrons	Orbital designation	Total electrons in a particular n level
$n = 1$	0	0	±1/2	2	1*s*	2
$n = 2$	0	0	±1/2	2	2*s*	
	1	+1	±1/2	2		
		0	±1/2	2 } 6	2*p*	8
		−1	±1/2	2		
$n = 3$	0	0	±1/2	2	3*s*	
	1	+1	±1/2	2		
		0	±1/2	2 } 6	3*p*	
		−1	±1/2	2		
	2	+2	±1/2	2		18
		+1	±1/2	2		
		0	±1/2	2 } 10	3*d*	
		−1	±1/2	2		
		−2	±1/2	2		
$n = 4$	0	0	±1/2	2	4*s*	
	1	+1	±1/2	2		
		0	±1/2	2 } 6	4*p*	
		−1	±1/2	2		
	2	+2	±1/2	2		
		+1	±1/2	2		
		0	±1/2	2 } 10	4*d*	32
		−1	±1/2	2		
		−2	±1/2	2		
	3	+3	±1/2	2		
		+2	±1/2	2		
		+1	±1/2	2		
		0	±1/2	2 } 14	4*f*	
		−1	±1/2	2		
		−2	±1/2	2		
		−3	±1/2	2		

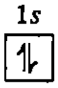
Thus, an *s* orbital can accommodate a maximum of 2 electrons, *p* orbital 6 electrons, *d* orbital 10 electrons and *f* orbital 14 electrons.

Let us take some examples and study the electron configurations; here the superscript indicates the number of electrons occupying that particular orbital.

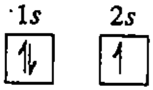
H – $1s^1$



He – $1s^2$



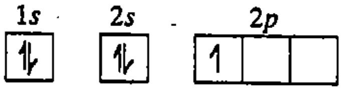
Li – $1s^2 2s^1$



The lowest energy orbital is $1s$. So the electron in hydrogen atom has the configuration $1s^1$. Helium having two electrons has the configuration $1s^2$ because the $1s$ orbital can hold two electrons, provided the two electrons have opposite spins. The third electron in case of lithium is in the next higher level, i.e., $2s$ orbital. Similarly, the fourth electron in case of berylium is in $2s$ orbital.

The next element, boron, has five electrons and its configuration can be written as

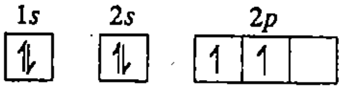
$1s^2 2s^2 2p^1$



because $2p$ orbital is the next higher energy level.

The next element, carbon, has six electrons. In conformity with Hund's rule which says that there should be a maximum number of unpaired electrons, the carbon has the configuration,

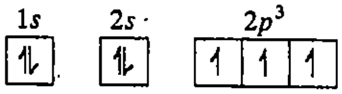
$1s^2 2s^2 2p_x^1 2p_y^1$



i.e., both the electrons in the $2p$ orbitals occupy the p orbitals singly and remain unpaired.

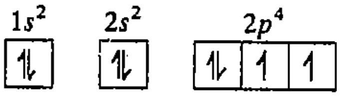
Similarly, in case of nitrogen (7 electron system), the configuration is

$1s^2 2s^2 2p^3$



with all the three electrons in $2p$ level remaining unpaired. Then, we have oxygen having eight electrons which can be represented as

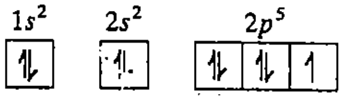
$1s^2 2s^2 2p^4$



Now since $2p$ orbitals contain four electrons, they can be filled as $2p_x^2\, 2p_y^1\, 2p_z^1$.

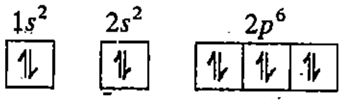
Similarly, in case of fluorine having nine electrons, the electron configuration is,

$1s^2 2s^2 2p^5$



Then, we have neon (10 electrons) which has the configuration

$1s^2 2s^2 2p^6$



with all the orbitals completely filled. You will learn in Inorganic Chemistry course that the elements having completely or exactly half-filled orbitals have more stable configuration as compared to those which have partially-filled orbitals. You can easily remember the sequence of filling of energy levels, using the diagram given in Fig. 2.15.

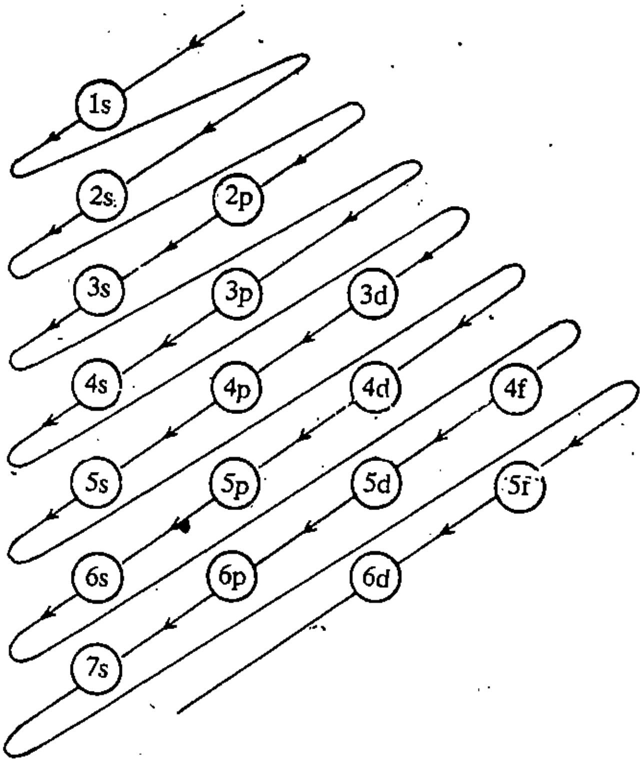


Fig. 2.15 : Sequence of filling of various orbitals.

Based upon the above sequence of filling of various orbitals, it is possible to write the electron configuration of any given element provided its atomic number is known.

Table 2.3 gives the electron configuration of all the elements. Certain anomalies are marked by asterisks (*) and are explained at the bottom of the table. You will learn more about these elements, i.e., their electron configuration and its relationship to various periodic properties in Inorganic Chemistry course.

Table 2.3 : Electron Configuration of Elements

Shell		K	L	M	N	O	P	Q
Orbital		1s	2s 2p	3s 3p 3d	4s 4p 4d 4f	5s 5p 5d 5f	6s 6p 6d 6f	7s 7p
Element	At. No.							
H	1	1						
He	2	2						
Li	3	2	1					
Be	4	2	2					
B	5	2	2 1					
C	6	2	2 2					
N	7	2	2 3					
O	8	2	2 4					
F	9	2	2 5					
Ne	10	2	2 6					
Na	11	2	2 6	1				
Mg	12	2	2 6	2				
Al	13	2	2 6	2 1				
Si	14	2	2 6	2 2				
P	15	2	2 6	2 3				
S	16	2	2 6	2 4				
Cl	17	2	2 6	2 5				
Ar	18	2	2 6	2 6				

	Shell		K	L		M			N				O				P				Q	
	Orbital		1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p	5d	5f	6s	6p	6d	6f	7s	7p
	Ele-ment	At. No.																				
n = 4	K	19	2	2	6	2	6		1													
	Ca	20	2	2	6	2	6		2													
	Sc	21	2	2	6	2	6	1	2													
	Ti	22	2	2	6	2	6	2	2													
	V	23	2	2	6	2	6	3	2													
	*Cr	24	2	2	6	2	6	5	1													
	Mn	25	2	2	6	2	6	5	2													
	Fe	26	2	2	6	2	6	6	2													
	Co	27	2	2	6	2	6	7	2													
	Ni	28	2	2	6	2	6	8	2													
	*Cu	29	2	2	6	2	6	10	1													
	Zn	30	2	2	6	2	6	10	2													
	Ga	31	2	2	6	2	6	10	2	1												
	Ge	32	2	2	6	2	6	10	2	2												
	As	33	2	2	6	2	6	10	2	3												
	Se	34	2	2	6	2	6	10	2	4												
	Br	35	2	2	6	2	6	10	2	5												
	Kr	36	2	2	6	2	6	10	2	6												
n = 5	Rb	37	2	2	6	2	6	10	2	6			1									
	Sr	38	2	2	6	2	6	10	2	6			2									
	Y	39	2	2	6	2	6	10	2	6	1		2									
	Zr	40	2	2	6	2	6	10	2	6	2		2									
	**Nb	41	2	2	6	2	6	10	2	6	4		1									
	*Mo	42	2	2	6	2	6	10	2	6	5		1									
	Tc	43	2	2	6	2	6	10	2	6	5		2									
	**Ru	44	2	2	6	2	6	10	2	6	7		1									
	**Rh	45	2	2	6	2	6	10	2	6	8		1									
	*Pd	46	2	2	6	2	6	10	2	6	10											
	*Ag	47	2	2	6	2	6	10	2	6	10		1									
	Cd	48	2	2	6	2	6	10	2	6	10		2									
	In	49	2	2	6	2	6	10	2	6	10		2	1								
	Sn	50	2	2	6	2	6	10	2	6	10		2	2								
	Sb	51	2	2	6	2	6	10	2	6	10		2	3								
	Te	52	2	2	6	2	6	10	2	6	10		2	4								
	I	53	2	2	6	2	6	10	2	6	10		2	5								
	Xe	54	2	2	6	2	6	10	2	6	10		2	6								
n = 6	Cs	55	2	2	6	2	6	10	2	6	10		2	6			1					
	Ba	56	2	2	6	2	6	10	2	6	10		2	6			2					
	La	57	2	2	6	2	6	10	2	6	10		2	6	1		2					
	Ce	58	2	2	6	2	6	10	2	6	10	1	2	6	1		2					
	Pr	59	2	2	6	2	6	10	2	6	10	2	2	6	1		2					
	Nd	60	2	2	6	2	6	10	2	6	10	3	2	6	1		2					
	Pm	61	2	2	6	2	6	10	2	6	10	4	2	6	1		2					
	Sm	62	2	2	6	2	6	10	2	6	10	5	2	6	1		2					
	Eu	63	2	2	6	2	6	10	2	6	10	6	2	6	1		2					
	Gd	64	2	2	6	2	6	10	2	6	10	7	2	6	1		2					
	Tb	65	2	2	6	2	6	10	2	6	10	8	2	6	1		2					
	Dy	66	2	2	6	2	6	10	2	6	10	9	2	6	1		2					
	Ho	67	2	2	6	2	6	10	2	6	10	10	2	6	1		2					
	Er	68	2	2	6	2	6	10	2	6	10	11	2	6	1		2					
	Tm	69	2	2	6	2	6	10	2	6	10	12	2	6	1		2					
	Yb	70	2	2	6	2	6	10	2	6	10	13	2	6	1		2					
	Lu	71	2	2	6	2	6	10	2	6	10	14	2	6	1		2					
	Hf	72	2	2	6	2	6	10	2	6	10	14	2	6	2		2					
	Ta	73	2	2	6	2	6	10	2	6	10	14	2	6	3		2					
	W	74	2	2	6	2	6	10	2	6	10	14	2	6	4		2					

	Shell		K	L	M	N	O	P	Q
	Orbital		1s	2s 2p	3s 3p 3d	4s 4p 4d 4f	5s 5p 5d 5f	6s 6p 6d 6f	7s 7p
	Element	At. No.							
n = 6	Re	75	2	2 6	2 6 10	2 6 10 14	2 6 5	2	
	Os	76	2	2 6	2 6 10	2 6 10 14	2 6 6	2	
	Ir	77	2	2 6	2 6 10	2 6 10 14	2 6 7	2	
	**Pt	78	2	2 6	2 6 10	2 6 10 14	2 6 9	1	
	*Au	79	2	2 6	2 6 10	2 6 10 14	2 6 10	1	
	Hg	80	2	2 6	2 6 10	2 6 10 14	2 6 10	2	
	Tl	81	2	2 6	2 6 10	2 6 10 14	2 6 10	2 1	
	Pb	82	2	2 6	2 6 10	2 6 10 14	2 6 10	2 2	
	Bi	83	2	2 6	2 6 10	2 6 10 14	2 6 10	2 3	
	Po	84	2	2 6	2 6 10	2 6 10 14	2 6 10	2 4	
	At	85	2	2 6	2 6 10	2 6 10 14	2 6 10	2 5	
	Rn	86	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	
n = 7	Fr	87	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	1
	Ra	88	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	2
	Ac	89	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6 1	2
	Th	90	2	2 6	2 6 10	2 6 10 14	2 6 10 1	2 6 1	2
	Pa	91	2	2 6	2 6 10	2 6 10 14	2 6 10 2	2 6 1	2
	U	92	2	2 6	2 6 10	2 6 10 14	2 6 10 3	2 6 1	2
	Np	93	2	2 6	2 6 10	2 6 10 14	2 6 10 4	2 6 1	2
	Pu	94	2	2 6	2 6 10	2 6 10 14	2 6 10 5	2 6 1	2
	Am	95	2	2 6	2 6 10	2 6 10 14	2 6 10 6	2 6 1	2
	Cm	96	2	2 6	2 6 10	2 6 10 14	2 6 10 7	2 6 1	2
	Bk	97	2	2 6	2 6 10	2 6 10 14	2 6 10 8	2 6 1	2
	Cf	98	2	2 6	2 6 10	2 6 10 14	2 6 10 9	2 6 1	2
	Es	99	2	2 6	2 6 10	2 6 10 14	2 6 10 10	2 6 1	2
	Fm	100	2	2 6	2 6 10	2 6 10 14	2 6 10 11	2 6 1	2
	Md	101	2	2 6	2 6 10	2 6 10 14	2 6 10 12	2 6 1	2
	No	102	2	2 6	2 6 10	2 6 10 14	2 6 10 13	2 6 1	2
	L	103	2	2 6	2 6 10	2 6 10 14	2 6 10 14	2 6 1	2

* As a result of inter-electronic repulsions, the electrons differing slightly in their energies have a preference to enter into those orbitals which thereby get either completely filled or just half-filld. This explains the anomalous configurations of Cr, Cu, Mo, Ag, Pd, *Au, etc.

** Anomalous configurations of Nb, Ru, Rh and Pt can be explained on the basis of nucleus-electron and electron-electron forces.

Based on their electron configuration, the various elements can be arranged in the form of the periodic table as shown in Table 2.4.

These elements are classified into various blocks according to the filling of the electrons in the various orbitals, e.g., when the *s* orbitals are being filled, the elements constitute the *s* block. Similarly, *p*, *d* and *f* block elements can be interpreted. The various groups are numbered according to both the old and the new conventions of numbering. Numbering the groups from 1 to 18 has been recently adopted by IUPAC.

SAQ 7

Write electron configuration of P and Ca and indicate the block of the periodic table, in which they occur.

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Table 2.4 Periodic trends in electron configuration, showing the outermost or differentiating electrons for each element

Group =	IA (1)	IIA (2)	IIIB (3)	IVB (4)	VB (5)	VIB (6)	VIIB (7)	— (8)	VIIIB (9)	— (10)	IB (11)	IIB (12)	IIIA (13)	IVA (14)	VA (15)	VIA (16)	VIIA (17)	VIIIA (18)	Closed Shell
Period = 1	1 H $1s^1$																	2 He $1s^2$	*K*
2	3 Li $2s^2$	4 Be $2s^2$											5 B $2p^1$	6 C $2p^2$	7 N $2p^3$	8 O $2p^4$	9 F $2p^5$	10 Ne $2p^6$	*L*
3	11 Na $3s^1$	12 Mg $3s^2$											13 Al $3p^1$	14 Si $3p^2$	15 P $3p^3$	16 S $3p^4$	17 Cl $3p^5$	18 Ar $3p^6$	*M*
4	19 K $4s^1$	20 Ca $4s^2$	21 Sc $4s^2 3d^1$	22 Ti $4s^2 3d^2$	23 V $4s^2 3d^3$	24 Cr $4s^1 3d^5$	25 Mn $4s^2 3d^5$	26 Fe $4s^2 3d^6$	27 Co $4s^2 3d^7$	28 Ni $4s^2 3d^8$	29 Cu $4s^1 3d^{10}$	30 Zn $4s^2 3d^{10}$	31 Ga $4p^1$	32 Ge $4p^2$	33 As $4p^3$	34 Se $4p^4$	35 Br $4p^5$	36 Kr $4p^6$	*N*
5	37 Rb $5s^1$	38 Sr $5s^2$	39 Y $5s^2 4d^1$	40 Zr $5s^2 4d^2$	41 Nb $5s^1 4d^4$	42 Mo $5s^1 4d^5$	43 Tc $5s^2 4d^5$	44 Ru $5s^1 4d^7$	45 Rh $5s^1 4d^8$	46 Pd $5s^0 4d^{10}$	47 Ag $5s^1 4d^{10}$	48 Cd $5s^2 4d^{10}$	49 In $5p^1$	50 Sn $5p^2$	51 Sb $5p^3$	52 Te $5p^4$	53 I $5p^5$	54 Xe $5p^6$	*O*
6	55 Cs $6s^1$	56 Ba $6s^2$	57 La $6s^2 5d^1$	72 Hf $6s^2 5d^2$	73 Ta $6s^2 5d^3$	74 W $6s^2 5d^4$	75 Re $6s^2 5d^5$	77 Os $6s^2 5d^6$	77 Ir $6s^2 5d^7$	78 Pt $6s^1 5d^9$	79 Au $6s^1 5d^{10}$	80 Hg $6s^2 5d^{10}$	81 Tl $6p^1$	82 Pb $6p^2$	83 Bi $6p^3$	84 Po $6p^4$	85 At $6p^5$	86 Rn $6p^6$	*P*
7	87 Fr $7s^1$	88 Ra $7s^2$	89 Ac $7s^2 6d^1$	104	105	106	107	108	109										

s-Block Elements

d-Block Elements

p-Block Elements

58 Ce $6s^2$ $5d^0 4f^2$	59 Pr $6s^2$ $5d^0 4f^3$	60 Nd $6s^2$ $5d^0 4f^4$	61 Pm $6s^2$ $5d^0 4f^5$	62 Sm $6s^2$ $5d^0 4f^6$	63 Eu $6s^2$ $5d^0 4f^7$	64 Gd $6s^2$ $5d^0 4f^7$	65 Tb $6s^2$ $5d^0 4f^9$	66 Dy $6s^2$ $5d^0 4f^{10}$	67 Ho $6s^2$ $5d^0 4f^{11}$	68 Er $6s^2$ $5d^0 4f^{12}$	69 Tm $6s^2$ $5d^0 4f^{13}$	70 Yb $6s^2$ $5d^0 4f^{14}$	71 Lu $6s^2$ $5d^0 4f^{14}$
90 Th $7s^2$ $6d^2 5f^0$	91 Pa $7s^2$ $6d^1 5f^2$	92 U $7s^2$ $6d^1 5f^3$	93 Np $7s^2$ $6d^1 5f^4$	94 Pu $7s^2$ $6d^0 5f^6$	95 Am $7s^2$ $6d^0 5f^7$	96 Cm $7s^2$ $6d^1 5f^7$	97 Bk $7s^2$ $6d^0 5f^9$	98 Cf $7s^2$ $6d^0 5f^{10}$	99 Es $7s^2$ $6d^0 5f^{11}$	100 Fm $7s^2$ $6d^0 5f^{12}$	101 Md $7s^2$ $6d^0 5f^{13}$	102 No $7s^2$ $6d^0 5f^{14}$	103 L $7s^2$ $6d^1 5f^{14}$

f-Block Elements

2.8 SUMMARY

We have learnt in this unit about the wave nature of the electrons in the light of de Broglie's ideas. Then we studied the Heisenberg uncertainty principle and observed that both these concepts are applicable to sub-atomic particles only. We then shifted our attention to Schrödinger wave equation and studied its applications to various simple systems, e.g., particle in a one-dimensional box, particle in a three-dimensional box and hydrogen atom. In case of hydrogen atom, we studied in detail about the solutions of the Schrödinger equation in terms of cartesian and polar coordinates. We extended these ideas to predict the shapes of various orbitals. Finally, we learnt about the filling of electrons in these orbitals in the light of various principles like ***aufbau* principle, Hund's rule** and **Pauli's exclusion principle.**

Bohr atom model calculates energy of hydrogen atom on electrostatic considerations. Schrödinger calculates the same based on amplitude variation in wave motion and de Broglie relationship.

2.9 TERMINAL QUESTIONS

1) Calculate the de Broglie wavelength associated with a body of mass 1 kg moving with a velocity 1500 m s^{-1}.
2) An electron has a speed of 300 m s^{-1} measurable accurately upto 0.01%. With what maximum accuracy, can you determine its position? ($m = 9.109 \times 10^{-31}$ kg).
3) Calculate the degeneracy of the first three energy levels for hydrogen atom.
4) Which of the following combinations of quantum numbers are allowed:

	n	l	m_l	m_s
a)	3	2	1	0
b)	2	0	0	–1/2
c)	7	2	–2	1/2
d)	3	–3	–2	–1/2

5) Write the electron configuration for the following elements:
   Si, S, Cl, Ar.
6) Write electron configuration for the following ions:
   H^-, Li^+, O^{2-}, Na^+ and Mg^{2+}

2.10 ANSWERS

Self-Assessment Questions

1) In our daily life, we come across the macroscopic objects having large mass; hence, λ associated with them is very small and cannot be measured. So we do not recognise de Broglie waves in our daily life.

2) ψ^2 gives the probability of finding an electron in a given region of space and when ψ^2 approaches unity, the probability approaches certainty of finding the electron in that particular region.

3. $$E_1 = \frac{n^2h^2}{8ma^2} = \frac{1^2 \times (6.626 \times 10^{-34})^2}{8 \times 9.109 \times 10^{-31} \times (10^{-9})^2} = 6.024 \times 10^{-20} \text{J}.$$

$$E_2 = \frac{4h^2}{8ma^2} = 24.1 \times 10^{-20} \text{ J}.$$

$$E_3 = \frac{9h^2}{8ma^2} = 54.2 \times 10^{-20} \text{ J}.$$

4) 9.10510×10^{-31} kg.

5) The four quantum numbers are
   a) Principal quantum number, n which gives the major energy level.
   b) Azimuthal quantum number, l which gives the angular momentum and shape of the orbital.

c) Magnetic quantum number, m_l, which gives the orientation of the angular momentum.

d) Spin quantum number, m_s, which gives the spin of the electron.

6) The term degenerate orbitals signify that the orbitals in question have same values of energies.

7) Electron configuration of P (At. No. 15) and Ca (At. No. 20) are,

$P = 1s^2 2s^2 2p^6 3s^2 3p^3$ *p* block

$Ca = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ *s* block

Terminal Questions

1) Use $\lambda = \frac{h}{mv}$

$$= \frac{6.626 \times 10^{-34}\ \text{J s}}{1\ \text{kg} \times 1500\ \text{m s}^{-1}}$$

$$= 4.417 \times 10^{-37}\ \text{m}$$

2) Use $\Delta p \cdot \Delta x = h$

i.e. $\Delta p = m \cdot \Delta v$. Calculate first Δv.

Hence, $\Delta x = \frac{h}{m \cdot \Delta v} = 2.427 \times 10^{-2}$ m

3) $n^2 = 1$ for first level,

$n^2 = 2^2 = 4$ for the second energy level and

$n^2 = 3^2 = 9$ for the third energy level.

So, the degeneracies are 1, 4 and 9, respectively.

4) a) Not allowed because m_s cannot be 0.
   b) allowed.
   c) allowed.
   d) Not allowed because l cannot be negative.

5) Si $1s^2 2s^2 2p^6 3s^2 3p^2$

S $1s^2 2s^2 2p^6 3s^2 3p^4$

Cl $1s^2 2s^2 2p^6 3s^2 3p^5$

Ar $1s^2 2s^2 2p^6 3s^2 3p^6$

6) H^- $1s^2$

Li^+ $1s^2$

O^{2-} $1s^2 2s^2 2p^6$

Na^+ $1s^2 2s^2 2p^6$

Mg^{2+} $1s^2 2s^2 2p^6$

APPENDIX

Value of *A* in one-dimensional box

Let us now determine the value of the constant *A* appearing in Eq. 2.31. To do this, we assume that the probability of locating the particle inside the box should be equal to unity. This can be ensured by integrating $\psi^2 dx$ within the limits $x = 0$ and $x = a$.

$$\int_0^a \psi^2\, dx = 1$$

Substituting ψ from Eq. 2.31,

$$\int_0^a A^2 \sin^2 \frac{n\pi}{a} x \cdot dx = 1 \qquad \text{....(A.1)}$$

From the fundamental rules of trigonometry, we can write

$$\cos 2\theta = 1 - 2 \sin^2\theta$$

or $\sin^2\theta = \frac{1}{2}(1 - \cos 2\theta)$

So, we can write Eq. A.1 as

$$\int_0^a A^2 \cdot \frac{1}{2}\left(1 - \cos 2 \cdot \frac{n\pi}{a} x\right) \cdot dx = 1$$

or $A^2\left[\int_0^a \frac{1}{2}\ dx - \int_0^a \frac{1}{2} \cos \frac{2n\pi}{a} x \cdot dx\right] = 1$

or $A^2\left[\int_0^a \frac{dx}{2} - \frac{1}{2}\int_0^a \cos \frac{2n\pi}{a} x \cdot dx\right] = 1$

But $\int \cos ax dx = \frac{\sin ax}{a}$

Then,

$$A^2\left\{\frac{a}{2} - \frac{1}{2}\left[\frac{\sin \frac{2n\pi x}{a}}{\frac{2n\pi}{a}}\right]_0^a\right\} = 1$$

$$A^2\left\{\frac{a}{2} - \frac{a}{4n\pi}\left[\sin \frac{2n\pi \cancel{a}}{\cancel{a}} - 0\right]\right\} = 1$$

$$A^2\left\{\frac{a}{2} - \frac{a}{4n\pi}[0 - 0]\right\} = 1$$

(because, $\sin 2n\pi = 0$)

i.e. $A^2\left(\frac{a}{2}\right) = 1$

$\therefore A^2 = \frac{2}{a}$

or $A = \sqrt{\frac{2}{a}}$

UNIT 3 ELECTRONIC THEORY OF VALENCY

Structure

3.1 INTRODUCTION

In Units 1 and 2, some concepts regarding atomic structure have been discussed in detail. These ideas naturally lead you to think as to why, the atoms of only a few elements combine among themselves or with those of others, to form stable structures, called molecules. Hydrogen gas, for example, consists of H_2 molecules, each of which is made up of two atoms of hydrogen. In contrast to this, the He_2 molecule is not formed by the combination of two atoms of helium. You may like to know the nature of attractive forces, known as chemical bonds, that are responsible for the stability of some structures. Such an analysis can also help you in correlating the physical and chemical characteristics of molecules to the type of bonding available in them.

Many attempts were made in the past to explain the formation of stable molecules. On the basis of electrolysis experiments, Berzelius (1812) concluded that some elements have a positive electric charge and some a negative charge and that the attraction between these opposite charges holds the elements together. This dualistic theory was proposed before the discovery of electrons and protons. But Cannizzaro (1860) showed that the elements like oxygen, hydrogen etc., are diatomic. This fact could not be explained by the dualistic theory of Berzelius. In 1852, Frankland proposed the theory that elements have a definite capacity for combining to which the name valence, was given later. It was for Kossel and Lewis (1916) to put forward theories of electrovalent and covalent compounds, respectively.

In this unit, we shall study the theories of Kossel and Lewis. The properties of ionic compounds, the importance of the ratio of ionic radii in deciding the crystal geometry and the significance of lattice energy are also discussed. We shall explain some of the characteristics associated with the covalent molecules, such as bond enthalpy and covalent radii. Finally we shall discuss, the relationship between the number of electron pairs around the central atom and the shape of the molecules.

Objectives

After studying this unit, you should be able to :

- define the terms such as effective nuclear charge, ionisation energy, electron affinity, electronegativity and utilise them in predicting bond character,

- define ionic bond and list the properties of ionic compounds,
- explain the role of ionic radii in deciding crystal geometry,
- calculate lattice energy and explain its importance in deciding stoichiometry, stability and solubility of a crystal,
- define covalent bond and compare the properties of covalent compounds with those of ionic compounds,
- correlate bond enthalpy and bond stability,
- explain the importance of covalent radii in estimating bond length, and
- explain the shapes of molecules and ions based on VSEPR theory.

3.2 BASIC CONCEPTS

Atoms can combine with each other in different ways to form a large variety of molecules. Really speaking the description of chemical bonds between atoms in a molecule is essentially the description of electron distribution around nuclei of the atoms in a molecule. There are three main types of bonding in molecules. One of them is ionic bonding and it arises when one or more valence electrons are transferred from one atom to another, resulting in the formation of positively and negatively charged ions.

The second type of arrangement that holds atoms together in a molecule is known as covalent bond. In this case, the bond results from the mutual sharing of electrons between atoms of the same or different elements. The formation of H_2 molecule is a case of covalent bond formation. Third type of bonding is coordinate bond and it arises when both the shared electrons are provided by one atom only, known as the donor. A coordinate bond differs from the covalent bond only in the mode of formation. Once a coordinate bond is formed, there is no way to distinguish it from the covalent bond. The salient features of the three types of bonds described above are listed in Table 3.1.

Table 3.1 : Bonding in Molecules

Bonding type	**Type of electronic interaction**	**Examples**
Electrovalent or ionic bond	Transfer of electron(s) from one atom to another	Na^+Cl^-, K^+Cl^-, Cs^+Cl^-
Covalent bond	Equal contribution and sharing of electrons between atoms	H_2, F_2, CH_4
Coordinate bond	Contribution of electrons by one atom and sharing by both the bonding atoms	$(CH_3)_3NO$, NH_4^+

One would like to know the factors on which the tendency of an atom to transfer or share one or more of its electrons depends. There are various factors such as effective nuclear charge, ionisation energy, electron affinity and electronegativity which determine the above tendency. We shall explain the salient features of these factors before going into the details of chemical bonding.

3.2.1 Effective Nuclear Charge

The hold the nucleus has over an electron in a particular level, is decreased by other electrons in the same and lower levels. In an atom with atomic number Z, the effect of nuclear charge is not felt uniformly by the electrons in the various orbitals. The extent to which other electrons decrease the nuclear charge over a particular electron is given by **screening constant**, S. Hence the effective nuclear charge, Z^*, is given by the equation,

$$Z^* = Z - S \qquad .....(3.1)$$

It is possible to calculate Z^* from the values of Z and S. It is observed that there is a steady increase in Z^* across the elements in a period. The values of effective nuclear charge felt by electrons in the valence shell of some elements are given in Table 3.2.

The outermost shell in an atom is called the valence shell. The electrons in this shell are called valence electrons.

Table 3.2 : Effective Nuclear Charge Felt by Valence Shell Electrons

H							He
1							1.7
Li	Be	B	C	N	O	F	Ne
1.3	1.95	2.6	3.25	3.9	4.55	5.2	5.85
Na	Mg	Al	Si	P	S	Cl	Ar
2.2	2.85	3.5	4.15	4.8	5.45	6.1	6.75

Screening constant for a particular electron tells you how much the other electrons in the same and lower levels decrease the nuclear charge due to Z protons in the atom

The high value for the effective nuclear charge felt by an electron signifies that the nucleus exhibits more attraction towards such an electron and hence more energy is needed in removing that electron from the atom. From effective nuclear charge values given in Table 3.2, you can infer that the loss of valence shell electron is more difficult for Ar than for Na. That is, formation of Na^+ is easier than the formation of Ar^+. **Any how values of Z^* alone are not sufficient to make generalisation regarding cation or positively charged ion formation.** You shall study about other factors concerning cation formation, in section 3.2.2. Before that, try the following SAQ.

SAQ 1

Justify the fact that Li^+ ion formation is easier than that of Ne^+ ion.

....

....

....

3.2.2 Ionisation Energy

Ionisation energy, in electron volt (ev), is known as ionisation potential.

1 ev = 96.5 kJ mol^{-1}

Ionisation energy is defined as the amount of energy to be supplied, to remove the most loosely bound electron, from an isolated gaseous atom of an element in its lowest energy state. The unit for ionisation energy is kJ mol^{-1} and we use the symbol I for representing ionisation energy of an element.

For an element X, the formation of singly charged cation can be represented by the following equation :

In a chemical reaction, g stands for gaseous state, l for liquid state and s for solid state.

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

The energy required for the above process, $I(X)$, is called first ionisation energy of X.

In the case of multielectron atoms, more than one electron can be removed; that is, second, third and higher ionisation energies are also possible.

Energy required to form a dipositive ion in the gaseous state is the sum of first and second ionisation energies.

It is also observed that the second ionisation energy is larger than the first ionisation energy, since during the second ionisation, the electron is to be removed from a positively charged ion against forces of attraction. Normally ionisation energy means first ionisation energy only. In Table 3.3, the ionisation energy values of some elements are given. The values with * mark indicate second ionisation energies.

Table 3.3 : Ionisation Energy Values in kJ mol^{-1}

H							He
1312							2372
Li	Be	B	C	N	O	F	Ne
520	900 1757*	800	1086	1403	1314	1681	2081
Na	Mg	Al	Si	P	S	Cl	Ar
495	738 1450*	577	787	1060	1000	1255	1520
K						Br	Kr
418						1142	1350
Rb						I	Xe
403						1007	1170
Cs							Rn
374							1037

In the last section, in Table 3.2, we studied that effective nuclear charge increases along the elements of a period. We would expect ionisation energy also to increase accordingly. But a scrutiny of first ionisation energies of second period elements shows that the values increase from lithium to beryllium, decrease for boron, increase up to nitrogen, again decrease in oxygen and finally increase up to neon, Fig. 3.1. At the outset this seems difficult to understand. But you can correlate the dependence of ionisation energy on electron configuration as discussed below :

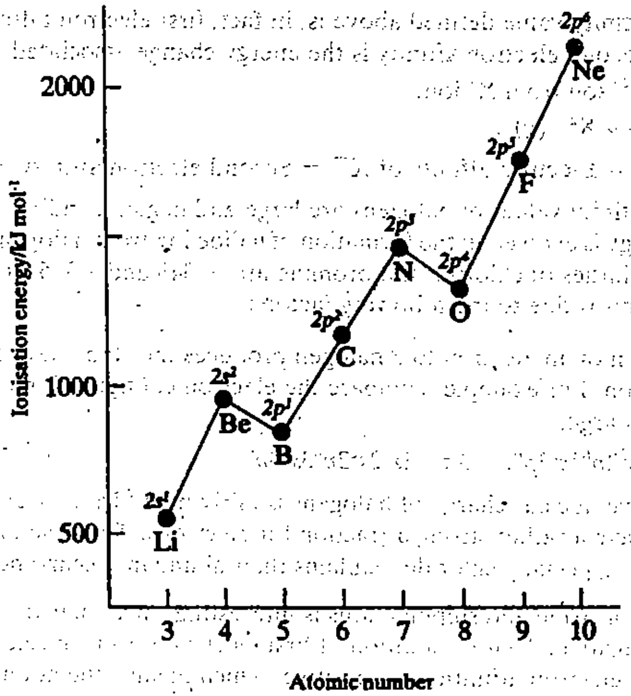

Fig. 3.1 : Ionisation energy of second period elements; only the orbital involved in ionisation indicated.

i) The electrons in *np* orbitals are in higher energy level than those in ns level. Hence it is easier to remove np electron than ns electron. Thus boron needs lower ionisation energy than beryllium.

ii) The half-filled and fully filled orbitals are more stable than partially filled orbitals. Thus nitrogen, with exactly half-filled *p* orbitals, is more stable than oxygen, with partially filled orbitals.

	2s	2p		
N	↑↓	↑	↑	↑
O	↑↓	↑↓	↑	↑
F	↑↓	↑↓	↑↓	↑
Ne	↑↓	↑↓	↑↓	↑↓

Hence, ionisation energy of nitrogen is larger than that of oxygen. For the same reason, neon with fully filled orbitals has larger ionisation energy than fluorine with partially filled orbitals.

Within a group, the ionisation energy decreases as atomic number increases. It is so since, increasing the energy level and increasing the average distance from the nucleus cause reduction of attraction between nucleus and the electron. With this background, you can understand the decrease in ionisation energies of group 1 elements, from hydrogen to caesium, as shown in Table 3.3.

The high ionisation energies of noble gases indicate the greatest stability of ns^2np^6 configuration (except in the case of helium having $1s^2$ configuration) known, in general, as **noble gas configuration**. You will soon see that **attainment of noble gas configuration** is one of the guiding factors in bond formation. When elements of group 1 (except hydrogen) lose their single ns^1 electron, their configuration becomes that of the preceding noble gas. Hence ionisation energy is low for alkali metals and they form cations easily.

Ionisation energies can be measured experimentally. In Unit 1, section 1.12, you have studied how ionisation energy of hydrogen can be determined from the atomic spectra of hydrogen.

Ionisation energy values of elements are useful in deciding their electron configuration

3.2.3 Electron Affinity

In the last section, we studied about ionisation energies which tell us about cation forming tendency of elements. Now we turn our attention to electron affinity values of elements which inform us about the ability of elements to form negatively charged ions, known as anions. **The energy change associated with the gain of an electron by a neutral gaseous atom is defined as electron affinity of an element.** It is expressed in kJ mol^{-1} and is represented by the symbol E_A. For an element X, the formation of X^- can be represented as,

$X(g) + e^- \longrightarrow X^-(g)$

Energy change = first electron affinity of X = $E_A(X)$

The electron affinity value defined above is, in fact, first electron affinity of an element. The second electron affinity is the energy change associated with the formation of X^{2-} ion from X^- ion.

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

Energy change = Electron affinity of X^- = Second electron affinity of X = $E_A(X^-)$

Since the removal of an electron from an atom or ion needs energy, *I* is always positive. The electron addition may be energy demanding or releasing, hence E_A may be positive or negative.

The electron affinity values of halogens are large and negative indicating that a large amount of energy is evolved in the formation of halide ion from halogen. For example, the electron affinities of chlorine and bromine are − 348 and −325 kJ mol^{-1}, respectively. This is due to the following factors:

i) The addition of an electron to a halogen produces the stable noble gas configuration. For example, compare the electron configuration of chloride ion with that of argon.

   Cl^- $1s^22s^22p^63s^23p^6$; Ar $1s^22s^22p^63s^23p^6$

ii) The effective nuclear charge of halogens is fairly high (Table 3.2). Therefore, halogens have a rather strong attraction for electrons. The ease of formation of halide ions, especially chloride, explains their abundant occurrence in ores.

The formation of oxide and sulphide ions is interesting since their first electron affinities are negative. That is, addition of first electron results in release of energy. But the second electron affinities are positive, which means, the addition of second electron is an energy demanding process. This is understandable since addition of an electron to $O^-(g)$ or $S^-(g)$ must overcome repulsion between like charges.

	O	S
First electron affinity/(kJ mol^{-1})	−141	−200
Second electron affinity/(kJ mol^{-1})	+701	+565

Electron affinity values indicate anion forming capacity of an element. Born-Haber cycle is used for determining electron affinity values of elements.

The energy required for the formation of $O^{2-}(g)$ ion from oxygen atom can be calculated as follows :

$O(g) + e^- \rightarrow O^-(g)$	First electron affinity of oxygen	= −141 kJ mol^{-1}
$O^-(g) + e^- \rightarrow O^{2-}(g)$	Second electron affinity of oxygen	= +701 kJ mol^{-1}

Adding both,

$O(g) + 2e^- \rightarrow O^{2-}(g)$	Total energy for the formation of $O^{2-}(g)$	= +560 kJ mol^{-1}

Similarly, the transformation $S(g) + 2e^- \rightarrow S^{2-}(g)$ requires a total energy of (− 200 + 565 =) + 365 kJ mol^{-1}. These values indicate that the reaction, $O(g) + 2e^- \rightarrow O^{2-}(g)$ or $S(g) + 2e^- \rightarrow S^{2-}(g)$ is energetically unfavourable. Even then, many metallic oxides and sulphides occur natively as ores. We shall explain this in section 3.3.3.

SAQ 2

Electron affinity of carbon is −122 kJ mol^{-1} while that of nitrogen is +9 kJ mol^{-1}. Explain.

....

....

....

3.2.4 Electronegativity

The use of values of ionisation energies and electron affinities to express the tendency of isolated atoms to lose or gain electrons is somewhat cumbersome in practice. To reduce this difficulty, Linus Pauling and Robert Mulliken, using the concept of electronegativity, developed empirical expressions for the attraction of bonding electrons to each of the two bonded atoms.

Electronegativity is the attraction of an atom for bonding electrons in a chemical bond. It can be defined as a measure of the tendency of an atom to attract the electrons which bind it to another atom. In a molecule containing two different atoms, one may have more attraction for the shared electrons, and that atom is said to be more electronegative. For example, in the molecule hydrogen fluoride, fluorine is more electronegative than hydrogen. Hence the shared electron pair is attracted by fluorine to a greater extent. In the case of molecules composed of two identical atoms like H_2, F_2 etc., the shared pair is pulled equally by both the atoms, since there is no difference in electronegativity.

Electronegativity is not a directly measurable quantity but it is a concept that a chemist uses frequently on an intuitive basis.

There are different scales for electronegativity like Pauling scale, Allred and Rochow scale etc. The electronegativity values of some elements are given in Table 3.4 on Pauling scale. Electronegativity is represented by the symbol χ (chi). It is expressed as a number only.

Table 3.4 : Electronegativities of Elements in Pauling Scale

H						
2.1						
Li	Be	B	C	N	O	F
1.1	1.5	2.0	2.5	3.0	3.5	4.0
Na	Mg	Al	Si	P	S	Cl
0.9	1.2	1.5	1.8	2.1	2.5	3.0
K	Ca					Br
0.8	1.0					2.8
Rb	Sr					I
0.8	1.0					2.5
Cs	Ba					
0.7	0.9					

From Table 3.4, you can understand that electronegativity increases from left to right along a period and decreases in a group from top to bottom in the periodic table. It is seen that oxygen group elements and halogens have higher electronegativities than alkali and alkaline earth metals. Caesium is the least electronegative element while fluorine is the most electronegative.

Electronegativity has proved to be an extremely useful concept in the estimation of molecular properties such as ionic character of bonds, dipole moments, bond dissociation energies, covalent radii etc. We shall soon define electrovalent and covalent bonding on the basis of electronegativity values of atoms.

3.3 ELECTROVALENT OR IONIC BOND

Before trying to understand ionic bonding using basic concepts, let us know how it was formulated originally. Kossel pointed out that the ions are formed by the loss or gain of electrons and that they would be stable, if they attain noble gas electron configuration, ns^2np^6. A reaction between sodium and chlorine results in the formation of sodium ions and chloride ions both types being held together by electrostatic attraction. In this process one mole electrons are transferred from one mole atoms of sodium to one mole atoms of chlorine. The resulting Na^+ and Cl^- ions have stable inert gas configurations :

In ionic bonding, there is complete transfer of one or more electrons from one atom to another.

$$Na\,(2,8,1) + Cl\ (2,8,7) \rightarrow \underset{\substack{\text{Electron}\\ \text{configuration}\\ \text{of neon}}}{Na^+(2,8)} + \underset{\substack{\text{Electron}\\ \text{configuration}\\ \text{of argon}}}{Cl^-(2,8,8)}$$

Compounds like potassium chloride, magnesium oxide, calcium fluoride and caesium chloride are also formed similarly. In all these compounds, the positive and negative ions are held together by strong electrostatic attraction known as ionic bonds.

From what you have studied in sections 3.2.2 and 3.2.3, you can infer that alkali and alkaline earth elements, which have low ionisation energies, can combine with halogens, which have large negative electron affinity values forming ionic compounds. Even oxides and sulphides of metals are known to have ionic character to a large extent, although second electron affinity values for oxygen and sulphur are positive.

Low ionisation energy for the metal and high, negative elect affinity for the nonmetal favo ionic bonding.

This is facilitated by higher lattice energy values of metallic oxides and sulphides. You will study about this aspect in section 3.3.3.

On the basis of electronegativity values, it has been observed that if the difference in electronegativity between two elements is more than 1.7, these two elements form compounds which are largely ionic in character. If $\Delta\chi < 1.7$, the molecule has large covalent character. The difference in electronegativity values, $\Delta\chi$, for some ionic compounds are given below:

$$\Delta\chi(\mathrm{NaCl}) = \chi(\mathrm{Cl}) - \chi(\mathrm{Na}) = 3.0 - 0.9 = 2.1$$
$$\Delta\chi(\mathrm{CsCl}) = \chi(\mathrm{Cl}) - \chi(\mathrm{Cs}) = 3.0 - 0.7 = 2.3$$
$$\Delta\chi(\mathrm{KBr}) = \chi(\mathrm{Br}) - \chi(\mathrm{K}) = 2.8 - 0.8 = 2.0$$

An octahedron has eight faces and six corners. Each face is an equilateral triangle.

Six Na^+ ions surrounding a Cl^- ion or six Cl^- ions surrounding a Na^+ ion prefer an octahedral arrangement, since, then the repulsion between like charges is minimum.

Ionic substances exist as charged particles whether in solid or liquid state. These charged particles form an array or a three-dimensional crystal lattice, as shown for sodium chloride crystal in Fig. 3.2 (a). X-ray analysis of sodium chloride crystal has established the presence of Na^+ and Cl^- ions. In ionic crystal lattice, each ion is attracted by several ions of opposite charge. In sodium chloride crystal, each Cl^- ion is surrounded octahedrally by six Na^+ ions and *vice versa*, Fig. 3.2 (b). In this context, it is apt to point out that a molecule of NaCl does not exist as such. The formula of an ionic substance is the lowest ratio of the component ions and can be determined from the charges of the respective ions. Thus in sodium chloride crystal, electrical neutrality is maintained if Na^+ and Cl^- ions are present in the ratio 1:1.

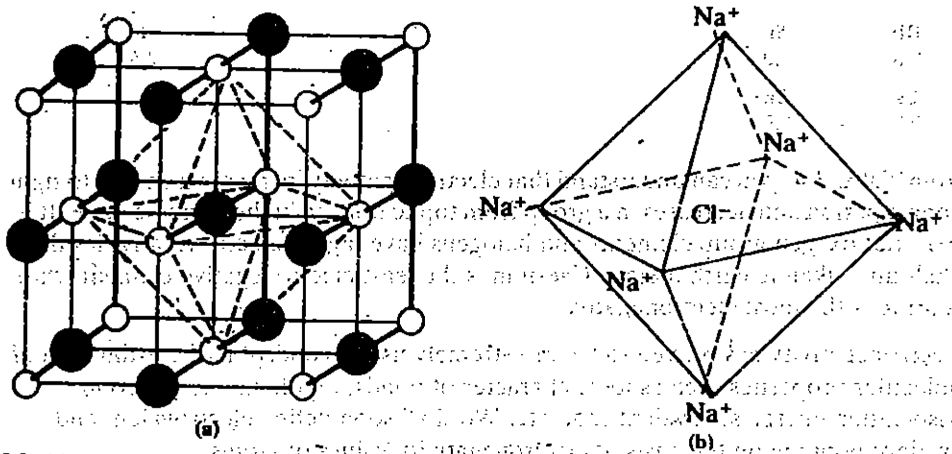

Fig. 3.2 : (a) Arrangement of Na^+(○) and Cl^-(●) ions in sodium chloride crystal. Note, the central Cl^- ion is surrounded by six Na^+ ions, as indicated by red lines. (b) Octahedral arrangement of six Na^+ ions around a Cl^- ion.

We shall next take up some characteristics of ionic compounds.

3.3.1 Properties of Ionic Compounds

Ionic compounds conduct electricity when melted or in solution. But in solid state, they are generally insulators due to very low mobility of the ions. The migration of ions towards electrodes explains their conducting capacity. The ionic compounds are usually soluble in solvents like water.

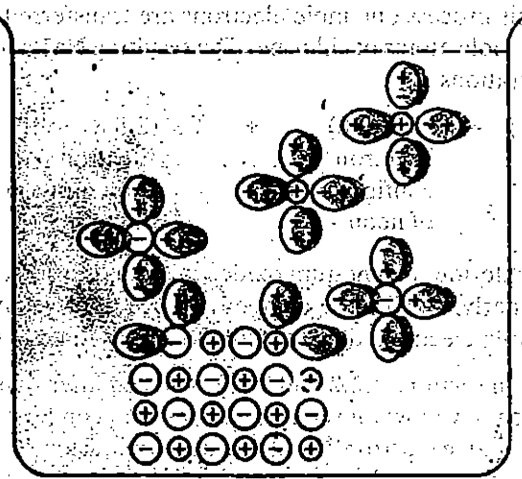

Fig. 3.3 : Solution of an ionic crystal in water; ⊕ and ⊖ indicate ions from the crystal, while (+−) stands for water. Enclosed area shows the undissolved solid.

In Fig. 3.3, we see that positive and negative ions of an ionic substance are surrounded by a sheath of water molecules in such a way that oxygen, the negative end of water, is directed towards cation and hydrogen the positive end of water, is directed towards anion. This type of solute-solvent interaction is called ion-dipole interaction and it reduces the force of attraction between the cation and anion. Solvents like water are called polar solvents.

In Fig. 3.2 (a), you have seen alternating layers of structure containing sodium ions and chloride ions, one around the other. Due to strong electrostatic forces operating in ionic compounds, higher energy is required to overcome such elecrostatic forces. Hence melting and boiling points of ionic substances are high. The stabilisation, an ionic crystal lattice attains due to electrostatic forces, is usually described in terms of lattice energy about which we will study in a detailed way in section 3.3.3 after understanding the importance of ionic radii.

Let us see, if you can answer the following SAQ.

SAQ 3

Sodium chloride does not have high solubility in benzene. What do you infer from this?

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3.3.2 Ionic Radii

The geometrical arrangement of ions in a crystal lattice depends on the relative sizes of cation and anion which are theoretically referred to in terms of ionic radii. The principles of quantum mechanics do not allow assigning definite size to an atom or ion. However, for the purposes of defining crystalline shape, cations and anions are assumed to be spherical, incompressible and having a sharply defined surface. Radius of an ion then becomes the radius of such a spherical charge, Fig. 3.4.

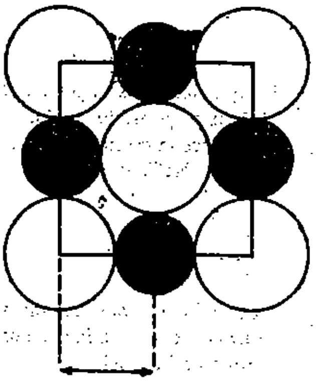

Fig. 3.4. : Hard sphere model; radii of cation and anion.

Using X-ray diffraction methods, a large number of ionic crystals have been studied and their interionic distances determined. For an ionic substance, AB, the interionic distance, a_{AB}, is assumed to be equal to the sum of the ionic radii, ($r_{A^+} + r_{B^-}$).

$$a_{AB} = r_{A^+} + r_{B^-} \qquad \text{...(3.2)}$$

It has been experimentally found that for a pair of ions having same electron configuration, known as isoelectronic pair, there is an inverse relationship between effective nuclear charge felt by an outermost electron of an ion and its radius. Let us assume that the ions A^+ and B^- are isoelectronic.

$$\frac{r_{B^-}}{r_{A^+}} = \frac{Z^*_{A^+}}{Z^*_{B^-}} \qquad \text{... (3.3)}$$

$Z^*_{A^+}$ and $Z^*_{B^-}$ — Effective nuclear charge values felt by an electron in the outermost shell of cation and anion.

r_{A^+} and r_{B^-} — Radius values of cation and anion.

The above equation has been used by Pauling in estimating individual ionic radii and some of the values are given in Table 3.5. For your easy identification, isoelectronic ions are grouped together.

Table 3.5 : Ionic Radii Values

Number of electrons in the ion	Anionic radii (pm)		Cationic radii (pm)	
2	H^-	208	Li^+	60
			Be^{2+}	31
10	F^-	136	Na^+	95
	O^{2-}	140	Mg^{2+}	65
			Al^{3+}	50
18	Cl^-	181	K^+	133
	S^{2-}	184	Ca^{2+}	99
36	Br^-	195	Rb^+	148
54	I^-	216	Cs^+	169

In an isoelectronic system of ions, the anion with largest charge has the largest radii value while the cation with the largest charge has the smallest radii.

Thus $r_{O^{2-}} > r_{F^-} > r_{Na^+} > r_{Mg^{2+}} > r_{Al^{3+}}$. Two factors responsible for this trend among isoelectronic ions are as follows :

i) The effective nuclear charge felt by the valence electrons is more for the cation than for the anion. Due to greater attraction from the nucleus, cation is smaller than the anion.

ii) In a highly charged anion, interelectronic repulsion is partly decreased by increase in size.

The ratio of cationic radius to anionic radius is useful in determining crystal geometry. Based on principles of geometry and X-ray diffraction experiments, the relationship among radius ratio, coordination number and crystal shape is given in Table 3.6. The terms r_{A^+} and r_{B^-} refer to cationic and anionic radius, respectively.

Coordination number is the greatest number of oppositely charged ions surrounding a particular ion. In Fig. 3.2, you see that each Cl^- ion is surrounded octahedrally by six Na^+ ions and *vice-versa*. It means coordination number for this system is six.

Table 3.6 : Radius Ratio and Crystal Geometry

Coordination number	Shape	Limiting value of radius ratio (r_{A^+}/r_{B^-})	Example
3	Triangular	0.155 – 0.225	BN
4	Tetrahedral	0.225 – 0.414	ZnS
6	Octahedral	0.414 – 0.732	NaCl
8	Cubic	0.732 – 1.000	CsCl

Larger size of Cs^+, compared to Na^+, is responsible for the difference in crystal geometry between NaCl and CsCl.

Let us see whether we get the same conclusion by using Tables 3.5 and 3.6.

$$r_{Na^+} = 95 \text{ pm}; \; r_{Cl^-} = 181 \text{ pm}$$

$$r_{Na^+}/r_{Cl^-} = 95/181 = 0.525$$

Hence in sodium chloride crystal, each ion is octahedrally surrounded by six ions of opposite charge, as per Table 3.6.

A tetrahedron has four faces and four corners, each face being an equilateral triangle.

To illustrate tetrahedral and cubical types, crystal structures of ZnS and CsCl are given in Figs. 3.5 and 3.6, respectively.

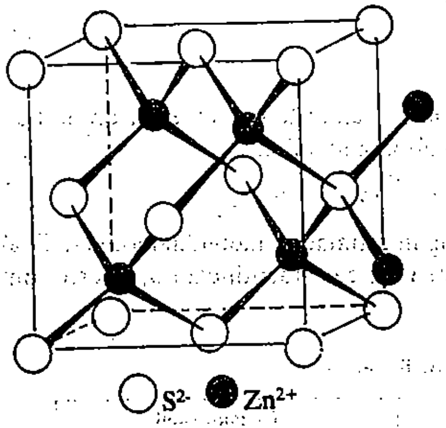

Fig. 3.5 : Tetrahedral structure; zinc sulphide (zinc blende).

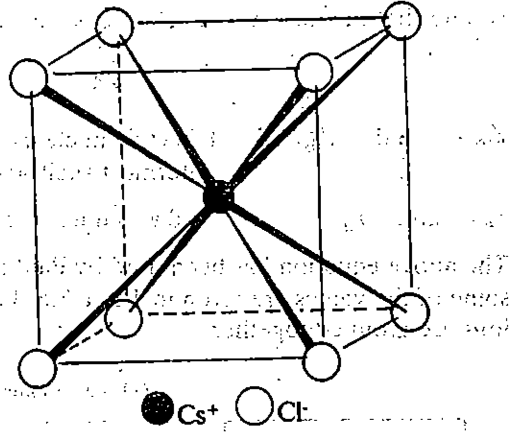

Fig. 3.6 : Cubic structure; caesium chloride.

But radius ratio need not be overemphasised since other factors such as lattice energy and pressure also play a role in determining the crystal shape.

3.3.3 Lattice Energy

In the last section, we saw, how in an ionic crystal the geometrical shape depends on radius ratio. In this section, we focus our attention on lattice energy which is an important factor in lattice formation and stability.

For an ionic crystal to be formed, its lattice energy and enthalpy of formation must be negative.

In Table 3.3, the first and second ionisation energies of magnesium are given as 738 and 1450 kJ mol^{-1}. The sum of these two values, that is 2188 kJ mol^{-1}, is the energy required to form Mg^{2+} ion. In section 3.2.3, it has been calculated that the formation of O^{2-} ion needs 560 kJ mol^{-1}. Thus energy is needed for the formation of both Mg^{2+} and O^{2-} ions. Yet solid magnesium oxide is actually formed along with the liberation of heat and light, when a magnesium wire is ignited. The interesting feature in the formation of magnesium oxide is that energy liberated in the lattice arrangement of magnesium oxide crystal, known as its lattice energy, is more than the energy required for the formation of Mg^{2+} and O^{2-} ions. The arrangement of positive and negative ions alternately in a three-dimensional lattice is a stabilising structural feature due to strong electrostatic attraction.

Before defining lattice energy of a crystal, it is better we know the significance of enthalpy change in a reaction. Heat change accompanying a reaction at constant pressure is represented as enthalpy change and is represented by the symbol ΔH. It is expressed in kJ mol^{-1} units. As you know, in exothermic reactions, heat is evolved and ΔH is negative; in endothermic reactions, heat is absorbed and ΔH is positive. You may recollect that a reaction is feasible if the change in free energy, ΔG, is negative. Using the values of change in enthalpy, ΔH, and the change in entropy, ΔS, the value of ΔG is calculated from the following equation :

$$\Delta G = \Delta H - T\Delta S$$

In this expression, T is the temperature. For the type of reactions discussed in this unit it is assumed that exothermic reactions are feasible. It is allowed since the entropy change is too small for such reactions.

Lattice energy, ΔH_{latt}, is the energy released when one mole of an ionic compound is formed from its constituent gaseous ions. Remember, lattice energy is different from the enthalpy of formation, ΔH_f, of the ionic compound in that the ΔH_f refers to the energy involved in the formation of the ionic compound from its elements. Lattice energy and enthalpy of formation of sodium chloride are the heat changes accompanying the reactions represented below :

$$Na^+(g) + Cl^-(g) \rightarrow NaCl(s) \quad \text{Heat change = Lattice energy of NaCl} = \Delta H_{latt}(NaCl)$$

$$Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s) \quad \text{Heat change = Enthalpy of formation of NaCl} = \Delta H_f(NaCl)$$

The formation of a stable crystal from the elements or ions is exothermic; hence the values of ΔH_f and ΔH_{latt} for such a crystal are negative. Let us now study about the methods of determining lattice energy.

Calculation of Lattice Energy

Two of the important methods for obtaining lattice energy values of crystals are based on electrostatic model and Born-Haber cycle. The electrostatic model is a theoretical approach and it is based on the assumption that the bond is wholly ionic in the crystal. It is possible to derive Eq. 3.4, on the basis of electrostatic model.

$$\text{Lattice energy} = \frac{-1.389 \times 10^{-4} A Z^+ Z^-}{a} \left(\frac{n-1}{n}\right) \text{ kJ mol}^{-1} \qquad \dots (3.4)$$

In this equation, A and n are known as Madelung constant and Born constant, respectively and for each crystalline shape, their values are available in literature. The quantities a, Z^+, Z^- are characteristic of a particular compound; a = internuclear distance, which is equal to the sum of ionic radii; Z^+ and Z^- = positive integers representing the positive and negative charges on the ions. For example, in NaCl crystal, $Z^+ = Z^- = 1$ and in CaF_2 crystal, $Z^+ = 2$ and $Z^- = 1$. Let us calculate the lattice energy value of NaCl crystal using Eq. 3.4. The literature values of A, a and n for NaCl crystal are given below :

a = 276 pm; A = 1.748; n = 9.1

$$\text{Lattice energy of NaCl} = \frac{-1.389 \times 10^{-4} \times 1.748 \times 1^2 \times 8.1}{276 \times 10^{-12} \times 9.1} = -783 \text{ kJ mol}^{-1}$$

The second method, Born-Haber cycle, is a thermochemical method of calculating lattice energy and it is based on Hess' law of heat summation which states that the heat change in a reaction is same, whether it takes place in one or in many steps. In Table 3.7, the formation of sodium chloride crystal is depicted in two ways; first through five stages, (i) through (v), and the second directly by the reaction between solid sodium and gaseous chlorine namely through (vi). According to Hess' law, the heat change either way is equal. That is, total heat change for the steps (i) through (v) is equal to the heat change in (vi). Let us calculate lattice energy of sodium chloride using data in Table 3.7.

Table 3.7 : Born — Haber Cycle for Sodium Chloride Crystal

Name of the reaction	Reaction	Heat change Name	Term	ΔH/kJ mol^{-1}
i) Sublimation of solid sodium	$Na(s) \rightarrow Na(g)$	Heat of sublimation	ΔH_s	+108
ii) Formation of sodium ions in gaseous state	$Na(g) \rightarrow Na^+(g) + e^-$	Ionisation energy of sodium	$I(Na)$	+495
iii) Dissociation of chlorine	$\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$	Heat of dissociation	$\frac{1}{2}\Delta Hd$ (one mole of atoms results from half a mole of chlorine)	$(\frac{1}{2} \times 242)$ = + 121
iv) Formation of chloride ions in gaseous state	$Cl(g) + e^- \rightarrow Cl^-(g)$	Electron affinity of chlorine	$E_A(Cl)$	−348
v) Formation of solid sodium chloride from gaseous ions	$Na^+(g) + Cl^-(g) \rightarrow NaCl(s)$	Lattice energy of sodium chloride	ΔH_{latt}	To be calculated
vi) Formation of solid sodium chloride from the elements [(i) + (ii) + (iii) + (iv) + (v)]	$Na(s) + \frac{1}{2} Cl_2(g) \rightarrow NaCl(s)$	Heat of formation of sodium chloride	ΔH_f	−411

$$\Delta H_f = \Delta H_s + I(Na) + \frac{1}{2}\Delta H_d + E_A(Cl) + \Delta H_{latt}$$

$$\begin{aligned}\Delta H_{latt} &= \Delta H_f - [\Delta H_s + I(Na) + \frac{1}{2}\Delta H_d + E_A(Cl)] \\ &= -411 - (108 + 495 + 121 - 348)\ \text{kJ mol}^{-1} \\ &= -787\ \text{kJ mol}^{-1}\end{aligned}$$

It is usual to express the above tabular column in a cyclic way as given in Fig. 3.7.

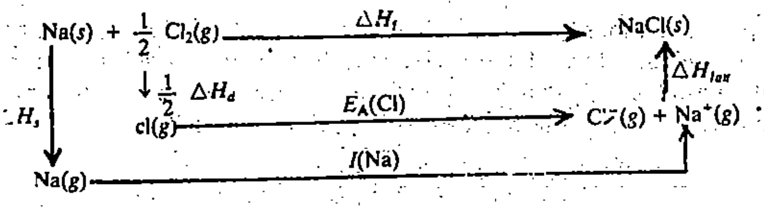

Fig. 3.7 : Born — Haber cycle for sodium chloride.

You can see that there is fair agreement between the lattice energy values derived from the two methods discussed above. A still better agreement between the values is possible if some refinements suggested for electrostatic model are taken into account. A large disparity between the values from the two methods suggests that bonding in the crystal is not wholly ionic and some covalent character may also be present. Thus for cuprous bromide, the electrostatic model gives a value of −882 kJ mol^{-1} whereas Born-Haber cycle value is −956 kJ mol^{-1}. Poor agreement hints at low ionic character of cuprous bromide.

Lattice energy calculations help us in predicting the stability and stoichiometry of compounds. Let us assume that we want to find the stoichiometric formula for magnesium chloride. We suggest three tentative formulae, MgCl, $MgCl_2$ and $MgCl_3$, and corresponding to each formula, lattice energy is calculated using Eq. 3.4. These lattice energy values are then used in Born-Haber cycles designed individually for the three formulae and the enthalpies of formation of magnesium chloride corresponding to the three formulae are calculated. Of the different stoichiometric formulae available, we can choose the one giving rise to largest negative value for the enthalpy of formation; it is so since a large negative enthalpy value corresponds to a stable structure. Thus, of the various suggested formulae for magnesium chloride, $MgCl_2$ is acceptable since it corresponds to the largest negative enthalpy of formation, as given below :

MgCl	-130	kJ mol^{-1}
$MgCl_2$	-642	kJ mol^{-1}
$MgCl_3$	$+3909$	kJ mol^{-1}

Lattice energy values play an important role in deciding the solubility of ionic solids. Higher lattice energy value means, necessity of larger energy to break the crystal lattice. Thus alkali metal chlorides are more soluble than alkaline earth chlorides since for the latter class, lattice energy values, given in kJ mol^{-1}, are high.

NaCl	-787	$MgCl_2$	-2525
KCl	-718	$CaCl_2$	-2253

SAQ 4

Write down Born-Haber cycle for $BaCl_2$ formation.

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3.4 COVALENT BOND

In a covalent bond, the bonding pair of electrons is supposed to be contributed and shared equally.

In the previous sections, we discussed ionic bonds, which are formed by the complete transfer of electrons from one atom to another. Another type of bonding, called covalent bond, was proposed by Lewis and it is defined as equal sharing of one or more electron pairs between atoms involved in the bond formation. The bonding pair(s) of electrons must also be contributed equally by bonding atoms. Elements having a difference of less than 1.7 in electronegativity form bonds, which are predominantly covalent in character.

By sharing one or more electron pairs, a non-metal atom other than hydrogen can acquire an octet of electrons and attain stable inert gas configuration. This is familiarly known as octet rule. The number of bonding electron pairs decides the number of bonds in a molecule. Examples of molecules having single, double and triple bonds are given in Table 3.8. A single bonding pair leads to a single bond; similarly two and three bonding pairs lead to double and triple bonds, respectively.

A pair of electrons which belongs to one atom only is called a lone or unshared or nonbonding pair. For example, hydrogen chloride, as represented in Table 3.8, has one bonding pair and three lone pairs. A lone pair is not directly involved in bonding but it has a role in deciding the shape of molecules. We shall study this in section 3.6.

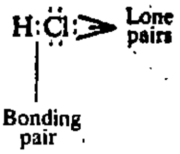
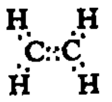
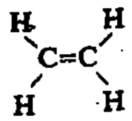


Table 3.8 : Examples of covalent compounds

Name of the compound	Lewis electron dot formula	Structure	Bond type
1) Hydrogen	H:H	H–H	Single
2) Hydrogen chloride	$\text{H}:\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{Cl}}}:$	$\text{H}–\underset{\cdot\cdot}{\overset{\cdot\cdot}{\text{Cl}}}:$	Single
3) Ammonia	$\text{H}:\underset{\text{H}}{\overset{\cdot\cdot}{\text{N}}}:\text{H}$	$\text{H}–\underset{\overset{\vert}{\text{H}}}{\overset{\cdot\cdot}{\text{N}}}–\text{H}$	Single

4) Carbon dioxide	$:\ddot{O}::C::\ddot{O}:$	$:\ddot{O}=C=\ddot{O}:$	Double
5) Ethylene			Double and Single
6) Nitrogen	$\ddot{N}::\ddot{N}$	$\ddot{N}\equiv\ddot{N}$	Triple
7) Acetylene	$H:C\vdots\vdots C:H$	$H-C\equiv C-H$	Triple and Single

In a coordinate bond, the bonding pair originates from one of the two linked atoms.

A special type of covalent bonding known as coordinate or dative bond is formed, if the shared electron pair has originated from one atom only. If atom A donates an electron pair for the bonding between A and B, then the molecule can be represented as $A \rightarrow B$. With formal charges on A and B, it can be represented using covalent bond as, $A^+ - B^-$.

If the electrons for bonding between A and B come only from A, it has a formal positive charge and B has a formal negative charge. Formal charge on an atom can be calculated as per the following equation:

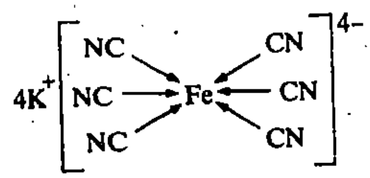
$$\text{Formal charge} = \text{Number of valence electrons} - \text{number of bonds} - \text{number of electrons present as lone pairs} \quad ....(3.5)$$

For example, in trimethyl amine oxide, the shared pair between nitrogen and oxygen originates from nitrogen. Hence for nitrogen and oxygen, formal charges can be calculated using Eq. 3.5. You should bear in mind that nitrogen and oxygen have five and six valence electrons, respectively.

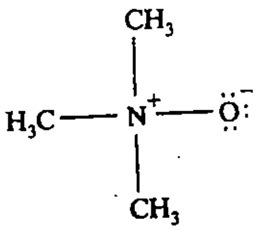
Formal charge on nitrogen $= 5 - 4 - 0 = +1$

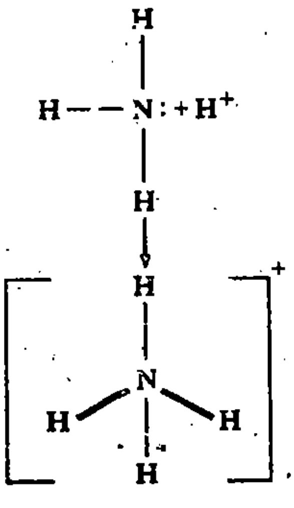
Formal charge on oxygen $= 6 - 1 - 6 = -1$

Hence, with formal charges, the structure is,



Potassium ferrocyanide





The formation of coordinate bond is possible only between an atom or ion with a lone pair of electrons in the valence shell and an atom or ion that needs a pair of electrons to acquire a more stable electron configuration. There is a separate class of compounds, known as **coordination complexes**, where a central metal ion is coordinated to lone pair containing groups or molecules, known as ligands. A typical example for a coordination complex is potassium ferrocyanide. In this complex, cyanide groups are ligands, which utilise their lone pair electrons to link to the empty *d* orbitals of Fe^{2+} ion.

The difference between the coordinate bond and covalent bond is in the mode of formation; that is, whether each atom contributes one electron or one atom contributes both. Once a bond is established, covalent bonds are indistinguishable from the coordinate bond since electrons are identical regardless of their source. For example, ammonium ion is formed when an ammonia molecule combines with H^+ ion, using the lone pair electrons of nitrogen. That is, a coordinate bond is formed between nitrogen and H^+ ion. But once ammonium ion is formed, all the four N − H bonds are equal.

SAQ 5

In phosphorus oxychloride, calculate the formal charges on phosphorus and oxygen.

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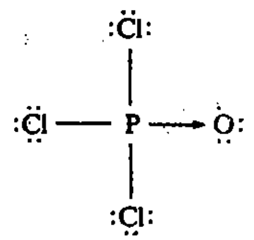


Phosphorus oxychloride

3.4.1 Characteristics of Covalent Molecules

By and large, the properties of covalent molecules are opposite to those of ionic substances. Thus many organic compounds, which are largely covalent, possess low melting and boiling points. This is due to the fact that the forces of attraction between covalent molecules, known as *van der Waals* forces, are weaker than the electrostatic forces operating in ionic substances. *Van der Waals* forces arise due to rapid fluctuations of electron clouds in covalent molecules.

Van der Waals forces account for the liquid or solid forms of molecules such as dry ice (solid carbon dioxide) or iodine.

Covalent bonds are directional in nature and therefore, molecules with covalent bonds have shapes.

Secondly, covalent molecules dissolve mostly in nonpolar solvents like benzene, carbon tetrachloride etc., but not in polar solvents like water. The nonpolar solvents have, more or less, symmetric charge distribution throughout the molecule. Hence there is no preferred arrangement of covalent solvent molecules around covalent solute molecules. For example, toluene is a covalent compound and it forms solutions with benzene in all proportions, but not so with water. It is so because bonding is covalent, both in toluene and in benzene. As you have seen earlier, water molecule, although covalent, has some polar character due to difference in electronegativity between oxygen and hydrogen. Thus dissolution proceeds well, if the solute and solvent molecules have similar type of bonding. A generalisation regarding solubility is — "like dissolves the like". Is it not like saying, "birds of the same feather flock together"?

Thirdly, covalently bonded molecules do not conduct electricity. But caution must be exercised in generalising the behaviour of covalently linked substances. A wide disparity in characteristics is evident if we compare graphite and diamond, Figs. 3.8 and 3.9.

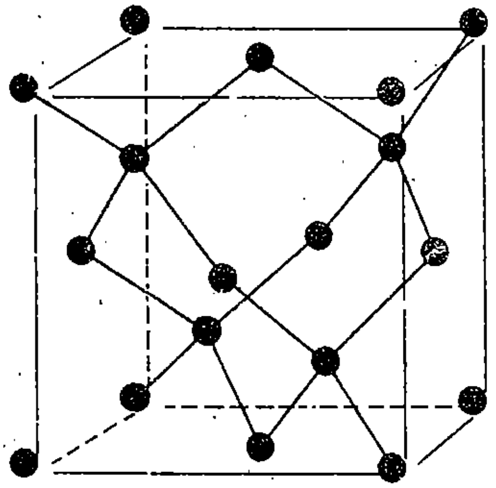


Fig. 3.8 : Diamond

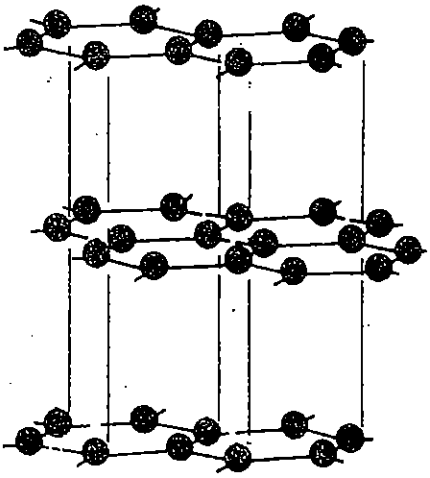


Fig. 3.9 : Graphite

Diamond is a nonconductor of electricity since all the four valence electrons of carbon are firmly held in bond formation with four different carbon atoms. But in graphite, each carbon uses three of its electrons in bond formation with three different neighbours. The fourth electron of each carbon atom is known as p_z electron; the p_z electrons are paired into a system of π bonds. The π electrons are relatively labile and this accounts for electrical conduction of graphite.

3.4.2 Bond Enthalpy

Bond dissociation enthalpy and covalent radii are some aspects of molecules, arising out of covalent linkage. Bond dissociation enthalpy is the energy required for breaking a bond. For example, for hydrogen molecule, bond dissociation enthalpy, is the enthalpy change for the reaction,

$$H_2(g) \rightarrow H(g) + H(g); \text{ Enthalpy change} = 436 \text{ kJ mol}^{-1}$$

This tells us that the energy required to dissociate one mole of hydrogen is 436 kJ.

Iodine is often used as a catalyst in organic reactions. Its low bond enthaply favours easy breakage of I-I bond. The bond enthaply for C-I also is not high. Hence, both formation and breakage of C-I bond is smooth.

By convention, mean bond dissociation enthalpy or simply bond enthalpy, E, is calculated as the average of energy values required to dissociate a particular bond by considering a series of similar compounds. Thus bond enthalpy for O-H bond, obtained from water and similar compounds, such as methanol, ethanol etc., has been found to be 463 kJ mol^{-1}. The bond enthalpies of some bonds calculated similarly, are given in Table 3.9.

Table 3.9 : Bond Enthalpy (E) Values in kJ mol^{-1}

Bond	E	Bond	E	Bond	E
H—H	436	C—F	484	C≡C	813
O—H	463	C—Cl	338	N—N	163
C—H	412	C—Br	276	N=N	409
F—F	155	C—I	238	N≡N	945
Cl—Cl	242	C—C	348	O—O	146
Br—Br	193	C=C^a	612	O=O	497
I—I	151	C=C^b	518		

a → in alkenes   b → in aromatic compounds.

Bond enthalpy values are useful in calculating enthalpies of reactions.

A stronger bond has larger bond enthalpy value. This means that a bond having a large bond enthalpy value is more difficult to be broken. The inspection of Table 3.9 indicates that C≡C is stronger than C=C bond and C=C bond in turn is stronger than C−C bond. It is to be borne in mind that when a covalent bond is formed, energy is released, which is equal in magnitude to bond enthalpy value. Thus in the formation of hydrogen molecule from hydrogen atoms, energy to the tune of 436 kJ mol^{-1} is released. For the dissociation of hydrogen, which is the reverse of formation, energy of the order of 436 kJ mol^{-1} is required.

3.4.3 Bond Lengths and Covalent Radii

Number of bonds between two atoms is known as bond order. As bond order increases, bond length decreases.

In section 3.3.2, we saw how ionic radii are related to interionic distance in an ionic substance. In this section, we study the relationship between bond length and covalent radii in covalently linked molecules. Bond length of a covalent bond is the distance between the nuclei of two covalently bonded atoms and it can be measured by diffraction using X-rays or electron or neutron. Half the bond length between like-atoms joined by a single covalent bond is known as the single bond covalent radius of the atom concerned. Values for double and triple bond covalent radii are obtained in a similar way. The bond distance in hydrogen molecule is 74 pm and so single bond covalent radius of hydrogen is 37 pm. The C−C bond distance of 154 pm, in diamond is taken as standard value for C−C bond length and half its value, 77 pm is the single bond covalent radius of carbon. Multiple bond radii, like C=C and C≡C, are obtained by studies in alkenes and alkynes, respectively. Some covalent radii are given in Table 3.10.

Table 3.10 : Covalent Radii

Type	Element	Value (pm)
Single bond radii	H	37
	C	77
	N	74
	F	72
	Cl	99
	Br	114
	I	133
Double bond radii	C^a	67
	C^b	69.5
	N	65
Triple bond radii	C	60
	N	55

a → in alkenes;   b → in aromatic compounds.

It is interesting to find that in many covalently linked molecules, the bond distance is equal to the sum of the covalent radii of the two elements involved in bond formation. Let us cite an example for this. From Table 3.10 covalent radii of chlorine and bromine are 99 and 114 pm, respectively. Hence the calculated bond distance in Cl–Br is (99 + 114 =) 213 pm and it agrees well with the experimental bond length of Cl–Br, viz., 214 pm. Although Table 3.10 is generally useful in calculating bond lengths in covalent compounds, caution must be exercised when the molecule has appreciable ionic character or the atoms connected are in different hybridisation states or the molecule has resonance structures. You will study about this particular aspect in a detailed way in the next unit. Using the above principles attempt the following

SAQ 6

Calculate the bond length in the following molecules :

(a) N_2 (b) Cl_2 (c) ICl.

3.5 BOND POLARITY

The bonding in most compounds is intermediate between purely ionic and purely covalent. The extent of ionic character in a covalent bond is called 'polarity of a bond'. Polarity in a bond, taking HCl as an example, can be shown by writing the bond as either $H^{\delta+} - Cl^{\delta-}$ or as $\overset{+\!\!\longrightarrow}{H - Cl}$. In this molecule, hydrogen is at the positive end and chlorine at the negative end of dipole. Polarity is measured in terms of dipole moment and you will study about this in Block II, Unit 6.

Internuclear distance for a polar molecule is different from the sum of covalent radii.

A covalent bond, with some ionic character, has electrical charges associated with it. Such charges render the bond more liable to be attacked by other charged atoms or groups thereby, affecting their chemical reactivity. For example, alkyl halides are more reactive than alkanes. It is so, since C–X bond in alkyl halides has more polarity than C–H bond in alkanes.

Small cation, large anion and large charge on either of the ions — are some of the factors which favour large covalent character.

3.6 VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

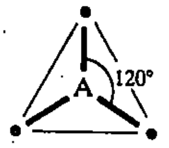
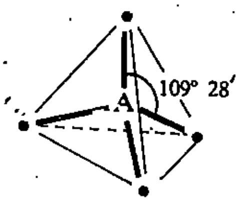
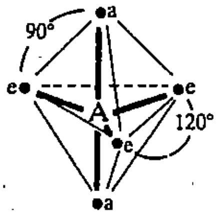
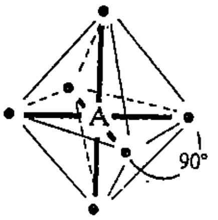
So far we studied about some theories of bonding. Our next concern is to explain the shape of molecules in relation to the number of shared and lone electron pairs around the central atoms. Electron pair repulsion theory of Gillespie sums up the factors deciding the shapes of molecules in the following four rules :

i) The preferred arrangement of a given number of electron pairs of an atom is that which maximises their distance apart, and thereby minimises the mutual repulsion. Because of their negative charge, the pairs of electrons surrounding an atom are mutually repulsive and orient themselves as far apart as possible. The geometrical arrangement of electron pairs around a central atom varies depending on the number of electron pairs around it. Thus, two electron pairs around a central atom prefer a linear arrangement. Three electron pairs prefer a planar triangular arrangement; similarly four, five and six electron pairs prefer tetrahedral, trigonal bipyramidal and octahedral arrangements, respectively. The relationship between the number of electron pairs and their geometrical arrangement around a central atom is given in Table 3.11.

   It is worth mentioning that in trigonal bipyramidal arrangement, there are two types of bonding, namely equatorial (e) and axial (a). The equatorial – equatorial angle of separation is 120° while axial – equatorial angle is 90°.

   This rule is useful only in predicting the geometrical arrangements of electron pairs. Anyhow, the shape of the molecule depends on the arrangement of surrounding atoms around the central atom. In the next rule, we shall see how the shape of a molecule can be determined based on the number of bonding pairs and lone pairs of electrons around the central atom.

Table 3.11 : Geometrical Arrangement of Electron Pairs

Molecule	Number of electron pairs	Predicted geometry	Example
AX_2	2	 Linear	$HgCl_2$
AX_3	3	 Triangular planar	BF_3
AX_4	4	 Tetrahedral	CH_4
AX_5	5	 Trigonal bipyramidal	PCl_5
AX_6	6	 Octahedral	SF_6

ii) According to the second rule, a lone pair of electrons occupies more space than a bond pair. This is due to the fact that a lone pair is loosely held, being under the influence of only one nucleus, while a bonding pair is held tightly by two nuclei. The mutual repulsion varies as follows: lone pair – lone pair > lone pair – bonding pair > bonding pair – bonding pair. Using this rule, we can predict the shapes of molecules. The bonding pairs define the shape of the molecule, although bond angle values depend on the number of both the bonding pairs and lone pairs around the central atom.

Thus, a central atom with two bonding pairs, but with no lone pairs, adopts a linear shape in which the two electron pairs are as far apart as possible. Mercuric chloride (Fig. 3.10) and beryllium chloride are examples of this type.

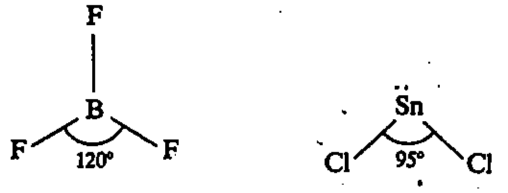
In Table 3.11, you have studied that if a central atom has three electron pairs, these pairs assume a triangular planar configuration. The shape of the molecule is also triangular planar, if all the three pairs are of bonding type. For example, boron trifluoride molecule is triangular and planar (Fig. 3.11a), with a bond angle of 120°, since this arrangement provides greatest separation between three electron pairs. Ions like CO_3^{2-} and NO_3^- also have triangular planar arrangement.

If the central atom has two bonding pairs and one lone pair, then the molecule is angular. For example, in stannous chloride, Fig. 3.11b, the three electron pairs occupy a planar triangular configuration. But its shape is decided by the position of the two bond pairs only and hence the molecule is angular. The bond angle in

$SnCl_2$ is 95°, which is less than 120° expected of a triangular arrangement of electron pairs. This is due to the fact that two Sn—Cl bonds are forced closer together due to more space occupied by the lone pair of tin. Other examples of this type are NO_2^- and ClNO.

Mercuric Chloride — linear

Fig. 3.10 : Shape of molecule with two bonding pairs around central atom.



a) Boron trifluoride— three bonding pairs; planar triangular

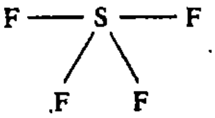
b) Stannous chloride— two bonding pairs and one lone pair; angular

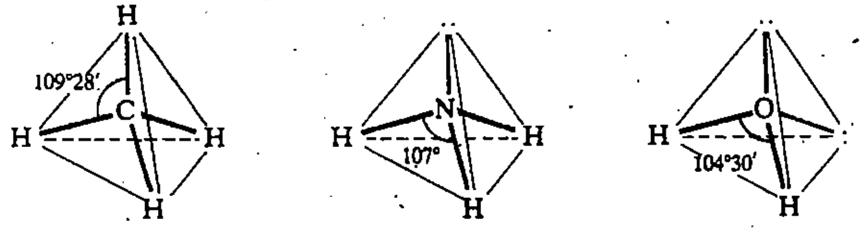
Fig. 3.11 : Shapes of molecules with three electron pairs around central atom.

Let us now examine the shapes of molecules with four electron pairs around a central atom. As per Table 3.11, four pairs of electrons prefer a tetrahedral arrangement around a central atom. Thus, if all the four are bonding pairs, the shape is tetrahedral as in the case of CH_4 molecule (Fig. 3.12a), NH_4^+ and BF_4^- ions. But if there are three bond pairs and one lone pair, the shape is trigonal pyramidal. It is so since one of the corners of the tetrahedron is occupied by a lone pair. Some typical examples for this type are NH_3 (Fig. 3.12b), and PF_3.

If there are two bonding pairs and two lone pairs occupying the four corners of the tetrahedron, then the shape of the molecule is angular, as in the case of H_2O molecule (Fig. 3.12c), NH_2^- and ICl_2^+ ions.

See-saw shape of SF_4 molecule can be understood, if seen in terms of children's see-saw in parks.





a) Methane—four bonding pairs; tetrahedral

b) Ammonia—three bonding pairs and one lone pair; trigonal pyramidal

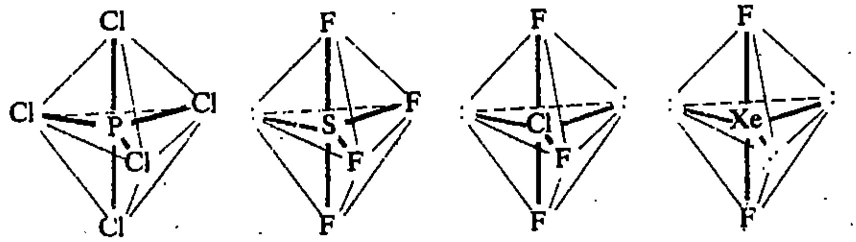
c) Water—two bonding pairs and two lone pairs; angular

Fig. 3.12 : Shapes of molecules with four electron pairs around the central atom.

The single lone pair on nitrogen of ammonia and two lone pairs on oxygen of water occupy more space than the bonding pairs; hence the bonding pairs are compressed resulting in a bond angle reduction in ammonia and water from the tetrahedral angle of 109° 28′.

Similarly the shapes of molecules with five or six electron pairs around the central atom can be explained. The shapes of such molecules and ions are described in Figs. 3.13 a – d and Figs. 3.14 a – c.

T-shape of ClF_3 can be recognised, if viewed as follows:



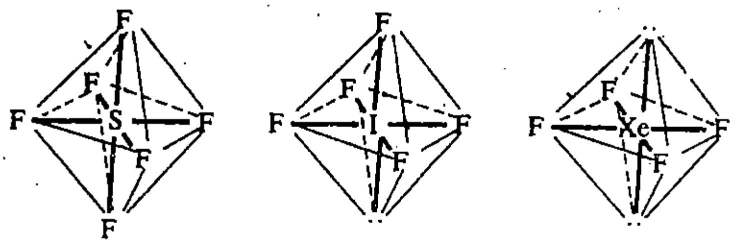
a) Phosphorus pentachloride—five bonding pairs; trigonal bipyramidal

b) Sulphur tetrafluoride— four bonding pairs and one lone pair; see-saw shaped

c) Chlorine trifluoride— three bonding pairs and two lone pairs; T-shaped

d) Xenon difluoride—two bonding pairs and three lone pairs; linear.

Fig. 3.13 : Shapes of molecules with five electron pairs around the central atom. Lone pairs, if present, occupy equatorial positions.



a) **Sulphur hexafluoride—six bonding pairs; octahedral**

b) **Iodine pentafluoride—five bonding pairs and one lone pair; square pyramid**

c) **Xenon tetrafluoride—four bonding pairs and two lone pairs; square planar**

Fig. 3.14 : Shapes of molecules with six electron pairs.

A summary of the applications of this rule is given in Table 3.12 and justification for inclusion of groups like CO_3^{2-} and NO_3^- having multiple bonds is discussed in rule (iii).

Table 3.12 : Number of Electron Pairs in the Valence Shell of the Central Atom, and Shape of Molecule or Ion.

No. of Electron Pairs				
Total	Bond pairs	Lone pairs	Shape	Examples
2	2	0	linear	$HgCl_2$, $BeCl_2$
3	3	0	triangular planar	BF_3, BCl_3, CO_3^{2-}, NO_3^-
3	2	1	angular	$SnCl_2$, NO_2^-, ClNO
4	4	0	tetrahedral	CH_4, BF_4^-, NH_4^+
4	3	1	trigonal pyramidal	NH_3, PF_3
4	2	2	angular	H_2O, ICl_2^+, NH_2^-
5	5	0	trigonal bipyramidal	PCl_5, $SnCl_5^-$
5	4	1	see-saw	$TeCl_4$, IF_4^+, SF_4
5	3	2	T-shaped	ClF_3, BrF_3
5	2	3	linear	XeF_2, ICl_2^-
6	6	0	octahedral	SF_6, PF_6^-
6	5	1	square pyramidal	IF_5, SbF_5^{2-}
6	4	2	square planar	BrF_4^-, XeF_4

In a trigonal bipyramid structure, the lone pairs prefer more spacious equatorial positions. Thus SF_4, Fig. 3.13b, has see-saw shape, with the lone pair occupying an equatorial position of the trigonal bipyramid. Similarly ClF_3, Fig. 3.13c, is T-shaped with two lone pairs occupying two equatorial positions of trigonal bipyramid; while XeF_2, Fig. 3.13d, is linear with three lone pairs occupying three equatorial positions.

In case of octahedral geometry, a lone pair of electrons can occupy any of the six positions since all of them are equivalent. But if there are two lone pairs, they orient themselves as far apart as possible, that is, at an angle of 180°. Thus IF_5, Fig. 3.14b, and XeF_4, Fig. 3.14c, with one and two lone pairs, around the central atom have square pyramidal and square planar structure, respectively. You can understand other examples given in Table 3.12 in the light of above discussion.

iii) Third rule states that multiple bonds also act as a single shared pair of electrons, in deciding the shape of molecules. The only difference is that the three electron pairs of a triple bond occupy more space than two electron pairs of a double bond which, in turn occupy more space than the single electron pair of a single bond.

We shall illustrate this rule, taking three examples. Carbon dioxide, for example, has two double bonds around carbon and these are equal to two "effective" shared pairs only according to this rule. Since a central atom with two electron pairs prefers a linear arrangement, carbon dioxide, like $HgCl_2$ is linear, Fig. 3.15a.

In COF_2, there are three effective electron pairs around the central atom and the molecule has triangular shape, like BF_3, Fig. 3.15b. Anyhow, in BF_3, all the bond

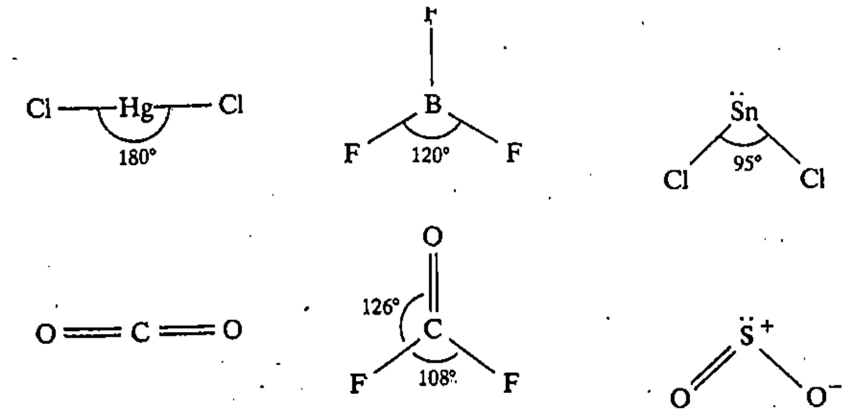


Fig. 3.15

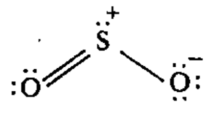
a) Linear due to two "effective" electron pairs in CO_2; compared with two electron pairs in $HgCl_2$

b) Triangular due to three "effective" bonding pairs in COF_2, compared with three electron pairs in BF_3

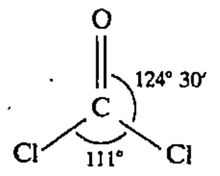
c) Angular due to three "effective" electron pairs in SO_2, one of them being a lone pair; compared with three electron pairs in $SnCl_2$.

angles are equal whereas in COF_2, the bond angles are different. The two electron pairs in C=O occupy more space and compress the F $\overset{C}{\wedge}$ F angle.

An inspection of Fig. 3.15c brings out the similarity in shape between SO_2 and $SnCl_2$. You can understand the formal charges on sulphur and oxygen by indicating lone pair electrons around oxygen atoms and using Eq. 3.5.



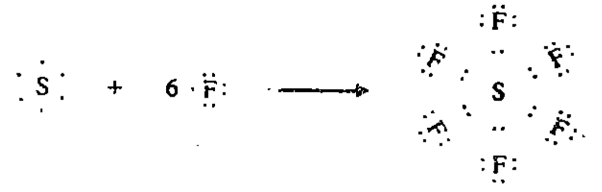
iv) The fourth rule is that, the bond pair size and also the bond angle decrease with increasing electronegativity of the atoms connected to the central atom. You compare the bond angles in Cl_2CO with those of F_2CO given above. The reason for the lower value of the angle between the two C–F bonds than that between the two C–Cl bonds, is the higher electronegativity of fluorine than chlorine.



In the next section, we shall see how VSEPR theory can be used to predict the shapes of molecules.

3.7 PREDICTION OF SHAPES OF MOLECULES AND IONS USING VSEPR THEORY

In using VSEPR theory to predict the shape of a molecule or ion, first its Lewis structure has to be drawn. The Lewis structure of a molecule or ion is written assuming that it is formed by linking individual atoms through single or multiple bonds by pairing up the unpaired electrons on the constituent atoms. For example, sulphur hexafluoride is assumed to be formed by the pairing of the unpaired electrons of sulphur and fluorine atoms.



The steps involved in arriving at Lewis structure of a molecule or ion are explained with illustrations below:

Step 1 : Determine the total number of valence electrons in the molecule or ion. There are three types to be considered.

Type i) For a neutral molecule, the total number of valence electrons is equal to the sum of valence electrons on each atom. By valence electrons of an atom, we mean the number of electrons in the outer most shell. We apply this rule to calculate the number of valence electrons in ClF_3 and SF_6.

	ClF_3	SF_6
	7 (one Cl)	6 (one S)
	21 (three F)	42 (six F)
Number of valence electrons	28	48

Type ii) For a positive ion, the total number of valence electrons is equal to the sum of the valence electrons of each atom minus the number of positive charges on the ion. The positive charge is to be subtracted since one electron is lost for each positive charge. We apply this rule to calculate the valence electrons in NH_4^+ ion.

	5	(one N)
	4	(four H)
	−1	(unit positive charge)
Number of valence electrons	8	

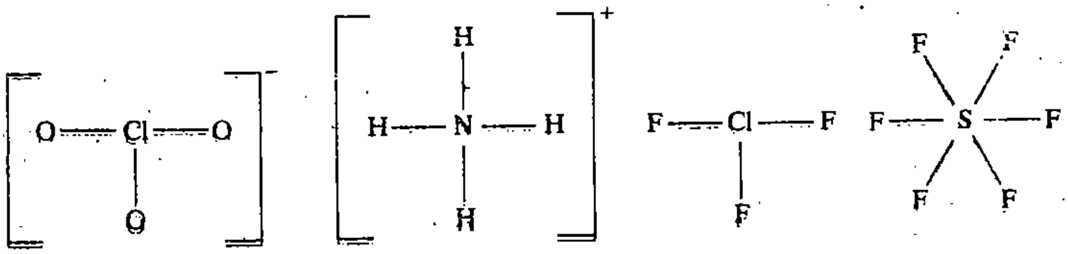
Type iii) For a negative ion, total number of valence electrons is equal to the sum of the valence electrons of each atom plus the number of negative charges on the ion. For attaining a unit negative charge, an atom has to gain an electron. To calculate the valence electrons in ClO_3^- ions, the following rule is applied.

	7	(one Cl)
	18	(three O)
	1	(unit negative charge)
Number of valence electrons	26	

Step 2 : Draw a skeleton structure of a molecule or an ion showing the arrangement of atoms and connect the central atom to others through a single bond. As a rule, the less electronegative element is often the central atom. For example, in ClF_3, chlorine is less electronegative than fluorine, and chlorine is the central atom in this molecule. Of course, you will not expect hydrogen to be the central atom in its compounds.

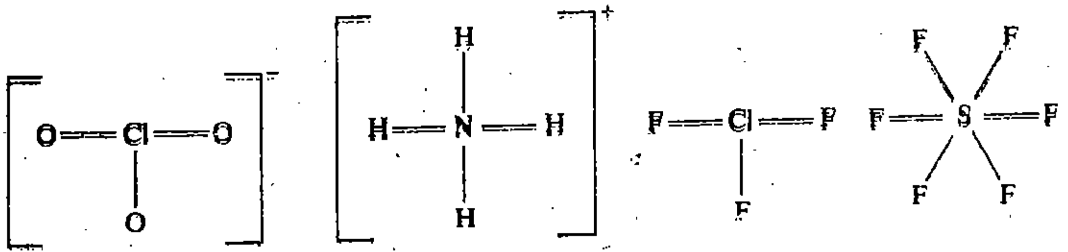
Calculate the total number of electrons for the skeleton structure. You must bear in mind that two electrons are required for each bond.

Skeleton structure



* Number of bonds	3	4	3	6
Electrons required for skeleton structure	6	8	6	12

Step 3 : Calculate the number of electrons which are in excess of that required for a single bonded structure. This is equal to the difference between the answers obtained in step 1 and step 2.

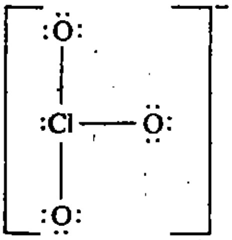


Electrons in excess for a single bond structure

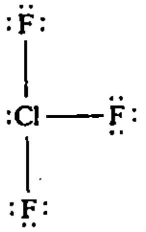
26 − 6 = 20	8 − 8 = 0	28 − 6 = 22	48 − 12 = 36

Since NH_4^+ ion has only four bond pairs of electrons, we consider it further in step 5 only.

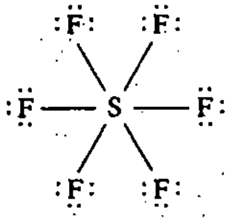
Step 4 : Distribute the excess electrons obtained in the last step to each atom, except hydrogen, such that each atom has eight electrons if possible. If there are too few electrons to give eight electrons to each atom, convert single bonds to multiple bonds, where possible. Remember, the ability to form multiple bonds is limited almost exclusively to bonds between carbon, nitrogen, oxygen, sulphur and phosphorus.



20 electrons distributed as 10 lone pairs. No balance.



Of the 22 electrons 20 electrons, as ten lone pairs, are just sufficient to give eight electron structure to each atom. Two electrons yet remain to be accommodated.

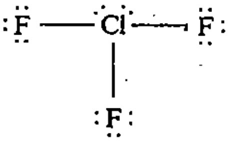


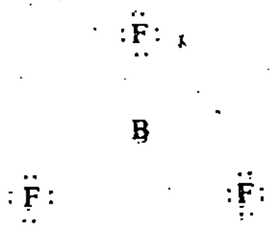
36 electrons distributed as 3 lone pairs per each fluorine atom. No balance!

Distribution of excess electrons facilitating eight electrons for each atom.

Hence, except in the case of ClF_3, we have accounted for the valence electrons of other molecules or ions.

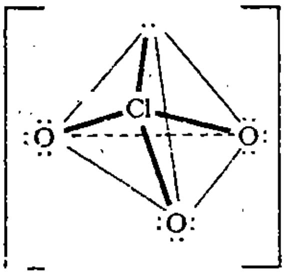
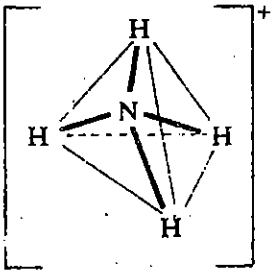
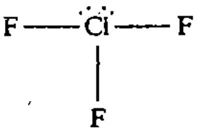
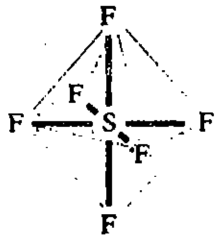
Step 5 : Any balance of electrons remaining in step 4, after providing eight electron structure to all elements, except hydrogen must be assigned to the central atom. However, note that the outer atoms contain a maximum of eight electrons in their valence shells. Thus, in ClF_3, two electrons remaining after assigning eight electron structure to each atom, are assigned to chlorine atom which is the central atom. Hence, the structure of ClF_3 is :





The elements of third and higher periods can accommodate more than eight electrons due to availability of empty *d* orbitals. But Lewis formula with more than eight electrons for an atom of the first or second period is almost certainly incorrect and should be re-examined. Also, you must remember that some elements like boron may have fewer than eight electrons in their valence shells when they function as central atoms. For example, in the Lewis formula for BF_3, boron has only six electrons around it.

Having arrived at the Lewis structure of a molecule or an ion you can predict its shape, by counting the number of bond pairs and lone pairs around the central atom and by matching this with the entries in Table 3.12. You must consider a double or triple bond as a single bond pair only as per rule (iii) stated in the last section.

	$[ClO_3]^-$	$[NH_4]^+$	ClF_3	SF_6
Bond pairs around the central atom	3	4	3	6
Lone pairs around the central atom	1	0	2	0
Shape:	 Trigonal Pyramidal	 Tetrahedral	 T-Shaped	 Octahedral

There are other approaches for relating the shape of a molecule to its electronic arrangement. We shall study in Unit 4, one such method, namely, hybridisation to arrive at the shape of molecules.

SAQ 7

Derive Lewis formula and then apply VSEPR theory to predict the shape of following :
(i) AsF_5 (ii) SO_4^{2-} (iii) CO_3^{2-}.

3.8 SUMMARY

In this unit, we have explained some of the basic concepts of molecular structure. You have learnt the following aspects of chemical bonding :

- Kossel's theory of ionic bonding,
- Lewis theory of covalency,
- characteristics of ionic compounds with special reference to ionic radii and lattice energy,
- characteristics of covalent compounds such as bond enthalpy and covalent radii, and
- VSEPR theory and its use in the prediction of shapes of molecules and ions.

3.9 TERMINAL QUESTIONS

1) Which of the following pairs has higher ionisation energy? Justify your prediction
(a) K or Rb (b) Si or Cl.

2) Why are the electron affinities of noble gases positive?

3) How do you define an ionic compound, based on the concepts of ionisation energy, electron affinity and electronegativity?

4) Arrange the following four compounds in the increasing order of stability :
CF_4, CI_4, CBr_4, and CCl_4.

5) How can you predict the geometry of ionic crystals?

6) Test the validity of the following statements by marking "T" for true and "F" for false :

i) Covalent compounds are by and large soluble in nonpolar solvents ☐

ii) Graphite owes its electric conduction to the availability of π electrons ☐

iii) Multiple bonds lead to larger bond length and lower bond enthalpy ☐

iv) The anionic radius of iodine is smaller than its covalent radius ☐

v) Shape of H_3O^+ ion is trigonal pyramidal ☐

7) Explain the reason for the following ;

i) PCl_5 is formed easily but not NCl_5

ii) $Z^*_{Na^+}$ is different from Z^*_{Na}

iii) Ionic radius of H^- ion is greater than that of F^- ion.

8) Calculate the lattice energy of magnesium chloride using the following energy values given in kJ mol^{-1}.
$\Delta H_s(\mathrm{Mg}) = 150$; $I(\mathrm{Mg}) = 738$; $I(\mathrm{Mg}^+) = 1450$; $\Delta H_d(\mathrm{Cl_2}) = 242$;
$E_A(\mathrm{Cl}) = -348$; $\Delta H_f = -642$

9) Predict the shapes of the following ions :

(a) $\mathrm{BeF_3^-}$ (b) $\mathrm{BF_4^-}$ (c) $\mathrm{IF_4^-}$ (d) $\mathrm{IBr_2^-}$ (e) $\mathrm{GeF_3^-}$

3.10 ANSWERS

Self Assessment Questions

1) Z^* values increase along a period; that is $Z^*_{Ne} > Z^*_{Li}$. Hence, formation of Li^+ is easier than that of Ne^+.

2) Carbon by accepting an electron becomes C^- ion and attains stable half-filled p^3 configuration; nitrogen is in stable p^3 configuration as such, but on adding an electron, it becomes partially filled and attains less stable p^4 configuration.

3) Benzene is a nonpolar solvent and cannot favourably orient itself around the cations and anions just as water can do.

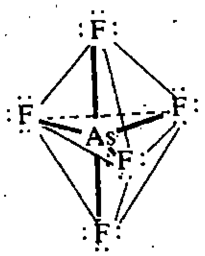
4) Born-Haber cycle for $\mathrm{BaCl_2}$ formation :

$$\begin{tikzcd}
\mathrm{Ba}(s) + \mathrm{Cl_2}(g) \arrow[rr, "\Delta H_f"] \arrow[dd, "\Delta H_s"'] & & \mathrm{BaCl_2}(s) \\
& 2\mathrm{Cl}(g) \arrow[ul, leftarrow, "\Delta H_d"'] \arrow[r, "2E_A(\mathrm{Cl})"] & 2\mathrm{Cl}^-(g) + \mathrm{Ba}^{2+}_a(g) \arrow[u, "\Delta H_{latt}"'] \\
\mathrm{Ba}(g) \arrow[rru, "I(\mathrm{Ba}) + I(\mathrm{Ba}^+)"'] & &
\end{tikzcd}$$

5) Formal charge on P = 5 − 4 − 0 = +1
Formal charge on O = 6 − 1 − 6 = −1

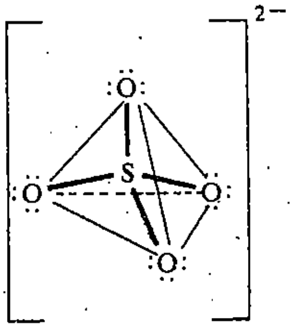
6) $a_{\mathrm{N_2}} = 110$ pm; $a_{\mathrm{Cl_2}} = 198$ pm; $a_{\mathrm{ICl}} = 232$ pm.

7) i)



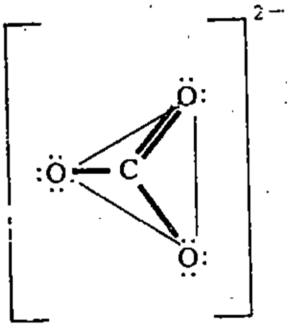
; trigonal bipyramidal

ii)



; tetrahedral

iii)



; triangular planar

Terminal Questions

1) (a) $I(\text{K}) > I(\text{Rb})$; since the 4*s* electron of K, being nearer to the nucleus, is more difficult to remove than the 5*s* electron of Rb.

   (b) $I(\text{Cl}) > I(\text{Si})$; effective nuclear charge on the valence electrons is higher for chlorine than for silicon.

2) An electron is added to a system which is already stable due to fully filled orbitals. The added electron has to go to $(n+1)s$ orbital.

3) An element of low I value, combines with an element of high negative E_A value, to form an ionic compound. Two elements, differing in electronegativity by more than 1.7 form an ionic compound.

4) The stability increases in the following order :
   $CI_4 < CBr_4 < CCl_4 < CF_4$; this conclusion is based on bond enthalpy values of C – X bonds.

5) Using radius ratio, ionic crystal geometry can be predicted.

6) (i) T (ii) T (iii) F (iv) F (v) T.

7) i) Nitrogen atom has only four orbitals in the valence level, 2*s* and 2*p*; therefore, it can form a maximum of four bonds. But phosphorus atom, having nine orbitals in the valence level namely, 3*s*, 3*p* and 3*d*, can form five bonds with five chlorine atoms.

   ii) The screening constant value for the outer most electrons is less for Na^+ than for Na.

   iii) Effective nuclear charge on the valence electrons of H^- ion is less than that for F^- ion.

8) Use Born-Haber cycle for calculation of lattice energy; lattice energy of $MgCl_2 = -2524\ \text{kJ mol}^{-1}$.

9) a) triangular b) tetrahedral c) square planar d) linear
   e) trigonal pyramidal.

UNIT 4 VALENCE BOND THEORY

Structure

4.1 INTRODUCTION

In Unit 3, covalent bond formation was explained on the basis of Lewis theory. For the same purpose, two quantum mechanical approaches namely valence bond theory and molecular orbital theory are available. These two theories seek to describe the structure of molecules, their shape and their energy. Valence bond method, proposed by Heitler and London (1927), is based on the assumption that a molecule is formed by the interaction of valence electrons and that atoms in a molecule maintain their individuality so far as the inner electrons are concerned. Molecular orbital theory, developed by Hund, Mulliken and Hückel (1930) considers the entire molecule as a new unit with all the electrons moving under the influence of all the nuclei and all the other electrons. Molecular orbital theory will be discussed in Unit 5; here we concentrate on valence bond theory.

In this unit, we shall explain the main principles of valence bond approach and apply the same to describe the structural aspects of hydrogen and other simple molecules. The concepts, resonance and hybridisation, are explained as developments in the evolution of valence bond theory. In Unit 3, shapes of some molecules were derived by using VSEPR theory. It is interesting to see how same conclusions are arrived at in a different way using hybridisation concept.

Objectives

After studying this unit, you should be able to :

- explain the principles of valence bond method and apply the same to derive the structure of hydrogen molecule,
- list and illustrate the rules of resonance,
- explain the term hybridisation and list its types,
- explain the structures of methane, ethane, ethylene and acetylene using hybridisation theory, and
- apply valence bond theory to explain the structure of benzene.

4.2 THE ORIGIN OF VALENCE BOND AND MOLECULAR ORBITAL THEORIES

The two approaches, valence bond theory and molecular orbital theory, arise by the different ways of arriving at the solution of the Schrödinger equation for the molecules. The Schrödinger equation (Eq. 4.1) can be written for the molecules as in the case of atoms.

$$H\psi = E\psi \qquad \text{.... (4.1)}$$

Here H is the Hamiltonian operator for the system and E is the energy of the system.

The exact solution of Eq. 4.1 in the case of any molecule is impossible. Even for the simplest molecule hydrogen, H has the form,

$$H = \frac{-h^2}{8\pi^2 m}[\nabla_1^2 + \nabla_2^2] - \frac{e^2}{4\pi\epsilon_0}\left(\frac{Z_a}{r_{a1}} + \frac{Z_b}{r_{b1}} + \frac{Z_a}{r_{a2}} + \frac{Z_b}{r_{b2}} - \frac{Z_a Z_b}{R} - \frac{1}{r_{12}}\right)$$

where 1 and 2 denote the two electrons and a and b the two nuclei. R is the internuclear distance, r_{a1} distance between electron 1 and nucleus a etc.; r_{12} is the interelectronic distance between the electrons 1 and 2.

In the above H, the kinetic energy of nuclei has not been considered as they, being too massive relative to electrons, are assumed to be stationary. This is known as **Born Oppenheimer Approximation.** The solution of Eq. 4.1 is impossible due to the presence of $1/r_{12}$ term in the Hamiltonian H. Therefore, one has to solve Eq. 4.1 by an approximate method.

Two types of mathematical approaches are used to solve the Eq. 4.1. These approaches differ in the manner of choosing ψ. Once ψ is constructed, the average energy E of the molecule can be calculated using the equation,

$$E = \frac{\int \psi^* H \psi \, d\tau}{\int \psi^* \psi \, d\tau} \qquad \ldots. (4.2)$$

Also E is calculated as a function of the internuclear distance R. In Eq. 4.2, ψ^* is the complex conjugate of the wave function, ψ.

In one of the approaches, known as Valence Bond (VB) method, approximate wave functions are constructed from those of the separate atoms. This approach is, in a sense, the quantum mechanical description of the Lewis concept of electron pair bond; hence the name—valence bond method. In the second approach, the molecular orbital (MO) method, the approximate wave functions are constructed from the molecular orbitals which in turn are constructed from the atomic orbitals of the constituent atoms. The electrons of the molecule are then assigned to these molecular orbitals on the basis of Aufbau principle. In this unit, we take up the study of valence bond approach and its application to simple molecules. We shall study the details of the molecular orbital theory in Unit 5.

4.3 PRINCIPLES OF VALENCE BOND THEORY

The main steps used in valence bond method, in arriving at the structure of a molecule, are given below :

i) Molecular wave function for the combining electrons is formed as a product of wave functions of electrons of the constituent atoms. For example, if the wave functions for 1*s* electron on each of the two hydrogen atoms are ψ_A and ψ_B, then the molecular wave function ψ is given by,

$$\psi = \psi_A \cdot \psi_B \qquad \ldots. (4.3)$$

In other words the **constituent atoms retain their identity** when they combine to form a molecule.

ii) Various trial functions ψ are designed, depending on the assumptions regarding molecule formation. Setting up different trial functions, indicates our attempts to describe the structure of molecule in different ways, taking into account various factors such as effective nuclear charge, resonance, indistinguishability of bonding electrons etc.

iii) Each trial function is fitted into an appropriate Schrödinger equation (Eq. 4.2) and the energy values, E, are obtained as a function of interatomic distance, R.

iv) E vs R diagrams, known as energy diagrams, are drawn for each trial function (Fig. 4.1). **The curves with minima represent stabilising features for molecule formation.** The difference between the total energy of the two isolated atoms and the energy corresponding to minima of the curve, gives the bond energy, calculated according to a particular trial function. The value of R at the minima point is the equilibrium interatomic distance or bond distance.

These steps are repeated for various trial functions. That trial function, for which calculated bond energy and bond distance values, agree closely with experimental values, is taken as the correct one, and the structural features assumed in designing such a trial function, are also considered valid.

In the next section, the above procedure is applied to determine the structural features of hydrogen molecule. Before we take that up, you can try the following SAQ.

SAQ 1

What are the deciding factors in choosing a particular trial function for a molecule? Give the answer in three lines.

....

....

....

4.4 VALENCE BOND THEORY OF HYDROGEN MOLECULE

In this section, we will apply the principles of valence bond theory, discussed in the last section, to the case of H_2 molecule.

We shall begin with two hydrogen atoms far apart so that no appreciable interaction between them occurs. Let us assume that the total energy of these two hydrogen atoms is represented by the point L in Fig. 4.1. Arbitrarily this has been placed on the zero of the scale. Although the two hydrogen atoms are identical, for the sake of convenience, we may label the electrons as 1 and 2 and the nuclei as A and B; the orbital wave functions of the two electrons 1 and 2 contained in two hydrogen atoms A and B would then be given by $\psi_A(1)$ and $\psi_B(2)$, respectively. Using Eq. 4.3, the trial molecular wave function for the hydrogen molecule (in reality a system of two separated H atoms) can be written as,

$$\psi_1 = \psi_A(1).\psi_B(2)$$

Using the above wave function in Eq. 4.2, the energy E of the system comprising two identical hydrogen atoms can be calculated as a function of the internuclear distance R. From the values of E and R, energy diagram 4.1a is drawn. The energy difference between L (total energy of the two isolated hydrogen atoms) and the minima of the curve 4.1a, gives the calculated bond energy of 24 kJ mol^{-1}. The equilibrium interatomic distance is calculated to be 90 pm. But the actual bond energy and interatomic distance for hydrogen molecule are 436 kJ mol^{-1} and 74 pm, respectively.

At the equilibrium interatomic distance r_0, a molecule has a stable existence. At interatomic distance greater than or less than r_0, it is less stable.

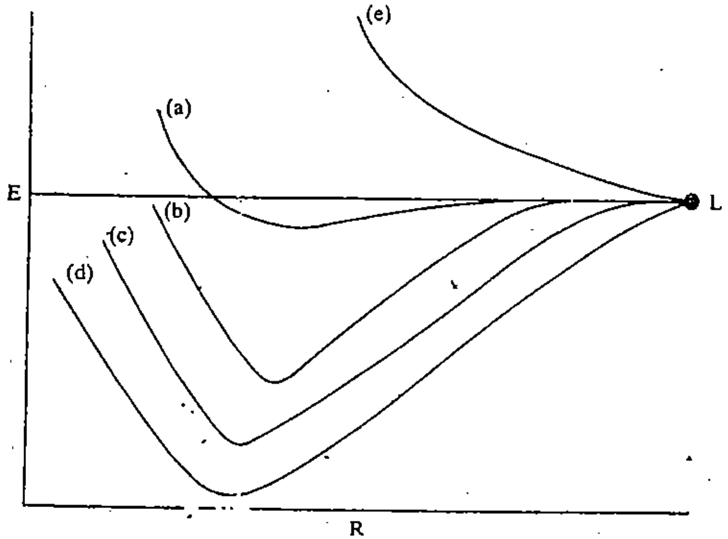


Fig. 4.1 : Theoretical energy curves (a–c, e) for hydrogen molecule compared with the experimental curve (d).

This means that the assumption used in trial function ψ_1 that electron 1 resides on hydrogen atom A and electron 2 resides on hydrogen atom B is not acceptable.

A refined wave function, ψ_{cov}, is then designed which allows for either of the electrons to reside on either of the hydrogen atoms. Also it is assumed that the two electrons are shared equally since the atoms are identical. This trial function is called ψ_{cov} to denote covalent bonding.

$$\psi_{cov} = \psi_A(1).\ \psi_B(2) + \psi_A(2).\ \psi_B(1) \qquad \ldots (4.4)$$

This trial function ψ_{cov} is tried in Eq. (4.2) in place of ψ and energy values at different R values are obtained. The bond energy and bond distance, according to this calculation are 303 kJ mol^{-1} and 86.9 pm, respectively. The E vs R curve is shown in Fig. 4.1(b). This trial function again requires further refinement.

A wave function ψ_2, is then designed keeping in mind the following features :

i) The two electrons mutually shield one another from the nuclear charge. Hence, the effective nuclear charge value Z^* must be used, instead of $Z = 1$.

ii) Hydrogen molecule can be given covalent structure (I) and ionic structures (II and III) as shown below :

$$\underset{\text{I}}{H : H} \qquad \underset{\text{II}}{{}^{-}H : H^{+}} \qquad \underset{\text{III}}{{}^{+}H : H^{-}}$$

The wave function corresponding to ionic forms is given by,

$$\psi_{ion} = \psi_A(1).\ \psi_A(2) + \psi_B(1).\ \psi_B(2) \qquad \ldots (4.5)$$

The first term in the right hand side denotes a situation, when both the electrons are on hydrogen atom A, and the second term, when the two electrons are on hydrogen atom B. The structures (I – III) are called canonical or resonating structures and the actual structure is the resonance hybrid of all these three structures. You will study more about resonance in the next section. This mixing of ionic and covalent forms is called **ionic - covalent resonance.**

A combined wave function ψ_2 is formed using ψ_{cov} and ψ_{ion} as follows :

$$\psi_2 = C_1\ (C_2\ \psi_{cov} + C_3\ \psi_{ion}) \qquad \ldots (4.6)$$

In this equation, C_1, C_2 and C_3 are constants depending on how much of the ionic wave function is mixed with the covalent wave function. When the wave function ψ_2 is used in Eq. 4.2, and energy values calculated for various values of R, curve of the type 4.1(c) is obtained. The bond energy and bond distance values, according to this calculation, are found to be 388 kJ mol^{-1} and 74.9 pm, respectively. Thus the addition of new terms to the trial function, brings the bond energy and bond distance values closer to experimental values. The resonance structures (I – III) seem to describe the structure of hydrogen molecule much better than covalent structure (I) alone. In Table 4.1, a summary of bond energy and bond distance values, obtained for trial functions mentioned above, is given.

Table 4.1 : Bond Energy and Bond Distance For Various Trial Functions of Hydrogen Molecule

Trial Function		Energy	Distance	Curve representing trial function
Type	**Significance**	**(kJ mol^{-1})**	**(pm)**	
ψ_1	A system of two isolated H atoms; two electrons are distinguishable	24	90	4.1a
ψ_{cov}	Covalent structure and indistinguishable electrons	303	86.9	4.1b
ψ_2	Effective nuclear charge and ionic-covalent resonance recognised	388	74.9	4.1c
Experimental curve		436	74	4.1d

A trial function, combining as much as 100 terms, has been found to yield bond energy and bond distance values almost equal to experimental values. The energy diagram corresponding to experimental values is given in Fig. 4.1(d).

Valence bond theory throws light on the fact that no bond is 100% ionic or 100% covalent. It is further inferred that the electron density distribution is symmetrical about the axis passing through the nuclei, Fig. 4.2. Such bonds, with symmetrical electron density about internuclear axis, are called σ bonds.

Fig. 4.2 : σ bond in hydrogen molecule.

In constructing atomic wave functions such as ψ_A (1), ψ_B (2), etc., the spins of combining electrons have been assumed to be opposite. Hence hydrogen molecule formation can also be considered as a **process of spin pairing**. On the other hand, if the two *H* atoms approach in such a way that the spins are in the same direction, then the net force of interaction is strongly repulsive. As two hydrogen atoms having same spin value approach each other, the energy of the system increases. This situation is indicated by the curve 4.1 (e). Try the following SAQ, to see if you have understood the ideas developed above.

SAQ 2

Explain the fact that for H_2 molecule, covalent structure is more important than ionic structures. (Hint : Use the bond energy values).

……………………………………………………………………………………………………

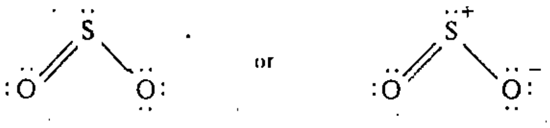
……………………………………………………………………………………………………

……………………………………………………………………………………………………

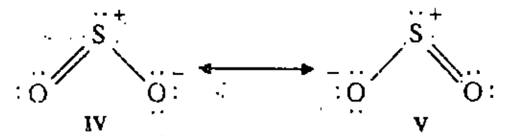
4.5 RESONANCE OR ELECTRON DELOCALISATION

Sometimes the properties of a molecule or ion are not adequately represented by a single Lewis structure. In the last section, we saw how the structure of hydrogen could not be represented by one of the three structures (I), (II) and (III) alone and had to be conceived on the basis of contribution from all the three. Such structures are known as resonance structures. They differ in the arrangement of electrons, keeping the atomic arrangement the same.

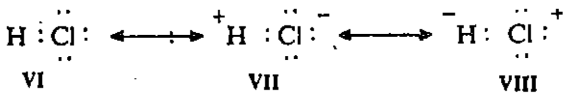
Let us take another example: say sulphur dioxide.



The charges represented are formal charges, which you studied in section 3.4 of Unit 3. According to the above structure, the two sulphur-oxygen bonds must be of different types, one being a single bond and the other a double bond. But in sulphur dioxide molecule, both the bonds are of same length. So in the case of this molecule also, two or more valence bond structures such as (IV) and (V), have to be used to depict the molecule. The molecule is said to be a resonance hybrid of the structures (IV) and (V), which are in turn known as **resonating or canonical structures.**



The actual structure of sulphur dioxide does not correspond to either of the resonance structures alone; but it is intermediate between these two resonance structures. There is only one type of sulphur dioxide molecule and it can have only one structure. The electrons do not flip within the molecule; i.e., for no moment of time, the molecule has any one resonance structure. The two resonance structures of sulphur dioxide are equivalent. But in some cases, like hydrogen chloride, all the resonance structures may not be equivalent.



$$H:\ddot{\underset{..}{Cl}}: \longleftrightarrow \overset{+}{H}\ :\ddot{\underset{..}{Cl}}:^{-} \longleftrightarrow \overset{-}{H}:\ \ddot{\underset{..}{Cl}}:^{+}$$

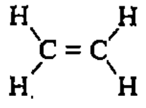
VI VII VIII

A π bond is formed by the lateral (sideways) overlap of atomic orbitals. The electrons giving rise to a π bond are called π electrons.

The ionic – resonance structures, having lower bond order value than covalent structures, are of less importance. Thus, ionic structures (VII) and (VIII) of hydrogen chloride having zero bond order are of less importance than covalent structure (VI) having bond order value of one. This is due to the involvement of σ electrons which is rarely significant in resonance structures. Resonance structures in majority of cases, involve variable distribution of π electrons. Hence, resonance is also known as delocalisation of π electrons.

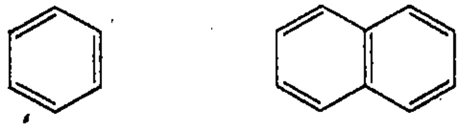
Double bond in alkenes is said to be localised since its location is fixed between two particular carbon atoms.

Localisation of π electrons means fixing π electrons between two particular atoms, as in ethylene.



Ethylene

Compounds like benzene and naphthalene have a delocalised π electron structure which means π electrons are not fixed between any two particular carbon atoms.



Benzene Naphthalene

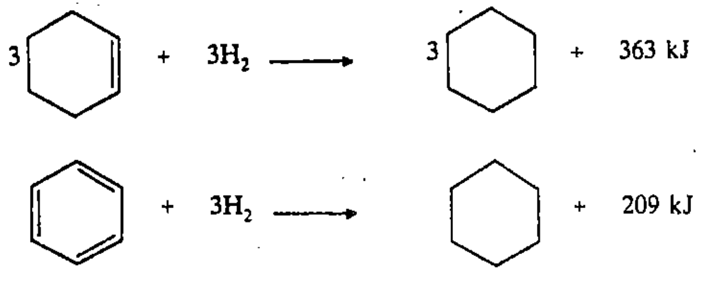
π electron delocalised over all the carbon atoms.

The percentage contribution each resonating structure makes to the resonance hybrid indicates how far the characteristics of the molecule are explained by a particular structure.

Some structures may be of lower energy than others and hence make major contribution to the hybrid. The resonance forms must be evaluated to determine their importance and relative contribution to the resonance hybrid. The percentage contribution, that each resonance structure makes to the resonance hybrid, is derived by the solution of Schrödinger equation, set up for the molecule.

The heat of hydrogenation is the quantity of heat evolved or absorbed when one mole of an unsaturated compound adds on hydrogen.

The stabilisation, a molecule or ion attains, due to contributing resonance structures, is described in terms of resonance energy. A substance that has a considerable resonance energy is said to be resonance stabilised. As an illustration, let us calculate resonance energy for benzene. The resonance energy for benzene is the difference between the heat of hydrogenation calculated for a structure with three localised double bonds and the experimental value. The heat of hydrogenation for the localised structure of benzene is calculated on the assumption that the three double bonds of benzene add on hydrogen like three molecules of cyclohexene. That is, the calculated heat of hydrogenation of benzene is thrice the heat of hydrogenation of cyclohexene (363 kJ). But the experimentally determined heat of hydrogenation of benzene is 209 kJ mol^{-1}.



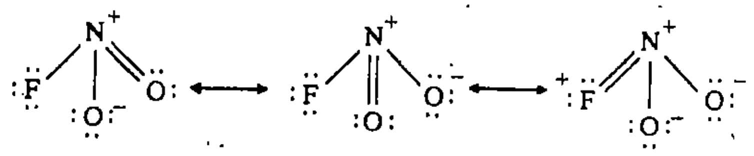
The difference between the calculated and the experimental values of heat of hydrogenation for benzene is (363 – 209 =) 154 kJ mol^{-1}. Thus, the resonance energy of benzene is 154 kJ mol^{-1}. Compared to this, the resonance energy of naphthalene is 315 kJ mol^{-1}. Hence, naphthalene has greater resonance stability than benzene.

Let us now see the rules that are useful in deciding the relative importance of resonance structures of a molecule or ion.

1) The resonance forms of a given species differ in the arrangement of electrons, and not in the arrangement of nuclei.

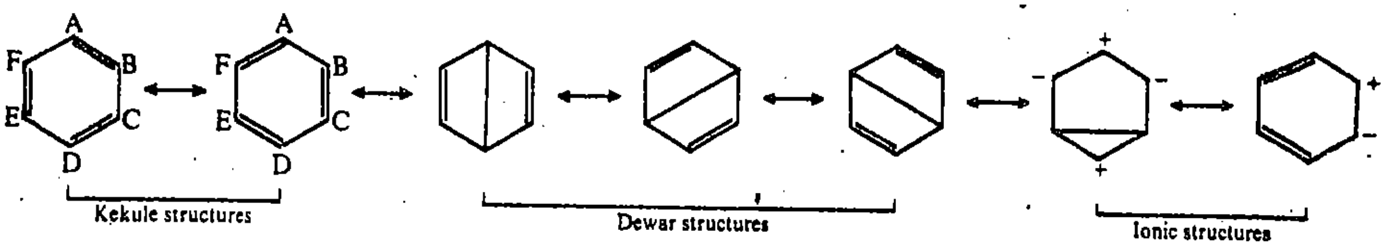
   Thus for carbon dioxide, having the arrangement of atoms as OCO, the structure, OOC, is not a resonance structure.

2) In case resonance structures have charge separation, two atoms that are bonded together should not have formal charges with the same sign. Thus, of the three structures for FNO_2, structure (XI) is not a resonance structure, since it suffers from electrostatic repulsion from adjacent positive charges.



IX X XI

3) The structures without formal charges are more important than those with formal charges. For benzene, the resonance structures of Kekule (XII and XIII) and Dewar types (XIV–XVI) which do not have formal charges are more important than the ionic structures (XVII and XVIII).



XII XIII XIV XV XVI XVII XVIII

4) While giving formal charges, the more electronegative atom should carry a formal negative charge and the less electronegative atom should carry a formal positive charge. Thus, of the resonance structures of hydrogen chloride, structure (VIII) is less important since the more electronegative atom chlorine has a formal positive charge.

5) The resonance forms of a molecule or ion have usually the same number of shared electrons. Of the three structures (XIX – XXI) for cyanate ion, (XXI) is less important as a resonance structure, since it has only three shared pairs. The other two structures (XIX) and (XX) have four shared pairs each.

$$^{-}:\ddot{\underset{\cdot\cdot}{O}}-C\equiv N: \longleftrightarrow :\ddot{O}=C=\underset{\cdot\cdot}{N}:^{-} \longleftrightarrow {}^{-}:\ddot{\underset{\cdot\cdot}{O}}-\overset{+}{C}=\underset{\cdot\cdot}{\ddot{N}}^{-}$$

XIX XX XXI

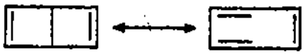
6) Resonance hybrid is said to be stabilised if two or more of its resonating structures are energetically equivalent. The two Kekule structures of benzene which are equivalent are largely responsible for its considerable resonance energy and resonance stabilisation.

7) Delocalisation of electrons in an unsaturated system is maximum when the molecule is coplanar.

Benzene, a resonance stabilised molecule, has been found to be a planar molecule with equal electron density around six carbon atoms, as per X-ray diffraction studies. On the other hand, bicyclohexadiene, **an isomer of benzene**, is not much resonance stabilised due to its nonplanarity.

Isomers have individual existence: resonating structures do not have.

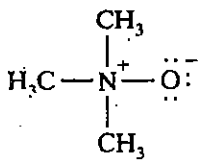
Diffraction is the bending of light rays over the edges of an object. The diffraction of x-rays is maximum in places of atomic sites. X-ray diffraction helps in the location of atomic sites.



Bicyclohexadiene **Very minor**

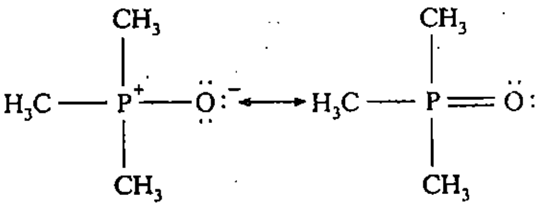
8) The compounds of third and higher period elements can have resonance structures involving *d* orbitals whereas those of second period elements do not have. The compounds of phosphorus and sulphur, for example, exhibit resonance structures involving *d* orbitals. These two elements in their compounds can expand their outer shells to more than eight electrons. This behaviour is not expected of compounds of second period elements such as nitrogen due to nonavailability of *d* orbitals.

Trimethylamine oxide, for example has only a single structure while trimethylphosphine oxide has two resonance structures.



$H_3C-\overset{CH_3}{\underset{CH_3}{\overset{+}{N}}}-\ddot{\underset{..}{O}}:^-$

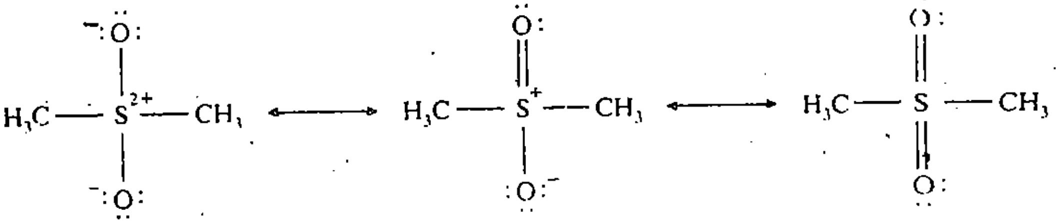
Trimethylamine oxide; resonance structures not possible.



$H_3C-\overset{CH_3}{\underset{CH_3}{P^+}}-\ddot{\underset{..}{O}}:^- \longleftrightarrow H_3C-\overset{CH_3}{\underset{CH_3}{P}}=\ddot{O}:$

Trimethylphosphine oxide

Similarly, dimethylsulphone has the following resonance structures :



$H_3C-\overset{^-:\ddot{O}:}{\underset{^-:\ddot{\underset{..}{O}}:}{S^{2+}}}-CH_3 \longleftrightarrow H_3C-\overset{\ddot{O}:}{\underset{:\underset{..}{O}:^-}{S^+}}-CH_3 \longleftrightarrow H_3C-\overset{\ddot{O}:}{\underset{\underset{..}{O}:}{S}}-CH_3$

Dimethylsulphone

Using the above rules, attempt the following SAQ

SAQ 3

Write the resonance structures of nitrate ion. (*Hint* : Start with Lewis structure of NO_3^- ion).

....

....

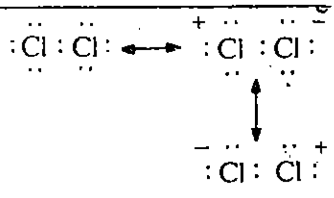
....

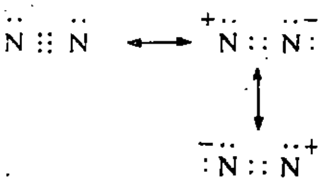
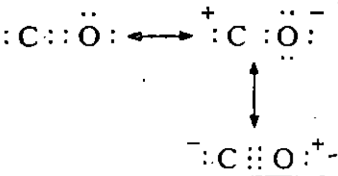
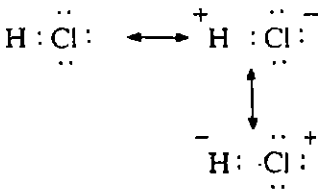
4.6 VALENCE BOND DESCRIPTION OF SOME MORE MOLECULES

Valence bond method can be applied to describe the structure of many covalent molecules. According to valence bond method, whenever we have two atoms, each with at least one unpaired electron, they may unite to form a bond in which these two electrons are paired. In order to arrive at the structure of a molecule, various trial functions are designed, as was done in the case of hydrogen molecule, till a satisfactory trial function, which can explain the properties of the molecule, such as bond energy and bond length, is obtained. The structural features corresponding to the acceptable trial function are taken into account while describing the actual molecular structure.

The resonance structures of some molecules, obtained using the above procedure, are given in Table 4.2.

Table 4.2 : Valence Bond Structures of Some Molecules

Molecule	Electron configuration of the combining atoms	Unpaired electrons	Resonance structures
Cl_2	Cl $1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^1$	$3p_z$ electron in each chlorine atom	 $:\ddot{\underset{..}{Cl}}:\ddot{\underset{..}{Cl}}: \longleftrightarrow \overset{+}{:\ddot{Cl}}\ :\overset{-}{\ddot{\underset{..}{Cl}}}:$ $\updownarrow$ $\overset{-}{:\ddot{Cl}:}\ \overset{+}{\ddot{Cl}:}$

N_2	N $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$	$2p_x$, $2p_y$, $2p_z$ electrons in each nitrogen atom	
CO	C $1s^2 2s^2 2p_x^1 2p_y^1$ O $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$	$2p_x$ and $2p_y$ electrons of carbon and $2p_y$ and $2p_z$ electrons of oxygen	
HCl	H $1s^1$ Cl $1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^1$	$1s^1$ electron of hydrogen and $3p_z$ electron of chlorine	 (VIII) VIII is of little importance since chlorine has higher electronegativity.

Based on the above principles, we would be tempted to give the following structures for oxygen molecule :

But these structures do not explain the experimentally known paramagnetic character of oxygen. Let us see if molecular orbital theory, which we are going to study in next unit, is able to explain this behaviour of oxygen.

In the next section, we shall see hybridisation of orbitals which is another aspect of valence bond theory. Using the above principles, attempt the following SAQ.

SAQ 4

Explain valence bond structures of fluorine molecule.

....

....

....

4.7 HYBRIDISATION OF ORBITALS

Principles of valence bond theory used so far in describing the structure of molecules, are not sufficient to explain the structure of methane. The electron configuration of carbon in the ground state is $1s^2 2s^2 2p_x^1 2p_y^1$. The concepts of valence bond approach enunciated above predict the pairing of two unpaired electrons in $2p_x$ and $2p_y$ orbitals of carbon with $1s$ electron of each of the two hydrogen atoms to form CH_2 molecule. But CH_2 is not a stable molecule. The simplest stable hydrocarbon is methane, CH_4. How are we to explain this?

To reconcile the valence bond theory with experimental evidence, Pauling devised a model in which one of the $2s$ electrons of carbon atom is promoted to the empty $2p_z$ orbital. The $2s$ and three $2p$ orbitals of carbon atom are mixed to form four equivalent orbitals, known as **sp^3 hybrid orbitals.** The axes of sp^3 orbitals are oriented in space, toward the corners of a regular tetrahedron. That is, the angle between any two orbital axes is 109°28′ [Fig. 4.3(a)]. **The process of mixing two or more orbitals of different energies to give an equal number of new hybrid orbitals of lower energy is known as hybridisation.** Anyhow, it should be remembered that hybridisation is a mathematical concept. The promotion of electrons to higher levels and mixing of orbitals are both mental construction which are useful in thinking about bond formation.

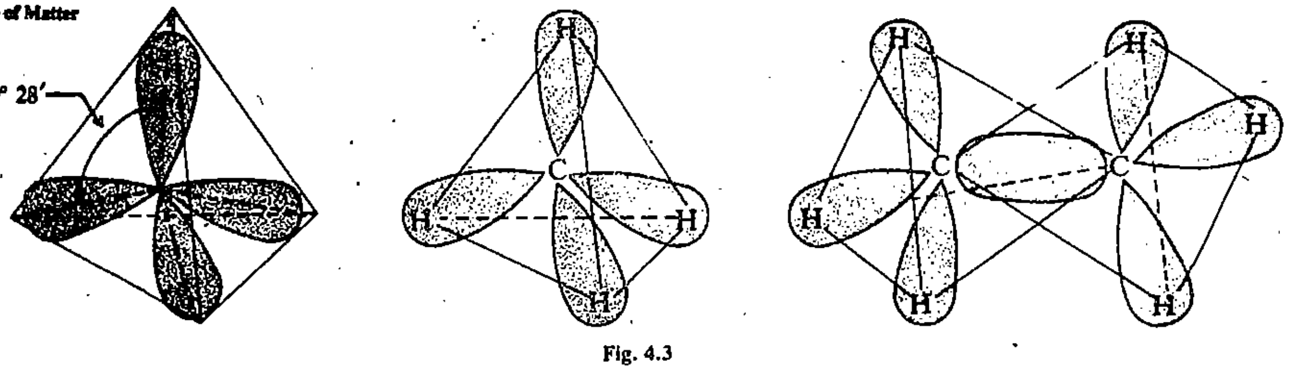


Fig. 4.3

a) Four sp^3 atomic orbitals for carbon (small back lobes of orbitals omitted).

b) Tetrahedral structure of methane.

c) Structure of ethane.

The most acceptable trial function for methane indicates that the hybrid orbital has one-fourth s character and three-fourth p character. The four unpaired electrons in the four sp^3 hybrid orbitals of carbon, combine with $1s$ electron of each of the four hydrogen atoms, to form four σ bonds. The energy liberated in the formation of four C-H bonds is more than that required for :

i) the promotion of $2s$ electron to $2p_z$ orbital.

ii) mixing s and p orbitals.

iii) keeping the four unpaired electrons free from mutual or orbital spin interactions.

Methane is tetrahedral in shape, Fig. 4.3b, with a bond angle of 109°28′. In section 3.6 of last unit, we derived the same conclusion based on VSEPR theory. In ethane, (Fig. 4.3c), and in other higher alkanes also, carbon atoms are in sp^3 hybridised state. The C-C bond length in ethane has been found to be 154 pm. The covalent radius for sp^3 hybridised carbon is 77 pm.

Let us now focus our attention on the structure of ethylene. One of the $2s$ electrons in each of the two carbon atoms is promoted to the empty $2p_z$ level as before. The $2s$, $2p_x$ and $2p_y$ orbitals are hybridised to yield three sp^2 hybrid orbitals (Fig. 4.4a). The $2p_z$ orbital is not used for hybridisation. Each sp^2 hybrid orbital has one-third s character and two-third p character.

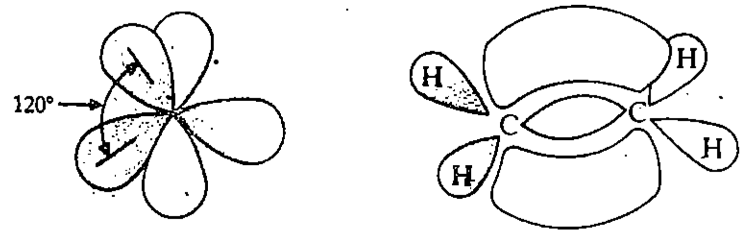
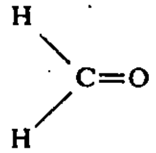


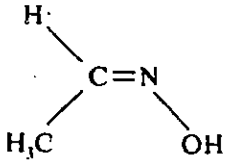
Fig. 4.4

a) Diagram illustrating the three trigonal sp^2 hybrid orbitals of the carbon atom (shown in grey colour), which lie in the same plane and the one unhybridised p orbital (shown in red colour), which is perpendicular to the plane.

b) Structure of ethylene.



Formaldehyde



Acetaldoxime

Each of the two carbon atoms in ethylene forms three σ bonds, two σ bonds being formed with two hydrogen atoms and one σ bond with the other carbon atom. The fourth bond, a π bond, is formed by the lateral overlap of the $2p_z$ orbitals of the two carbon atoms. Ethylene, therefore, has a double bond between the two carbon atoms [Fig. 4.4(b)], one being a σ bond and the other a π bond, the latter being perpendicular to the plane of the molecule. The C=C bond length is 134 pm which is less then C—C bond length in ethane. The covalent radius for sp^2 hybridised double bonded carbon is 67 pm. The bond angle in ethylene and other sp^2 hybridised systems is approximately 120° and the molecule is said to have trigonal shape. That is, the orbitals around each carbon atom are directed towards the vertices of a triangle. On the basis of VSEPR theory also, the same conclusion can be obtained. The structural aspects around the double bonded carbon atoms in other alkenes also are similar to those in ethylene. In compounds like formaldehyde and acetaldoxime, double bonded carbon atom is in sp^2 hybridised state.

In the next section, you will see as to how sp^2 hybridisation concept is used in combination with resonance to explain the structure of benzene.

Wherever carbon atom is attached to four other atoms, it is sp^3 hybridised. When it is attached to three other atoms it is sp^2 other atoms, it is sp hybridised.

In acetylene, the carbon atoms are in sp hybridised state. Again one of $2s$ electrons is promoted to empty $2p_z$ level in each of the two carbon atoms. The mixing of $2s$ orbital and $2p_x$ orbital produces two sp hybrid orbitals with their axes arranged in a linear fashion [Fig. 4.5(a)]. Each sp hybrid orbital has 50% s character and 50% p character. The two sp hybrid orbitals of each of the carbon atoms form two σ bonds, one between each carbon and a hydrogen and another between the two carbon atoms. The two $2p_y$ and $2p_z$ orbitals of each carbon atom, which are not used in hybridisation, combine to give two π bonds, which are perpendicular to each other and also to the plane of the molecule. The two π bonds are represented as a cylindrical envelope around the two carbon atoms. Thus, in acetylene, there is a triple bond between the two carbon atoms, Fig. 4.5(b). The bond angle is 180° and the molecule is linear; VSEPR theory, also could be used to get the same conclusion. The C≡C length is 120 pm and the covalent radius for sp hybridised triple bonded carbon is 60 pm.

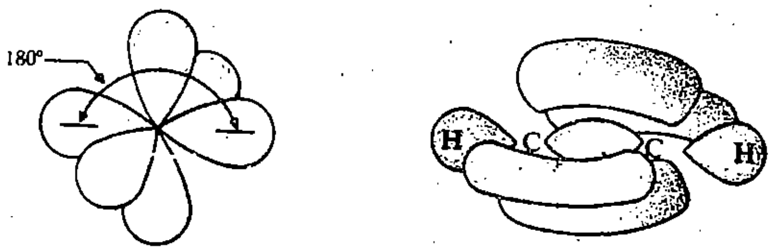


Fig. 4.5

a) Diagram of the two linear sp hybrid orbitals of the carbon atom, which lie in a straight line (shown in grey colour) and the two unhybridised p orbitals (shown in red colour).

b) structure of acetylene.

You can see that among sp^3, sp^2 and sp hybridised carbon atoms, covalent radius is the highest for sp^3 and least for sp hybridised state; s character is the highest for sp and least for sp^3. Increase of s character in the hybridised carbon atom causes a decrease in its covalent radius since s electrons are more tightly held than p electrons. It is worth remembering that in section 3.4.3 of the previous unit, we have mentioned that the bond length decreases as bond order increases. From Table 4.3, you can have a comparative account of ethane, ethylene and acetylene with respect to structural features.

A substance, which releases H^+ ion more readily than another, is said to be more acidic. Since s character is the highest for sp hybridised carbon (50%) and least for sp^3 hybridised carbon (25%), C-H bond in acetylene is the most acidic, that in ethylene is less acidic and that in ethane is the least acidic. The greater s character results in the bond electrons of C-H bond being pulled strongly towards carbon atom, thereby releasing H^+ more easily.

Table 4.3 : Comparison of Ethane, Ethylene and Acetylene

Name of the Compound	Hybridisation type	Structure	Shape	Type of bonds for each carbon atom	Bond Angle	Carbon-carbon bond	
						Bond type	Bond length/pm
Ethane	sp^3	H H \ / H — C—C — H / \ H H	Tetrahedral	4 σ bonds	109°28′	Single bond	154
Ethylene	sp^2	H H \ / C=C / \ H H	Trigonal	3 σ bonds & 1 π bond	120°	Double bond	134
Acetylene	sp	H — C≡C — H	Linear	2 σ bonds & 2 π bonds	180°	Triple bond	120

Carbon-carbon bond lengths given in Table 4.3 correspond to single, double and triple bonds formed by sp^3, sp^2 and sp carbon atoms, respectively. But single bond can occur between any two similarly or dissimilarly hybridised carbon atoms. Similarly double bonds of the type $sp^2 - sp^2$, $sp^2 - sp$ and $sp - sp$ are possible. Some examples are given below :

$$\underset{sp^3}{H_3C}-\underset{sp^3}{CH_3} \qquad \underset{sp^3}{H_3C}-\underset{sp^2}{CH}=\underset{sp^2}{CH_2} \qquad \underset{sp^2}{H_2C}=\underset{sp}{C}=\underset{sp^2}{CH_2}$$

$$\underset{sp^3}{H_3C}-\underset{sp}{C}\equiv\underset{sp}{CH} \qquad \underset{sp^2}{H_2C}=\underset{sp^2}{CH}-\underset{sp^2}{CH}=\underset{sp^2}{CH_2}$$

Carbon-carbon bond lengths depend both on bond type and hybridisation state of linked carbon atoms, as given in Table 4.4.

Table 4.4 : Hybridisation States, Bond Types and Bond Lengths

Bond type	(Bond length)/pm	Bond type	(Bond length)/pm	Bond type	(Bond length)/pm
C – C		C = C		C – H	
$sp^3 - sp^3$	154	$sp^2 - sp^2$	134	$C_{sp^3} - H$	111
$sp^3 - sp^2$	150	$sp^2 - sp$	131	$C_{sp^2} - H$	110
$sp^3 - sp$	146	$sp - sp$	128	$C_{sp} - H$	108
$sp^2 - sp^2$	148				
$sp^2 - sp$	143	C ≡ C			
$sp - sp$	138	$sp - sp$	120		

Hybridisation is not limited to *s* and *p* orbitals only but may, in general, involve the mixing of other types of orbitals also, provided energy difference is not much. Hybrid orbitals involving *d* orbitals occur quite commonly among the heavier elements and are particularly important in complexes of the transition elements. Although hybrid orbitals are generally equivalent, in some cases nonequivalent hybrid orbitals also occur. Thus, in dsp^3 hybridisation, whether it is trigonal bipyramid or square pyramid, two types of bonds, axial (a) and equatorial (e) are seen. Under VSEPR theory of the previous unit, you studied that two types of bonds, axial and equatorial are present in a molecule having a total of five electron pairs around the central atom. In Table 4.5, hybridisations involving *d* orbitals are given.

Table 4.5 : Hybridisations Involving *d* Orbitals

Type	Orbitals used	Geometry	Hybrid orbitals equivalent (E) or nonequivalent (N)	Example
d^2sp^3 or sp^3d^2	$s, p_x, p_y, p_z, d_{z^2}, d_{x^2-y^2}$	Octahedral	E	SF_6, $[Fe(CN)_6]^{4-}$
dsp^3 or sp^3d	$s, p_x, p_y, p_z, d_{z^2}$	Trigonal bipyramid	N	PF_5, PCl_5
dsp^3 or sp^3d	$s, p_x, p_y, p_z, d_{x^2-y^2}$	Square pyramid	N	IF_5
dsp^2	$s, p_x, p_y, d_{x^2-y^2}$	Square planar	E	$[Cu(NH_3)_4]^{2+}$
sd^3	$s, d_{xy}, d_{yz}, d_{zx}$	Tetrahedral	E	CrO_4^{2-} and MnO_4^- (both sd^3 and sp^3 possible)

The structure of many of the coordination complexes and of molecules like phosphorus pentachloride and sulphur hexafluoride can be explained using hybridisation theory. Earlier you studied in Unit 3, based on VSEPR theory, that sulphur hexafluoride is octahedral in shape. We can arrive at this conclusion using the concept of hybridisation also. For sulphur, the ground state configuration is $1s^2\,2s^2\,2p^6\,3s^2 3p_x^2\,3p_y^1\,3p_z^1$. The $3s$ and $3p_x$ electrons are unpaired, excited to $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals and the six orbitals, namely, $3s$, $3p_x$, $3p_y$, $3p_z$, $3d_{x^2-y^2}$ and $3d_{z^2}$ are hybridised to obtain six orbitals of sp^3d^2 type. Each of these six orbitals has an unpaired electron. Pairing of these six unpaired electrons with the $2p_z$ electron in each of the six fluorine atoms gives rise to sulphur hexafluoride molecule. This is diagrammatically illustrated below :

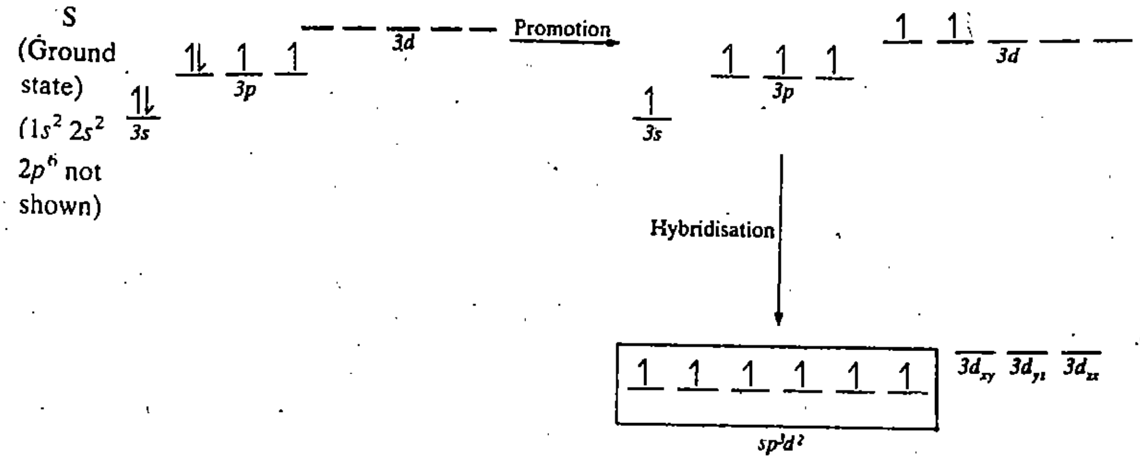


Fig. 4.6 : sp^3d^2 hybridisation in sulphur atom; six unpaired electrons available for pairing with $2p_z$ electrons of six fluorine atoms.

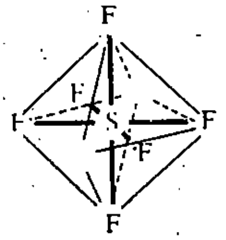


Fig. 4.7 : Structure of sulphur hexafluoride.

The orbitals of sp^3d^2 type have lobes directed to the vertices of an octahedron. In other words, sulphur hexafluoride is octahedral, Fig. 4.7.

Using the above ideas, why don't you try the following SAQ?

SAQ 5

Explain the type of hybridisation in phosphorus pentachloride.

....

....

....

4.8 VALENCE BOND DESCRIPTION OF BENZENE

The valence bond picture of benzene can be explained using the two concepts, hybridisation and resonance. Each of the six carbon atoms in benzene is in sp^2 hybridised state, forming three bonds, two to adjacent carbon atoms and one to a hydrogen atom. Because sp^2 orbitals are planar, all the six carbon and six hydrogen atoms are in the same plane and the bond angles are 120°. Each carbon atom has still an unpaired electron in the $2p_z$ orbital. The next question is to see how these six $2p_z$ electrons pair up. The valence bond description of pairing of $2p_z$ electrons can be understood first by considering Kekule structures and then Dewar and ionic structures.

Even among the two Kekule structures, the overall wave function is formed for only the first Kekule structure (XII), to start with. If the carbon atoms are labeled A, B, C, ...F and the electrons, 1, 2, ...6, then wave function for one π bond is $\Psi_A(1)\cdot\Psi_B(2) + \Psi_A(2)\cdot\Psi_B(1)$ because formally it is like an isolated hydrogen molecule. For second π bond, the wave function is $\Psi_C(3)\,\Psi_D(4) + \Psi_C(4)\cdot\Psi_D(3)$ and for the third, it is $\Psi_E(5).\ \Psi_F(6) + \Psi_E(6)\cdot\Psi_F(5)$. The overall wave function for the first Kekule structure is

$$\psi_{VB}^{KI} = \{\psi_A(1).\,\psi_B(2) + \psi_A(2)\cdot\psi_B(1)\}.\ \{\psi_C(3).\,\psi_D(4) + \psi_C(4).\,\psi_D(3)\}.$$
$$\{\psi_E(5).\,\psi_F(6) + \psi_E(6)\ \psi_F(5)\} \quad \ldots.(4.7)$$

The overall wave function is obtained as the product of the independent wave functions as per the principle explained in section 4.3. The expression in Eq. 4.7 may look complicated but it can be analysed in the same way as for the hydrogen molecule. As it stands, Eq. 4.7 does not permit any π electron density between carbon atoms B and C, D and E, and F and A. This structure implies that two sets of bond lengths, 148 pm and 134 pm, must exist, one for sp^2 hybridised single bonded carbon atoms and other for double bonded ones. Experimentally determined carbon-carbon bond lengths are all equal, viz., 139.7 pm. Hence, the above trial function needs to be improved.

As a next step, another wave function ψ_{VB}^{K2} is formed, for the second Kekule structure, where the π bond formation is assumed between carbon atoms B and C, D and E and F and A (XIII). Mixing these two wave functions for Kekule structures, wave function ψ_K is written as,

$$\psi_K = \psi_{VB}^{K1} + \psi_{VB}^{K2} \qquad \text{....(4.8)}$$

From energy considerations, it can be shown that even ψ_K needs to be improved.

Further refinements are possible, if we take into account the following features :

i) Bonding may occur between non-neighbouring atoms and a better description is obtained by considering Dewar structures (XIV – XVI). However, Dewar structures imply the presence of diagonal C–C bonds having bond distance value of 280 pm. This is larger than even the C–C bond length in alkanes. These diagonal bonds are weak rendering small contribution of Dewar forms to the resonance hybrid.

ii) As in the case of hydrogen molecule, we should allow ionic – covalent mixing, taking into account structures of the kind (XVII) and (XVIII). Actually there are many such ionic structures. Anyhow, ionic structures (XVII) and (XVIII), are less important than covalent structures, (XII – XVI), as per rule (3) stated in section 4.5.

Resonance hybrid of benzene is said to have around 80% contribution from Kekule structures and 20% contribution from Dewar structures. This means properties of benzene are better explained by Kekule structures than by Dewar structures.

Although inclusion of more terms in the trial function gives a better description of the structure of benzene, the treatment becomes much more complicated. In spite of all the mathematical complexity, valence bond theory leads to the following facts regarding benzene structure :

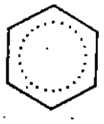
i) All carbon-carbon bond lengths are equal to 139.7 pm which is in between single and double bond lengths. This means double bonds are not localised between any two carbon atoms, i.e., benzene has a delocalised π electron structure.

ii) The actual structure of benzene is a resonance hybrid of the structures of the type (XII – XVIII).

iii) The resonance stabilisation energy, has been found to be 154 kJ mol

iv) It predicts a planar hexagonal structure with a bond angle of 120°.

From the above discussion we can infer that the π electrons are not localised between particular pairs of carbon atoms. The six π electrons are delocalised over all the carbon atoms. Summing up all the above structural features, a delocalised π electron structure of benzene can be written as :



Inner circle denotes symmetrical distribution of π electron density over all the six carbon atoms.

Using the above ideas, try to answer the following SAQ.

SAQ 6

Between ethylene and benzene, suggest two structural aspects of similarity and dissimilarity.

....

....

....

4.9 SUMMARY

In this unit, we have described the development of valence bond theory and its applications to simple molecules. The concepts of resonance and hybridisation have also been explained. Using the principles of valence bond theory, the structures of methane, ethylene, acetylene and benzene are discussed. In the next unit, you will study the structure of molecules like hydrogen, oxygen and carbon monoxide in the light of molecular orbital theory.

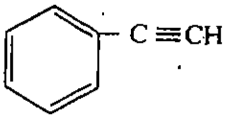
4.10 TERMINAL QUESTIONS

1) What are the essential steps involved in arriving at the structure of a molecule using valence bond theory?

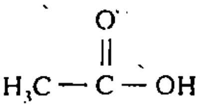
2) Identify the type of hybridisation for each of the carbon atoms.

   i) $H_3C-CH=CH_2$

   ii)



   iii)



$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-OH$

3) Explain the shape of CCl_4 molecule on the basis of VSEPR and hybridisation theories.

4) For the following statements, mark T for correct statements and F for false ones.

   a) Electrons in a hydrogen molecule are distinguishable ☐

   b) More terms in the trial function lead to a more acceptable bond energy value ☐

   c) Homonuclear molecules like N_2, O_2 etc. do not have ionic terms in their valence bond structures ☐

   d) Carbon atom, in carbonate ion, is in sp^2 hybridised state ☐

   e) Covalent radius of carbon increases with increase of *s* character in different hybridisation states ☐

5) Explain the structure of mercuric chloride on the basis of hybridisation theory.

6) Differentiate the following isomers on the basis of theoretical carbon-carbon bond lengths :

$H_3C-CH_2-CH=CH_2$	$H_3C-CH=CH-CH_3$
1 – Butene	2 – Butene

7) Carbon dioxide is linear as per VSEPR theory. Explain the type of hybridisation in the carbon atom of this molecule, in keeping with its linear structure.

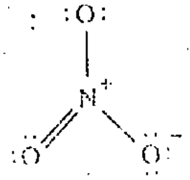
4.11 ANSWERS

Self Assessment Questions

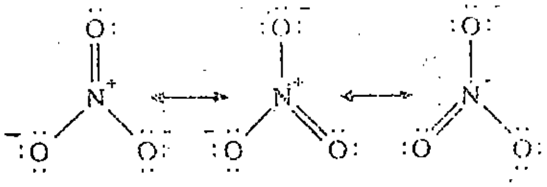
1) That trial function, for which bond energy and bond length values are closest to experimental values, is accepted as the correct one.

2) By assuming a covalent structure with indistinguishable electrons, the bond energy is improved from a value of 24 kJ mol^{-1} to 303 kJ mol^{-1}. But this value is improved to only 388 kJ mol^{-1} by taking into account the screening effect of the electron and the possibility of ionic and covalent structures. Hence, covalent structure has greater importance than other factors.

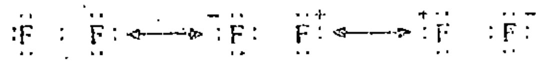
3) Lewis structure for nitrate ion is



The resonance structures are :

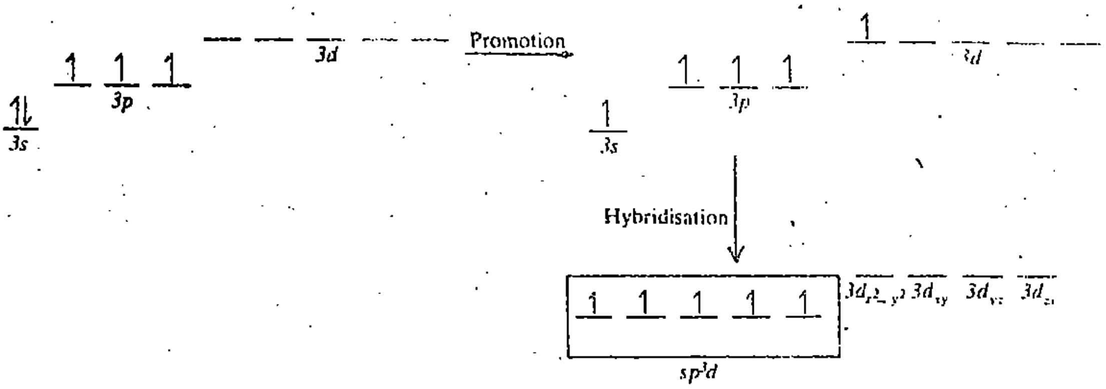


4) The $2p_z$ electrons in the two fluorine atoms get paired to give fluorine molecule. The following resonance structures are possible :



5)

P
(Ground state)
($1s^2 2s^2 2p^6$
not shown)



The five unpaired electrons in the sp^3d hybrid orbitals pair up with five unpaired electrons, one from each of the five chlorine atoms.

6) **Similarities :**

i) Both have sp^2 hybridised carbon atoms.

ii) Both have bond angle of 120°.

Dissimilarities :

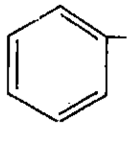
i) Carbon-carbon bond lengths are different in the two molecules.

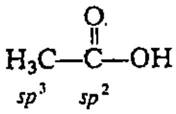
ii) Ethylene has localised π electrons while benzene has a delocalised π electron structure.

Terminal Questions

1) Molecular wave functions are formed and E vs R curves are drawn. The wave function giving E and R values, agreeing closely with experimental bond energy and bond distance, is taken as the acceptable wave function. The structural features assumed in arriving at the wave function are assumed to be correct.

2) i) $\underset{sp^3}{H_3C} - \underset{sp^2}{CH} = \underset{sp^2}{CH_2}$

ii)  $-\underset{sp}{C} \equiv \underset{sp}{CH}$; all the carbon atoms of benzene ring are sp^2 hybridised.

iii) 

$\underset{sp^3}{H_3C}-\underset{sp^2}{\overset{\overset{O}{\|}}{C}}-OH$

3) Tetrahedral on the basis of both the concepts.

4) (a) F (b) T (c) F (d) T (e) F.

5) *sp* hybridisation; its structure is linear.

6) The bond lengths are given in Table 4.4.

$\underset{4}{CH_3} - \underset{3}{CH_2} - \underset{2}{CH} = \underset{1}{CH_2}$: $C_1 - C_2$ 134 pm;
$C_2 - C_3$ 150 pm;
$C_3 - C_4$ 154 pm.

$\underset{4}{CH_3} - \underset{3}{CH} = \underset{2}{CH} - \underset{1}{CH_3}$: $C_1 - C_2$ 150 pm;
$C_2 - C_3$ 134 pm;
$C_3 - C_4$ 150 pm.

7) Carbon atom is *sp* hybridised.

UNIT 5 MOLECULAR ORBITAL THEORY

Structure

5.1 INTRODUCTION

You have learnt in Units 1 and 2 the basic concepts of atomic structure and you know that the electrons occupy different orbitals namely *s*, *p*, *d*, and *f*, depending upon their energy. These orbitals are filled up in accordance with various rules like Pauli's exclusion principle, *aufbau* principle and Hund's rule. Let us now extend these ideas to molecules and try to understand the molecular structure on the basis of formation of molecular orbitals. When we talk about molecules, we know that molecules are made of atoms and in a molecule, the constituent atoms are held together by forces of attraction. In ionic compounds, these forces of attraction are electrostatic in nature. In case of covalent molecules, the atoms share the electron pairs. In the last unit, the formation of covalent linkage has been explained on the basis of valence bond theory. You will now study an alternative approach for the formation of molecules which is called Molecular Orbital Theory. Here you will learn how electrons are assigned into various molecular orbitals in homonuclear and heteronuclear diatomic molecules.

Objectives

After studying this unit, you should be able to :

- state the principles of molecular orbital theory and linear combination of atomic orbitals,
- define bonding, antibonding and nonbonding orbitals,
- illustrate the various combinations of *s* and *p* orbitals with diagrams,
- write the various molecular orbitals in a homonuclear diatomic molecule according to the increasing order of energy and draw their energy level diagram,
- state the molecular orbital configuration for simple homonuclear diatomic molecules, and
- predict the electron configuration for simple heteronuclear diatomic molecules.

5.2 MOLECULAR ORBITAL THEORY

A molecule is defined as a stable combination of two or more atoms. By stable combination, we mean that when two atoms form a molecule, the energy of the new entity is less than the sum of the energies of the isolated atoms. In case the atoms constituting a molecule are identical, they form the homonuclear molecules and examples are molecules of various elements, like H_2, N_2 and O_2. In other cases, when the atoms constituting a molecule are of different elements, they form heteronuclear molecules; examples being the molecules of compounds, like HCl and H_2O. Molecules of varying complexities exist in nature including the simple ones like CO_2, SO_2, CH_4, NH_3 and the complex polyatomic molecules like proteins and carbohydrates. Whatever be the nature of molecules, they are built up from the atoms according to certain basic laws. In the last unit you have already read about the valence bond approach. Let us now study the molecular orbital theory which also deals with the formation of the molecules from the atoms from a different angle.

Consider a system in which the nuclei are in their equilibrium positions and the electrons occupy the molecular orbitals. These molecular orbitals are similar to atomic orbitals. The procedure for constructing the molecular orbitals is given below :

1) The molecular orbital will be polynuclear, i.e., it will be associated with all the nuclei present in the molecule and the wave function for the molecular orbital will have the same significance that it has for the atom, i.e., $\psi^2\, d\tau$ is proportional to the probability of finding the electron in a given volume $d\tau$. Each electron is placed in a molecular energy level or orbital which is determined by the sets of various quantum numbers.

2) Each molecular wave function corresponds to a definite energy value and the sum of the individual energies of electrons in the molecular orbitals, after correction for interaction, represents the total energy of the molecule.

3) The electrons occupy the available molecular orbitals one at a time; the lowest energy molecular orbital being filled first. In assigning configuration to the electrons, the *aufbau* principle and Hund's rule are applied. Also, according to the Pauli's exclusion principle, each molecular orbital can accommodate a maximum of two electrons, provided their spins are opposite.

We can write Schrödinger equation for molecules also, as in case of atoms. Again, the exact solutions cannot be obtained and some approximations are to be made. There are two approximation methods, one is linear combination of atomic orbitals or the LCAO method and the other is United Atom method. We will study only the LCAO method.

5.2.1 LCAO Method

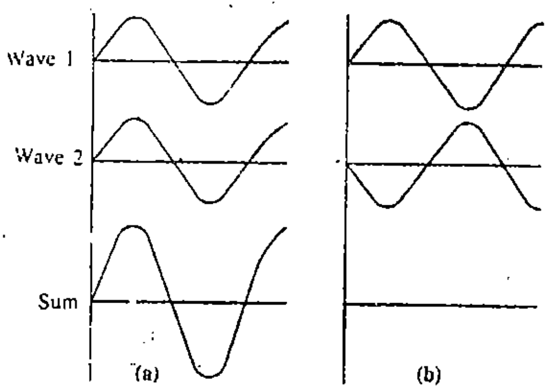
Consider two atoms A and B having atomic orbitals of similar energy and described by the wave functions ψ_A and ψ_B, respectively. When these atoms form a bond, the electrons of the atoms occupy molecular orbitals. These molecular orbitals can be written using linear combination of atomic orbitals. The number of molecular orbitals produced is always equal to the sum of the number of atomic orbitals involved. Hence, we can write the molecular orbitals as

$$\psi_{(g)} = \psi_A + \psi_B \qquad \ldots (5.1)$$

$$\psi_{(u)} = \psi_A - \psi_B \qquad \ldots (5.2)$$

where 'g' stands for **gerade** (even) and 'u' for **ungerade** (odd). The letters *g* and *u* refer to the symmetry of the orbitals about its centre. If the sign of the wave function ψ is unchanged when the orbital is reflected about its centre (i.e., axes *x, y* and *z* are replaced by $-x$, $-y$ and $-z$), it is called **gerade**. If you recall the types of atomic orbitals from Unit 2 (Fig. 2.11), you will agree that *s* orbital is symmetrical about its centre; hence it will be **gerade**. Similarly, an **ungerade** orbital is one which changes sign on reflection about the centre; for example, each *p* orbital having lobes with different signs (Fig. 2.11, Unit 2) is **ungerade.** Can you guess about the *d* orbitals? Yes, they are all **gerade.**

Let us assign a positive sign for ψ_A. Then, ψ_B may be positive or negative. Wave functions of the same sign represent the waves that are in phase and such waves combine by constructive interference to give a wave, whose amplitude is the sum of ψ_A and ψ_B at every point (Fig. 5.1a). Similarly, wave functions of opposite sign represent the out of phase waves which on combination will cancel each other by destructive interference (Fig. 5.1b).



(a) (b)

Fig. 5.1 : Superposition of Waves (a) Constructive interference (b) Destructive interference.

When ψ_A and ψ_B having same symmetry combine, the resulting molecular orbital would be $\psi_{(g)}$, leading to an increased electron density in between the nuclei. This is called the **bonding molecular orbital** and it is lower in energy than the atomic orbitals ψ_A and ψ_B. Conversely, $\psi_{(u)}$ will result when ψ_A and ψ_B, having different symmetry, combine, resulting in zero electron density in between the nuclei. This type of molecular orbital is known as the **antibonding molecular orbital** and it is higher in energy, as compared to the atomic orbitals ψ_A and ψ_B. We can represent these ideas pictorially using Fig. 5.2.

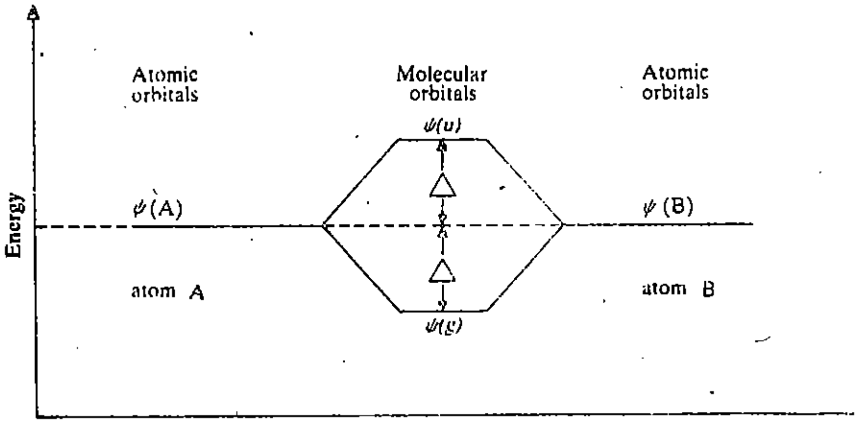


Fig. 5.2 : Energy levels of atomic and molecular orbitals.

The energy of the bonding molecular orbital $\psi_{(g)}$ is lower than that of the constituent atomic orbitals by an amount Δ, known as the **stabilisation energy**. Similarly the energy of the antibonding molecular orbital is higher by the same amount Δ, as compared to the parent atomic orbitals. Let us now study how the various combinations of *s* and *p* atomic orbitals yield different type of molecular orbitals.

s – *s* Combination of Orbitals

Consider the case of hydrogen molecule ion, H_2^+. This ion exists and can be detected spectroscopically when hydrogen is subjected to electrical discharge under reduced pressure. It has a bond length of 106 pm and a bond energy of 269.5 kJ mol^{-1}. Here, there are two protons and one electron; ψ_A and ψ_B in this case are two 1*s* orbitals. Their linear combination will produce two molecular orbitals: one bonding and the other antibonding. The single electron in the ground state occupies the bonding orbital. You can visualise the shape of molecular orbitals formed by the combination of two 1*s* orbitals as shown in Fig. 5.3.

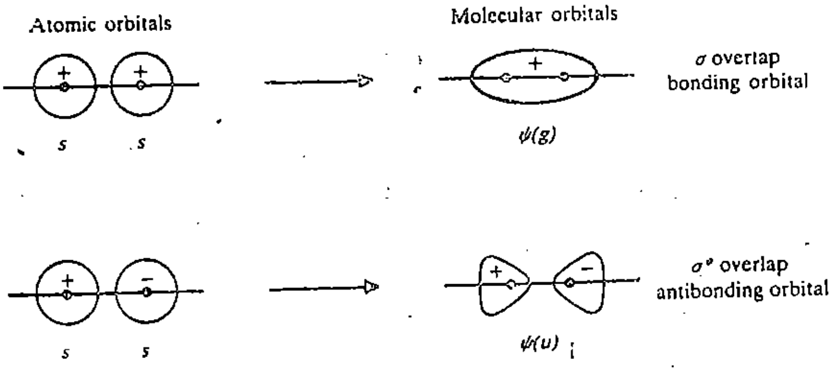


Fig. 5.3 : *s*–*s* combination of atomic orbitals.

We represent the molecular orbitals formed from the 1*s* orbitals as σ 1*s* and σ* 1*s*. The former is a bonding orbital and the latter, an antibonding orbital. One typical feature of σ orbitals is that they are symmetrical about the molecular axis. The electron probability density graphs for bonding and antibonding combinations are given in Fig. 5.4.

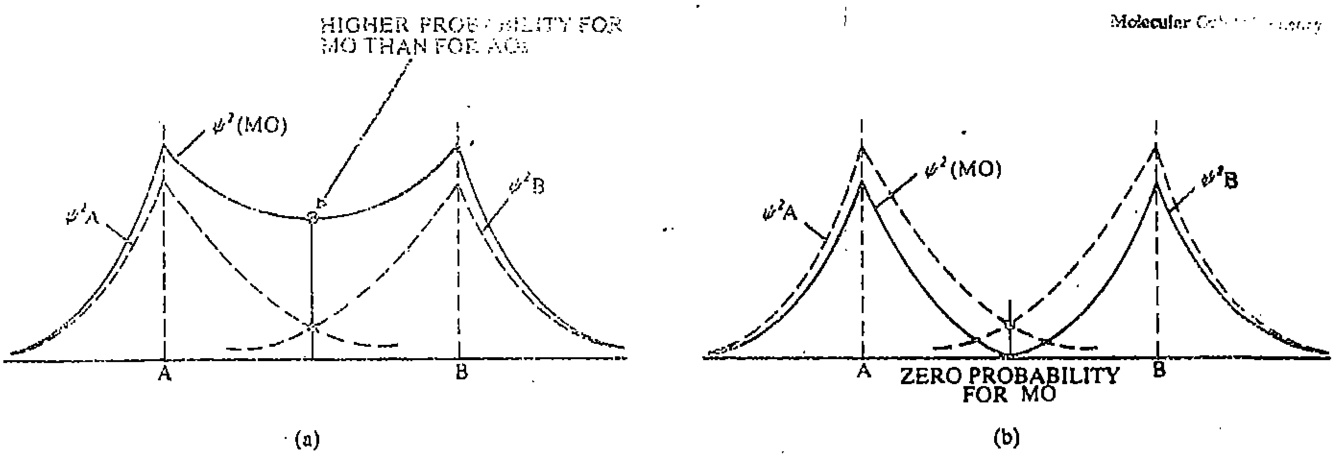


Fig. 5.4 : (a) Individual electron densities of atoms A and B and bonding orbital showing increased electron density between the atoms A and B.

(b) Antibonding orbital showing decreased electron density between the atoms A and B.

$s-p$ Combination of Orbitals

Next let us study the molecular orbitals obtained by the combination of s and p atomic atomic orbitals. There are three equivalent p orbitals for a given principal quantum number, namely p_x, p_y and p_z. An s orbital may combine with a p orbital, provided that the lobes of the p orbital are pointing along the axis joining the nuclei. Let us first consider the $s-p_x$ combination. When the lobes of s and p_x orbitals have the same sign, the molecular orbital produced is bonding molecular orbital, whereas the antibonding molecular orbital results when the lobes are of opposite sign (Fig. 5.5). The other combinations, i.e., combination of s orbital with p_y and p_z orbitals will be discussed later.

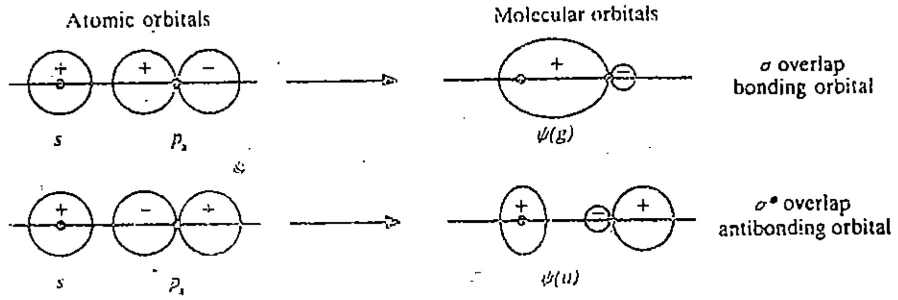


Fig. 5.5 : s-p_x combination of atomic orbitals.

You have already studied in Unit 2 that + and – signs of the orbitals refer to the symmetry of the wave function and have nothing to do with the electrical charges because the electron cloud is always negatively charged.

Note that the combination of s and p_x atomic orbitals is also leading to σ type of molecular orbitals, as they are symmetric about the internuclear axis.

$p-p$ Combination of Orbitals

As the two lobes of a p orbital are of opposite sign, the combination of two p_x orbitals, which have lobes pointing along the axis joining the nuclei, lead to σ bonding as well as σ^* antibonding orbitals depending on the nature of the signs of the wave functions, Fig. 5.6.

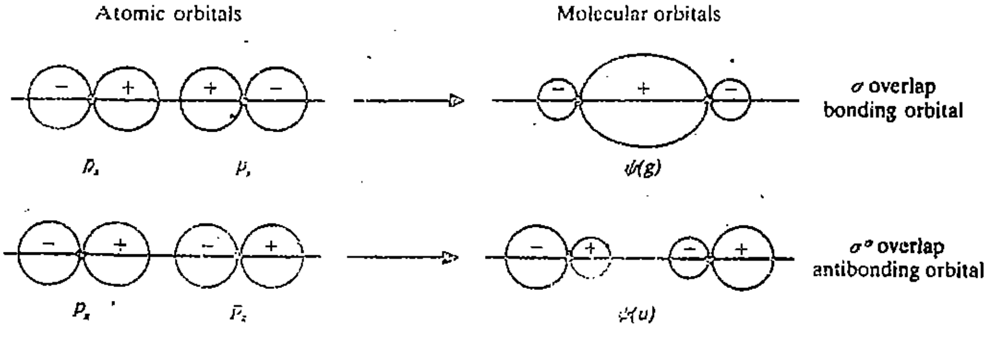


Fig. 5.6 : p_x - p_x combinations of atomic orbitals.

Let us now focus our attention on the combination of two p orbitals which have their lobes perpendicular to the axis joining the nuclei. Lateral overlap of these orbitals will result in the π bonding and π^* antibonding molecular orbitals. Both p_y and p_z orbitals form π and π^* orbitals in the above fashion. In Fig. 5.7, the $p-p$ combination using p_y orbitals is depicted. Similarly, you can draw the π and π^* orbitals using p_z orbitals. You are already familiar (Unit 4) with compounds like ethylene, acetylene and benzene which contain π bonds.

$s-s$, $s-p_x$ and p_x-p_x combinations lead to *sigma* bond formation whereas p_y-p_y and p_z-p_z combinations lead to *pi* bond formation.

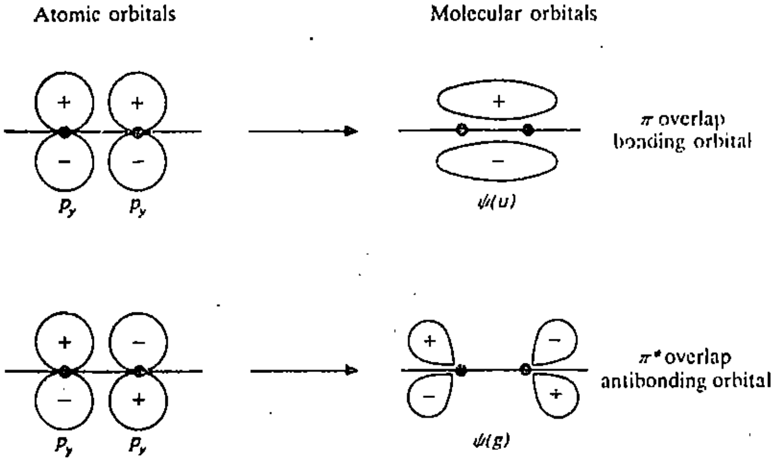


Fig. 5.7 : $p_y - p_y$ combination giving *pi* bonding.

Similarly, a p orbital can overlap with a d orbital giving bonding and antibonding combinations. The $d-d$ combination of orbitals is also possible and it produces δ bonding and δ^* antibonding orbitals.

Upto this stage, you have learnt about two types of molecular orbitals viz. bonding and antibonding. There is a third category called **nonbonding molecular orbitals** which can be understood when we consider the combination of an $s-p_y$ or $s-p_z$ atomic orbitals as shown in Fig. 5.8.

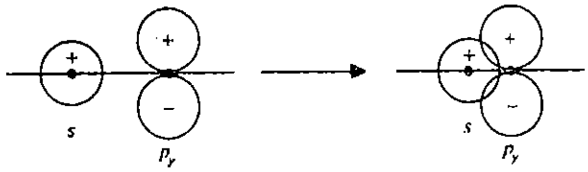


Fig. 5.8 : s and p_y combination of atomic orbitals leading to nonbonding situation; $s-p_z$ combination is also similar.

In this type, any stabilisation from overlaping of + and + parts of atomic orbitals is cancelled by the equal amount of overlaping between + and − parts of atomic orbitals. This evidently indicates that there is no net change in energy and hence no bonding occurs. Thus, this situation is called nonbonding combination of orbitals.

After studying various combinations of atomic orbitals, let us now sum up the rules governing the linear combination of the orbitals.

Rules for Linear Combination of Atomic Orbitals

1) The constituent atomic orbitals mut be of similar energy, i.e., combination of 1s and 2s or 1s and 2p orbitals will not give any effective combination in case of homonuclear diatomic molecules because they are of different energy. However, such combinations may be possible in heteronuclear molecules, since the energies of the orbitals of atoms A and B may become comparable in such cases, e.g., HF molecule.

2) The atoms must be close enough to give effective overlap, i.e., the radial distribution functions $R_{(r)}$ must be similar at this distance. You are already familiar with the radial distribution functions, discussed in Unit 2.

3) In order to produce bonding and antibonding molecular orbitals, either the symmetry of the two atomic orbitals must remain unchanged (as in the case of $p_x - p_x$ combination) when rotated about the internuclear axis, or both atomic

orbitals must change symmetry in an identical manner (as in the case of $p_y - p_y$ or $p_z - p_z$ combinations). For example, in Fig. 5.6 when p_x orbitals are rotated along the internuclear axis, no change in their symmetry is observed, hence the bonding and antibonding molecular orbitals are produced as given in Fig. 5.6. But in the case of $p_y - p_y$ combination of orbitals leading to π bonding, if the p_y orbitals (Fig. 5.7) are rotated about the internuclear axis, the atomic orbitals obtained after rotation will yield the molecular orbital as shown in Fig. 5.9 (a). Similarly the rotation for second possibility will yield the antibonding orbitals for the other combination, Fig. 5.9 (b).

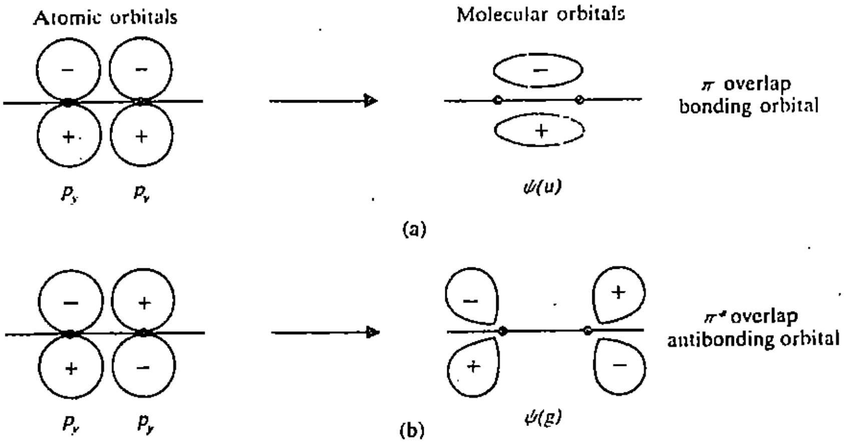


Fig. 5.9 : $p_y - p_y$ combination after rotation of p_y orbitals around the internuclear axis giving : (a) π bonding orbital (b) π^* antibonding orbital.

SAQ 1

Assume that you are starting with two p_y orbitals. Show the type of molecular orbitals formed under the hypothetical situation when only one of the two p_y atomic orbitals changes symmetry, on rotation, about the internuclear axis.

....

....

....

Various molecular orbitals have different energies and are represented by the four quantum numbers similar to atomic orbitals. The principal quantum number, n and the subsidiary or azimuthal quantum number, l are retained from the atomic orbitals and have the same significance here also. But the magnetic quantum number, m_l is replaced by a new quantum number, λ. In case of diatomic molecules, the internuclear axis is taken as the reference axis and the quantisation of angular momentum in $\frac{h}{2\pi}$ units is represented with respect to this axis similar to the case of atoms. λ can take same values for molecules as m_l has for the atoms, i.e., $\lambda = -l \ldots -2, -1, 0, 1, 2, \ldots l$. When $\lambda = 0$, orbitals are symmetrical about the internuclear axis and hence are called σ orbitals. When $\lambda = \pm 1$, orbitals are known as π orbitals. Similarly, $\lambda = \pm 2$, represents the δ orbitals. The spin quantum number, m_s, is similar to that for the atomic orbitals and can take the values ± 1/2.

The order of energy of molecular orbitals has been determined from the spectroscopic data. For homonuclear diatomic molecules the order of increasing energy is

$$\sigma 1s,\ \sigma^* 1s,\ \sigma 2s,\ \sigma^* 2s,\ \sigma 2p_x,\ \left\{ \begin{array}{l} \pi 2p_y \\ \pi 2p_z \end{array} \right. \left\{ \begin{array}{l} \pi^* 2p_y \\ \pi^* 2p_z, \end{array} \right. \sigma^* 2p_x$$

The energy level diagram for homonuclear diatomic molecules is shown, in Fig. 5.10.

Here, the energies of the $\pi 2p_y$ and $\pi 2p_z$ orbitals are the same and hence they are called **degenerate orbitals.** Similarly, $\pi^* 2p_y$ and $\pi^* 2p_z$ orbitals constitute another set of **degenerate orbitals.** The energies of $\sigma 2p_x$ and $\pi 2p_y/\pi 2p_z$ orbitals are very close to one another; in some cases, the above order is reversed, i.e., $\pi 2p_y$ or $\pi 2p_z$ orbitals are lower in energy than $\sigma 2p_x$ orbital.

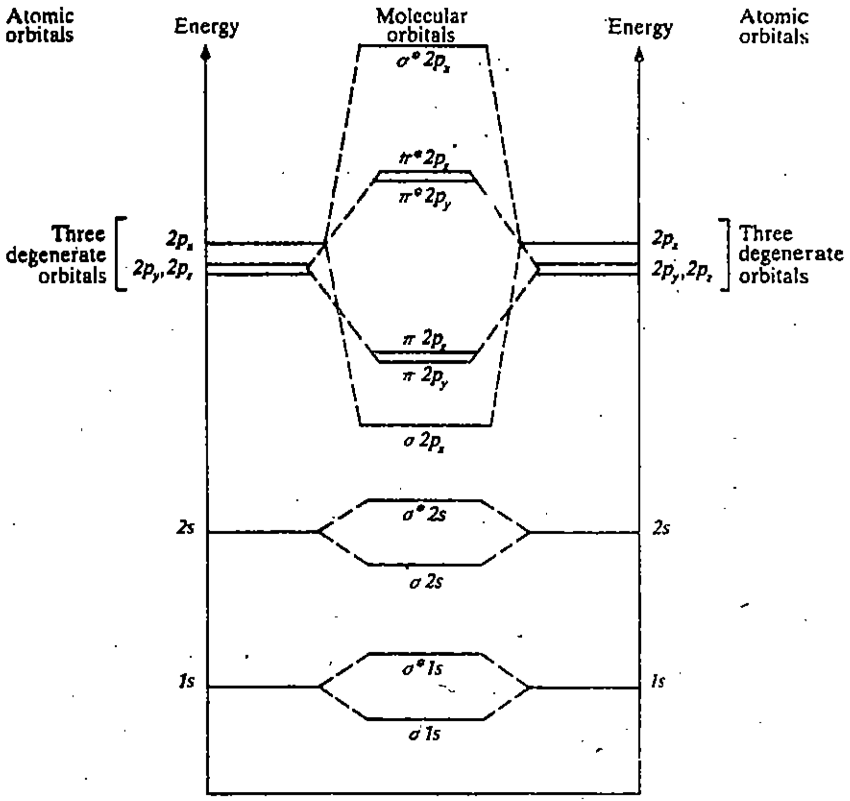


Fig. 5.10 : Energy pattern for homonucleur diatomic molecules; although three 2p orbitals are degenerate, for the sake of clarity, p_x has been shown slightly above p_y and p_z orbitals.

SAQ 2

Fill in the blanks using appropriate words:

i) In case of σ overlap, the lobes of atomic orbitals point .... the internuclear axis whereas for π overlap, the lobes are .... to the line joining the nuclei.

ii) In contrast to σ orbitals, π orbitals have both ψ and ψ^2 .... along the internuclear axis.

SAQ 3

Classify the following molecular orbitals as **gerade** or **ungerade** :

i) π bonding orbital
ii) σ bonding orbital
iii) σ* antibonding orbital
iv) π* antibonding orbital

5.3 HOMONUCLEAR DIATOMIC MOLECULES

By now, you are familiar with many details of the LCAO method. Let us apply these ideas to some simple homonuclear diatomic molecules, i.e., the molecules containing both the atoms of the same nuclei.

H_2^+ molecular ion – As studied before, it has only one electron, so you can write its molecular orbital configuration as $\sigma 1s^1$. This means, H_2^+ ion has one electron in σ 1s bonding orbital.

H_2 molecule – Each hydrogen atom contributes one electron. So the two electrons go to the lower energy σ1s bonding orbital and the electron configuration can be written as $\sigma 1s^2$. The bond energy of H_2 is 436 kJ mol^{-1} and bond length is 74 pm. On comparing these data with those of H_2^+ given in section 5.2.1, you will realise that placement of an additional electron in the bonding σ1s orbital of the H_2 molecule has resulted in a more stable arrangement; hence, the bond energy of H_2 is more and bond length is less than those of H_2^+ ion.

He_2^+ Ion – Since He_2^+ has three electrons, the configuration is $\sigma 1s^2, \sigma^* 1s^1$. Here, one electron is in antibonding orbital and it reduces the bond strength. The bond energy in this case is 238 kJ mol^{-1} and the internuclear distance is 108 pm.

He_2 – Theoretically, each He atom contributes two electrons giving a total of four electrons which can be accommodated into the orbitals as $\sigma 1s^2, \sigma^* 1s^2$.

Since both the bonding and antibonding orbitals are equally filled, there is no net decrease in energy as compared to the helium atoms and hence, He_2 does not exist under ordinary conditions.

We can introduce a term **bond order** here. As you know, the two bonding electrons constitute a bond; the bond order is given as one half the difference between the number of bonding electrons (N_b) and the number of antibonding electrons (N_a), i.e.

A stronger bond has higher bond energy and lower bond length.

Bond Order $= \frac{1}{2}(N_b - N_a)$

For He_2, N_b and N_a are both equal to two; hence bond order $= \frac{1}{2}(2-2) = 0$, i.e., there is no bond between the two He atoms and He_2 does not exist. However, He_2 is detected in discharge tubes and is formed there due to the promotion of two electrons from $\sigma^* 1s$ level to $\sigma 2s$ level. Thus, it has a configuration

$\sigma 1s^2, \sigma 2s^2$

which corresponds to higher energy than that of two normal uncombined helium atoms. But it appears to be more stable than two separate excited atoms.

Li_2 – Each lithium atom has two electrons in its inner 1s orbital and one in the outer 2s orbital, making a total of six electrons in Li_2 which can be arranged as

$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2$

The filled $\sigma 1s$ and $\sigma^* 1s$ molecular orbitals do not contribute to the bonding as explained in the case of He_2. The electrons in these orbitals could be collectively represented as *KK* and hence the configuration of Li_2 is $KK, \sigma 2s^2$. Here, bonding occurs due to the filling of $\sigma 2s$ orbital and Li_2 has been found to exist in the vapour state.

Be_2 — Combination of four electrons from each Be atom leads to eight electrons in Be_2 molecule which can be arranged as $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2$, or $KK, \sigma 2s^2, \sigma^* 2s^2$. Again, the effect of bonding and antibonding 2s levels would cancel each other, so there is no net stabilisation and the molecule would not be expected to be stable.

B_2 — B_2 molecule has a total of ten electrons and the molecular orbital configuration is

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \begin{cases} \pi 2p_y^1 \\ \pi 2p_z^1 \end{cases}$$

Note that the $\pi 2p$ orbitals here are lower in energy than $\sigma 2p_x$ orbital. Since $\pi 2p_y$ and $\pi 2p_z$ are degenerate, they are singly occupied in accordance with the Hund's rule. Here, the stabilisation occurs due to the filling of $\pi 2p$ orbitals and B_2 molecule is known to exist.

C_2 molecule — It has 12 electrons, each carbon atom contributing six electrons to the molecule. So filling of molecular orbitals can be represented as,

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2 \end{cases}$$

Here again, as in the case of B_2, the $\pi 2p$ orbitals are lower in energy as compared to $\sigma 2p_x$ orbital which is in contrast to the general order of filling of electrons in molecular orbitals according to the sequence given before.

In case of B_2 and C_2, $\sigma 2p_x$ is of higher energy as compared to the $\pi 2p_y$ and $\pi 2p_x$ orbitals due to the repulsion among 2s and $2p_x$ orbitals as they tend to occupy the same region of space. This effect decreases for the higher elements and in O_2 and F_2, $\sigma 2p_x$ orbital is of lower energy than $\pi 2p_y$ and $\pi 2p_x$ orbitals.

N_2 molecule — In the nitrogen molecule, there are fourteen electrons arranged in the molecular orbitals as,

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2, \begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2 \end{cases}$$

Assuming that the inner orbitals do not participate in bonding, stabilisation will be produced by filling six electrons in the bonding $\sigma 2p_x$, $\pi 2p_y$ and $\pi 2p_z$ orbitals. Hence, the bond order will be $\frac{1}{2}(N_b - N_a) = \frac{1}{2}(6 - 0) = 3$.

O_2 — Each oxygen atom has eight electrons, making a total of sixteen electrons for the molecule, which can occupy the molecular orbitals as

$$\sigma 1s^2,\ \sigma^* 1s^2,\ \sigma 2s^2,\ \sigma^* 2s^2,\ \sigma 2p_x^2 \left\{ \begin{array}{l} \pi 2p_y^2 \\ \pi 2p_z^2 \end{array} \right. \left\{ \begin{array}{l} \pi^* 2p_y^2 \\ \pi^* 2p_z^2 \end{array} \right.$$

Paramagnetic substances are those which have unpaired electron spins and they have a tendency to be drawn into a magnetic field.

The $\pi^* 2p_y$ and $\pi^* 2p_z$ orbitals are singly occupied according to the Hund's rule. Since the two unpaired electrons have parallel spins, oxygen is paramagnetic in nature.

Bond order in oxygen molecule is two because there are six electrons in $\sigma 2p_x$ and $\pi 2p$ bonding orbitals and two electrons in the π^* antibonding orbitals.

F_2 — Fluorine molecule has a total of eighteen electrons and the filling of molecular orbitals can be represented as,

$$\sigma 1s^2,\ \sigma^* 1s^2,\ \sigma 2s^2,\ \sigma^* 2s^2,\ \sigma 2p_x^2 \left\{ \begin{array}{l} \pi 2p_y^2 \\ \pi 2p_z^2, \end{array} \right. \left\{ \begin{array}{l} \pi^* 2p_y^2 \\ \pi^* 2p_z^2 \end{array} \right.$$

The inner shell is nonbonding and the filled bonding $\sigma 2s$, $\pi 2p_y$, $\pi 2p_z$ orbitals are cancelled by their corresponding antibonding orbitals. This leaves only filled $\sigma 2p_x$ orbital to contribute for bonding. Since there are two electrons in the bonding $\sigma 2p_x$ orbital, bond order is one.

In Unit 3, sections 3.4.2 and 3.4.3, we have indicated that as the bond order increases, bond length decreases and bond energy increases; the same principle has again been stressed in section 4.7 of Unit 4. Molecular orbital theory predicts bond orders of fluorine, oxygen and nitrogen as 1, 2 and 3, respectively. You can see from Table 5.1 that this prediction is in keeping with the bond length and bond energy values of the molecules.

Table 5.1 : Bond Length, Bond Energy and Bond Order

Molecule	Bond order as per M.O. theory	Experimental Values	
		Bond Length (pm)	Bond Energy (kJ mol^{-1})
F_2	1	144	155
O_2	2	121	497
N_2	3	110	945

SAQ 4
Calculate the bond order for the following :
a) H_2^+ b) H_2 and c) He_2^+.

SAQ 5
Which of the following is paramagnetic and why?
a) O_2 b) O_2^{2-}.

5.4 HETERONUCLEAR DIATOMIC MOLECULES

The principles which apply to the homonuclear molecules are valid for heteronuclear molecules also. You may recollect that heteronuclear molecules contain two different nuclei. To form the molecular orbitals, the atomic orbitals must have

1) similar energies
2) charge clouds that overlap as much as possible, and
3) the same symmetry properties with respect to the internuclear axis.

Let us consider HF molecule. The electron configuration of the constituent atoms are

H $1s^1$
F $1s^2 2s^2 2p^5$

The inner $1s$ and $2s$ electrons of fluorine do not participate in bonding since they are much lower in energy as compared to the $1s$ orbital of hydrogen. The effective overlap is possible between $1s$ orbital of hydrogen and only $2p_x$ orbital of fluorine because the $2p_x$ orbital points along the internuclear axis. This leads to the bonding and antibonding molecular orbitals as shown earlier in Fig. 5.5 for $s - p_x$ combination of orbitals. The other possibilities, i.e., $s - p_y$ and $s - p_z$ combinations will lead to the nonbonding situation as was shown earlier in Fig. 5.8. Thus, we can write the configuration of ten available electrons in HF molecule as,

$\sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2, \sigma 2p_x{}^2$

As the electrons in the inner $\sigma 1s$ and σ^*1s orbitals do not participate in bonding and $\sigma 2s$ orbital is cancelled by the filling of σ^*2s orbital; the two electrons in the bonding $\sigma 2p_x$ orbital lead to the bond order of one.

Bond Order $= \frac{1}{2}(N_b - N_a)$
$= \frac{1}{2}(2 - 0) = 1.$

Let us next consider CO molecule. Carbon and oxygen atoms supply six and eight electrons, respectively, making a total of fourteen electrons which can be arranged as

$$\sigma 1s^2, \sigma^*1s^2, \sigma 2s^2, \sigma^*2s^2, \begin{cases} \pi 2p_y^2, \\ \pi 2p_z^2 \end{cases} \sigma 2p_x^2$$

Again, the inner electrons do not contribute to bonding and $\sigma 2s^2$ orbital is cancelled by σ^*2s^2. We are now left with six electrons in the bonding $\sigma 2p_x$, $\pi 2p_y$ and $\pi 2p_z$ orbitals. This leads to a bond order of 3. Here, due to different electronegetivities of carbon and oxygen, the constituent atomic orbitals are of different energies, i.e., the $2s$ atomic orbital of oxygen is lower in energy than the analogous carbon orbital, Fig. 5.11.

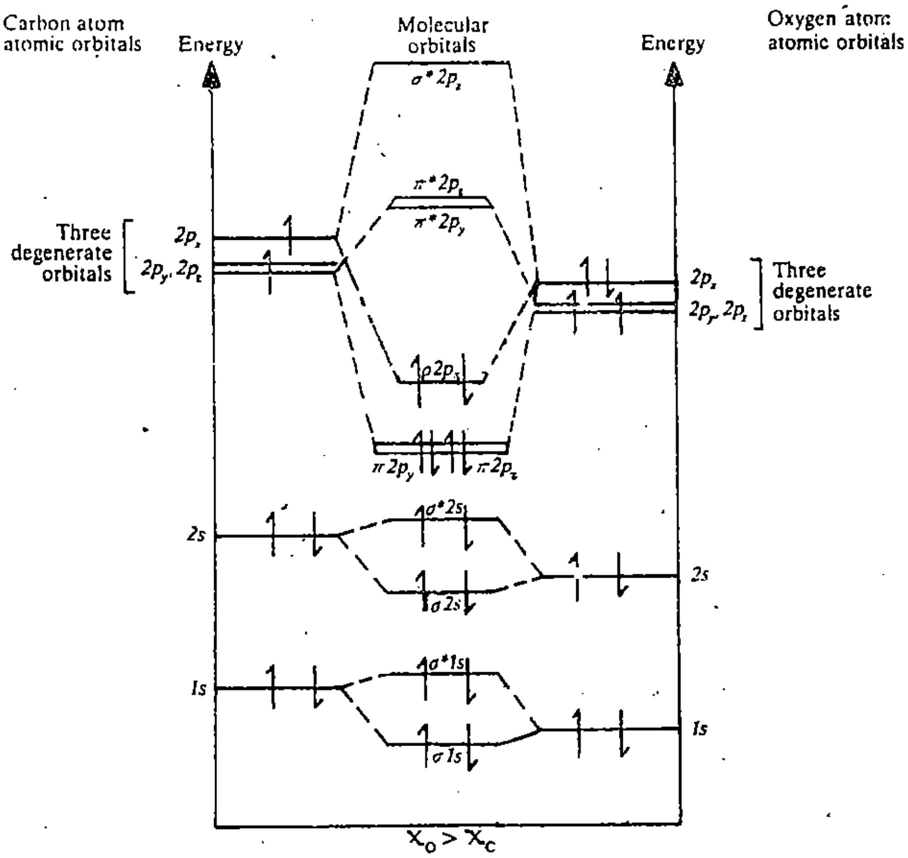


Fig. 5.11 : Molecular orbitals for carbon monoxide.

Note that the bonding $\pi 2p$ orbitals of Carbon monoxide are lower in energy than the $\sigma 2p_x$ orbial.

In case of **NO molecule** nitrogen has seven electrons and oxygen has eight electrons. So, the NO molecule has a total of fifteen electrons for which the molecular orbital configuration can be given as.

$$\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x{}^2 \begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2, \end{cases} \begin{cases} \pi^* 2p_y^1 \\ \pi^* 2p_z^0 \end{cases}$$

The energy pattern for this molecule is shown in Fig. 5.12.

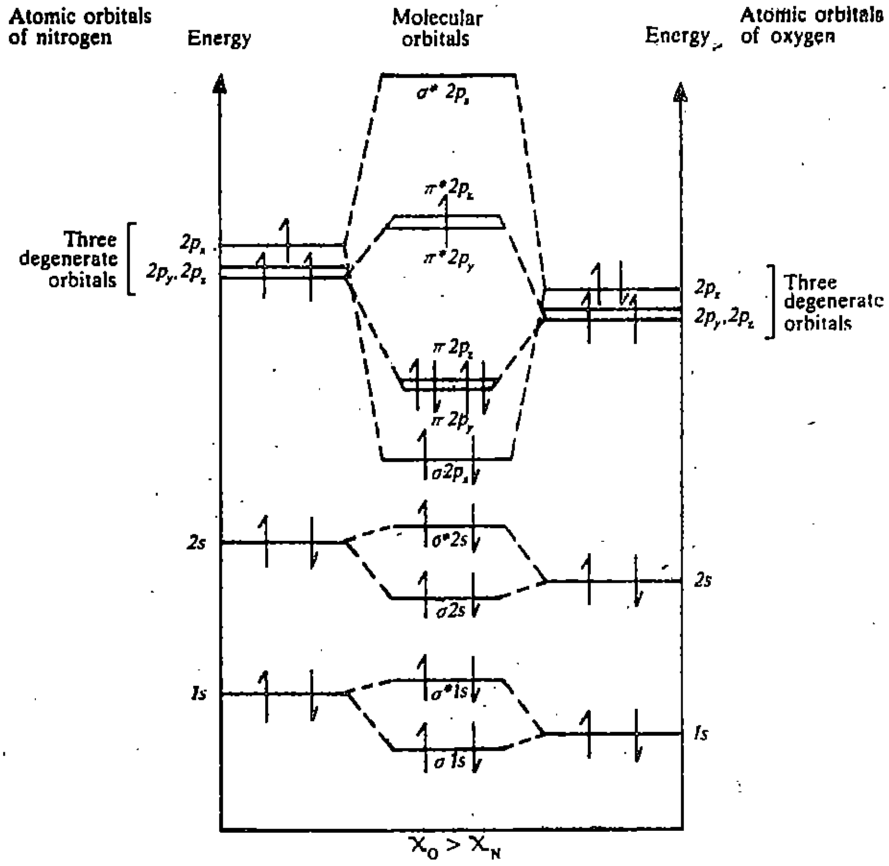


Fig. 5.12 : Energy pattern for NO molecule.

SAQ 6

a) Calculate the bond order of NO molecule.

……………………………………………………………………………………………

……………………………………………………………………………………………

……………………………………………………………………………………………

b) State whether NO is paramagnetic or not.

……………………………………………………………………………………………

5.5 COMPARISON OF VALENCE BOND AND MOLECULAR ORBITAL THEORIES

You have studied in the last unit about the valence bond theory and you are now familiar with the molecular orbital approach also. Let us now compare these two approaches. The principles which govern the filling of orbitals in both the theories are same, i.e., Hund's rule and *aufbau* principle. The valence bond theory retains the individuality of the atoms but the bonding is described in terms of the pairing of unpaired electrons. The molecular orbital theory states that molecular orbitals are formed by the linear combination of atomic orbitals. These molecular orbitals are similar to the atomic orbitals but they encompass all the nuclei and hence are polycentric in nature. Thus, according to this approach the atoms do not retain their individuality and all the nuclei are assumed to behave as a single unit around which the electrons are present in molecular orbitals. This approach uses the linear combination of atomic orbitals or the LCAO method, whereas the valence bond approach utilises the resonance and hybridisation concepts to explain the structures of molecules. However, unlike the valence bond theory, the molecular orbital theory explains the paramagnetic character of oxygen molecule on the basis of the presence of two unpaired electrons.

The molecular orbital treatment gives an equal weightage to the ionic and covalent structures, whereas in valence bond treatment, the contribution of ionic and covalent structures is not equal.

5.6 SUMMARY

You have learnt in this unit about the molecular orbital theory which involves the linear combination of atomic orbitals to give molecular orbitals. You studied about various combinations of *s* and *p* atomic orbitals to yield bonding, antibonding and nonbonding orbitals. Then a description was given regarding the energies of these molecular orbitals and their filling. These ideas were applied to various simple homonuclear and heteronuclear diatomic molecules and electron configurations were assigned to them. The electron configurations were used to calculate the bond order and comparative stability in some cases. Finally, we compared the valence bond approach which you studied in the previous unit, with the molecular orbital theory.

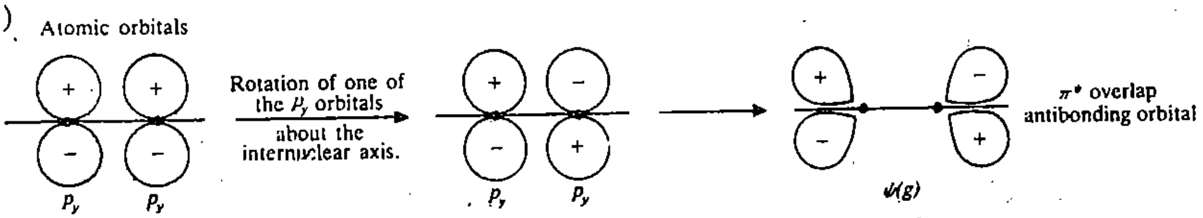
5.7 TERMINAL QUESTIONS

1) Draw $p_y - d_{xy}$ bonding and antibonding molecular orbitals.
2) a) Define bond order.
   b) Calculate the bond order for the following :
      i) He_2^{2+} ii) Li_2
      iii) B_2 iv) C_2
3) Arrange the following in increasing order of stability : O_2, O_2^+, O_2^-, O_2^{2-}.
4) Write molecular orbital configuration of Na_2.
5) Discuss the molecular orbitals of the HCl molecule, considering that the 1*s*, 2*s*, 2*p* and 3*s* atomic orbitals of chlorine are of lower energy as compared to 1*s* atomic orbital of hydrogen.

5.8 ANSWERS

Self Assessment Questions

1)



When only one p_y orbital changes sign on rotation as shown in figure, the resultant combination will lead to the antibonding situation.

2) i) along, perpendicular
   ii) Zero
3) i) Ungerade ii) Gerade
   iii) Ungerade iv) Ungerade
4) (a) ½ (b) 1 (c) ½
5) O_2 – $\sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p^2 \begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2 \end{cases}, \begin{cases} \pi^* 2p_y^1 \\ \pi^* 2p_z^1 \end{cases}$; O_2 has two unpaired electrons

   and hence, paramagnetic. Similarly.

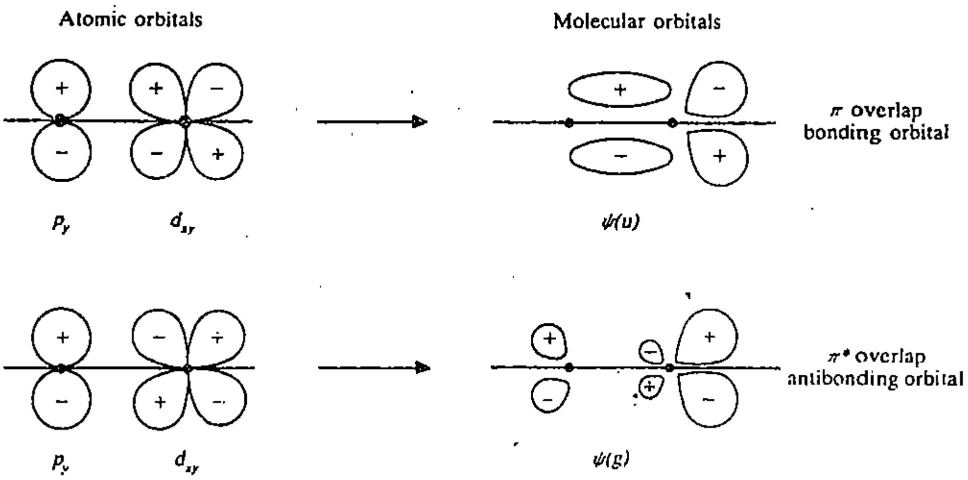
$O_2^{2-} - \sigma 1s^2, \sigma^* 1s^2, \sigma 2s^2, \sigma^* 2s^2, \sigma 2p_x^2 \begin{cases} \pi 2p_y^2 \\ \pi 2p_z^2, \end{cases} \begin{cases} \pi^* 2p_y^2 \\ \pi^* 2p_z^2 \end{cases}$; O_2^{2-} has no unpaired electron and hence, not paramagetic.

6) a) 2.5

b) Paramagnetic due to one unpaired electron in $\pi^* 2p_y$ level.

Terminal Questions

1)



2) (a) It is half the difference of number of electrons occupying bonding and antibonding orbitals.

(b) (i) 1 (ii) 1 (iii) 1 (iv) 2

3) $O_2^{2-} < O_2^- < O_2 < O_2^+$.

Calculate first the bond order which is as follows :

$O_2 - 2$, $O_2^+ - 2.5$, $O_2^- - 1.5$, $O_2^{2-} - 1$
and then arrange according to increasing bond order.

4) Na_2 : KK, LL, $\sigma 3s^2$.

5) Out of the three available $3p$ orbitals of chlorine, the combination of $3p_y$ or $3p_z$ orbital with $1s$ orbital of hydrogen will lead to the nonbonding situation. Hence, effective overlap is possible only with $3p_x$ orbital. Here, all the atomic orbitals of chlorine except $3p_x$ will retain their original atomic orbital status and electrons in $3s$, $3p_y$ and $3p_z$ orbitals will be regarded as nonbonding lone pairs. The combination of $1s$ and $3p_x$ atomic orbitals will give a bonding orbital which is occupied by the two electrons; and the corresponding antibonding orbital is empty. Hence, bond order is one in HCl according to molecular orbital theory.

FURTHER READING

1) *Principles of Physical Chemistry,* Samuel H. Maron and Carl F. Prutton, Oxford and IBH Publishing Co., New Delhi, 4th ed., 1985.

2) *Physical Chemistry,* Gilbert W. Castellan, Narosa Publishing House, Addison — Wesley/Narosa (Indian Student Edition), Delhi, 3rd ed., 1983.

3) *Physical Chemistry,* P.C. Rakshit, Sarat Book House, Calcutta, 5th ed., 1988.

4) *Physical Chemistry through Problems,* S.K. Dogra and S. Dogra, Wiley Eastern Ltd., New Delhi, 1984.

5) *Physical Chemistry — Principles and Problems,* D.V.S. Jain and S.P. Jauhar, Tata McGraw-Hill Pub. Company Ltd., New Delhi, 1988.

Table of SI Units

Physical quantity	Name of the Unit	Symbol
Length, Wavelength	metre	m
Area	metre^2	m^2
Volume	metre^3	m^3
Mass	kilogram	kg
Time	second	s
Density	kilogram metre^{-3}	kg m^{-3}
Velocity	metre second^{-1}	m s^{-1}
Acceleration	metre second^{-2}	m s^{-2}
Force	newton	N = kg m s^{-2}
Work, Energy	joule	J = kg m^2 s^{-2} = N m
Frequency	hertz	Hz = s^{-1}
Temperature	kelvin	K
Amount of a substance	mole	mol
Electric charge	coulomb	C
Electric potential difference	volt	V
Dipole moment	coulomb metre	C m

Table of Physical Constants

Physical Constant	Symbol	Value
Speed of light in vacuum	c	2.998×10^{8} m s^{-1}
Permittivity of free space	ϵ_0 $1/4\pi\epsilon_0$	8.854×10^{-12} C^2 N^{-1} m^{-2} 8.988×10^{9} N m^2 C^{-2}
Charge of the proton	e	1.602×10^{-19} C
Charge of the electron	$-e$	-1.602×10^{-19} C
Planck's constant	h	6.626×10^{-34} J s
Mass of the electron	m	9.109×10^{-31} kg
Avogadro constant	N_A	6.022×10^{23} mol^{-1}
Universal gas constant	R	8.314 J K^{-1} mol^{-1}
Boltzmann constant	k	1.381×10^{-23} J K^{-1}

Greek Alphabets

A	α	Alpha	N	ν	Nu
B	β	Beta	Ξ	ξ	Xi
Γ	γ	Gamma	O	o	Omicron
Δ	δ	Delta	Π	π	Pi
E	ϵ	Epsilon	P	ρ	Rho
Z	ζ	Zeta	Σ	σ	Sigma
H	η	Eta	T	τ	Tau
Θ	θ	Theta	Y	υ	Upsilon
I	ι	Iota	Φ	ϕ	Phi
K	κ	Kappa	X	χ	Chi
Λ	λ	Lambda	Ψ	ψ	Psi
M	μ	Mu	Ω	ω	Omega

Long Form of Periodic Table

(s-block)

p-block elements

d-block elements

1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.90	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.91	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.21	42 Mo 95.94	43 Tc 98.91	44 Ru 101.07	45 Rh 102.91	46 Pd 106.6	47 Ag 107.87	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.90	54 Xe 131.30
55 Cs 132.91	56 Ba 137.34	57 La* 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 197.97	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.98	84 Po 210	85 At 210	86 Rn 222
87 Fr 223	88 Ra 226.03	89 Ac** 227.03	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une									

f-block elements

Lanthanides →	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm 146.92	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.92	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.93	71 Lu [illegible]
** Actinides →	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu 239.05	95 Am 241.06	96 Cm 247.07	97 Bk 249.08	98 Cf 251.08	99 Es 254.09	100 Fm 257.10	101 Md 258.10	102 No 255	103 Lr 257

Logarithms

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											1	2	3	4	5	6	7	8	9
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11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
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42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

											differences								
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55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
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57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
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64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9653	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

Antilogarithms

											differences								
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1302	1306	1309	1312	1315	0	1	1	1	2	2	2	2	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

	0	1	2	3	4	5	6	7	8	9	differences								
											1	2	3	4	5	6	7	8	9
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	3	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

UTTAR PRADESH
RAJARSHI TANDON OPEN UNIVERSITY

UGCHE - 01

Atoms and Molecules

Block

2

STRUCTURE OF MATTER — II

UNIT 6

UNIT 7

UNIT 8

UNIT 9

BLOCK 2 STRUCTURE OF MATTER–II

In Block 1, we started with the ideas of Democritus and Dalton that matter is composed of tiny indivisible particles, called atoms; we then described the development of the theories of atoms and molecules up to the recent times. In this block, which starts with Unit 6, we shall describe some of the physical methods which a chemist uses to determine the structure of molecules and also present some degree of validity of the models of bonding discussed in Block 1.

The physical methods commonly used for investigation of chemical structure are as follows :

i) Methods based on electrical, magnetic and optical properties

ii) Spectroscopic methods

iii) Mass spectrometry

iv) Diffraction methods (using X rays, electron and neutron).

Of the above, we take up only methods (i) and (ii) in this block. The diffraction methods will be taken up in the physical chemistry course and mass spectrometry in the course on spectroscopy along with a detailed account of all the spectroscopic methods.

In Unit 6, we discuss methods of deriving structural information based on electrical, magnetic and optical properties of matter. We explain how the electrical charges and magnetic moments of the molecules respond to the applied electrical and magnetic fields. The study of such responses can provide valuable information about the structure of molecules. The interaction of some types of molecules with plane polarised light has also been discussed.

In Block 1, we described atomic spectroscopy and showed how the frequency of the light absorbed or emitted by an atom is related to the energy difference between the quantum levels of the atom. Spectroscopy is now widely used for the study of the energy levels of the molecules; this particular branch is called molecular spectroscopy. We shall study in Units 7 and 8, how microwave, infrared, ultraviolet and visible spectra can be used to obtain information regarding bond length, moment of inertia, force constant and aspects of molecular structure.

In Unit 9, we discuss some aspects of nuclear chemistry, such as nuclear reactions, radioactive decay series, nuclear energy, uses of radioisotopes and biological effects of radiation. This discussion combined with what we have said about the electronic arrangement in atoms in Units 1 and 2, gives us a complete perspective of the atomic structure.

In short, we describe the structural features of atoms and molecules along with elementary aspects of some physical methods useful in verifying the same.

After studying this block, you should be able to :

- explain the importance of electrical, magnetic and optical characteristics in assigning structure to molecules,
- describe the principles of microwave and infrared spectra with reference to the calculation of bond length and force constant,
- state and explain Beer-Lambert law,
- discuss the importance of ultraviolet and visible spectroscopy in the study of conjugated molecules, and
- explain the main aspects of nuclear chemistry.

UNIT 6 MOLECULAR PROPERTIES

Structure

6.1 INTRODUCTION

The molecules do not move with identity cards, although for our convenience, we would like them to ! However, the molecules don't feel shy to "send" a coded message indicating their building plan and architecture (i.e., bond length, bond angle and spatial arrangement), if a proper situation is created. By situation, we mean exposing the molecules to an energy source such as electric field, magnetic field or electromagnetic radiation (i.e., light). The choice regarding the energy type and its intensity depends on the nature and the capacity of the molecule to interact. In this unit, we discuss three of physical characteristics of the molecules. namely, dipole moment, magnetic susceptibility and specific rotation as an index for the ability of the molecules to interact with electric field, magnetic field and (plane polarised) light, respectively. These three parameters are studied to understand their application in obtaining information regarding molecular structure.

In the next two units, we will take up the spectroscopic methods for unravelling the structure of the molecules. The idea of dipole moment of molecules is necessary to understand spectroscopic transitions.

The development of the theories regarding dipole moment and magnetic susceptibility is based on the analogy between the behaviour of an electric dipole in an electric field and a magnetic dipole in a magnetic field. In order to help you understand this treatment without breaking the continuity in the unit, electric and magnetic parameters along with SI units are explained in the Appendix. **You are advised to get familiarised with these parameters and the SI units before going through this unit.**

Objectives

After studying this unit, you should be able to:

- define a polar and a nonpolar molecule,
- define and explain the term dielectric constant,
- explain the term dipole moment and describe its experimental determination,
- calculate the percentage ionic character in polar molecules,
- estimate the bond angle in simple polar molecules,
- explain three types of magnetic behaviour of substances,
- correlate the paramagnetic molar susceptibility of a substance to the electron configuration,
- compare the experimental and theoretical molar diamagnetic susceptibility values of a substance, as a test for the structure assigned, and
- calculate the specific rotation of an optically active substance.

6.2 POLAR AND NONPOLAR MOLECULES

In Unit 3, you studied the theories of bonding in detail. In homonuclear diatomic molecules, like hydrogen or chlorine, the electrons are shared equally between the two atoms. But when the bonding atoms in a molecule are different, the electrons are not shared equally. The centres of positive and negative charges do not coincide in such a molecule. For example, in hydrogen halides, the halogen atom, being more electronegative than hydrogen, pulls the bonding pair to a greater extent. Thus, the bond is said to have partial ionic character; hydrogen and fluorine in hydrogen fluoride, for example, have partial positive and negative charges (poles), respectively.

Polarity in a chemical bond is due to the difference in electronegativity between the atoms forming the bond.

Hence the molecules like HF and HCl are called polar molecules. In contrast to this, hydrogen and chlorine molecules are called nonpolar molecules. We will define polar and nonpolar molecules based on an electrical property, called dipole moment in Sec. 6.6.1. It is better to introduce the property of matter called dielectric constant in order to help you understand the dipole moment concept.

$^{\delta+}H—F^{\delta-}$

6.3 DIELECTRIC CONSTANT

The polar and nonpolar molecules are collectively known as dielectrics or insulators, since these materials have low electrical conductivity in comparison to that of a metal. Compared to the strength of an electric field in vacuum, it is less in the presence of a dielectric. The electric field is reduced when a dielectric is used, due to the 'polarisation' of the molecules of the dielectric. The term polarisation refers to the disturbance in the positive and negative charge locations. You will study in Sec. 6.5 regarding three types of polarisation.

The ratio of the electric field strength in vacuum to that in a dielectric medium is called the dielectric constant or the relative permittivity (ϵ_r) of the latter. It is also defined as the ratio of the capacitance (C) of a capacitor filled with a dielectric to the capacitance (C_0), when the capacitor is evacuated.

The unit for capacitance is farad (F). 1 F = 1 C V^{-1}

$$\epsilon_r = \frac{C}{C_0} \qquad \ldots(6.1)$$

It is a dimensionless quantity. The dielectric constant for vacuum (also known as free space) is unity. The dielectric constant of air is also nearly unity. Its actual value is 1.00054. The dielectric constant of a substance depends on the temperature, and if an alternating electric field is used, on the frequency of the field. Table 6.1 lists ϵ_r values for some common substances.

Table 6.1 : Dielectric Constant (ϵ_r) Values at 298 K

Dielectric	ϵ_r
Benzene	2.3
$CHCl_3$	4.7
CH_3OH	32.6
Nitrobenzene	34.9
Water	78.3
HCN	107.0
Acetone	20.7

The knowledge of dielectric constant helps in selecting suitable solvents for dissolving compounds. In Unit 3, you have studied that ionic compounds are more soluble in water than in benzene. This is so since solvents with high dielectric constant, like water, decrease the interionic forces of attraction as compared to solvents like benzene.

We will see in Sec. 6.5.2 how dielectric constant measurements are useful in dipole moment calculations.

SAQ 1

The capacitance of a capacitor in vacuum is 8.9×10^{-12} F. When the capacitor is filled with a dielectric, the capacitance is 80.1×10^{-12} F. Calculate the dielectric constant of the dielectric material. (Hint : Use Eq. 6.1).

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6.4 DIPOLE MOMENT – AN EXPLANATION

Let us consider the general case of a chemical bond, constituted by two atoms of different electronegativity. An electric dipole results with charges $+q$ and $-q$ (say) separated by the interatomic distance r (Fig. 6.1).

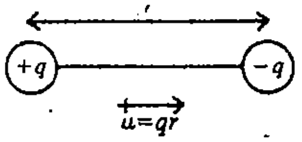

Fig. 6.1 : Representation of a dipole.

A vector quantity, by name, electric dipole moment or simply dipole moment, can be associated with such a system. Dipole moment is represented by the letter μ, and is given by

$$\mu = q\,r \qquad \ldots(6.2)$$

It is diagrammatically represented by an arrow pointing from the positive to negative pole. The SI unit is C m. If a negative charge equivalent to that of an electron (of magnitude 1.602×10^{-19} C) is separated from a positive charge of equal magnitude at a distance of 10^{-10} m, then dipole moment would be

$$\begin{aligned}\mu &= 1.602 \times 10^{-19}\,(\mathrm{C}) \times 1 \times 10^{-10}\,(\mathrm{m}) \\ &= 16.02 \times 10^{-30}\ \mathrm{C\,m}\end{aligned}$$

In literature, the dipole moment values are given in debye (D) units.

$1\ \mathrm{D} = 3.336 \times 10^{-30}\ \mathrm{C\,m}$

In the next section, we study how dipole moment is estimated for polar molecules. You try the following SAQ, using Eq.6.2. It would help you in understanding Sec. 6.6.2.

SAQ 2

The dipole moment and the bond distance in hydrogen chloride are 3.57×10^{-30} C m and 127.5 pm. Calculate the magnitude of charge on hydrogen and chlorine atoms. Compare the result with the charge on the electron.

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6.5 DETERMINATION OF DIPOLE MOMENT

When a polar molecule is subjected to an electric field, the positive and negative charge distribution in the molecule is disturbed which is known as **polarisation**. Polarisation is a threefold disturbance caused by an electric field in a molecule. This disturbance is in the alignment of dipoles, electronic distribution and in the nuclear skeleton. Let us study this in detail.

6.5.1 Molar Polarisation

The polarisation so caused is quantified in terms of molar polarisation (P_M) which is the polarisation for one mole of a substance. Let us consider the three types of polarisation individually.

i) Orientation Polarisation

In the absence of an electric field, due to thermal motions, the molecular dipoles are generally randomly distributed. But the application of an electric field causes the molecular dipoles to **orient** along the field direction. For this reason, this type of polarisation is called orientation polarisation. In other words, the alignment of the dipoles is due to the rotating force, known as **torque**, caused by the electric field. The degree of this alignment would depend upon the strength of the electric field. Also the alignment is affected adversely by an increase in temperature, since it disrupts the orderly arrangement of dipoles. The expression for orientation polarisation, P_0, for one mole (called **molar orientation polarisation**) is given by,

Application of force brings about a linear motion. But torque is applied to bring about circular motion. In opening a door or a screw, you apply, not force, but torque.

$$P_0 = \frac{N_A \mu^2}{9 \epsilon_0 k T} \qquad ...(6.3)$$

Here N_A, μ, ϵ_0, k and T stand for Avogadro number, dipole moment of the molecules constituting the dielectric material, permittivity of vacuum, Boltzmann constant and temperature, respectively.

ii) Distortion Polarisation

This is due to the **distortion of the electronic charge cloud** in a molecule caused by the applied electric field. This polarisation is independent of temperature. Its value depends on the strength of an applied field in distorting the electron cloud of the molecule. The ability of a molecule to undergo distortion of its electronic distribution is called polarisability (α_e). If a molecule contains large atoms with electrons fairly distant from the nucleus, the nuclear control is less, the electron distribution is flabbier and the polarisability is greater. For one mole of the substance, the expression for distortion polarisation (P_D) is given by

Polarisability, α_e, of a molecule speaks of its "willingness" to get its electron cloud deformed by an applied electric field.

$$P_D = \frac{N_A \alpha_e}{3 \epsilon_0} \qquad ...(6.4)$$

iii) Vibrational Polarisation

This is caused by the **deformation of the nuclear skeleton** of the molecule by the electric field. Its value depends on the vibrational polarisability (α_v), which is a measure of the extent to which nuclei can be deformed. Again, the vibrational polarisation for one mole (P_v) is given by,

Distortion polarisation measures the disturbance in the electronic distribution in the molecules whereas vibrational polarisation indicates the dislocation of the nuclei.

$$P_v = \frac{N_A \alpha_v}{3 \epsilon_0} \qquad ...(6.5)$$

The **total molar polarisation** (P_M) of a substance is the sum of P_0, P_D and P_V. Thus, we have,

$$P_M = \frac{N_A}{3 \epsilon_0} \left(\alpha_e + \alpha_v + \frac{\mu^2}{3 k T} \right) \qquad ...(6.6)$$

The unit of total molar polarisation is $m^3 mol^{-1}$.

This equation is useful in the calculation of dipole moment.

6.5.2 Experimental Method

For measurement of dipole moment of a substance, we find the dielectric constant of its vapour (if the substance is volatile or it exists as a gas). The dipole moment of a nonvolatile substance (as well as volatile) can be determined by measuring the dielectric constant of its solutions in a suitable solvent.

For Gases and Vapours: To calculate the dipole moment of gases and vapours, first their dielectric constant (ϵ_r) values are measured at different temperatures. Then, at each temperature, total molar polarisation is calculated from the relationship,

$$P_M = \frac{\epsilon_r - 1}{\epsilon_r + 2}\frac{M}{\rho} \qquad \ldots(6.7)$$

Here M and ρ stand for molecular mass (in kg mol^{-1}) and density (in kg m^{-3}), respectively. Then P_M is plotted against $1/T$, which should yield a straight line as per Eq. 6.6. The slope of this straight line is equal to $\frac{N_A \mu^2}{9 \epsilon_0 k}$

$$\text{Hence, } \mu = \sqrt{\frac{9 \epsilon_0 k \times \text{slope}}{N_A}} \qquad \ldots(6.8)$$

The slope of P_M against $1/T$ plot is to be substituted in Eq. 6.8 to calculate the dipole moment of polar molecules in gas phase.

For Solids and Liquids: In case of solid or liquid substances, molar polarisation values are obtained by an indirect method. This method is based on the assumption that a dilute solution is equivalent to a gas as far as freedom of orientation of the dipoles is concerned. The substance under investigation is to be dissolved in an excess of solvent to have its dilute solution. The molar polarisation of the solvent must be known. The dielectric constant of the solution is to be experimentally determined; by using Eq.6.7, the molar polarisation of the solution has to be found out from which the molar polarisation of the substance can be calculated, after substracting the molar polarisation contributed by the solvent. This has to be repeated for a few temperatures and from the slope of the plot, P_M against $1/T$, the dipole moment of the substance in solid or liquid phase can be calculated.

Having studied the method of finding out the dipole moment of molecules, let us now take up some of its applications. Before that, attempt the following SAQ.

SAQ 3
Using Eq. 6.3, show that molar orientation polarisation has the unit, m^3 mol^{-1}

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6.6 APPLICATIONS OF DIPOLE MOMENT STUDIES

First let us see how dipole moment studies help us redefine polar and nonpolar molecules.

6.6.1 Polar and Nonpolar Molecules Redefined

In Sec. 6.2, we defined polar and nonpolar molecules based on electronegativity. Now let us define them in a different way. In Fig. 6.2, the P_M Vs $1/T$ curves a, b and c are drawn for CH_3Cl, HCl and CCl_4 molecules, respectively.

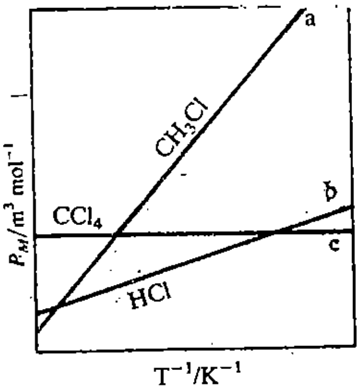


Fig. 6.2 : P_M against $1/T$ plot for CH_3Cl (a), HCl (b), and CCl_4 (c).

You can see that total molar polarisation (P_M) increases with $1/T$ for CH_3Cl and HCl (as shown by the rising curves a and b). That is, for CH_3Cl and HCl, P_M against $1/T$ curves have a **finite, positive slope.** Such a behaviour is characteristic of polar molecules. Since the polar molecules have a finite positive slope for the plot, P_M against $1/T$, these molecules have a finite dipole moment value too, as per Eq.6.8. But, for CCl_4, the molar polarisation is constant at all temperatures (as shown by the curve c which is parallel to x - axis, denoting **zero slope value**), and such molecules are nonpolar.

In other words, for polar molecules, the molar polarisation increases with decrease in temperature; for nonpolar molecules, the molar polarisation does not depend on temperature.

6.6.2 Percentage Ionic Character

In the last sub-section, we defined polar and nonpolar molecules based on dipole moment values. It is interesting to see how percentage ionic character of a polar molecule can be calculated using dipole moment values. Before reading further, if you have not tried SAQ 2 so far, it is worth doing it before proceeding with this section. Consider for example, HCl molecule, for which the observed dipole moment ($\mu_{observed}$) is 3.57×10^{-30} C m. But, if it were 100% ionic, the bonding electron pair should have completely moved to chlorine. Then there should be a negative charge (of magnitude 1.602×10^{-19} C) on chlorine and an equal positive charge on hydrogen, both being separated by the bond distance of 127.5 pm. (Look at your answer for SAQ 2 for the actual charge on hydrogen and chlorine in hydrogen chloride molecule.) For this situation, dipole moment can be calculated using Eq. 6.2 and represented as $\mu_{calculated}$.

A polar molecule has a permanent dipole moment and for a nonpolar molecule, $\mu = 0$.

$$\mu_{calculated} = 1.602 \times 10^{-19}\ (\mathrm{C}) \times 127.5 \times 10^{-12}\ (\mathrm{m})$$

$$= 20.42 \times 10^{-30}\ \mathrm{C\ m}$$

We can estimate the % ionic character using the relationship,

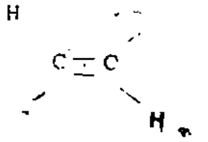
$$\text{Ionic character} = \frac{\mu_{observed} \times 100}{\mu_{calculated}}\ \% \qquad \ldots(6.9)$$

$$\text{Hence, ionic character in HCl} = \frac{3.57 \times 10^{-30}\ (\mathrm{C\ m}) \times 100}{20.42 \times 10^{-30}\ (\mathrm{C\ m})}\ \% = 17.5\%$$

6.6.3 Structure Elucidation

So far we have dealt only with diatomic molecules. For polyatomic molecules, different bonds have different dipole moments. It must be borne in mind that the dipole moment is a vector quantity and it is the vector sum of the bond moments. By bond moment, we mean the moment associated with a chemical bond. Again, the absence of a permanent dipole moment in a molecule may be due to the fact that either all the bonds present are nonpolar or the individual bond moments add vectorially to zero. In the case of a **molecule with a centre of symmetry, dipole moment is zero.** The dipole moment studies are helpful in defining the shape of a molecule. Let us illustrate these principles using simple molecules.

If at equal distances from a particular point in the structure of a substance, you find identical groups in opposite directions, the structure is said to have centre of symmetry. Ethylene molecule has a centre of symmetry. In its structure, atoms which are identical and equidistant from the centre are shown using the same colour.



ethylene

Ethylene: centre of symmetry indicated as a dot in the middle of the double bond.

Perhaps you are curious to know how we would look like, if our body were to have a centre of symmetry. Look at the following figures, each having a centre of symmetry (with two heads and no legs!). Of course, these figures depict one of the possible models.

Are you not happy that our body does not have a centre of symmetry (atleast after seeing their serious faces, although in royal dress) ?

i) Carbon monoxide

It is interesting to note that it has a dipole moment of 4×10^{-31} C m only, whereas the individual C = O bond moment is 7.67×10^{-30} C m. The observed dipole moment of carbon monoxide can be explained only if it has a structure, C = O where oxygen donates a bonding pair to form a co-ordinate bond with carbon. The bond moment of this co-ordinate bond acts in a direction opposite to that of the C = O bond moment, thus resulting in a low dipole moment value of 4×10^{-31} C m.

ii) Let us next take up the structure of carbon dioxide. As said earlier, C = O bond moment ($\mu_{c=o}$) is 7.67×10^{-30} C m. But the dipole moment of carbon dioxide (μ_{CO_2}) is zero. It implies that the two C = O bond moments nullify each other, acting in opposite directions. Again, using the parallelogram law of bond moments (discussed in the Appendix), the bond angle θ can be calculated as follows :

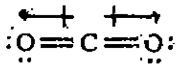
$$\cos\theta = \frac{\mu^2_{CO_2}}{2\mu^2_{c=o}} - 1 \qquad \text{...(6.10)}$$

$$= \frac{[0(C\ m)]^2}{2[7.67 \times 10^{-30}\ (C\ m)]^2} - 1$$

$$= -1$$

$$\theta = \cos^{-1}(-1) = 180°$$

That is, carbon dioxide molecule is linear. It is worth noting that this molecule has a centre of symmetry and evidently its dipole moment is zero.



Carbon dioxide

In the structure of CO_2, the carbon atom is at the centre of symmetry.

iii) Let us now study the structure of water. The bond moment, μ_{O-H} and the dipole moment μ_{H_2O} are reported to be 5.02×10^{-30} C m and 6.14×10^{-30} C m, respectively.

Again using the parallelogram law of bond moments, we can calculate the bond angle θ.

$$\cos\theta = \frac{\mu^2_{H_2O}}{2\mu^2_{O-H}} - 1$$

$$\cos\theta = \frac{\left[6.14 \times 10^{-30}\ (C\ m)\right]^2}{2 \times \left[5.02 \times 10^{-30}\ (C\ m)\right]^2} - 1$$

$$= -0.2520$$

$$\theta = \cos^{-1}(-0.2520) = 104° 36'$$

The above conclusions regarding the shapes of carbon dioxide and water are in keeping with the predictions of VSEPR theory (discussed in Unit 3).

iv) Again based on VSEPR theory, it was mentioned in Unit 3 that boron trifluoride (with three bond pairs) has a planar triangular structure, whereas ammonia (with three bond pairs and one lone pair) has a trigonal pyramidal structure. Based on these structures and the vector addition of moments, boron trifluoride must have zero dipole moment whereas ammonia must have a finite dipole moment. The experimental dipole moment values for boron trifluoride and ammonia are zero and 4.871×10^{-30} C m, respectively. This proves the validity of the shapes of these molecules assigned on the basis of VSEPR theory.

We shall study in the next unit how the presence of dipole moment in a molecule is a key factor for absorption in the microwave region.

SAQ 4

Is it true to say that the dipole moment of sulphur dioxide is zero? (Hint : Use VSEPR theory of sulphur dioxide discussed in Unit 3).

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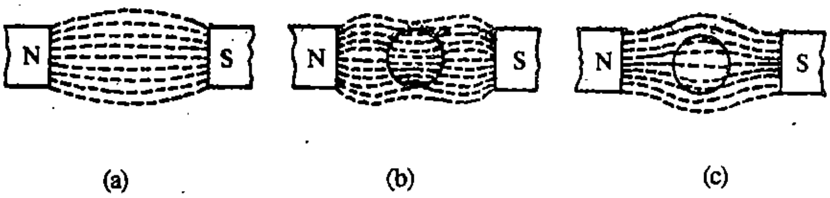
6.7 MAGNETIC PROPERTIES OF MATTER.

The electrical properties of matter arise due to the static distribution of electric charges whereas the magnetic properties are due to the electric currents. It was reported by Oersted that a magnetic field exists around a current-carrying wire. This is true for moving electronic and nuclear charges too. We intend studying the magnetic behaviour as related to the electron configuration of atoms, molecules and ions.

The SI unit of magnetic induction (B_0 or B) is tesla (T).
1 T = 1 N A^{-1} m^{-1}

The number of magnetic lines of force passing through a unit area of a material is called its **magnetic induction.** For vacuum or free space, the magnetic induction is represented by B_0 while for all other materials, it is represented as B. Based on the magnetic behaviour, the substances may be broadly classified into the following types: (i) paramagnetic (ii) diamagnetic and (iii) ferromagnetic. For a paramagnetic material, the number of magnetic lines of force passing through it are more than those passing through free space, i.e., B is greater than B_0. For a diamagnetic substance, B is less than B_0 and for a ferromagnetic material, B is far greater than B_0. For paramagnetic and diamagnetic substances, the magnetic behaviour is pictorially represented in Fig. 6.3. You may note that as compared to free space, the lines of force are more inside a paramagnetic material and less inside a diamagnetic material.



(a) (b) (c)

Fig. 6.3 : Magnetic lines of force: (a) in free space, (b) in paramagnetic substance and (c) in diamagnetic substance.

The differences in magnetic behaviour of substances arise on account of the values for their magnetic susceptibility. Three types of magnetic characteristics along with the range of susceptibility values are given in Table 6.2. It should be understood that the **susceptibility** (χ) measures the ease of magnetisation of a material. It is a dimensionless quantity.

Table 6.2 : Magnetic Characteristics of Materials

Type	Magnetic Induction (B)	Susceptibility (χ)
Paramagnetic	$B > B_0$	small positive value
Diamagnetic	$B < B_0$	small negative value
Ferromagnetic	$B >> B_0$	large positive value

The magnetic properties of a chemical substance are better studied in terms of its **molar magnetic susceptibility** (χ_M) which is given by,

$$\chi_M = \frac{\chi M}{\rho} \quad \text{...(6.11)}$$

where χ, M and ρ refer to the magnetic susceptibility, molecular mass (kg mol^{-1}) and density (kg m^{-3}), respectively. Evidently, χ_M has the unit, m^3 mol^{-1}. Susceptibility measurements are made using Gouy balance. The experimentally measured susceptibility of a paramagnetic substance gives the sum of paramagnetic and diamagnetic susceptibilities, but as the latter is small in comparison with the former, it can be neglected.

Since we want to study the magnetic characteristics of a substance in relation to structure, we consider the behaviour of paramagnetic and diamagnetic substances only.

6.8 PARAMAGNETISM

A species with one or more unpaired electrons shows paramagnetic behaviour. In paramagnetic materials, the individual atoms or molecules or ions have a net magnetic moment because of the spin and orbital motion of electrons. Usually the contribution due to spin is more important than that from the orbital motion.

The magnetic moments of the individual atoms in a paramagnetic bulk are oriented randomly due to thermal motions. Hence under normal conditions such a material does not have any net magnetic moment over its bulk. But when it is subjected to an external magnetic field, the individual magnetic dipoles experience a torque. The magnitude of this torque is given by the product of **magnetic induction** (B) and the **magnetic moment** (m). This helps in aligning the magnetic moment of the molecules or ions in the direction of the external magnetic field. Further this results in a net magnetisation of the sample in the direction of the magnetic field. Note that such an alignment of the magnetic moments of paramagnetic substances in a magnetic field is similar to the alignment of the dipole moments of polar molecules in an electric field.

Magnetic moment is a measure of the magnetic strength of a substance. The unit of magnetic moment is A m^2 or J T^{-1}.

Note that m (italicised) stands for magnetic moment, while m (Roman) is used as a symbol for the unit, metre.

If the torque Bm, is less than the thermal energy kT (where k is Boltzmann constant, equal to 1.381×10^{-23} J K^{-1}), then it is possible to derive the relationship between the molar paramagnetic susceptibility and temperature as given by,

The terms, kT and Bm, refer to thermal and magnetic energies; why don't you substitute the relevant units in the two terms, kT and Bm, and convince yourself that these two have units of energy?

$$\chi_M = \frac{\mu_0 N_A m^2}{3\,kT} \qquad \ldots(6.12)$$

In this expression, μ_0 stands for the permeability of free space and it is equal to $4\pi \times 10^{-7}$ T m A^{-1}. N_A stands for Avogadro constant.

Eq. 6.12 implies that the molar magnetic susceptibility of a paramagnetic material is inversely proportional to its temperature. This is known as Curie's law and it can be indicated by the relationship,

$$\chi_M \propto 1/T \qquad \ldots(6.13)$$

The magnetic moments are usually expressed in A m^2 (equivalent to J T^{-1}) units. In the case of atoms, molecules and ions, unit of magnetic moment is Bohr magneton (μ_B).

$$\mu_B = \frac{e\,h}{4\,\pi\,m_e} \qquad \ldots(6.14)$$

In this expression, e and m_e stand for the charge and mass of the electron, respectively.

$$\therefore\ \mu_B = \frac{1.602 \times 10^{-19}\,(C) \times 6.626 \times 10^{-34}\,(J\ s)}{4 \times 3.142 \times 9.109 \times 10^{-31}\,(kg)}$$

$$= 9.274 \times 10^{-24}\ \frac{C\ J\ s}{kg}$$

but $1\ J = 1\ kg\ m^2\ s^{-2}$ and

$1\ C = 1\ A\ s$

$$\text{Hence, } \mu_B = 9.274 \times 10^{-24}\ \frac{A\ s\ kg\ m^2\ s^{-2} s}{kg}$$

$$= 9.274 \times 10^{-24}\ A\ m^2$$

The magnetic moment due to n unpaired electrons is given by the expression,

$$m = \sqrt{n\,(n+2)}\ \mu_B \qquad \ldots(6.15)$$

In this equation, the magnetic moment due to electron spin alone is considered, since the orbital contribution is much less.

Based on the magnetic properties, there are two spectroscopic methods for structural elucidation – one is **nuclear magnetic resonance,** which depends on the magnetic characteristics of some nuclei and another is **electron spin** resonance based on the magnetic behaviour of odd-electron species.

In Table 6.3, the magnetic moment values in μ_B and A m^2 units are given for different values of n. You can verify the entries in column 2 of this Table by assigning values 1, 2, 3 ...etc., to n in Eq. 6.15.

Table 6.3 : Magnetic Moment (m) Values for Different n Values

Number of unpaired electrons (n)	(Magnetic moment) / μ_B	(Magnetic moment) / 10^{-23} A m^2
1	1.732	1.606
2	2.828	2.623
3	3.873	3.592
4	4.899	4.543
5	5.916	5.486

It is more useful to combine Eqs. 6.12 and 6.15, to get,

$$\chi_M = \frac{\mu_0 N_A n \ (n + 2) \ \mu_B^2}{3 \ k \ T} \qquad \ldots(6.16)$$

It is interesting to see how Eq. 6.16 can be used to predict the number of unpaired electrons in a molecule or ion. In Unit 5, you have studied the structure of oxygen molecule on the basis of molecular orbital theory. The support for this theory, regarding the presence of two unpaired electrons, came from the magnetic susceptibility studies.

The magnetic susceptibility measurements help us in the study of complex compounds. For example, in the case of complex compounds formed from metal ions with d^4, d^5, d^6 and d^7 configurations, two types of electron arrangements are possible for the metal ions. This is due to the fact that in the presence of some ligands, the five degenerate d orbitals are split into sets of three and two orbitals, which are no more degenerate. For example, for a metal ion with d^4 configuration, the two arrangements (i) and (ii) correspond to high spin and low spin values, respectively. The electron configuration of the metal ion (such as (i) or (ii)) depends on factors such as the nature of the ligand. It is possible to decide whether (i) or (ii) is correct by experimentally determining χ_M and then calculating n using Eq. 6.16. In Block 4 of Inorganic Chemistry course, you will study in detail, the applications of magnetic susceptibility in elucidating the structure of metal complexes.

Degenerate orbitals have same energy.

Two arrangements for d^4 configuration :

i) 4 unpaired electrons:
$m = 4.899\ \mu_B$; higher spin

ii) 2 unpaired electrons:
$m = 2.828\ \mu_B$; lower spin value

6.9 DIAMAGNETISM

For a diamagnetic substance, the net magnetic moment over each atom is zero, in the absence of an external magnetic field. This is possible, if the various contributions to the magnetic moment from all the electrons in the atom balance out completely. All diamagnetic atoms or molecules or ions have even number of electrons, although the converse is not true (as in the case of oxygen). **The electron spins in diamagnetic materials are paired.** (Remember the last two statements, while answering SAQ 5.)

Diamagnetism arises due to the fact that the applied magnetic field causes a change in the velocity of the electrons moving about their nuclei. The applied field induces a magnetic field in the substance, which opposes the applied magnetic field; hence diamagnetic susceptibility is negative.

The diamagnetic susceptibility is independent of temperature. Pascal showed that the molar diamagnetic susceptibility can be calculated from atomic and bond contributions. Table 6.4

presents some data for atomic and bond contributions. Note the difference in C=O group susceptibility values, between a ketone and an ester. That is, the susceptibility value of a structural unit depends on its environment. Such a property, which depends on its environment and is also additive, is called an additive and constitutive property. To sum up, the diamagnetic molar susceptibility value is the sum of the susceptibility values of the constituent units, which again depend on their structure.

Table 6.4 : Atomic and Bond Contributions to Molar Diamagnetic Susceptibility; $10^{12}\,\chi_M/\mathrm{m^3\,mol^{-1}}$

H	–2.93	Cl	–20.1
C	–6.00	Br	–30.6
O* (R–OH, R–OR)	–4.61	C=C	+5.5
O (ketone)	+1.73	C=N	+8.2
O (C=O in ester, acid etc.)	–3.36	N=N	+1.9
N (open chain)	–5.57	C≡C	+0.8
N (ring)	–4.61	C=C–C=C	+10.6
N (amines)	–1.54	Benzene ring	–1.4
F	–11.5		

* The contribution to molar diamagnetic susceptibility of C–O bond is same, irrespective of its environment.

To illustrate this, let us calculate χ_M for benzoic acid using Table 6.4. The molecular formula for benzoic acid is C_6H_5COOH. That is, it has 7 carbon atoms, 6 hydrogen atoms, one benzene ring, one C=O bond and one C–O bond. Adding all these contributions.

7 C = $7\,(-6.00\times10^{-12}) = -42.00\times10^{-12}$ $\mathrm{m^3\,mol^{-1}}$

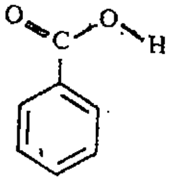
6 H = $6\,(-2.93\times10^{-12}) = -17.58\times10^{-12}$ $\mathrm{m^3\,mol^{-1}}$

1 C–O (same as R–OH) = $1\,(-4.61\times10^{-12}) = -4.61\times10^{-12}$ $\mathrm{m^3\,mol^{-1}}$

1 C=O = $1\,(-3.36\times10^{-12}) = -3.36\times10^{-12}$ $\mathrm{m^3\,mol^{-1}}$

1 benzene ring = $1\,(-1.4\times10^{-12}) = -1.4\times10^{-12}$ $\mathrm{m^3\,mol^{-1}}$

-68.95×10^{-12} $\mathrm{m^3\,mol^{-1}}$



Benzoic acid

It is close to the observed value of $-70.3\times10^{-12}\ \mathrm{m^3\,mol^{-1}}$.

Before proceeding further, why don't you consolidate your gain of knowledge regarding diamagnetism, by solving the following SAQ?

SAQ 5

The magnetic susceptibility measurements show that hypophosphoric acid is diamagnetic. Its empirical formula is H_2PO_3. Pick out its molecular formula from the following (Hints: Examine the sum of the valence electrons in each formula; also use the last two statements of the first para in this section) :

i) H_2PO_3 ii) $H_4P_2O_6$ iii) $H_6P_3O_9$

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6.10 OPTICAL ACTIVITY

In the last section, you have learnt about the behaviour of molecules in the magnetic field. Let us now see how the molecules interact with light. Ordinary light may be considered as an electromagnetic vibration of a range of different wavelengths, vibrating in many different planes at right angles to the direction of propagation of light. The electromagnetic radiation comprises of oscillating electric and magnetic fields directed perpendicularly to each other and also to the direction of propagation of light, as shown in Fig. 6.4.

A nicol prism consists of two pieces of transparent calcite (calcium carbonate) which together form a parallelogram. It is a device for producing plane polarised light.

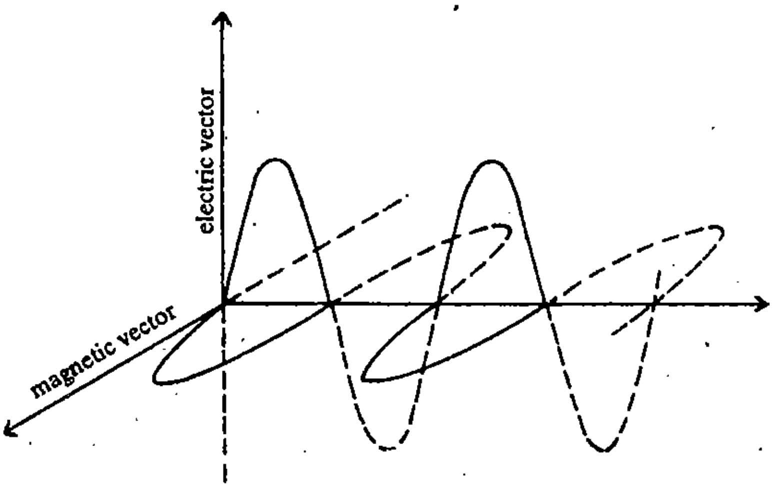


Fig. 6.4 : Oscillating electric and magnetic fields in light.

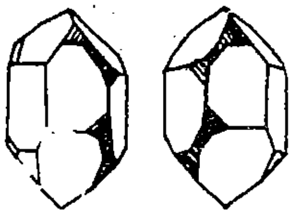


Fig. 6.5 : Quartz crystals having mirror image relationship.

Quartz is the most stable crystalline form of silica.

Monochromatic light can be defined as that consisting of distinct wavelength; but its electric and magnetic fields, still vibrate in infinite number of planes. When monochromatic light is passed through a nicol prism, the outcoming light vibrates in only one of these possible planes. Such a type of light is called **plane polarised light.** Any material which rotates the plane of the polarised light is said to be optically active. If a substance rotates the plane of polarised light to the right, it is called **dextrorotatory** (Latin: *dexter*, right); if the rotation is to the left, the substance is **laevorotatory** (Latin: *laevus*, left).

It was observed that the quartz crystals which have the odd faces inclined in a particular direction, rotate the plane of the polarised light in one and the same direction, whereas the mirror image crystals (Fig. 6.5), whose odd faces are inclined in the opposite direction, rotate the plane of the polarised light in the opposite direction.

Substances like quartz and sodium chlorate are optically active only in the solid state. The ability of these substances to rotate the plane polarised light is related to the fact that the atoms or molecules in the crystal are arranged in the form of either a right-handed or a left-handed spiral. Since this structure disappears on melting, the liquid shows no optical activity. There is a second variety of optically active substances in which the optical activity is due to a particular arrangement of atoms and groups within the molecule. Hence these substances exhibit optical activity in solid, liquid, gas or in solution phase. Since the optical activity of this class of compounds is related to molecular structure, we shall consider this in detail.

It was pointed out by Le Bel and van't Hoff that in organic compounds, the tetrahedral carbon atom would explain the existence of mirror image isomers. Such isomers are called **enantiomers** and are shown in Fig. 6.6 as I and II.

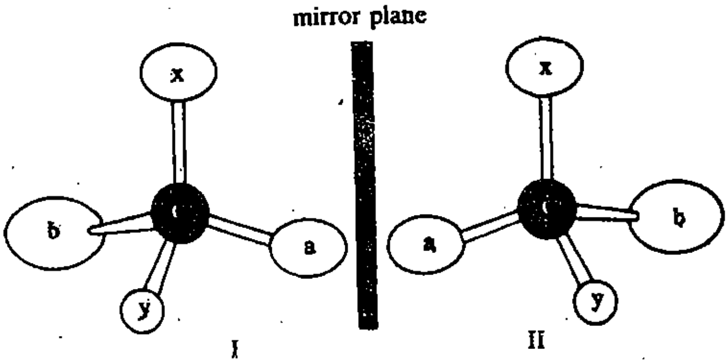
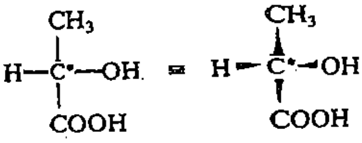


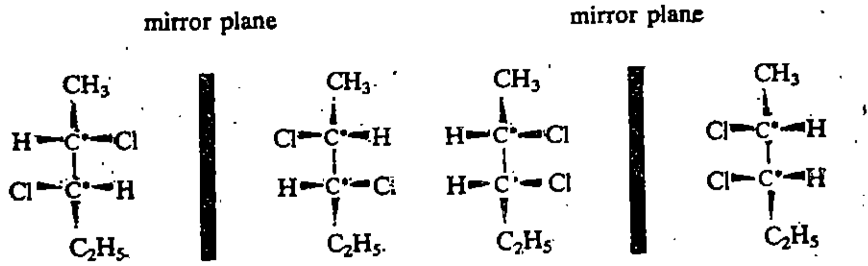
Fig. 6.6 : Mirror image relationship between enantiomers.



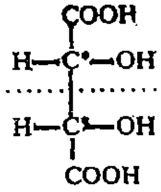
III

A carbon atom attached to four different groups is called a **chiral** carbon atom. If only one chiral carbon atom is present, the molecule can be expected to have two optically active enantiomers, one being dextro and the other, laevo. Note that in the structure of lactic acid (III) and in other optically active compounds, the chiral carbon is indicated by an asterik(*) mark. An equal mixture of dextro and laevo isomers is optically inactive and is called a **racemic** mixture. It is possible to separate the enantiomers from the racemic mixture.

If in a compound, more than one chiral carbon atoms are present, then the mirror image isomers are called enantiomers and those; which do not have a mirror image relationship, ar called diastereomers. For example, of the four isomers of 2, 3-dichloropentane, IV and V as also VI and VII are two pairs of enantiomers. But the pairs, IV and VI or V and VII are diastereomers.



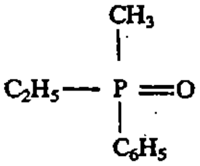
IV V VI VII



VIII

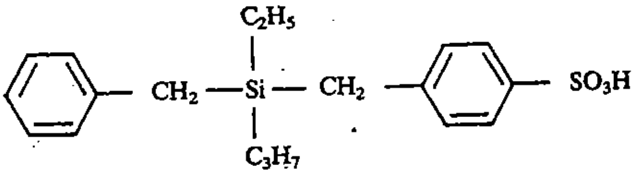
It is interesting to note that, if in a molecule, there are two or more chiral carbon atoms, and if one half of the molecule is a mirror image of the other half, then it would be optically inactive. Such an isomer is called a meso isomer and a familiar example is meso-tartaric acid (VIII). You will note that above and below the dotted line in this structure, there is an identical arrangement. In such a case, optical rotation by one part of a molecule is cancelled by that of the other part.

Chiral groupings other than a chiral carbon unit can also cause optical activity. Some such optically active compounds are substituted phosphine oxide (IX) and substituted silane (X), each of which has two enantiomers.



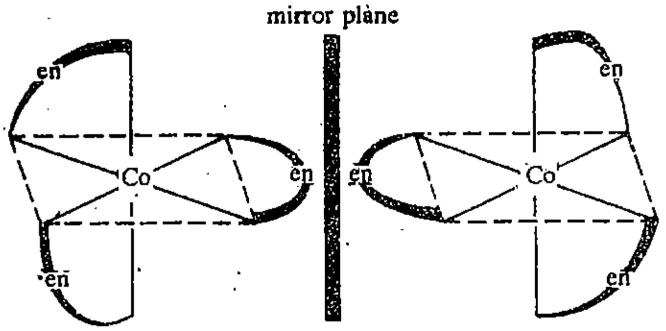
$$C_2H_5-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle C_6H_5}{|}}{P}}=O$$

IX



X

Many co-ordination complexes, having ligands such as ethylenediamine (en), have optical activity and the enantiomers have been isolated. An example is $CO\,(en)_3^{3+}$ (XI).



XI

The optical rotation is caused by the individual molecules. The amount of rotation depends on how many molecules the light encounters in passing through the tube. The extent of rotation can be represented by stating the specific rotation [α], which can be defined as the number of degrees of rotation observed when a 1 decimetre tube is used and the concentration of the solution is 1 kg dm^{-3}. Thus,

$$[\alpha]_\lambda^t = \frac{\text{Observed rotation (degree)}}{\text{length (dm)} \times \text{concentration (kg dm}^{-3})}$$

The specific rotation depends on the temperature (t) and the wavelength (λ) of the light used for measurement. Thus $[\alpha]_D^{20}$ indicates that the rotation is measured at 20°C with the D line of sodium having $\lambda = 589.3$ nm.

6.11 SUMMARY

In this unit, you have studied the interaction of matter with the electric field, magnetic field and electromagnetic radiation. The contents of this unit can be summarised as follows:

- The difference in electronegativity between the atoms forming a covalent bond causes polarity.
- The electric field strength decreases due to a dielectric material and the extent of decrease is related to its dielectric constant.
- Dipole moment is a measure of the polarity of the bond; it is related to the dielectric constant and molar polarisation of the substance.
- Dipole moment serves as a support for VSEPR predictions.
- Broadly speaking, there are three types of magnetic materials, namely, paramagnetic, diamagnetic and ferromagnetic.
- Paramagnetic molar susceptibility of a substance is related to the number of unpaired electrons present in its structural unit.
- Diamagnetic molar susceptibility is an additive and constitutive property.
- Optical activity of a substance is related to its structure.

6.12 TERMINAL QUESTIONS

1) Calculate the dipole moment of sodium chloride molecule at an internuclear separation of 500 pm.

   (Hint: Assume $q = 1.602 \times 10^{-19}$ C).

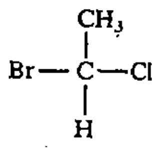
2) The dielectric constant of carbon tetrachloride is 2.238 at 293 K. Its density is 1.595×10^3 kg m^{-3}.

   i) Calculate its molar polarisation.

   ii) If its molar polarisation does not vary with temperature and its vibrational polarisation is negligible, what is its polarisation due to?

3) What is the predicted magnetic moment of Mn^{2+} ion in μ_B units (Assume high spin state)?

4) Which of the following can exhibit optical activity?

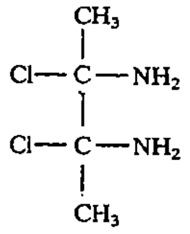


$$\mathrm{Br-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-Cl}$$

(i)

$CH_3—CH_2—Br$

(ii)



(iii)

6.13 ANSWERS

Self-Assessment Questions

1) Dielectric constant of the material is given by the ratio, $\frac{80.1 \times 10^{-12}\ (F)}{8.9 \times 10^{-12}\ (F)}$; it is equal to 9.

2) The charge on chlorine or hydrogen $(q) = \mu / r$

$$= \frac{3.57 \times 10^{-30}\ (C\ m)}{127.5 \times 10^{-12}\ (m)}$$

$$= 2.8 \times 10^{-20}\ C$$

Compared to the magnitude of the charge of an electron (1.602×10^{-19} C), the negative charge on chlorine of HCl is less, indicating that charge separation in HCl is not complete. See Sub-section 6.6.2 also.

3) The units of N_A, μ, ϵ_0, k and T are mol^{-1}, C m, $C^2\ m^{-2}\ N^{-1}$, $J\ K^{-1}$ and K, respectively. Substituting only the relevant units in Eq. 6.3, we get,

$$\text{Unit of } P_0 = \frac{mol^{-1}\ C^2\ m^2}{C^2\ m^{-2}\ N^{-1}\ J\ K^{-1}\ K}$$

$$= \frac{mol^{-1}\ m^4}{N^{-1}\ J} = \frac{mol^{-1}\ m^4}{N^{-1}\ N\ m} \quad \{\because 1\ J = 1\ N\ m\}$$

$$= m^3\ mol^{-1}$$

4) Not true; since SO_2 is angular, it has finite dipole moment value.

5) Sum of the valence electrons for H_2PO_3 can be calculated, knowing that valence electrons per hydrogen, phosphorus and oxygen atom are 1, 5 and 6, respectively. Sum of the valence electrons for H_2PO_3

$$= (2 \times 1) + (1 \times 5) + (3 \times 6)$$

$$= 2 + 5 + 18$$

$$= 25$$

Similarly, sum of the valence electrons for $H_4P_2O_6$ and $H_6P_3O_9$ are 50 and 75, respectively. Since hypophosphoric acid is diamagnetic, it must have even number of electrons. Hence, the possible formula is $H_4P_2O_6$.

Terminal Questions

1) $\mu = q \cdot r = 1.602 \times 10^{-19}\ (C) \times 500 \times 10^{-12}\ (m)$

$$= 8.010 \times 10^{-29}\ C\ m.$$

2) i) Its molecular mass is 0.154 kg mol^{-1}

$$P_M = \frac{\epsilon_r - 1}{\epsilon_r + 2} \cdot \frac{M}{\rho} = \frac{(2.238 - 1)}{(2.238 + 2)} \cdot \frac{0.154 \text{ (kg mol}^{-1}\text{)}}{1.595 \times 10^3 \text{ (kg m}^{-3}\text{)}}$$

$$= 2.820 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}.$$

ii) Since the molar polarisation of carbon tetrachloride does not vary with temperature, it is non-polar; its dipole moment and orientation polarisation are zero. Since its vibrational polarisation is also negligible, its molar polarisation is only due to distortion polarisation.

3) The electron configuration of Mn^{2+} is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$. Since it is in a high spin state, all the five $3d$ electrons have their spins unpaired. Hence using Table 6.3.
$m = 5.916\ \mu_B$.

4) Structure (i) alone can exhibit optical activity. The structure (ii) has no chiral centre, and in structure (iii), one half of the molecule is a mirror image of the other and hence (ii) and (iii) are optically inactive.

Appendix

It is our aim to explain some of the useful terms in understanding the electrical and magnetic properties of matter. Firstly let us study some of the parameters and principles required for understanding the concepts of dielectric constant and dipole moment (described in sections 6.3 – 6.6).

Quantity of charge: The quantity of electric charge (q) has the unit, coulomb (C). A coulomb is the amount of charge transported in a second (s) through a cross-section of wire that has a steady current of one ampere (A).

1 C = 1 A s

Coulomb's law: This law deals with electrostatic force, which is a force operating between stationary charges. This law states that the electrostatic force (F) between two charges (q_1 and q_2) is directly proportional to the product of the two charges and inversely proportional to the square of the distance (d^2) between the charges.

$$F \propto \frac{q_1 q_2}{d^2}$$

In this relationship, the value of the proportionality constant has been found to be equal to $1/4\pi\epsilon_0$ where ϵ_0 is the permittivity of vacuum.

$$\text{Hence, } F = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{d^2} \qquad \text{...(A.1)}$$

The SI units of force, charge and distance are newton (N), coulomb (C) and metre (m), respectively. Therefore, ϵ_0 has the unit, $C^2 N^{-1} m^{-2}$. The value of ϵ_0 is equal to $8.854 \times 10^{-12}\ C^2 N^{-1} m^{-2}$. Permittivity is a measure of the degree to which a medium can resist the flow of charge and permit the establishment of a steady electric field.

Potential Difference (V)

The increase in electric potential energy (or work w required to take from a point to another point) per unit charge (q) is called the potential difference (V) between the two given points.

$$V = \frac{w}{q} \qquad \text{...(A.2)}$$

The units for electrical energy, charge and potential difference are joule (J), coulomb (C) and volt (V), respectively.

Hence, 1 volt = 1 joule/1 coulomb ...(A.3)

You must bear in mind that V (italicised) stands for the potential difference, while V (Roman) is used as a symbol for volt.

Electric Field (E)

An electric charge experiences a force in the presence of another charge, the magnitude of which can be calculated using Coulomb's law. This force has a region under its influence. The space surrounding a charge within which it exerts a perceptible force is called **the electric field.** The intensity of the electric field (E) is defined as the electric force (F) acting on a small test charge divided by the magnitude of the test charge (q).

i.e., $E = F/q$ ...(A.4)

The SI unit for an electric field is the unit of force, divided by the unit of charge; that is, N C^{-1}. Electric field can also be defined as the potential difference (V) between two points divided by the distance of separation (d).

$E = V/d$ ...(A.5)

Hence, the electric field also has the unit V m^{-1}.

The two units, V m^{-1} and N C^{-1} are identical as shown below:

1 joule	=	1 volt coulomb (electrical energy)	=	1 newton metre (mechanical energy)

i.e., 1 J = 1 V C = 1 N m

or 1 V m^{-1} = 1 N C^{-1} ...(A.6)

Dielectric

A dielectric or an insulator is a material having electrical conductivity much lower in comparison to that of a metal. In a dielectric material, an electric field can be sustained with a minimum dissipation of power.

Capacitance

A capacitor is an arrangement of one or more pairs of conductors, separated by a dielectric, and between which an electric field can be produced. Two metal plates separated by a non-conducting material constitute a capacitor. Let $+q$ and $-q$ be the charges on the two plates of the capacitor. Assume that the area of each plate is A, while the potential difference and the distance between the plates are V and d, respectively.

The electric field (E_0) between the evacuated plates is found to be proportional to the quantity q/A, known as the density of the charge.

$$E_0 = k\,\frac{q}{A} \quad \text{...(A.7)}$$

The proportionality constant k, has been found to be equal to $(1/\epsilon_0)$, ϵ_0 being the permittivity of the vacuum.

$$\text{Hence, } E_0 = \frac{1}{\epsilon_0}\,\frac{q}{A} \quad \text{...(A.8)}$$

This equation is valid if there is a vacuum between the plates in the capacitor.

If the gap between the plates is filled by a dielectric material without altering the charges on the plates, then the electric field (E) is,

$$E = \frac{q}{\epsilon_r\,\epsilon_0\,A} \quad \text{...(A.9)}$$

where ϵ_r is the relative **permittivity or dielectric constant** of the material.

Using Eqs. A.5 and A.9 we can write,

$$q = \frac{\epsilon_r\,\epsilon_0\,A}{d}\,.\,V \quad \text{...(A.10)}$$

The term $\frac{\epsilon_r\,\epsilon_0\,A}{d}$ can be represented by the letter C. Hence Eq. A.10 can be written as,

$q = C\,V$ ...(A.11)

$$\text{or } C = \frac{q}{V} = \frac{\epsilon_r \epsilon_0 A}{d} \qquad \text{...(A.12)}$$

The term C is the capacitance of the capacitor which consists of two metal plates and a dielectric material between them. It is the capacity to store charge. The capacitance depends on the shape, size and the relative positions of the conductors and on the dielectric constant of the dielectric material in which the conductors are immersed. The SI unit of capacitance is the farad (F), named in honour of Faraday. Since the farad is too large a unit for ordinary use, smaller units, microfarad ($\mu F = 10^{-6}$ F) and picofarad ($pF = 10^{-12}$ F) are used commonly. Substituting the units in Eq. A.12 we can see that the unit F is equal to C V^{-1}. **(Again, you must bear in mind that** C (italicised) **is used as a symbol to denote the capacitance of a dielectric material, while** C (Roman) **denotes coulomb, the unit of electric charge.)**

For the vacuum, the dielectric constant, ϵ_r is equal to 1; therefore, capacitance (C_0) in vacuum as per Eq. A.12 is,

$$C_0 = \frac{\epsilon_0 A}{d} \qquad \text{...(A.13)}$$

Eq. A.13 is applicable to air too, since ϵ_r for air is almost equal to 1 (i.e. 1.00054); it is not much different from that of the vacuum.

You can see that the ratio of the capacitance values, C and C_0, in the dielectric material and air, respectively gives the dielectric constant of the material. Using Eqs. A.12 and A.13,

$$\epsilon_r = C/C_0 \qquad \text{...(A.14)}$$

Alternatively, dielectric constant of a material can also be defined as the ratio of the electric field in the vacuum to that in the given material.

The dielectric constant is a dimensionless quantity. Let us illustrate the calculation of the dielectric constant of mica using the above equations. Let us assume that the capacitor has two metal plates of area 0.01 m^2 separated by a distance of 0.01 m.

The capacitance of the air-filled capacitor,

$$\begin{aligned} C_0 &= \frac{\epsilon_0 A}{d} \\ &= \frac{8.854 \times 10^{-12} (C^2\,N^{-1}\,m^{-2}) \times 0.01\ (m^2)}{0.01\ (m)} \\ &= 8.854 \times 10^{-12}\ C^2\,N^{-1}\,m^{-1} \\ &= 8.854 \times 10^{-12}\ F \\ &= 8.854\ pF \end{aligned}$$

$$\left[\begin{aligned} 1\ C^2\,N^{-1}\,m^{-1} &= \frac{1\ C^2}{1\ N\ m} \\ &= \frac{1\,C^2}{1\ J} \\ &= \frac{1\ C^2}{1\ V.C} \\ &= \frac{1C}{1\ V} = 1\ F \end{aligned}\right]$$

The capacitance of the capacitor (C) filled with mica is found to be 47.81 pF. The dielectric constant of mica is,

$$\begin{aligned} \epsilon_r = \frac{C}{C_0} &= \frac{47.81 \times 10^{-12}\ (F)}{8.854 \times 10^{-12}\ (F)} \\ &= 5.4 \end{aligned}$$

Vectors and Scalars

A scalar quantity has only magnitude but no direction. Typical scalar quantities are mass, volume, density and speed. Some physical quantities like velocity, acceleration and force are fully described only when magnitude and direction are mentioned and such physical quantities are called vectors. A vector has numerical and geometric properties. A vector is denoted by using bold face letter(s). Thus, A denotes that it is a vector quantity, whereas A means it is scalar.

In this unit, electrical quantities like electric field strength, molar polarisation, dipole moment, and the magnetic quantities such as magnetic induction, magnetic field intensity and magnetisation are all vector quantities; but our discussion is restricted to their magnitudes only and hence we have used scalar notation for the above quantities. Let us see how the dipole moment of a substance can be calculated from the bond moments using vector algebra. Even with an elementary knowledge of trigonometry, you can understand the following discussion on the dipole moment.

Dipole Moment

Dipole moment is a measure of the polarity of a molecule. The dipole moment of a substance is the vector sum of its bond moments. For a simple triatomic molecule like H_2O or CO_2, the dipole moment can be calculated using **the parallelogram method** of addition of vectors. As per this method, when two bond moment vectors are represented by the adjacent sides of a parallelogram, the diagonal containing the two sides represents the dipole moment of the molecule in magnitude and direction.

Let us consider the general case of a triatomic molecule, XYZ, where the element Y is more electronegative than the elements X and Z. Let the bond moments for the two bonds, XY and ZY be $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ (being the two sides of a parallelogram (XYZD)). Let these bond moments be inclined at an angle θ (Fig.A.1). That is, the bond angle is θ. The dipole moment, $\boldsymbol{\mu}$ of this molecule XYZ is the resultant **DY** (diagonal of the parallelogram) of the two bond moments and is equal to $\boldsymbol{\mu}_1 + \boldsymbol{\mu}_2$

Hence, $\boldsymbol{\mu} = \boldsymbol{DY} = \boldsymbol{\mu}_1 + \boldsymbol{\mu}_2$

Let μ_1, μ_2 and μ represent the magnitude of the vectors $\boldsymbol{\mu}_1$, $\boldsymbol{\mu}_2$ and $\boldsymbol{\mu}$, respectively.

We can derive an equation relating the bond angle to the magnitudes of the bond moments and the dipole moment of the molecule XYZ, as described below:

From D, draw a perpendicular to meet XY extended up to E.

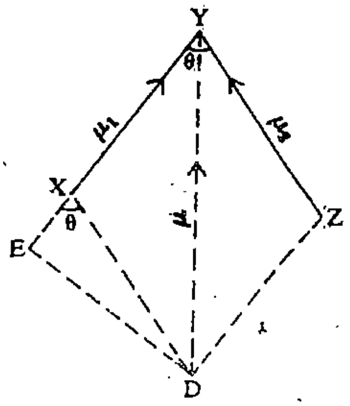


Fig A.1 : Dipole vectors for the bond moments and the resultant moment of the molecule XYZ.

From Fig. A.1, $\angle DXE = \angle ZYX = \angle \theta$

In the right angled Δ DYE,

$$\begin{aligned} DY^2 &= DE^2 + EY^2 \\ &= DE^2 + (EX + XY)^2 \\ &= DE^2 + EX^2 + 2EX.XY + XY^2 \\ &= DX^2 + 2 \,.\, DX \cos\theta \, XY + XY^2 \end{aligned}$$

$$\left[\begin{array}{l} \dfrac{EX}{DX} = \cos\theta \\ \text{and } DE^2 + EX^2 = DX^2 \end{array}\right]$$

$$DY^2 = ZY^2 + 2\,ZY \,.\, XY \cos\theta + XY^2$$

[DX = ZY ; opposite sides of a parallelogram]

i.e., $\mu^2 = \mu_1^2 + \mu_2^2 + 2\,\mu_1\mu_2 \cos\theta \quad \because \left\{\begin{array}{c} DY = \mu \\ ZY = \mu_2 \\ \text{and } XY = \mu_1 \end{array}\right\}$

$$\therefore \cos\theta = \frac{\mu^2 - (\mu_1^2 + \mu_2^2)}{2\,\mu_1\,\mu_2} \qquad (A.15)$$

Let us use Eq. A.15 to calculate the bond angle in water and carbon dioxide.

For water : $\mu_1 = \mu_2 = \mu_{O-H}$ = The O–H bond moment

$\mu = \mu_{H_2O}$ = Dipole moment of water

Hence, using Eq. A.15, $\cos\theta = \dfrac{\mu^2_{H_2O} - \mu^2_{O-H}}{2\mu^2_{O-H}}$

i.e., $\cos\theta = \dfrac{\mu^2_{H_2O}}{2\mu^2_{O-H}} - 1$

For carbon dioxide : $\mu_1 = \mu_2 = \mu_{C=O}$ = The C=O bond moment and
$\mu = \mu_{CO_2}$ = Dipole moment of carbon dioxide

$$\text{Hence, } \cos\theta = \frac{\mu_{CO_2}^2 - 2\mu_{C=O}^2}{2\mu_{C=O}^2} = \frac{\mu_{CO_2}^2}{2\,\mu_{C=O}^2} - 1$$

These expressions are used in Sub-sec. 6.6.3.

So far, we have discussed the terms concerning electrical properties of matter. Now let us study some of the parameters and terms used in describing magnetic properties of matter. An elementary knowledge of the magnetic characteristics of matter is essential; especially, the study of the effect of an applied magnetic field on the electrons revolving in the orbits is made easier, once we understand the effect of an applied magnetic field on a current-carrying coil. We make use of the parameters, magnetic moment and susceptibility in Secs. 6.7 – 6.9. To understand these two, we require to know a few more quantities and the first one is the magnetic field.

Magnetic Field

The force field surrounding a magnet is called a magnetic field. It is usual to represent a magnetic field surrounding a magnet by imaginary field lines (Fig. A.2). Iron filings sprayed around a magnet are often used to indicate the magnetic field lines. They align themselves along the field lines.

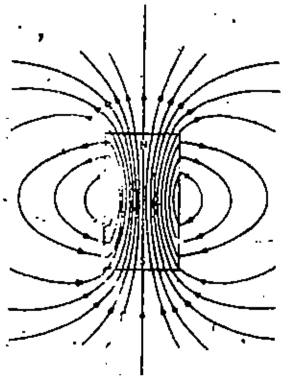


Fig. A.2 : Magnetic field lines directed from north pole to south pole.

Magnetic Induction (B)

If a charge moves perpendicularly to the magnetic field, it experiences a force. The direction of the force is always perpendicular to the velocity of the charge and to the direction of the field. The magnitude of the force (F) is proportional to the charge (q), its velocity (v) and another quantity, B, which is a measure of the strength of the magnetic field.

$$F = q\,v\,B \qquad \text{...(A.16)}$$

The parameter B is often called magnetic induction.

Rearranging Eq. A.16,

$$B = F/q\,v \qquad \text{...(A.17)}$$

The SI unit of magnetic induction is tesla (T) in honour of the American inventor Tesla; a tesla is that magnetic field which produces a force of 1 newton on a charge of 1 coulomb moving at 1 metre per second perpendicular to the field. Substituting the units of B, F, q and v in Eq. A.17, we get,

$$1\text{ T} = 1\text{ N (C m s}^{-1})^{-1}$$

$$= 1\text{ N (A s m s}^{-1})^{-1}$$

$$1\text{ T} = 1\text{ N A}^{-1}\text{ m}^{-1} \qquad \text{...(A.18)}$$

Magnetic Moment (m)

We are aware that current is a flow of charges. Hence we can expect the magnetic field to exert a force on a current-carrying wire. The maximum magnetic force is seen, if the current-carrying wire is perpendicular to the field. A current-carrying loop is more commonly in use rather than a wire in a magnetic field. Such a loop does not experience any net linear force, but it experiences a torque. If a current-carrying loop having a surface area A, number of turns N and current I is placed in a field of magnetic induction B, then the torque (τ) experienced by this loop, when it is placed perpendicular to the field is given by,

Torque is the rotational effect of a force. The unit of torque is N m or J.

$$\tau = I\,N\,A\,B$$

$$= m\,B \qquad \text{...(A.19)}$$

The product $I\,N\,A$ is called the magnetic moment (m) of the coil and evidently its unit is A m^2 (since N does not have a unit). Using Eq. A.19, m can be given the unit J T^{-1} also. Magnetic moment is a measure of the magnetic strength of the coil. Let us illustrate the calculation of magnetic moment for a rectangular coil which is 0.1 m long, 0.05 m wide, contains 100 turns of wire and has I = 20 A.

$m = I\,N\,A$ [$\because$ Area of a rectangular coil, A = length of the coil × its width]

$= 20\ (\mathrm{A}) \times 100 \times 0.1\ (\mathrm{m}) \times 0.05\ (\mathrm{m})$

$= 10\ \mathrm{A\ m^2}$

The effect of the external magnetic field on any current-carrying coil is to rotate the coil so as to align the magnetic dipole parallel to the external magnetic field. This behaviour is similar to that of an electric dipole placed in an external electric field, where the electric dipole experiences a torque. By analogy, a current loop is called a magnetic dipole.

A current-carrying wire experiencing a torque in the presence of a magnetic field has wide applications in electrical appliances such as electric motors and galvanometer.

Magnetic Field Around a Wire

Oersted discovered that a current-carrying wire has a magnetic field around it. A helical coil of wire with a large number of turns carrying a current is called a solenoid. An electromagnet, a magnet energised by an electric current, consists of a solenoid with or without magnetic material in its core. If a solenoid (in vacuum or air) of length l having N total number of turns carries a current I, then magnetic induction B_0 is given by,

$$B_0 = \frac{\mu_0 N I}{l} \qquad \text{...(A.20)}$$

Here μ_0 is the permeability of free space or air and is equal to $4\pi \times 10^{-7}\ \mathrm{T\ m\ A^{-1}}$. The presence of magnetic material inside the solenoid increases the field by several hundred times. The equation for magnetic induction when the solenoid has magnetic material inside is,

$$B = \frac{\mu N I}{l} \qquad \text{...(A.21)}$$

where μ is the permeability of the core material and it has the same units as μ_0, namely, $\mathrm{T\ m\ A^{-1}}$. The **permeability** of a substance indicates its tendency to allow the magnetic lines of force to pass through it, as compared to that of a non-magnetic substance like air. That is, the permeability of magnetic materials is much higher than the permeability of air or free space.

Magnetisation (M)

The effect of the external magnetic field is to produce a net magnetic moment in the bulk of the matter along the direction of the field; this effect is similar to that of the induced electric polarisation for a dielectric placed in an external electric field. The degree of magnetic polarisation in matter is specified by magnetisation (M) which is defined as the magnetic moment induced in unit volume of the medium, that is,

$$M = \frac{\text{Total magnetic moment in the bulk}}{\text{Volume of the bulk}}$$

The unit of M is $\mathrm{A\ m^{-1}}$ since magnetic moment and volume have $\mathrm{A\ m^2}$ and $\mathrm{m^3}$ units, respectively. The magnetisation is also known as the surface current per unit length of the cylinder.

Magnetic Field Intensity (H)

The magnetic field strength (H), also known as field intensity, is equal to the ratio of magnetic induction to the permeability of the material inside the solenoid.

$$H = B_0/\mu_0 \qquad \text{...(A.22)}$$

$$= B/\mu \qquad \text{...(A.23)}$$

Eq. A.22 is applicable when the solenoid is in a vacuum or in the air and Eq. A.23 is for a situation when there is a magnetic material inside the solenoid. For a coil magnetised by passing current I and having N turns within a length l, the magnetic field intensity is defined by the relationship,

$$H = \frac{N I}{l} \qquad \text{...(A.24)}$$

The unit of H is $\mathrm{A\ m^{-1}}$. The value of H depends only on the magnitude of the current passed and the number of turns in unit length (N/l) but is independent of the core material.

The total magnetic induction, B, in a solenoid due to the passage of the current is the sum of its induction in free space (B_0) and that due to the matter inside the solenoid, the latter being given by the product $\mu_0 M$.

Hence $B = B_0 + \mu_0 M$ ...(A.25)

Using Eq. A.22, we get, $B = \mu_0 H + \mu_0 M = \mu_0 (H + M)$ ...(A.26)

Magnetic Susceptibility (χ)

The ease with which a substance can be magnetised is measured by a quantity, called its magnetic susceptibility (χ). It is defined as the ratio of magnetisation to the field intensity.

$\chi = M/H$ ...(A.27)

The susceptibility is much larger for magnetic substances than for non-magnetic substances. The susceptibility of soft iron is greater than that of steel, nickel and cobalt. As seen from Eq. A.27, χ is a unitless quantity since M and H have the same units. Using Eqs. A.26 and A.27, we can write,

$$\begin{aligned} B &= \mu_0 (H + \chi H) \\ &= \mu_0 (1 + \chi) H \end{aligned}$$

or $B = \mu H$ ...(A.28)

where $\mu = \mu_0 (1 + \chi)$ ...(A.29)

You may recall that μ is the permeability of the medium and it is defined by the Eq. A.21. Since in a vacuum, there is no magnetisation ($M = 0$), χ is zero and $\mu = \mu_0$. This justifies the term "permeability of free space" for μ_0. The permeability of air is nearly the same as that of μ_0. Hence the magnetic effects in vacuum and air are practically the same.

UNIT 7 MOLECULAR SPECTROSCOPY – I

Structure

7.1 INTRODUCTION

In Unit 6, we studied the correlation between some of the molecular properties and molecular structure. Presently, we take up the study of molecular spectra with a view to obtain more direct information about molecular structure. It is worth recollecting that in Unit 1, we have seen how atomic spectra are useful in the understanding of the electronic arrangement in atoms. The transitions of the electrons between the various energy levels of the atom result in emission or absorption of electromagnetic radiations. Corresponding to energy difference between the levels, the spectral lines occur in different regions, and this gives rise to atomic spectra. Just as atomic spectra give information about the structure of the atom, molecular spectra give information regarding the molecular structure. We may define molecular spectroscopy as the study of the interaction of electromagnetic radiation with molecules.

In this unit, first of all we explain different types of energy levels in molecules and the conditions under which transitions occur among these levels. Then we describe various types of absorption spectra and general features of a spectrometer used in obtaining absorption spectra. We then explain how rotational spectra can be used to calculate simple molecular parameters like bond length and moment of inertia. In the next unit, we shall study how infrared, visible and ultraviolet spectra can be used to obtain some more molecular parameters.

Objectives

After studying this unit, you should be able to :

- define different types of energy levels in molecules,
- state various types of molecular spectra,
- explain the reason for the difference in the intensity of spectral lines,
- describe the general features of an absorption spectrometer,
- state the pre-requisite for exhibiting rotational spectra,
- explain the theory of rotational spectra, and
- calculate the parameters like bond length and moment of inertia of a heteronuclear diatomic molecule using microwave spectra.

7.2 ENERGY LEVELS IN MOLECULES

We have already discussed in Unit 1 the energy changes in an atom, accompanying the transfer of electrons from lower energy levels to high energy levels and *vice versa*. The electronic transitions in an atom are due to absorption or emission of electromagnetic radiation. We have further stated that electronic transitions in an atom are quantised and the resulting line emission spectra correlate with the difference between the electronic energy levels.

There are more possibilities for transition between various energy levels in the polyatomic molecules than those in individual atoms. The total energy of a molecule is the sum of four different types of energy, viz., translational, rotational, vibrational and electronic. Therefore, absorption or emission of energy (electromagnetic radiation) may cause changes in some or all of these types of energy, and molecular spectra provide a method of measuring these changes. Before going into further details of molecular energy changes, their measurements and interpretation, let us first define the energy types present in molecules.

Translational Energy (E_{trans}) is concerned with the overall movement of the molecules along the three axes. It is significant only in gases and to a lesser extent for liquids. In solids, translational energy is minimum.

Rotational Energy (E_{rot}) involves the spinning of molecules about the axes passing through their centre of gravity (see Fig. 7.1 a).

Vibrational Energy (E_{vib}) is associated with vibrations within a molecule such as the stretching or the bending of bonds (see Fig. 7.1 b, c and d). In stretching type, the bond length varies but in bending type, bond angle varies.

Electronic Energy (E_{elec}) involves changes in the distribution of electrons by the promotion of electrons to higher levels on absorption of energy. This is similar to electronic energy changes in atoms.

Fig. 7.1 : Rotation and vibration within molecules: (a) shows rotation about two different axes; (b), (c), and (d) show vibrations. (b) and (c) are referred to as stretching and (d) as bending.

Now, if E is the energy of a molecule, it can be expressed as the sum of translational, rotational, vibrational and electronic contributions.

Molecular energies in increasing order of their magnitude : $E_{rot} < E_{vib} < E_{elec}$.

$$E = E_{trans} + E_{rot} + E_{vib} + E_{elec} \qquad ...(7.1)$$

The translational energy levels of a molecule in a container are so close that they can be considered as continuous. The other three forms of energy are considered to be quantised in a manner similar to the electronic energy in atoms. The magnitude of the various forms of energy and the difference between adjacent levels vary considerably. Calculations indicate that the difference between the energy levels for electronic energy change is about 100 to 10^4 kJ mol^{-1}, for vibrational energy changes, it is generally between 1 and 100 kJ mol^{-1}, and for rotational changes, it is between 0.01 and 1 kJ mol^{-1}. On the other hand, at room temperature, the average translational energy of gas molecule is about 10^{-21} J $molecule^{-1}$.

We may use two different conventions to illustrate molecular energies further. The first shows a plot of energy of the molecule versus interatomic distance, as illustrated in Fig. 7.2. This figure shows how the energy of the molecule changes with the interatomic distance.

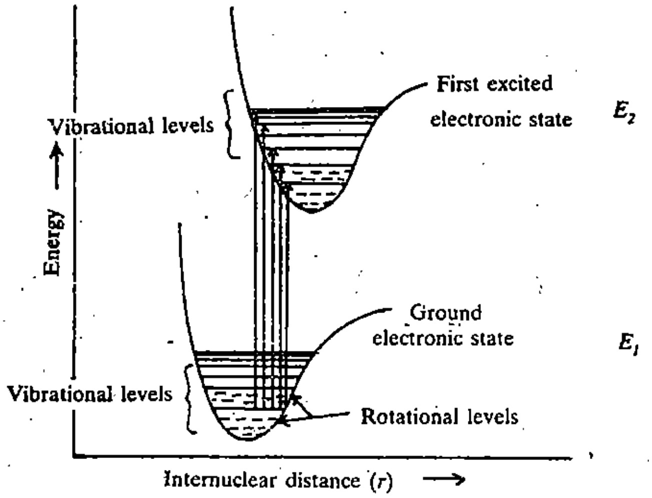


Fig. 7.2 : Representative plot for the potential energy of a diatomic molecule.

The two curves represent the ground and the first excited electronic state or electronic energy level. The individual, narrow lines indicate the allowed quantum vibrational and rotational levels. The molecule can reside in any one of the quantised rotational, vibrational and electronic energy levels that are indicated in this figure. A diagram such as this is usually used only for diatomic molecules because, for polyatomic molecules, there are too many different interatomic distances to be represented.

The second convention is to represent the energies of molecules as exemplified in Fig. 7.3. We show comparative spacing of energy levels of different types of energy. It is clear that electronic levels are much more widely spaced than vibrational levels, which in turn are more widely spaced than rotational levels.

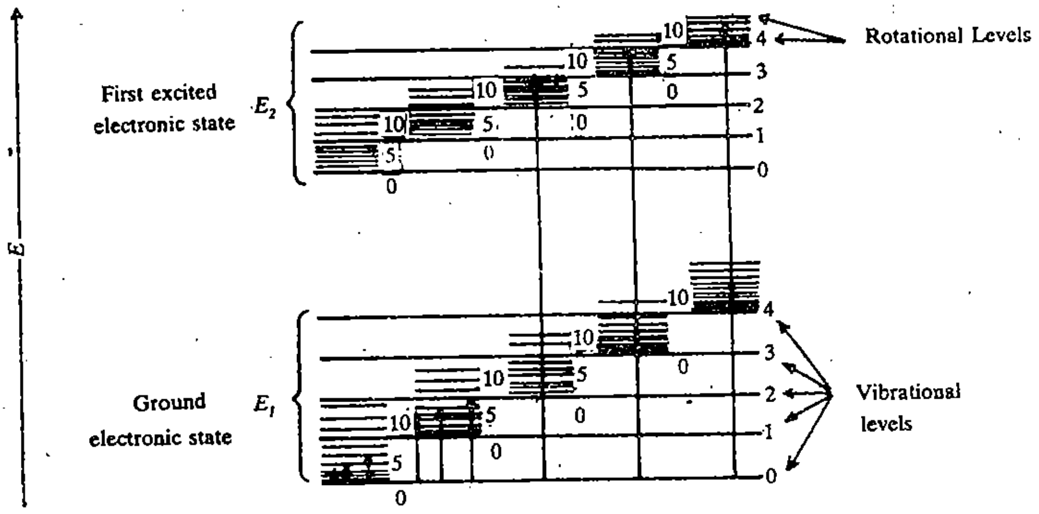


Fig. 7.3 : Diagrammatic representation of possible quantised energy levels and energy changes within a molecule.

As in the atomic spectra, quantised energy changes within a molecule are associated with the emission or absorption of electromagnetic radiation and these can be detected in the form of spectra using an instrument, known as **spectrometer**. The energy changes in a molecule are specified in terms of frequency (ν), wavelength (λ) and wave number ($\bar{\nu}$) as per Eq. 7.2.

$$\text{Energy change } (\Delta E) = h\nu = hc/\lambda = hc\bar{\nu} \qquad ...(7.2)$$

where h is the Planck's constant and c is the velocity of light.

You can find a list of units normally used in representing these quantities in Table 7.1. We use these quantities to express the position of a line or band in the absorption or emission spectrum.

Table 7.1 : Parameters Commonly Used for Representing Wavelength, Frequency and Wave Number

Parameter	Symbol	Unit
Wavelength	λ	nm(10^{-9}m)
Frequency	ν	Hz or s^{-1}
Wave number	$\bar{\nu}$	m^{-1} (or more commonly cm^{-1})

Further, the choice of the unit of a particular quantity depends on how far it can be expressed as a convenient small number. For example, 'nm' unit for wavelength is chosen to represent absorptions in ultraviolet and visible regions of electromagnetic spectrum since values of wavelength in this region lie between 200 – 800 nm. We have already discussed electromagnetic spectrum and its regions in Unit 1.

You should try the following SAQ to be convinced that $\bar{\nu}$, ν or ΔE values are not quite convenient in expressing absorptions in ultraviolet region.

SAQ 1

The absorption in ultraviolet and visible regions in wavelength units correspond to 200 – 800 nm. Calculate the following corresponding to λ = 200 nm :

a) ΔE (in kJ mol^{-1})

b) ν

c) $\bar{\nu}$

7.3 TYPES OF MOLECULAR SPECTRA

As you know, the molecules can exist in specific molecular energy levels. The rotational, vibrational and electronic energies are quantised in a manner similar to quantisation of electronic energy of an atom. As a result, spectra from even simple molecules exhibit large number of lines. To illustrate this, the emission spectrum of N_2 in the ultraviolet region is given in Fig. 7.4.

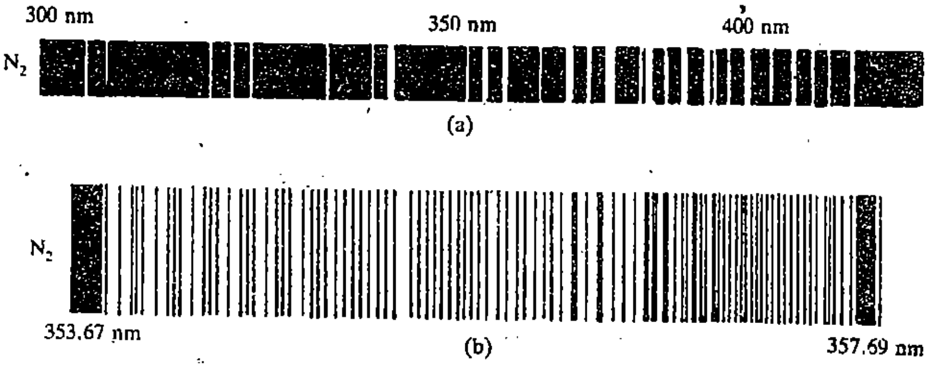


Fig. 7.4 : Spectra of nitrogen molecule : (a) bands of N_2 at low resolution; (b) bands of N_2 resolved into individual lines corresponding to transitions between rotational-vibrational sublevels of the electronic states.

Spectra can be recorded in two ways. The first method is to depict photographically the areas of greater and lesser exposure indicating the light intensity at each wavelength or wave number or frequency (See spectrum of N_2 in Fig. 7.4). The other method is to plot a graph with λ or ν or $\bar{\nu}$ in the x - axis and absorbance/ transmittance in the y - axis. (See the spectrum of benzene given in Fig. 7.5).

In this case, unlike atomic spectra, molecular spectra appear as **bands** at low resolution (see Fig. 7.4a). At high resolution, one finds that instead of the bands, the spectrum is composed of sharp lines. These lines arise from the presence of vibrational and rotational energy levels. Since there are many such levels, a large number of individual lines are possible for a single electronic transition. Such a high resolution spectrum is shown in Fig. 7.4b. This figure can give you an idea as to how complex the whole spectrum would look, with many electronic energy transitions, interspersed with vibrational and rotational changes.

In solid or in liquid phase, even at high resolution, these individual lines are broad and are known as **unresolved bands**. All the spectra that we use for analysis of condensed media (liquids and solids) have bands due to large number of unresolved spectral transitions. This is illustrated in Fig. 7.5. Notice that the absorption bands are more sharp for benzene vapour rather than for its solution in ethanol.

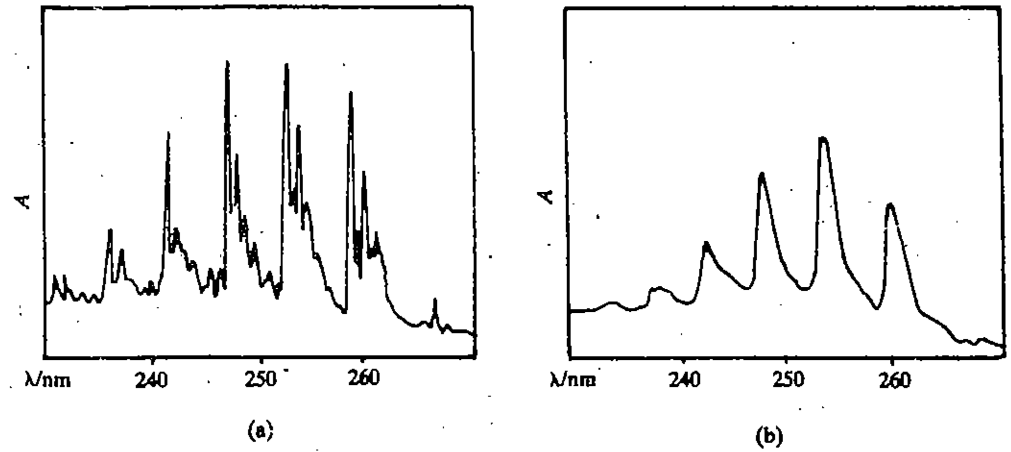


Fig. 7.5 : Absorption spectrum of benzene in ultraviolet region : (a) benzene vapour ; (b) benzene in ethanol.

Now we will consider molecular spectra in detail. Depending on the method of obtaining molecular spectra, it can be classified into three types, viz.,

i) Emission spectra

ii) Absorption spectra

iii) Spectra through scattering, such as, Raman spectra.

Let us study each of these types in a brief manner.

i) Emission Spectra

Molecules give emission spectra when subjected to intense heat or electric discharge. By this process, the molecules obtain the necessary energy to become excited. On returning to their lower energy state, molecules may emit radiation. Such emission is the result of a transition of a molecule from an excited state to one of lower energy, usually the ground state. This excess energy is emitted as a photon and the corresponding frequency is recorded as the **emission spectrum**. If the transition is from upper energy level E_2 to lower energy level E_1, the frequency (ν) of the emission spectrum is given by,

$$\nu = \frac{E_2 - E_1}{h} = \frac{\Delta E}{h} \qquad ...(7.3)$$

As an illustration, a portion of the emission spectrum of N_2 molecule is given in Fig. 7.4. The different spectral series in the atomic spectra of hydrogen discussed in Unit 1 are examples for atomic emission spectra.

ii) Absorption Spectra

When a substance is irradiated with electromagnetic radiation, the energy of the incident photons may be transferred to the molecules, raising them from the ground state to an excited state. This process is known as **absorption** and the resultant spectrum is known as **absorption spectrum**. Energy absorption occurs only when the energy difference between the ground state and higher energy level is exactly matched by the energy of the incident electromagnetic radiation. The frequency of the absorption spectrum is also given by the Eq. 7.3.

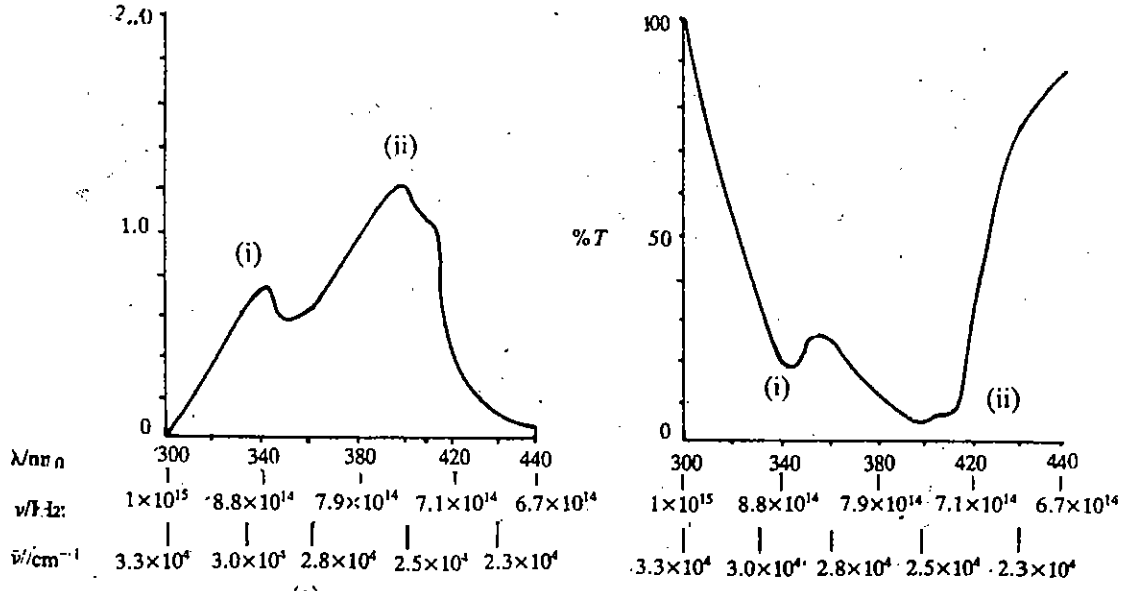
The difference between emission and absorption spectra is that in emission spectra, the molecule passes on from higher energy level to lower energy level ; in absorption spectra, it is raised from lower energy level to higher energy level. The energy absorbed, ΔE, by a molecule may bring about changes in one or more of its energy levels such as rotational, vibrational and electronic.

In an absorption spectrum, it can be seen that molecule absorbs some of the wavelengths (or frequencies or wave numbers) of electromagnetic radiation while the rest of it is transmitted. We can plot either absorbance (A) or percent transmittance ($\%T$) vs. wavelength or frequency or wave number to get the absorption spectrum. The plot of absorbance (A) vs. wavelength or frequency or wave number is illustrated in Fig. 7.6a. In this figure you can see that two maxima occur, corresponding to the points (i) and (ii), denoting intense absorptions at the corresponding wavelengths, frequencies and wave numbers. If the

Relationship between absorbance and % transmittance can be expressed by the relation:

$$A = \log\left(\frac{100}{\%T}\right) = 2 - \log(\%T)$$

absorptions are to be represented as % transmittance (%T) vs. wavelength or frequency or wave number, the plot will look like Fig.7.6b. Minima appear in Fig. 7.6b corresponding to the maxima of Fig.7.6a. We will discuss absorbance and transmittance in detail in Unit 8.



(a) (b)

Fig. 7.6 : Presentation of absorption spectral data.

iii) Raman Spectra

Besides the above two types of spectra, another variety is also observed. When a substance is irradiated with electromagnetic radiation, some of the radiation may be scattered as shown in Fig. 7.7.

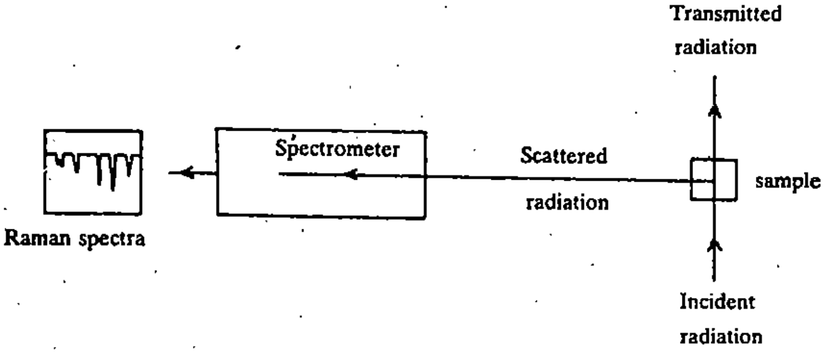


Fig. 7.7: Origin of Raman Spectra in scattered light.

The scattered radiation shows some lines of higher and some of lower frequency than that of incident radiation. This arises because incident radiation can lose energy in exciting the molecules or can alternatively gain energy from molecules already excited. The resulting spectrum so obtained is known as **Raman Spectrum.** The lines of lower frequency are called Stokes lines; those of higher frequency are known as anti Stokes lines. The experimental method of obtaining Raman spectra is different because the lines are very weak; but the use of lasers for the incident radiation has made the technique easier and of wider application.

A laser is a device that produces an intense beam of monochromatic coherent light. A laser beam remains a narrow pencil of light even after travelling a long distance. The word 'laser' stands for light amplification by the stimulated emission of radiation.

Absorption spectra are studied extensively in order to elucidate the structure of molecules. We shall concentrate only on absorption spectroscopy in this and the next unit. The molecular spectra are more complicated than atomic spectra; they range over wider regions of the electromagnetic spectrum and their interpretation is often more difficult. We divide absorption spectra into different types on the basis of the radiation absorbed. In this and the next unit, we are concerned with three types of molecular absorption spectra as given below:

Microwave Spectra: Region of electromagnetic spectrum (3×10^{10} to 3×10^{12} Hz or 1 cm^{-1} to 100 cm^{-1}) is concerned with the energy change of rotational levels which are of the order of 0.01 to 1 kJ mol^{-1}. Microwave radiation does not affect vibrational and electronic energy levels as it changes only the rotational energy and the resulting molecular spectra is called **rotational spectra.** The principles and the information given by rotational spectra will be dealt in sections 7.6 to 7.8.

Infrared Spectra: Electromagnetic radiation in the infrared region of the spectrum (3×10^{12} to 3×10^{14} Hz or 100 cm^{-1} to 10^4 cm^{-1}) results in changes of the vibrational energy of molecules. The energy change required for molecular vibrations is of the order of 1 to 100 kJ mol^{-1}, and changes in vibrational energy levels are accompanied by transitions between rotational levels too. So, in a vibrational spectrum, each line is accompanied by the rotational fine structures. Such a spectrum is evidently known as **vibrational-rotational spectrum.** If we do not consider the rotational fine structure, absorption spectrum is called **vibrational spectrum.**

Ultraviolet and Visible Spectra: Electromagnetic radiation in the ultraviolet and visible regions ($3 \times 10^{14} - 3 \times 10^{16}$ Hz or 1000 – 10 nm) of the spectrum results in changes in the electronic structure of molecules. The energy change observed in this region is of the order of 100 – 10^4 kJ mol^{-1}. This type of absorption spectra is also called **electronic spectra.** The vibrational and rotational transitions also accompany electronic transitions and these transitions appear as **broad band absorption spectra.** In practice, the region 200–800 nm is generally used by chemists to observe electronic spectra. In Table 7.2, we summarise the types of absorption spectra and information available from each type.

Table 7.2: Types of Absorption Spectra and the Information Obtained from these

Radiation absorbed	Effect on the molecule	Information deduced
Microwave $\nu = 3 \times 10^{10} - 3 \times 10^{12}$ Hz $\bar{\nu} = 1 - 100$ cm^{-1} $\lambda = 1$ cm – 0.01 cm $E = 0.01 - 1$ kJ mol^{-1}	Change in rotational energy levels of the molecule	Calculation of bond length, bond angle, etc.
Infrared $\nu = 3 \times 10^{12} - 3 \times 10^{14}$ Hz $\bar{\nu} = 100 - 10^4$ cm^{-1} $\lambda = 0.01$ cm – 1000 nm $E = 1 - 100$ kJ mol^{-1}	Change in the vibrational and rotational energy levels in the molecule	Detection of functional groups in compounds, calculation of force constant, bond length and bond angle, etc., and in quantitative analysis.
Ultraviolet and Visible $\nu = 3 \times 10^{14} - 3 \times 10^{16}$ Hz $\bar{\nu} = 10^4 - 10^6$ cm^{-1} $\lambda = 1000$ nm – 10 nm $E = 100 - 10^4$ kJ mol^{-1}	Change in electronic energy levels within the molecule. Vibrational and rotational transitions are also brought about; but their resolution is not possible in solid and liquid states.	In qualitative and quantitative analysis.

You try the following SAQ, which is based on the above discussion.

SAQ 2

Indicate the type of energy change brought about, when a gaseous molecule is exposed to the following radiation. Write your answer in the space provided.

a) Infrared

....

b) Ultraviolet

....

c) Microwave

....

d) Visible

....

7.4 THE INTENSITY OF SPECTRAL LINES OR BANDS

In the previous section, we have discussed the origin of spectral lines or bands in a spectrum. Now, in this section we are going to focus our attention on the factors which are responsible for the number and intensities of spectral lines or bands.

The number and the intensities of lines or bands which may appear in a spectrum are determined by the factors such as population of the energy levels and quantum mechanical **selection rules.**

The number of molecules present at each energy level is known as the population of that energy level. A large population at a particular level indicates that a large number of molecules may undergo a particular transition giving rise to an intense absorption band.

Quantum mechanical selection rules help us in deciding whether a particular transition is allowed or not. Again, the molecules, undergoing a transition which is permitted by the selection rules, give rise to an intense absorption line or a band. Forbidden transitions are those which are not permitted by the selection rules and give rise to weak absorption pattern. In our study of molecular spectroscopy, we will not go into the detailed reasoning for intensity pattern of spectral transitions; instead we will pay more attention to the applications of different types of spectra. Before taking up the details of the microwave spectra, let us first consider some features of an absorption spectrometer.

7.5 GENERAL FEATURES OF ABSORPTION SPECTROMETER

Let us now study the instruments used for obtaining molecular spectra. The instrument which we use to record the spectra of molecules, is called a **spectrometer**. The exact design of the instrument varies according to the spectral region being examined. But the basic features of all spectrometers are similar. A generalised schematic representation is shown in Fig. 7.8.

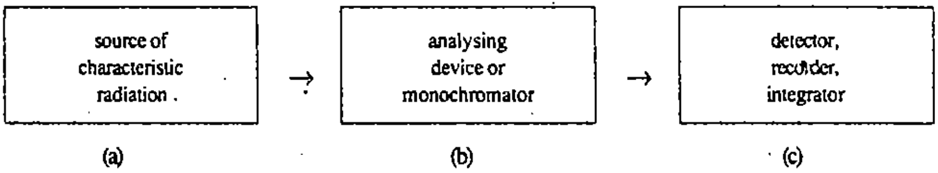


Fig. 7.8 : Schematic layout of spectrometer.

The essential features of an absorption spectrometer are fairly simple. It consists of a suitable source of electromagnetic radiation, a system to analyse the radiation or a monochromator and an appropriate detector to detect the intensity of the radiation absorbed. Depending on the technique, the sample may be positioned between (a) and (b) or between (b) and (c). These features are summarised in Table 7.3 for the different spectral types.

The final absorption spectrum is displayed either on a video screen or, more generally, recorded on a chart paper. In this manner, we can measure the extent to which a substance absorbs radiation at each wavelength (or frequency or wave number).

Table 7.3 : General Features of Absorption Spectrometer

	Ultraviolet	Visible	Infrared	Microwave
Source (a)	Hydrogen discharge lamp	Tungsten filament lamp	Electrically heated rod of rare earth oxides	Klystron valve
System of Analysis (b)	System of mirrors and rotating grating to select appropriate wavelength.		System of mirrors and rotating grating	Frequency varied electronically

A high frequency radio valve is called a klystron valve which can be tuned to emit monochromatic radiation over a limited range of frequency in the microwave region.

The fourteen elements from Ce to Lu are known as rare earth elements.

Sample	Generally dilute solutions but gases can be used. Quartz cell used in ultraviolet region.	Gases, liquids dilute solutions, solids ground with KBr and pressed into discs.	Gases or Vapours
Detector (c)	Photographic device or more generally, a photomultiplier tube.	Heat sensor or photo conductivity device.	Crystal detector for radio frequencies

With this background, we take up the study of microwave spectra in this unit. We shall study infrared, visible and ultraviolet spectra in the next unit.

7.6 REQUISITE FOR MICROWAVE ABSORPTION

We have mentioned earlier that absorption in the microwave region of electromagnetic spectrum can cause transition of the absorbing molecule from one rotational level to another. Therefore, the microwave spectra is also known as rotational spectra. The condition for a molecule to exhibit rotational spectra is that a molecule must possess permanent dipole moment. When a molecule having permanent dipole moment rotates, it generates an electric field which can interact with the electric component of the microwave radiation. During this interaction, energy can be absorbed or emitted and thus the rotation of the molecule gives rise to a spectrum. If molecules do not have permanent dipole moment, interaction is not quite prominent and these molecules are said to be **"microwave inactive"**. Examples of microwave inactive molecules are H_2, Cl_2, etc. On the other hand, the molecules like HCl, CH_3Cl, etc., which possess permanent dipole moment are **"microwave active"**.

Molecules that have no dipole moment can also have rotational spectra, although these are often weak. In this unit, we shall consider only the spectra of molecules which have permanent dipole moment.

Let us now see how microwave spectra can be utilised to derive information regarding bond length. Before that, answer the following SAQ.

SAQ 3

Which of the following molecules can absorb in the microwave region? Write YES or NO in the space given.

a) CO ....

b) SO_2 ....

c) N_2 ....

d) Cl_2 ....

e) HCl ....

7.7 THEORY OF ROTATIONAL SPECTRA

We have already mentioned that rotational energy, like other forms of molecular energy, is quantised. The permitted energy values (energy levels) may be calculated for any molecule by solving the Schrödinger equation for the molecule. For simple molecules, the derivations involved are somewhat simple while for large systems, it is more complicated and requires gross approximations. We are not concerned with tedious derivations of the expressions like Eq. 7.4, but we will only apply the same to simple cases such as heteronuclear diatomic molecules. For such a system, the rotational energy levels, as obtained by solving the Schrödinger equation, are given by the expression,

$$E_{rot} = \frac{h^2}{8\pi^2 I} J(J+1) \qquad \ldots(7.4)$$

where,

h = Planck's constant (6.626×10^{-34} J s),

I = Moment of inertia (kg m^2),

J = Rotational quantum number which has values 0, 1, 2, 3, etc. It is **dimensionless**.

The unit of E_{rot}

$= \text{Unit of } \frac{h^2}{8\pi^2 I} J\ (J+1)$

$= \frac{\text{J}^2\ \text{s}^2}{\text{kg m}^2}$

Note that J (italicised) stands for the rotational quantum number whereas J (roman) stands for the energy unit, joule. Here J stands for the energy unit, joule only. Also the rotational quantum number J is a mere number without a unit.

Hence, the unit of

$$E_{rot} = \frac{\text{J}^2\ \text{s}^2}{\text{kg m}^2}$$

$$= \frac{\text{J.J s}^2}{\text{kg m}^2}$$

$$= \frac{\text{J kg m}^2\ \text{s}^{-2}\ \text{s}^2}{\text{kg m}^2}$$

$[\because 1\ \text{J} = 1\ \text{kg m}^2\text{s}^{-2}]$

$= \text{J}$

By the application of simple mechanics, we can define moment of inertia. Consider a diatomic molecule AB, in which atomic masses of the atoms A and B are m_1 and m_2, respectively. Suppose that these two atoms are joined by a rigid bond of length r. Let the two atoms A and B be at distances r_1 and r_2, respectively, from the centre of gravity G of the molecule about which the molecule rotates end-over as shown in Fig. 7.9.

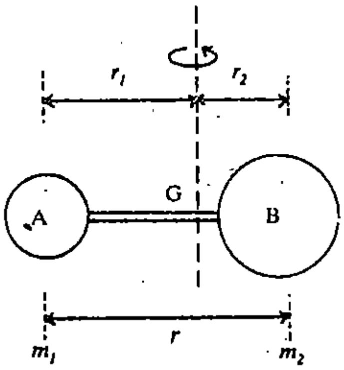


Fig. 7.9 : Simple model for rotational motion of a diatomic molecule.

It is evident that the bond length r must be equal to the sum of r_1 and r_2.

$$r = r_1 + r_2 \quad \text{...(7.5)}$$

In this case, the moment of inertia, I, about the axis of rotation is defined by,

$$I = m_1 r_1^2 + m_2 r_2^2 \quad \text{...(7.6)}$$

Since G is the centre of gravity, moments $m_1 r_1$ and $m_2 r_2$, must be equal.

$$\text{i.e., } m_1 r_1 = m_2 r_2 \quad \text{...(7.7)}$$

On rearranging this expression, we get,

$$\frac{r_1}{r_2} = \frac{m_2}{m_1}$$

using the characteristics of proportions, we can write,

$$\frac{r_1}{(r_1 + r_2)} = \frac{m_2}{(m_1 + m_2)}$$

i.e.,

$$r_1 = \frac{m_2}{(m_1 + m_2)}(r_1 + r_2) = \frac{m_2}{(m_1 + m_2)} r \quad \text{...(7.8)}$$

Similarly, rearranging Eq.7.7 as,

$$\frac{r_2}{r_1} = \frac{m_1}{m_2}$$

we get,

$$\frac{r_2}{(r_1 + r_2)} = \frac{m_1}{(m_1 + m_2)}$$

i.e.,

$$r_2 = \frac{m_1}{(m_1 + m_2)}(r_1 + r_2) = \frac{m_1}{(m_1 + m_2)} r \quad \text{...(7.9)}$$

On substituting Eqs. 7.8 and 7.9 in Eq. 7.6, we obtain the following expression,

$$I = m_1 \left(\frac{m_2}{m_1 + m_2}\right)^2 r^2 + m_2 \left(\frac{m_1}{m_1 + m_2}\right)^2 r^2 \quad \text{...(7.10)}$$

Rearranging, we get.

$$I = \frac{m_1 m_2}{(m_1 + m_2)^2} r^2 (m_2 + m_1) = \frac{m_1 m_2}{(m_1 + m_2)} r^2$$

$$= \mu r^2 \qquad \ldots(7.11)$$

where μ is the **reduced mass** of the diatomic molecule and its value is $\mu = m_1 m_2/(m_1 + m_2)$. The unit of reduced mass is kg. Eq. 7.11 defines the moment of inertia in terms of atomic masses and bond length.

Now consider again Eq. 7.4, which expresses the allowed energies in joules; we, however, generally express rotational energies, in terms of wave number. Since $E = hc\bar{v}$, Eq. 7.4 can be written as:

$$\bar{v} = \frac{h^2}{8\pi^2 Ihc} J(J + 1)$$

$$= \frac{h}{8\pi^2 Ic} J(J + 1) \qquad \ldots(7.12)$$

where c is the velocity of light expressed in m s^{-1} and the unit of wave number is reciprocal meter or m^{-1}.

Further, we generally write B for $h/8\pi^2 Ic$; so, Eq.7.12 can be expressed as,

$$\bar{v} = BJ(J + 1) \qquad \ldots(7.13)$$

where B is called the **rotational constant**. The literature values for B are in cm^{-1} unit. You can convert the values in cm^{-1} unit into m^{-1} unit, if you remember the relationship,
$1\ \text{m}^{-1} = (10^2\ \text{cm})^{-1} = 10^{-2}\ \text{cm}^{-1}$

We shall illustrate this conversion in Sec. 7.8.

Unit of $\bar{v}$ = unit of $\frac{h}{8\pi^2 Ic} J(J + 1)$

$$= \frac{\text{J s}}{\text{kg m}^2\ \text{m s}^{-1}}$$

Remember, the rotational quantum number, J, has no unit.

Unit of $\bar{v} = \frac{\text{J s}}{\text{kg m}^3\ \text{s}^{-1}}$

$$= \frac{\text{kg m}^2\ \text{s}^{-2}\ \text{s}}{\text{kg m}^3\ \text{s}^{-1}}$$

$$= \text{m}^{-1}$$

From Eq. 7.13, by using integral values 0, 1, 2, 3, 4, 5, etc. for J we can show the allowed rotational energy levels diagrammatically, as in Fig. 7.10.

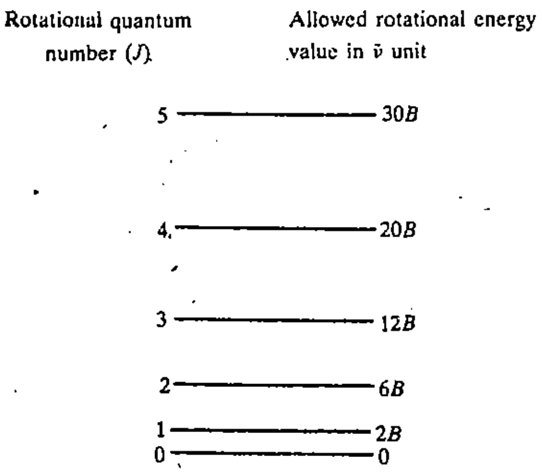


Fig. 7.10 : The allowed rotational energy levels of a rigid diatomic molecule.

In order to predict the rotational spectrum, we now need to consider the difference between the rotational energy levels. The energy difference between two levels will be given by,

$$\Delta E_{\text{rot}} = E_{J'} - E_J = \frac{h^2}{8\pi^2 I} J'(J' + 1) - \frac{h^2}{8\pi^2 I} J(J + 1) \qquad \ldots(7.14)$$

where J = lower quantum number, J' = higher quantum number.

When a molecule moves from one energy level to another, ΔE gives the amount of energy absorbed or emitted. This energy is detected by the spectrometer in the form of spectral lines. Since, we prefer mentioning the rotational transitions in wave number units, we can rewrite Eq. 7.14 as,

$$\bar{\nu}_{J\to J'} = \frac{\Delta E_{rot}}{hc} = \frac{h^2}{8\pi^2 Ihc}[J'(J'+1) - J(J+1)]$$

$$= \frac{h}{8\pi^2 Ic}[J'(J'+1) - J(J+1)]$$

$$= B[J'(J'+1) - J(J+1)] \qquad \ldots(7.15)$$

$$(\because B = \frac{h}{8\pi^2 Ic})$$

When $J = 0$ and $J' = 1$, Eq. 7.15 becomes :

$$\bar{\nu}_{0\to 1} = B[1(1+1) - 0(0+1)] = 2B$$

Thus, for $J = 0$ to $J' = 1$ transition, an absorption line will appear at $2B$. If the molecule is raised from $J = 1$ to $J' = 2$ level by the absorption of more energy in the microwave region, then the wave number corresponding to this transition is given by,

$$\bar{\nu}_{1\to 2} = B[2(2+1) - 1(1+1)]$$

$$= 4B$$

It means that corresponding to the transition, $J = 1$ to $J' = 2$, an absorption line will appear at $4B$. In general, when the molecule is raised from the level J to $J + 1$, the wave number for the transition is,

$$\bar{\nu}_{J\to J+1} = B[(J+1)(J+2) - J(J+1)]$$

$$= B(J+1)(J+2-J)$$

$$\bar{\nu}_{J\to J+1} = 2B(J+1) \qquad \ldots(7.16)$$

From Eq. 7.16, it is clear that stepwise, raising of rotational energy results in an absorption spectrum consisting of lines at $2B$, $4B$, $6B$, etc. The allowed energy transitions, the general pattern of rotational spectrum and rotational lines in the absorption spectrum of hydrogen chloride are shown in Fig. 7.11.

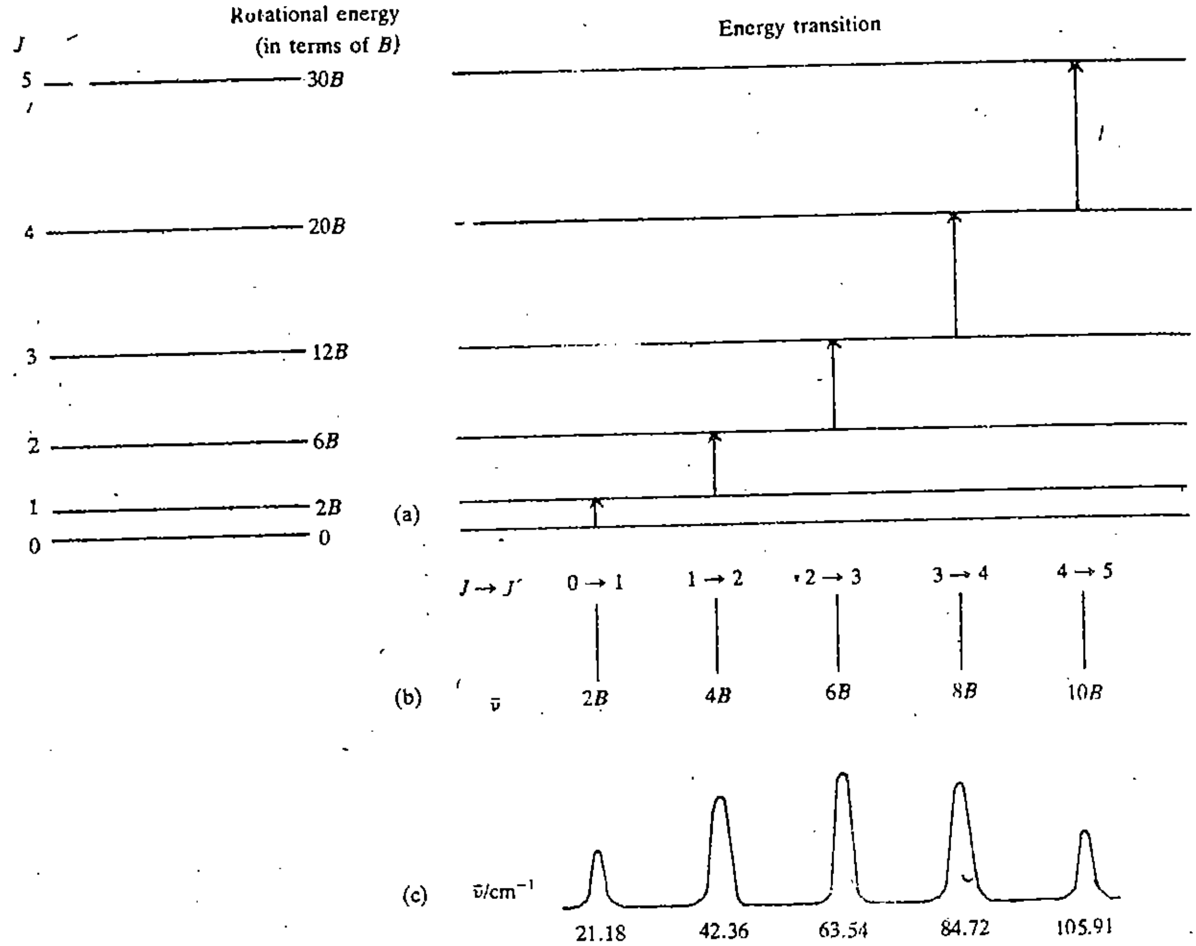


Fig. 7.11 : Rotational spectrum: (a) Allowed rotational transitions; (b) rotational lines in the absorption spectrum ; (c) rotational spectrum of hydrogen chloride.

Note a constant difference of $2B$ between adjacent lines ; this value, $2B$, is called rotational spacing. In the case of the spectra of $^1H^{35}Cl$ molecule, the rotational spacing is equal to 2118 m^{-1} or 21.18 cm^{-1}. It is assumed here that the molecule is rigid. Such a system is also called rigid rotator.

Selection rule for rotational spectra :

In the above discussion, we have not considered the sequence of transitions, $J = 0 \rightarrow J' = 2$, $J = 2 \rightarrow J' = 4$, etc. We considered transitions only to the immediate neighbouring energy level. It can be shown using quantum mechanics that only those transitions are possible in which J changes by one unit, all other transitions being spectroscopically forbidden. Such a result is called **selection rule**. Therefore, for rigid diatomic rotator, selection rule is:

$$\Delta J = \pm 1$$

For absorption spectra, $\Delta J = +1$; similarly, for emission, $\Delta J = -1$. That is, the allowed transition for absorption is $J \rightarrow J + 1$.

So far, we have discussed the theory of microwave spectra. In the next section, we shall consider the application of rotational spectra taking HCl molecule, as an example.

7.8 ROTATIONAL SPECTRA OF HCl MOLECULE

The rotational spectra of HCl molecule is shown in Fig. 7.11c. Let us now apply Eq. 7.16 to this spectrum to calculate the rotational constant, moment of inertia and bond length of the molecule.

The first line corresponding to $J = 0$ to $J' = 1$ appears in the rotational spectrum of HCl at 21.18 cm^{-1}. Hence, from Eq.7.16,

$$\bar{\nu}_{0 \rightarrow 1} = 21.18 \text{ cm}^{-1} = 2B \text{ cm}^{-1}$$

or $B = 10.59$ cm^{-1}. Since the literature values of B are given in cm^{-1}, whereas we use SI units throughout, it is better to convert B also into SI units.

$$B = 1059 \text{ m}^{-1} \qquad (\because 1 \text{ cm}^{-1} = 10^2 \text{ m}^{-1})$$

Since, $B = \dfrac{h}{8\pi^2 Ic}$, $I = h/8\pi^2 Bc$,

substituting the values of h, π, B and c,

$$I(\text{HCl}) = \frac{6.626 \times 10^{-34} \text{ (J s)}}{8 \times 3.142^2 \times 1059 \text{ (m}^{-1}) \times 2.998 \times 10^8 \text{ (m s}^{-1})}$$

$$= 2.646 \times 10^{-47} \text{ kg m}^2$$

Since the moment of inertia of HCl is known, we can calculate its bond length using the steps described below :

$$I = \mu r^2 = \frac{m_1 m_2}{m_1 + m_2} r^2$$

$$\text{Mass of an H atom} = \frac{1.008 \times 10^{-3}}{6.022 \times 10^{23}} \text{ kg}$$

$$\text{Mass of a Cl atom} = \frac{35.45 \times 10^{-3}}{6.022 \times 10^{23}} \text{ kg}$$

Thus, the reduced mass,

$$\mu = \frac{m_1 m_2}{(m_1 + m_2)} = \frac{1.008 \text{ (kg)} \times 35.45 \text{ (kg)}}{(1.008 + 35.45) \text{ (kg)}} \times \frac{10^{-3}}{6.022 \times 10^{23}} = 1.627 \times 10^{-27} \text{ kg}$$

$$r = \sqrt{\frac{I}{\mu}} = \sqrt{\frac{2.646 \times 10^{-47} \text{ (kg m}^2)}{1.627 \times 10^{-27} \text{ (kg)}}}$$

$$r = 127.5 \text{ pm.}$$

From the above discussion, it follows that rotational spectra can be used to calculate simple molecular parameters such as moment of inertia and bond length. Besides this, we can also obtain information regarding molecular symmetry and bond angle.

To test your understanding of the above discussion, try the following SAQ.

SAQ 4

The lowest wave number absorption line in the rotational spectrum of $^{1}H^{19}F$ is at 41.11 cm^{-1}. Answer the following questions.

a) What is the value of the lowest frequency of absorption in the rotational spectrum of HF?

b) Which are the two energy levels involved in this transition?

c) What is the value of the rotational constant (B) for HF?

d) Calculate the moment of inertia for HF molecule.

e) Calculate the bond length of HF molecule.

7.9 SUMMARY

In this unit, we have briefly described the principles of molecular spectroscopy with special reference to rotational spectra. We are summarising below what we have studied so far :

- Molecules have different types of quantised energy ; e.g., rotational, vibrational and electronic.
- Molecular spectra are more complex than atomic spectra ; the former can be classified into three types on the basis of the method to obtain them, namely, emission spectra, absorption spectra and Raman spectra.
- Different regions of electromagnetic radiations are used for different types of absorption spectra.
- The condition for a molecule to exhibit rotational spectra is that it must possess permanent dipole moment.
- The rotational spectra of a diatomic molecule is a series of equally spaced lines of wave numbers $2B$, $4B$, $6B$, etc. The wave numbers of the line can be used to provide accurate value of bond length.

7.10 TERMINAL QUESTIONS

1. Calculate ΔE, ν and $\overline{\nu}$ for visible radiation of wavelength 800 nm.
2. CO absorbs electromagnetic radiation at about 6.4×10^{13} Hz.
   a) In which region of the electromagnetic spectrum does this frequency lie?
   b) Which type of molecular energy is likely to be affected?
3. What is the selection rule for the microwave absorption spectra?
4. Complete the Table given below:

Rotational quantum number	Energy	Energy transition
0		
1		
2		
3		
4		
5		

5. The bond length of $^{1}H^{80}Br$ molecule is 141 pm. Calculate the wave numbers in cm^{-1} for the following rotational transitions :

$J = 0 \rightarrow J' = 1$;

$J = 1 \rightarrow J' = 2$; and

$J = 2 \rightarrow J' = 3$.

7.11 ANSWERS

SAQs

1. a) To calculate the energy per mole, multiply hc/λ by Avogadro constant (N_A)

Thus, $\Delta E = \frac{N_A hc}{\lambda}$

$$= \frac{6.022 \times 10^{23}\ (\text{mol}^{-1}) \times 6.626 \times 10^{-34}\ (\text{J s}) \times 2.998 \times 10^{8}\ (\text{m s}^{-1})}{200 \times 10^{-9}\ (\text{m})}$$

$= 5.981 \times 10^{5}\ \text{J mol}^{-1}$

$= 598.1\ \text{kJ mol}^{-1}$

b) $$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^{8}\ (\text{m s}^{-1})}{200 \times 10^{-9}\ (\text{m})} = 1.499 \times 10^{15}\ \text{s}^{-1} \text{ or Hz}$$

c) $$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{200 \times 10^{-9}\ (\text{m})} = 5 \times 10^{6}\ \text{m}^{-1}$$

$= 5 \times 10^{4}\ \text{cm}^{-1}$

2.

Radiation	Molecular energy changes
a) Infrared	Vibrational and rotational
b) Ultraviolet	Electronic, vibrational and rotational
c) Microwave	Rotational
d) Visible	Electronic, vibrational and rotational

3. a) Yes b) Yes c) No d) No e) Yes

4. a) First convert the unit of $\bar{\nu}$ into m^{-1}; then substitute this value in the equation, $\nu = \bar{\nu} c$.

Hence, $\nu = 1.232 \times 10^{12}$ Hz.

b) The lowest frequency absorption arises due to the transition from $J = 0$ level to $J = 1$ level.

c) $2B = 41.11\ \text{cm}^{-1}$, therefore $B = 20.56\ \text{cm}^{-1}$

$= 2056\ \text{m}^{-1}$

d) Since $B = \frac{h}{8\pi^2 Ic}$,

$$I = \frac{h}{8\pi^2 Bc} = \frac{6.626 \times 10^{-34}\ (\text{J s})}{8 \times (3.142)^2 \times 2056\ (\text{m}^{-1}) \times 2.998 \times 10^{8}\ (\text{m s}^{-1})}$$

$= 1.363 \times 10^{-47}\ \text{kg m}^2$

e) To calculate the bond length of HF molecule, first calculate reduced mass, μ;

$$\mu = \frac{m_H \times m_F}{(m_H + m_F)} \times \frac{10^{-3}}{6.022 \times 10^{23}}\ \text{kg}$$

$$= \frac{1 \times 19 \times 10^{-3}}{(1 + 19) \times 6.022 \times 10^{23}}\ \text{kg}$$

$= 1.578 \times 10^{-27}$ kg

From Eq. 7.11, bond length can be calculated as follows:

$$r = \sqrt{\frac{I}{\mu}}$$

$$= \sqrt{\frac{1.363 \times 10^{-47}\ (\text{kg m}^2)}{1.578 \times 10^{-27}\ (\text{kg})}}$$

$$= 92.94 \text{ pm}$$

Terminal Questions

1. $\Delta E = 149.5$ kJ mol^{-1}; $\nu = 3.748 \times 10^{14}$ Hz;

   $\bar{\nu} = 1.25 \times 10^{6}$ m^{-1} $= 1.25 \times 10^{4}$ cm^{-1}

2. a) Infrared

   b) Vibrational and rotational.

3. $\Delta J = \pm 1$.

4.

Rotational quantum number	Energy	Energy transition
0	0	
1	$2B$	$J = 0$ to $J = 1$, $2B$
2	$6B$	$J = 1$ to $J = 2$, $4B$
3	$12B$	$J = 2$ to $J = 3$, $6B$
4	$20B$	$J = 3$ to $J = 4$, $8B$
5	$30B$	$J = 4$ to $J = 5$, $10B$

5. Use Eq. 7.11 to calculate the moment of inertia.

$$I = \mu r^2$$

$$\mu = \frac{m_H m_{Br}}{m_H + m_{Br}} \times \frac{10^{-3}}{6.022 \times 10^{23}} \text{ kg}$$ (Atomic mass of hydrogen is 1 and that of bromine is 80)

$$= 1.640 \times 10^{-27} \text{ kg}$$

$$I = \mu r^2 = 1.640 \times 10^{-27}\ (\text{kg}) \times (141 \times 10^{-12})^2\ (\text{m})^2$$

$$= 3.260 \times 10^{-47} \text{ kg m}^2$$

Once I is known, we can calculate B using the equation,

$$B = \frac{h}{8\pi^2 Ic}$$

$$= \frac{6.626 \times 10^{-34}\ (\text{J s})}{8 \times (3.142)^2 \times 3.260 \times 10^{-47}\ (\text{kg m}^2) \times 2.998 \times 10^{8}\ (\text{m s}^{-1})}$$

$$= 858.4 \text{ m}^{-1}$$

$$= 8.584 \text{ cm}^{-1}$$

For the transition $J = 0$ to $J' = 1$, $\bar{\nu} = 2B = 17.17$ cm^{-1};

For the transition $J = 1$ to $J' = 2$, $\bar{\nu} = 4B = 34.34$ cm^{-1};

For the transition $J = 2$ to $J' = 3$, $\bar{\nu} = 6B = 51.50$ cm^{-1}.

UNIT 8 MOLECULAR SPECTROSCOPY– II

Structure

8.1 INTRODUCTION

In the previous unit, we have explained the different types of energy levels in a molecule. We also discussed how the transition between energy levels is responsible for the different types of absorption spectra. Later we discussed the rotational spectra in detail and used the same to calculate the moment of inertia and bond length for a diatomic molecule.

In this unit, firstly we study infrared spectra of diatomic molecules. Then we talk about the infrared spectra of polyatomic molecules. We discuss the applications of infrared spectra in the characterisation of group frequencies. We also take up ultraviolet and visible spectra in detail. We then explain how electronic spectra are useful in the identification of chromophores in a molecule. Finally we discuss applications of ultraviolet and visible spectra for quantitative analysis.

Objectives

After studying this unit, you should be able to:

- describe the condition for absorption of infrared radiation,
- explain the infrared spectra of diatomic molecules,
- calculate the force constant of simple diatomic molecules from their infrared spectra,
- state the number of vibrational modes for the polyatomic molecules,
- identify some specific functional groups present in organic compounds on the basis of infrared spectra,
- explain the significance of λ_{max} and ε values of a compound,
- state different types of electronic transitions in a molecule, and
- describe simple applications of ultraviolet and visible spectra in qualitative and quantitative analysis.

8.2 REQUISITE FOR INFRARED ABSORPTION

In the previous unit, we dealt with the rigid rotator model for the diatomic molecule, assuming that the bond is inflexible. The atoms in a molecule actually do not remain in fixed positions but vibrate about some mean positions. We have already noted that the absorption of infrared radiation by a molecule increases its vibrational energy. From the study of infrared absorption spectrum, we can, therefore, derive information about the spacings of the allowed vibrational energies. As in rotation spectra, all types of molecules cannot interact with infrared radiation. Only those molecules which show change in dipole moment during a vibration can exhibit infrared spectra. Homonuclear diatomic molecules such as O_2, N_2 or Cl_2 do not show change in dipole moment during vibration; therefore, they do not exhibit infrared spectra.

You are aware that the infrared radiation absorbed by a gaseous molecule changes both the vibrational and the rotational energies of the molecule. This further adds to the complexity of infrared spectrum. We first consider the diatomic molecule undergoing vibrational and rotational energy changes simultaneously, and then we focus our attention on the group frequencies of polyatomic molecules.

8.3 INFRARED SPECTRA OF DIATOMIC MOLECULES

Let us consider in detail, the absorption spectrum of gaseous hydrogen chloride, as a typical example of a diatomic molecule. Figure 8.1 shows the absorption spectrum of gaseous hydrogen chloride in the wave number region 2600-3100 cm^{-1}. The most important features to note are the regular spacings of about 20 cm^{-1} between adjacent lines and the fact that the spectrum is centred at about 2890 cm^{-1}.

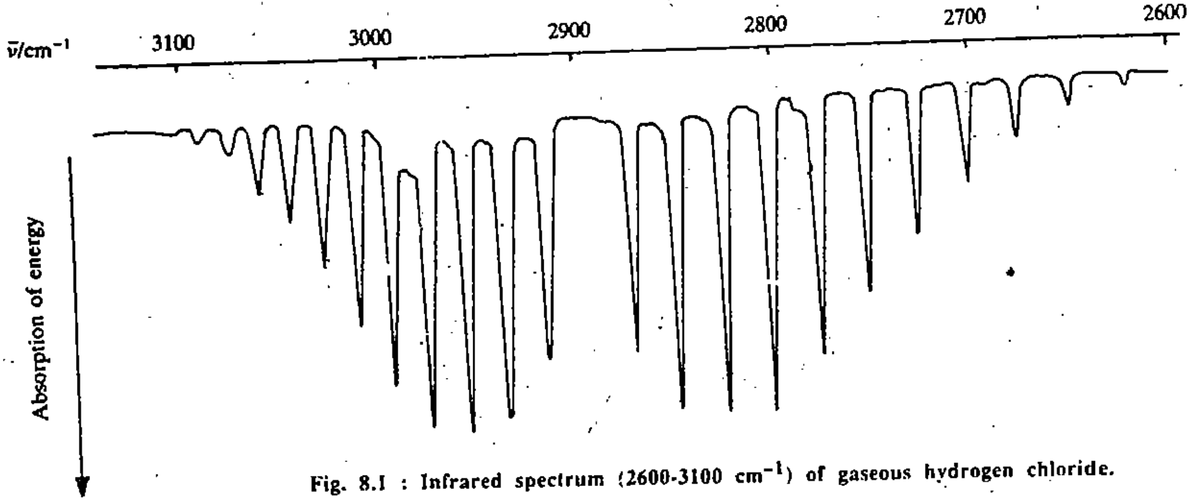


Fig. 8.1 : Infrared spectrum (2600-3100 cm^{-1}) of gaseous hydrogen chloride.

The spectra of hydrogen chloride molecule can be understood in terms of vibrational and rotational transitions. You are aware that energy needed for rotational transition is less than that for vibrational transition. The numerous vibrational transitions accompanied by the rotational transitions are responsible for the multiple lines in its infrared spectrum as shown in Fig. 8.1. This is explained in more detail in the next section.

8.4 THEORY OF INFRARED ABSORPTION SPECTRA

The quantum theory predicts that only certain vibrational energies (E_{vib}) are allowed. These values are governed by the expression:

$$E_{vib} = (v + \frac{1}{2}) h\nu_0 \qquad ...(8.1)$$

where v is the vibrational quantum number, with possible values of 0, 1, 2, etc. and ν_0 is the fundamental frequency.

The lowest two energy levels, $v = 0$ and $v = 1$, will have E_{vib} values of $1/2\, h\nu_0$ and $3/2\, h\nu_0$, respectively, so that the difference between them (i.e., the energy of the $v = 0 \rightarrow v = 1$ transition) is $h\nu_0$. The appropriate frequency of the electromagnetic radiation associated with this energy change is the fundamental frequency (ν_0). It should also be noted that even in the ground vibrational state, the molecule has the vibrational energy, $1/2\, h\nu_0$. This is called the **zero point energy**.

Zero point energy signifies that a molecule must always vibrate and can never be at rest. This is a significant wave-mechanical result which has been amply borne out by experiment.

When a molecule has rotational and vibrational changes simultaneously, the total energy associated with these changes is the sum of the rotational and vibrational energies, i.e.,

$$E_{vib} + E_{rot} = (v + \frac{1}{2}) h\nu_0 + \frac{h^2}{8\pi^2 I} J(J+1) \qquad ...(8.2)$$

Allowed energy levels are illustrated in Fig.8.2. Note that the vibrational energy levels are much more widely spaced than the rotational energy levels.

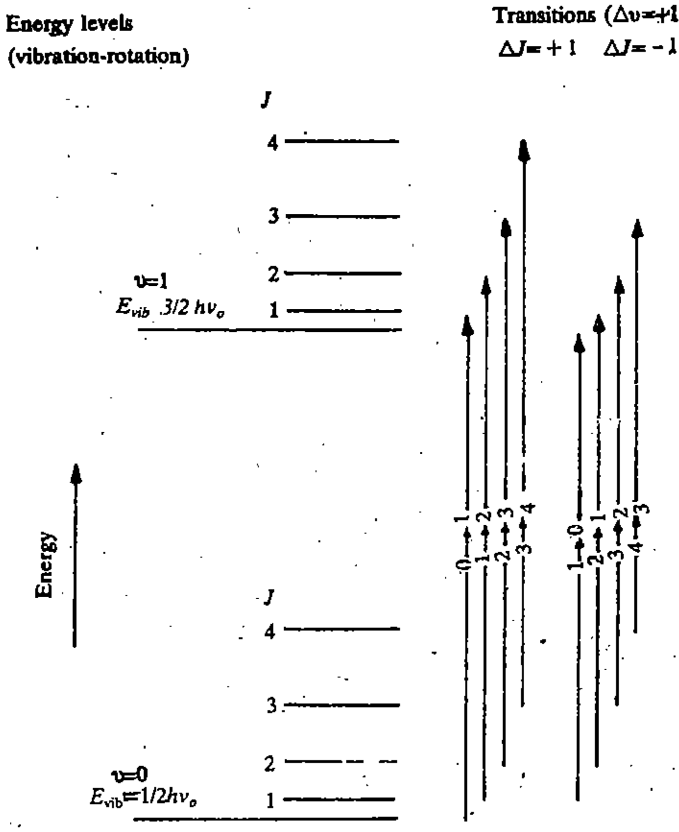


Fig. 8.2 : Vibrational energy levels with rotational sublevels for a diatomic molecule.

When a molecule absorbs energy in the infrared region of electromagnetic spectrum, it can change its vibrational and rotational levels and these energy changes account for the features of a typical spectrum (Fig. 8.1). The infrared absorption spectrum in the gas phase is much complicated due to the rotational fine structure (Fig. 8.3 a). We can avoid this complication by taking the spectrum for liquid (Fig. 8.3 b) or solid samples. For such cases, the rotational fine structure becomes buried and a broad peak is observed for a vibrational energy change. The interpretation of the infrared spectra is thus made simple even for polyatomic molecules.

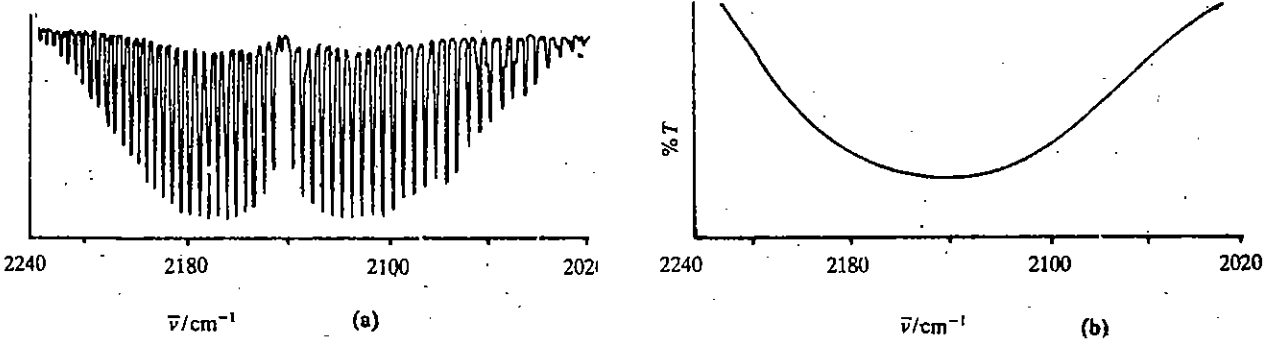


Fig. 8.3 : The spectra of CO (a) in the gas phase (b) in CCl_4 solution.

Now, we consider the theoretical basis of vibration spectra. It is simpler to understand the vibration of a diatomic molecule by classical mechanics than by quantum mechanics. If molecule undergoes only vibrational motion, we can explain the origin and changes in vibrational spectra using the ideas of the **harmonic oscillator model**, illustrated in Fig. 8.4. According to this model, each chemical bond acts like a spring; it connects two atoms of masses, m_1 and m_2, undergoing simple harmonic motion.

Such a system obeys Hooke's law; that is, when the masses are stretched or compressed away from the resting position, the restoring force is proportional to the extent of displacement (Δx) from that position. Algebraically stated,

$$\text{Restoring force} = -k\,\Delta x \qquad \ldots(8.3)$$

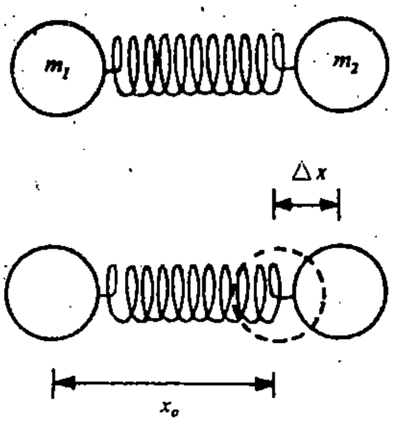


Fig. 8.4 : Ball and spring representation of a diatomic molecule.

where k is the proportionality constant known as **force constant**; it is the restoring force per unit displacement from the resting position. The negative sign in Eq. 8.3 indicates that the restoring force tends to pull the spring back to its original position. When the spring is compressed, it exerts a force to expand; when it is stretched, it exerts a force to pull back.

A set of masses that are connected by the spring, naturally tends to settle into a specific motion, when disturbed. The masses vibrate with a frequency that depends on the masses and the strength of the spring. **Such vibrations, which occur at characteristic frequencies, are what we measure in infrared spectra.** For the simple harmonic motion of the spring, it can be shown that the frequency of oscillation, ν, is given by,

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{1}{2\pi}\sqrt{\frac{k\,(m_1 + m_2)}{m_1 m_2}} \qquad \ldots(8.4)$$

where μ is the reduced mass (being equal to $\frac{m_1\ m_2}{(m_1 + m_2)}$) and k is the force constant of the spring. Similarly, the behaviour of chemical bonds can be interpreted in terms of a fundamental frequency, ν_0, given by Eq. 8.5.

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \ldots(8.5)$$

where μ is the reduced mass of the two connected atoms, and by analogy, k is the force constant of the bond. The energy of a classical oscillator is equal to $\frac{1}{2}kx^2$ or $2\pi^2\mu\ \nu_0^2 x^2$ (From Eq. 8.5, $k = 4\pi^2\mu\nu_0^2$); and hence can be varied continuously. But it can be shown that the energy of quantum mechanical oscillator is $(\upsilon + 1/2)\ h\nu_0$, with ν_0 having the same value as obtained for a classical oscillator. Now, on substituting the value of fundamental frequency from Eq. 8.5 in Eq. 8.1, we can get,

$$E_{\text{vib}} = (\upsilon + \frac{1}{2})\frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \ldots(8.6)$$

To raise the molecules from the state υ to state $\upsilon + 1$, the energy required is given by,

$$E_{\upsilon \rightarrow \upsilon + 1} = (\upsilon + 1 + \frac{1}{2})\,h\nu_0 - (\upsilon + \frac{1}{2})\,h\nu_0 = h\nu_0$$

The allowed vibrational energies for a diatomic molecule, as given by Eq. 8.6 are shown schematically in Fig. 8.5, where energy is plotted against internuclear distance. This representation contains information both about the energy levels and the energy changes that occur during the vibration. The energy levels are seen to be equally spaced with a spacing of $h/2\pi\sqrt{k/\mu}$ or more simply, $h\nu_0$. The selection rule for a harmonic vibrational transition, as per the solution of Schrödinger equation, is $\Delta\upsilon = \pm 1$. This means that the increase or decrease in the vibrational quantum number is by one unit only. That is, a molecule can absorb energy and get excited to the next higher vibrational level or emit a part of its energy to be transferred to the next lower vibrational level. Also the selection rule $\Delta\upsilon = \pm 1$ indicates that the energy difference between two vibrational levels involved in a transition would always be equal to the spacing ($h\nu_0$), and we would accordingly expect all lines in the spectrum to fall in the same place (see the diagram at the foot of Fig. 8.5).

Thus, for an ideal harmonic oscillator, the spectral absorption must occur exactly at the vibration frequency calculated from Eq. 8.6.

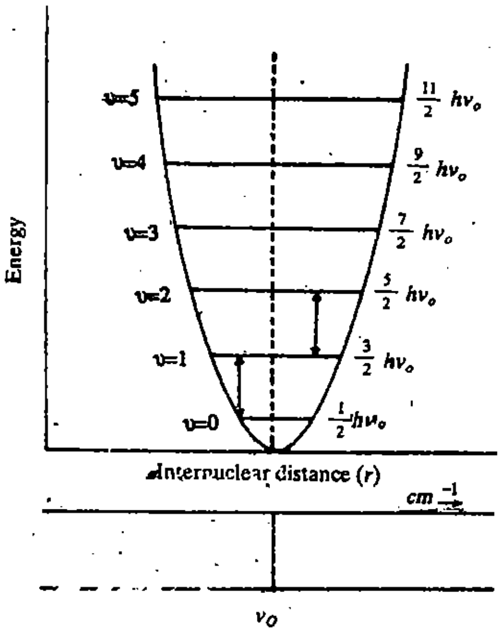


Fig. 8.5 : The allowed vibrational energy levels and the transitions between them.

To express the position of a spectral band in wave number (m^{-1}) unit, Eq. 8.7 is to be used.

$$\bar{\nu} = \frac{E_{vib}}{hc} = (\upsilon + \frac{1}{2}) \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \qquad \text{...(8.7)}$$

The literature values of the position of the spectral bands are in cm^{-1} units. Since
$1\ m^{-1} = 10^{-2} cm^{-1}$, $\bar{\nu}$ can be obtained in cm^{-1} unit as per the equation,

$$\bar{\nu} = (\upsilon + \frac{1}{2}) \frac{10^{-2}}{2\pi c} \sqrt{\frac{k}{\mu}} \qquad \text{...(8.8)}$$

Using Eq. 8.7 or Eq. 8.8, you can construct an energy level diagram from vibrational spectrum; alternatively, you can draw conclusions about the spectrum from an energy level diagram.

In reality, the molecules do not exhibit the simple harmonic motion exactly. That is, the resulting vibrational motion is **anharmonic** in nature and the mathematical calculation of the vibrational energy levels is necessarily more complex. The corresponding curve is modified in the manner shown in Fig. 8.6. We observe in this diagram that the spacing of the vibrational energy levels become closer with increasing energy (or increasing vibrational quantum number) due to the anharmonic nature of the vibration.

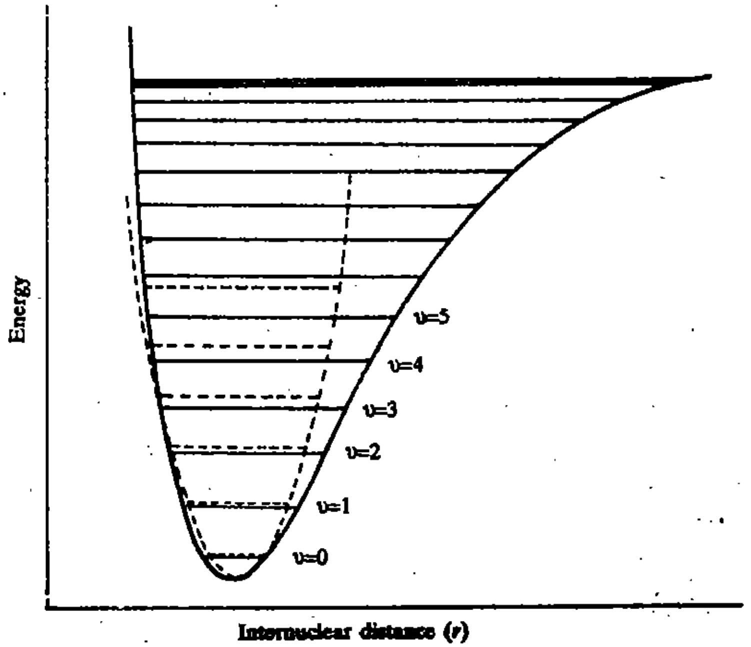


Fig. 8.6 : The energy of a diatomic molecule undergoing anharmonic vibration. Compare this curve with the dotted curve of a harmonic oscillator.

The selection rules for all the transitions in an anharmonic oscillator may be given as,

$\Delta\upsilon = \pm1, \pm2, \pm3, \ldots\ldots$

The transition in which

i) $\upsilon = 0$ to $\upsilon = 1$, gives fundamental band;

ii) $\upsilon = 0$ to $\upsilon = 2$, gives first overtone;

iii) $\upsilon = 0$ to $\upsilon = 3$, gives second overtone.

A typical vibrational spectrum with two overtones is shown in Fig. 8.7. Note the decreased intensity (as shown by lower value for $\% T$) of the overtones as compared to the fundamental band.

Energy levels are not equally spaced in the anharmonic oscillators, therefore, energy required for the first overtone is not exactly twice the fundamental band.

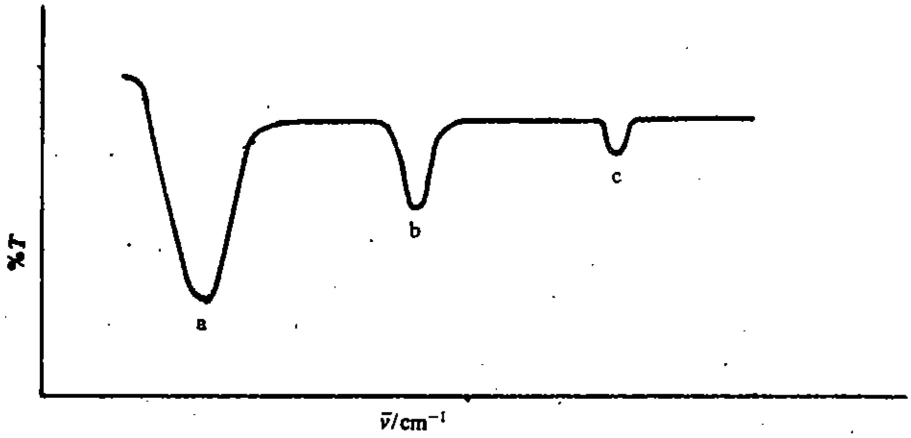


Fig. 8.7 : Infrared spectrum of a diatomic molecule in solution: (a) fundamental band; (b) first overtone; (c) second overtone.

Using the above discussion, we can calculate the fundamental frequency (ν_0) or the force constant (k), if one of them is known for a simple diatomic molecule. The value of force constant indicates the strength of the bond. For example, hydrogen chloride ($^1H^{35}Cl$), has a force constant value of 480 N m^{-1}. We can calculate its fundamental frequency, once its reduced mass is known.

$$\text{Reduced mass of } {}^1H^{35}Cl = \frac{m_1 m_2}{(m_1 + m_2)} = \frac{1 \times 35}{(1 + 35)} \times \frac{10^{-3}}{6.022 \times 10^{-23}}\ \text{kg}.$$

$$= 1.615 \times 10^{-27}\,\text{kg}.$$

Now, substituting the value of reduced mass and force constant in Eq. 8.5,

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} = \frac{1}{2 \times 3.142}\sqrt{\frac{480\ (\mathrm{N\ m^{-1}})}{1.615 \times 10^{-27}(\mathrm{kg})}}$$

$$= 8.676 \times 10^{13}\ \mathrm{Hz}$$

$$\bar{\nu} = \frac{\nu_0}{c} = \frac{8.676 \times 10^{13}\ (\mathrm{s^{-1}})}{2.998 \times 10^{8}\ (\mathrm{m\ s^{-1}})}$$

$$= 2.894 \times 10^{5}\ \mathrm{m^{-1}}$$

$$= 2.894 \times 10^{3}\ \mathrm{cm^{-1}} \qquad (\because 1\ \mathrm{m^{-1}} = 10^{-2}\ \mathrm{cm^{-1}})$$

$$= 2894\ \mathrm{cm^{-1}}.$$

$$\sqrt{\frac{1\ \mathrm{N\ m^{-1}}}{1\ \mathrm{kg}}} = \sqrt{\frac{1\ \mathrm{kg\ m\ s^{-2}\ m^{-1}}}{1\ \mathrm{kg}}} = \sqrt{\mathrm{s^{-2}}} = \mathrm{s^{-1}} \text{ or Hz.}$$

It is worth recollecting that the spectrum of hydrogen chloride given in Fig. 8.1 is centered around 2890 cm^{-1}. Now let us focus our attention on the significance of the force constant. Again consider the model given in fig. 8.4. Notice the way the frequency changes with k and the masses. m_1 and m_2. If the spring is stiffer, which means k becomes larger, then the frequency rises and the vibration is faster. Conversely, if the spring is weaker, k is reduced. and the frequency falls.

What happens if either of the masses is decreased and the same spring is retained? In that case, the value of μ decreases. Therefore, $1/\mu$ becomes larger, and as can be seen from Eq. 8.5, the fundamental frequency will rise. So decrease in mass yields the same effect as increase in the strength of the spring, and *vice versa*. Based on this analogy, we can generalise that the vibrational fundamental frequency is higher for,

i) stronger chemical bonds

ii) bonding between lighter atoms

The clause (i) suggests that we might expect the frequency to increase with bond order among C–C, C=C and $C\equiv C$ groups and among C–N, C=N and $C\equiv N$ groups. The trend expected from this simple model is indeed observed experimentally as seen in Table 8.1.

Table 8.1 : Variation of Vibrational Wave Number Values with Bond Order

Group	Wave number/cm^{-1}	Group	Wave number/cm^{-1}
C – C	900	C – N	1200
C = C	1650	C = N	1650
$C\equiv C$	2050	$C\equiv N$	2100

As per clause (ii) and the earlier discussion, we expect the frequency to decrease with increase in the vibrating masses. To understand this, consider the case of ^{1}HCl (which we shall represent as HCl in the following discussion) and ^{2}HCl (DCl). In case of HCl, the vibrational band, is centred at 2890 cm^{-1} and in case of DCl, it is centred at 2090 cm^{-1}. The force constant, is the same for HCl and DCl.

According to Eq. 8.5, ν_0 (HCl)/ν_0 (DCl) should be related inversely to the square root of the ratio of their reduced masses.

$$\frac{\nu_0(\mathrm{HCl})}{\nu_0(\mathrm{DCl})} = \sqrt{\frac{\mu(\mathrm{DCl})}{\mu(\mathrm{HCl})}}$$

Assume that the atomic masses of hydrogen, deuterium and chlorine are 1,2 and 35, respectively.

$$\text{Hence } \frac{\nu_0(\mathrm{HCl})}{\nu_0(\mathrm{DCl})} = \sqrt{\frac{2\times 35}{(2+35)} \times \frac{10^{-3}(\mathrm{kg})}{6.022\times 10^{23}} \times \frac{(1+35)}{35\times 1} \times \frac{6.022\times 10^{23}}{10^{-3}(\mathrm{kg})}}$$

$$= 1.395.$$

We can calculate the ratio ν_0 (HCl) /ν_0(DCl) also from the above mentioned experimental ν_0 values of the two molecules given above.

$$\frac{\nu_0(\mathrm{HCl})}{\nu_0(\mathrm{DCl})} = \frac{2890\ (\mathrm{cm}^{-1})}{2090\ (\mathrm{cm}^{-1})}$$

$$= 1.383.$$

It is interesting to note that the values of the ratio, ν_0(HCl)/ν_0 (DCl), obtained by both the methods are nearly the same. To test your understanding of the above discussion, try the following SAQ.

SAQ 1

Calculate the force constant for carbon monoxide, if this compound absorbs at 2.143 × 10^5 m^{-1} and its reduced mass is 1.139 × 10^{-26} kg.

....

....

....

8.5 INFRARED SPECTRA OF POLYATOMIC MOLECULES

So far, we have discussed the infrared spectra of simple diatomic molecules. Now, let us consider the vibrational spectra of polyatomic molecules.

For polyatomic molecules, there are several possible ways in which the bonds can vibrate. These are called the **vibrational modes** and each vibration has an associated fundamental frequency (ν_0). For example, the fundamental modes for the linear molecule CO_2 are illustrated in Fig. 8.8. Of these, ν_1 (the **symmetric stretching** mode) does not involve a dipole moment change and is "inactive" in the infrared region, there being no corresponding absorption of energy. However, absorption peaks are observed at ν_2 (2349 cm^{-1}) and ν_3 (667 cm^{-1}) because these modes of vibration involve dipole moment change. These are called **asymmetric stretching** (ν_2) and **bending** (ν_3) modes. We notice that less energy is involved in bending than in stretching; this is because, it is easier to bend a spring than to stretch. In symmetric stretching, both the bonds a and b are shortened or elongated to the same extent simultaneously. In asymmetric stretching, one of the bonds (a or b), is shortened, while the other is elongated.

During a stretching vibration, bond length varies; in a bending vibration, bond angle varies. Bending requires less energy than stretching.

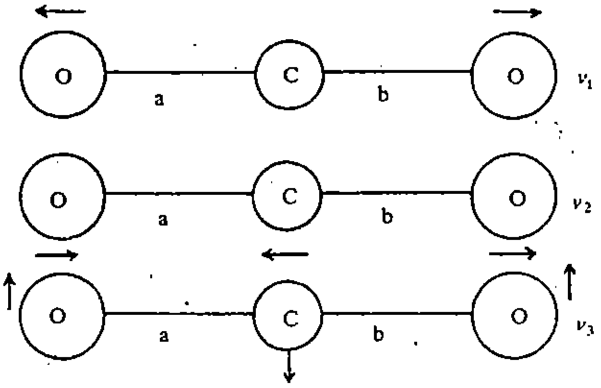


Fig. 8.8 : Vibrational modes for carbon dioxide.

The complexity of infrared spectra for molecules is increased as we progress from diatomic to triatomic and polyatomic molecules, because of the increase in the number of possible vibrations. For a nonlinear molecule with n atoms, the number of vibrational modes is ($3n-6$), so that methane theoretically possesses 9, and ethane has 18. On the other hand, for a linear molecule, the number of vibrational modes is $3n-5$. Actual number of observed vibration bands for a molecule is generally different from that calculated, because overtone and combination of overtones may increase the number of vibration bands or some other phenomenon may reduce the number of vibrations. In spite of these complications, it is often possible to obtain useful information about the structure of complex molecules from the infrared spectra, details of which we discuss in the following section. Before that try the following SAQ.

SAQ 2

How many normal modes of vibration do you expect for the following compounds ?

(**Hint** : Using the materials in Units 3 and 4, find out whether a structure is linear or not.)

a) CO_2 b) SO_2 c) $CHCl_3$

....

....

....

....

8.6 GROUP FREQUENCIES

We have stated earlier that for polyatomic molecules, infrared spectra is complex. So, it may not be easy to assign mode for every vibrational band. In such a case, the most important information we get is the recognition of **group frequencies**. To understand group frequencies, let us consider the organic compounds.

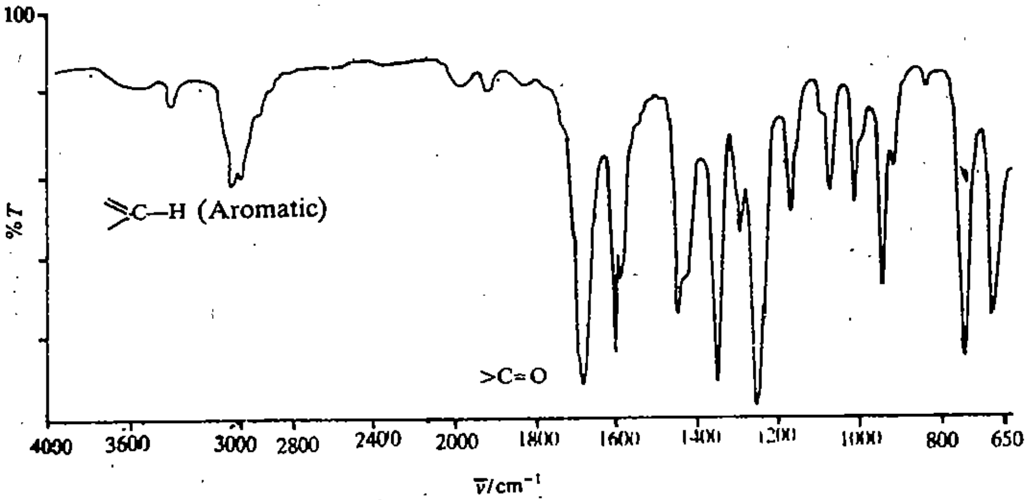


Fig. 8.9 : Infrared spectrum of acetophenone, ($C_6H_5COCH_3$).

Organic compounds show spectra in which many bands are spread over the wide scan-range (4000–600 cm^{-1}). Each band is associated with a particular vibration (or a combination of these). The complexity of the spectra, as illustrated in Fig. 8.9, reflects the large number of vibrations, which depend on the structure of the molecule. Fortunately, we can, to a certain extent, associate some absorptions with stretching or bending vibrations characteristic of particular functional groups in a molecule; for example, the absorptions at 3050 and 1700 cm^{-1} in the spectrum of acetophenone are typical of the stretching modes of C–H (aromatic) and C=O groups, respectively. These frequencies are called **group frequencies.** In this way, the infrared spectra allow recognition of the types of functional groups present in organic molecules. A list of some characteristic group frequencies is given in Table 8.2.

The group frequencies remain constant from molecule to molecule because of the following reasons :

i) The force constant for a particular bond is constant.

ii) The reduced mass is also nearly constant in big molecules. For example, in case of hydrocarbons :

$$\mu = \frac{m_H \times m_{rest\ of\ the\ molecule}}{(m_H + m_{rest\ of\ the\ molecule})}$$

$$\simeq m_H$$

Table 8.2 : Characteristic Group Frequencies

Group	(Bond Stretching vibration)/cm^{-1}	Group	(Bond Stretching vibration)/cm^{-1}
$\equiv C-H$	3300	$-\overset{\vert}{C}=O$	1700
$=\overset{\vert}{C}-H$	3020	$-\underset{\vert}{\overset{\vert}{C}}-\overset{\vert}{N}-$	1150
$-\underset{\vert}{\overset{\vert}{C}}-H$	2960	$-C\equiv N$	2100
		$-C\equiv C-$	2050
$-O-H$	3680 (gas)	$-\overset{\vert}{C}=\overset{\vert}{C}-$	1650
	3400 (liquid)		
$-\overset{\vert}{N}-H$	3350	$-\underset{\vert}{\overset{\vert}{C}}-\underset{\vert}{\overset{\vert}{C}}-$	900

SAQ 3

Match each absorption band with the functional group.

	Functional group	Wave number/cm^{-1}
a)	$-\overset{\vert}{C}=O$	2050
b)	$-\overset{\vert}{N}-H$	3400
c)	$=\underset{\vert}{\overset{\vert}{C}}-H$	1700
d)	$-C\equiv C-$	3350
e)	$-O-H$	3020

8.7 APPLICATIONS OF INFRARED SPECTRA

The usefulness of infrared spectra lies not only in the calculations of the molecular parameters for small molecules, but also, for the characterisation of organic molecules. We are considering some examples to illustrate further the importance of infrared spectra in identifying the structure of organic compounds:

Example 1: Pent-1-ene, $CH_3(CH_2)_2CH = CH_2$

The infrared spectrum of this compound is given in Fig. 8.10.

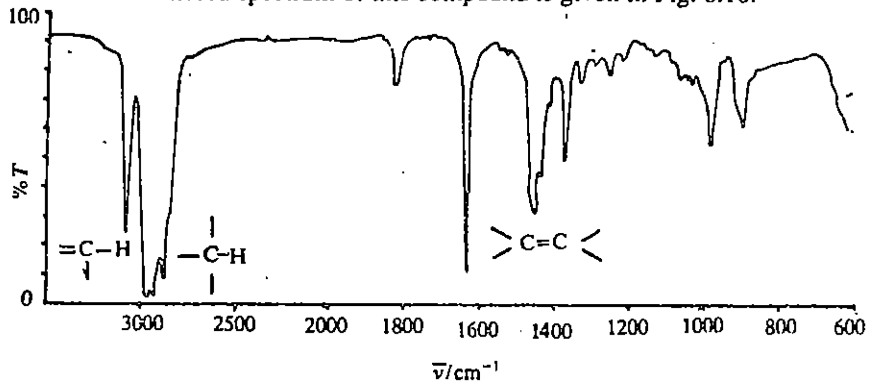


Fig. 8.10 : Infrared spectrum of Pent-1-ene.

The bands appearing at 3080 cm^{-1}, 2950 cm^{-1} and 1640 cm^{-1} are due to $=\overset{|}{C}-H$, $-\overset{|}{\underset{|}{C}}-H$ and $-\overset{|}{C}=\overset{|}{C}-$ stretching, respectively.

Example 2: 1-Butanol, $CH_3CH_2CH_2CH_2OH$

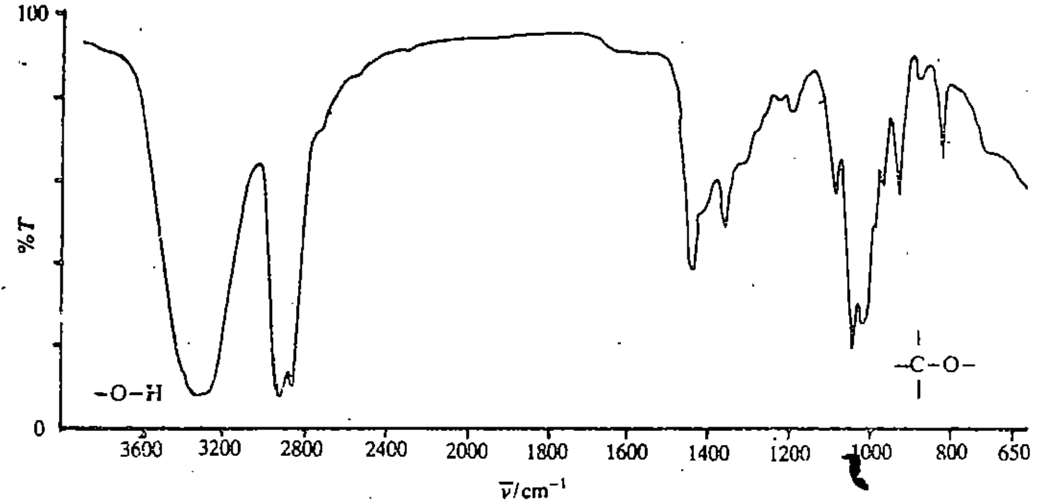
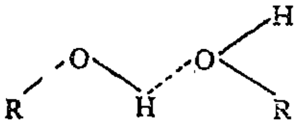


Fig. 8.11 : Infrared spectrum of 1-butanol.



Intermolecular hydrogen bonding in alcohol molecules.

In Fig. 8.11, the infrared spectrum of 1-butanol is given. Broad band at 3400 cm^{-1} indicates the presence of the O–H group in the molecule. This is due to the stretching of the O–H group. Broadening of the band suggests intermolecular hydrogen bonding. Here, intermolecular hydrogen bonding arises between hydrogen of the hydroxyl group of one molecule with the oxygen of the hydroxyl group of another molecule.

Example 3: Diethylamine $(C_2H_5)_2NH$

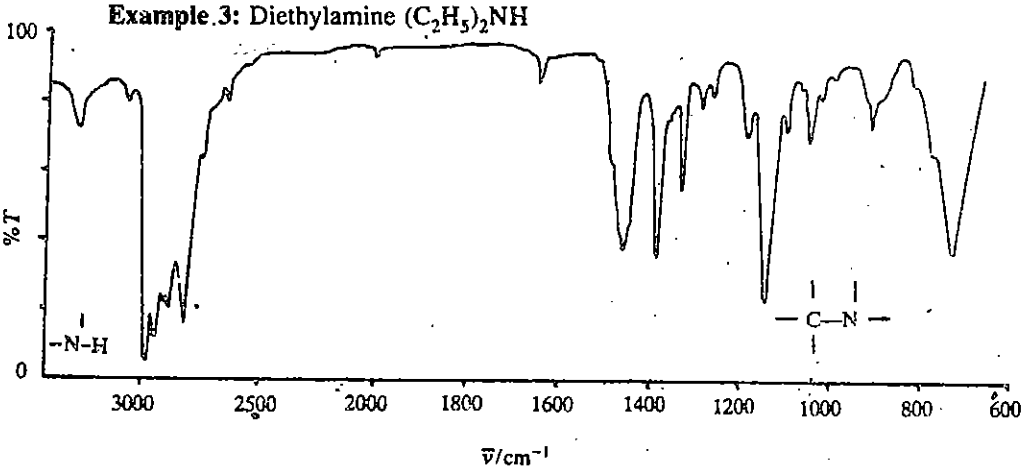
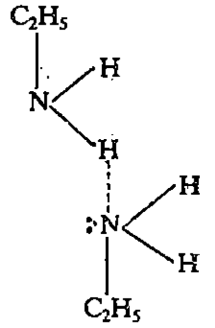


Fig. 8.12: Infrared spectrum of diethylamine.

The infrared spectra of diethylamine is given in Fig. 8.12. As in the case of alcohols, amines have a broad band, although at lower wave number region (3350 cm^{-1}); it is due to N–H stretching. The broadening suggests that the hydrogen atom takes part in intermolecular hydrogen bonding of the type $-\overset{|}{N}-H \cdots \underset{|}{\overset{|}{N}}-$



Intermolecular hydrogen bonding in diethylamine.

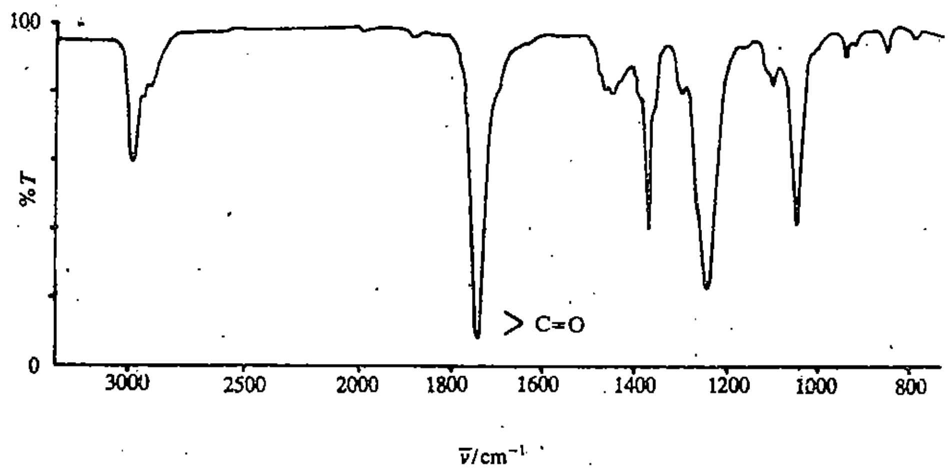


Fig. 8.13 : Infrared spectrum of ethyl acetate.

As an example of carbonyl compounds, the infrared spectrum of ethyl acetate is shown in Fig. 8.13. Note the intense band around 1700 cm^{-1} which is characteristic of C=0 stretching. Among the carbonyl compounds such as acids, esters, ketones and aldehydes, this is one of the prominent bands.

Finally, infrared spectra may also be employed for rapid quantitative analysis of a mixture of compounds. The infrared spectra are widely used in pollution detection and in milk analysis, etc. But the quantitative results obtained from infrared spectra are not as accurate as in the case of ultraviolet and visible spectra which we will discuss in Section 8.11.

Try the following SAQ before proceeding to the next section.

SAQ 4

From the infrared spectrum given in Fig. 8.14, identify the possible functional groups corresponding to the peaks indicated by the arrows.

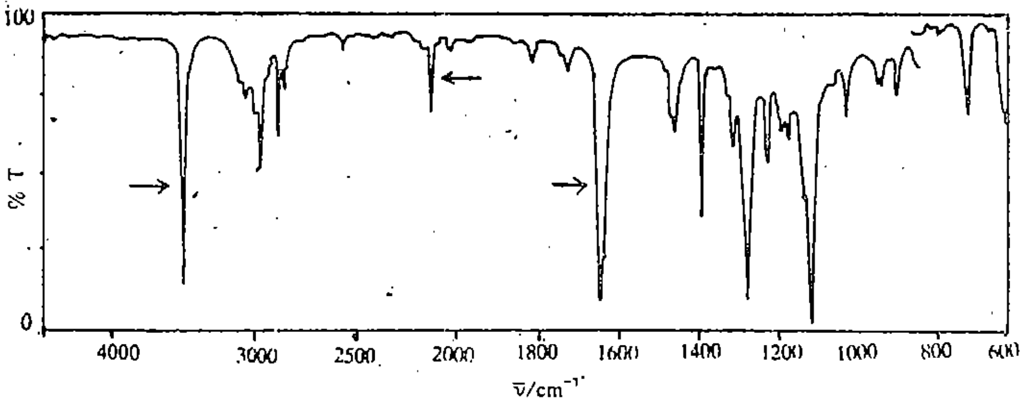


Fig. 8.14 : Infrared spectrum of the compound mentioned in SAQ 4.

8.8 MAIN FEATURES OF ULTRAVIOLET AND VISIBLE SPECTRA

We have already stated in Unit 7 that the absorption of radiation in the ultraviolet and visible regions of the electromagnetic spectrum results in transitions between electronic energy levels. Therefore, visible and ultraviolet spectra are also known as electronic spectra. The energy changes are relatively large, corresponding to 100-10^4 kJ mol^{-1}. This corresponds to wavelength range of 200-400 nm (ultraviolet region of electromagnetic spectrum) and 400-750 nm (visible region of electromagnetic spectrum). All molecules can undergo electronic transitions, but in some cases absorptions occur below 200 nm where atmospheric absorption necessitates the use of vacuum instrumentation.

The large energy changes involved in electronic transitions cause simultaneous change in rotational and vibrational energies also, as $E_{elec} > E_{vib} > E_{rot}$. For this reason, the spectra of simple molecules in the gaseous state contain narrow absorption peaks where each peak is representing a transition from a particular combination of vibrational and rotational levels in the electronic ground state to a different combination in the excited state. The allowed energy levels are shown in Fig. 8.15.

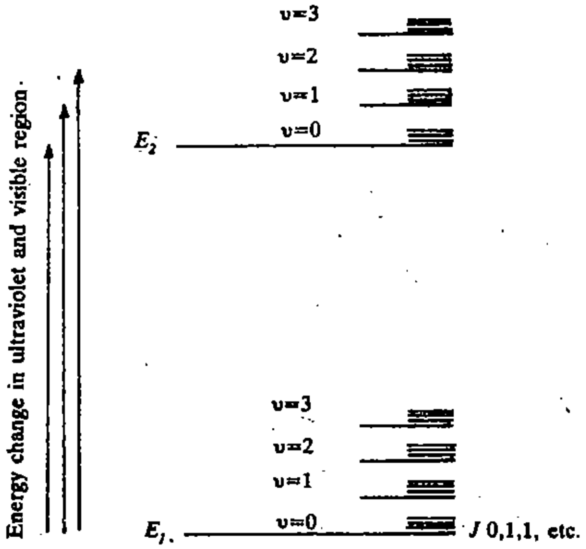


Fig. 8.15 : Allowed energy levels in ultraviolet and visible region.

Such vibrational and rotational fine structure lines are not usually observed if the spectrum is run in solution because of physical interactions between solute and solvent molecules, causing collisional broadening of the lines. The resulting overlapping bands coalesce to give one or more broad band envelopes (see Fig. 8.16).

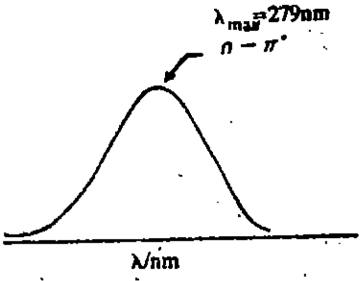


Fig. 8.16 : Electronic absorption spectrum of a solution of acetone $(CH_3)_2C=O$ in hexane.

In some cases, however, vibrational fine structures are visible as in the case of spectrum of benzene (see Fig. 8.17) around λ = 255 nm.

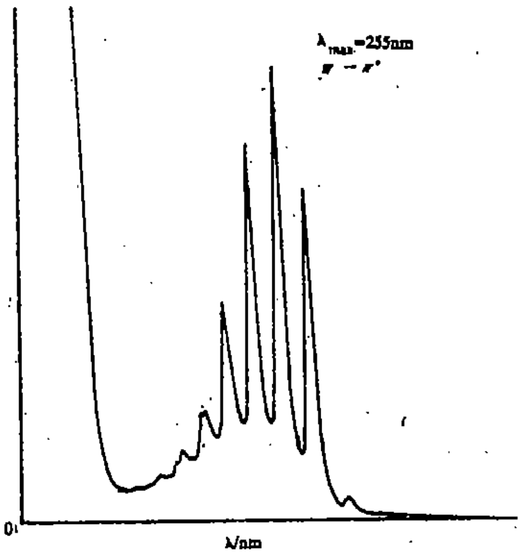


Fig. 8.17 : Electronic absorption spectrum of a solution of benzene in hexane.

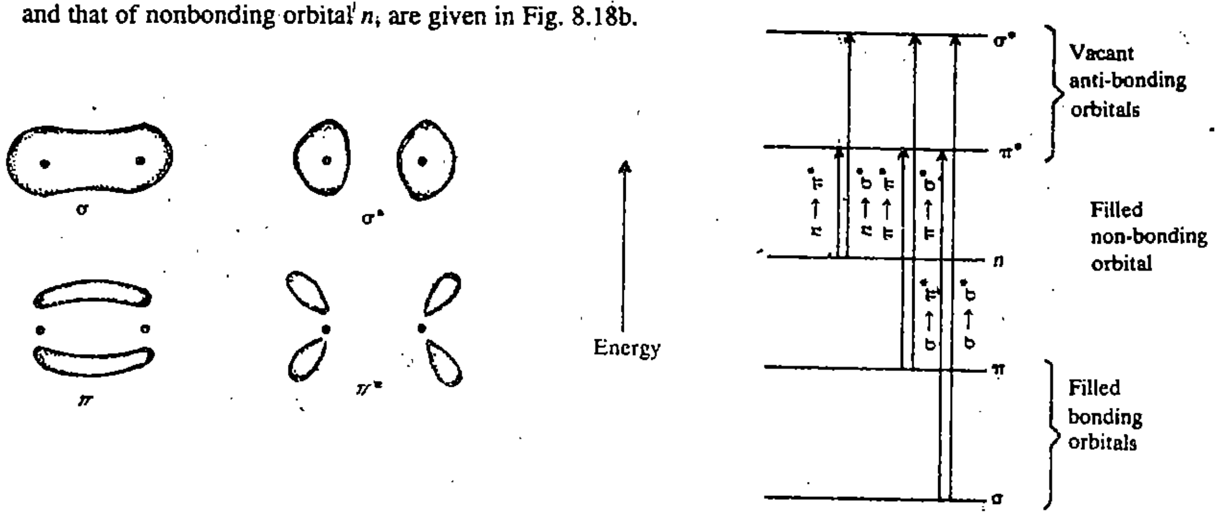
Bands observed in ultraviolet and visible spectra are usually characterised by two parameters :

i) λ_{max} **Value** : The value of the wavelength at which absorption maximum occurs is called λ_{max} value. From Figs. 8.16 and 8.17, you can understand that λ_{max} values are different for different molecules. For example, λ_{max} for acetone is 279 nm, whereas for benzene, it is 255 nm.

ii) **ε Value:** The extent of absorption, for a given concentration of a compound at any given wavelength is defined by molar absorptivity or molar extinction coefficient which is indicated as 'ε' value. It is related to the height of the absorption band. We shall define it precisely in Section 8.11. The parameters, λ_{max} (the position) and ε (the extent of absorption) are characteristic properties of a molecule. The parameters depend on the structure and concentration of the molecules in solution. Therefore, we extensively use ultraviolet and visible spectra in characterisation and also in quantitative detection. Now, the origin of the absorption bands is discussed in the following section.

8.9 ELECTRONIC TRANSITIONS

According to molecular orbital theory, which we discussed in Unit 5, the interaction of atomic orbitals leads to the formation of bonding and antibonding molecular orbitals. Depending on the nature of the overlapping atomic orbitals, bonding molecular orbitals may be of σ type, the electron density being concentrated along the internuclear axis, or of the π type where the electron density is concentrated above and below the internuclear axis. Electron density probability contours for electrons occupying σ and π (bonding), σ^* and π^* (antibonding) orbitals are shown in Fig. 8.18a. The relative energies of these orbitals and that of nonbonding orbital n, are given in Fig. 8.18b.



(a) (b)

Fig. 8.18: Shapes and relative energies of molecular orbitals : (a) Bonding and antibonding orbitals, (b) Relative energies of orbitals and possible transitions between them.

When excitation takes place, an electron from one of the filled orbitals (σ, π or n), gets excited to one of the vacant antibonding orbitals (σ^* or π^*). Since various excitations are possible, there are various absorptions, corresponding to these transitions :

$\sigma \rightarrow \pi^*$, $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $\pi \rightarrow \sigma^*$, $n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$

As expected, the σ electrons require a high energy for excitation to σ^* level. The order of decreasing energy for the absorptions is as follows :

$$\sigma \rightarrow \sigma^* > \sigma \rightarrow \pi^* \sim \pi \rightarrow \sigma^* > \boxed{\pi \rightarrow \pi^* \sim n \rightarrow \sigma^* > n \rightarrow \pi^*}$$

Of all the possible transitions, the last three account for absorptions in the region 200 – 800 nm, while others demand much higher energy. This then explains why only molecules with n or π electrons give rise to characteristic spectra in the region 200 – 800 nm, whereas alkanes, for example, absorb in the region below 200 nm. It is observed in the case of organic molecules that the part of the molecule having n or π electrons is essentially responsible for this absorption; these fragments are called **chromophores**. If two or more chromophores having π electrons are separated by a single bond in between, the system is said to be conjugated. For example, 1, 3-butadiene, benzene and crotonaldehyde are conjugated molecules. It has been found that for the conjugated molecules, λ_{max} values are somewhat larger. It is also reported that as conjugation length increases, λ_{max} also increases.

This is evident from Table 8.3, where λ_{max} and ε values for $\pi \rightarrow \pi^*$ transitions of a few chromophores are given. Note that λ_{max} value of benzene is larger than that of butadiene, which in turn, is larger than that of ethylene. Again, λ_{max} value of crotonaldehyde is larger than that of acetone or ethylene.

$CH_2=CH-CH=CH_2$;
1, 3 – Butadiene.

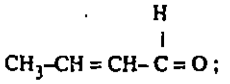
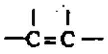
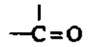
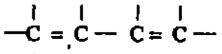
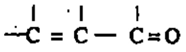

$CH_3-CH=CH-\overset{H}{\overset{|}{C}}=O$;
Crotonaldehyde

Table 8.3 : $\pi \rightarrow \pi^*$ Absorption Characteristics of Some Typical Chromophores and Conjugated Chromophores

Chromophore	Example	λ_{max} /nm	ε /m^2 mol^{-1}
 $-\overset{|}{C}=\overset{|}{C}-$	Ethylene	165	1500
 $-\overset{|}{C}=O$	Acetone	188	90
	Benzene	255	215
 $-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=\overset{|}{C}-$	Butadiene	217	2100
 $-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=O$	Crotonaldehyde	217	1600

The positions (λ_{max}) and extinction coefficients (ε) of the absorption bands are sensitive to the substituents close to the chromophore, and also to the solvents used.

While studying the λ_{max} values of benzene, butadiene and crotonaldehyde, from Table 8.3, you must remember that for conjugated molecules, as number of π bonds increases the possible number of $\pi \rightarrow \pi^*$ transitions also increases. In Table 8.3, λ_{max} values characteristic of benzene, butadiene and crotonaldehyde are given.

Try the following SAQs to check your understanding regarding ultraviolet and visible spectra.

SAQ 5

Identify the type of absorptions, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ or $n \rightarrow \sigma^*$ among the following compounds :

	Compound	λ_{max}/nm	Transition involved
a)	CH_3OCH_3	184	....
b)	CH_3SH	228	....
c)	$CH_2=CH-CH=CH_2$	217	....
d)	$CH_2=CH_2$	165	....

SAQ 6

Which will have greater λ_{max}? Reason out your answer.

$CH_3-CH=CH_2$ or $CH_3-CH=CH-CH=CH-CH_3$

....

....

....

8.10 APPLICATIONS OF ULTRAVIOLET AND VISIBLE SPECTRA

Electronic absorption spectra are useful in the characterisation of organic and inorganic compounds which show absorption in ultraviolet and visible regions of the electromagnetic spectrum. The transition metal complexes are often highly coloured and absorb in the visible region.

Also it is possible to estimate quantitatively the compounds absorbing in the ultraviolet and visible regions. This estimation is based on Beer-Lambert law. In the next section, we shall discuss this in detail.

8.11 QUANTITATIVE ANALYSIS

It is known to us that when light is passed through a sample as the absorbing medium, the intensity of the transmitted light is less than that of the incident light. This idea is expressed mathematically by Beer-Lambert law and it is useful in the quantitative estimation of compounds.

8.11.1 Beer-Lambert Law

Beer-Lambert law is actually a combined form of Lambert's law and Beer's law.

We shall first take up Lambert's law.

Lambert's Law

This law states that when a monochromatic beam of light is passed through a homogeneous medium absorbing this light, the absorption at each infinitesimally small section is proportional to the intensity of the incident light and the thickness of the layer. We can explain this using Fig. 8.19 given below :

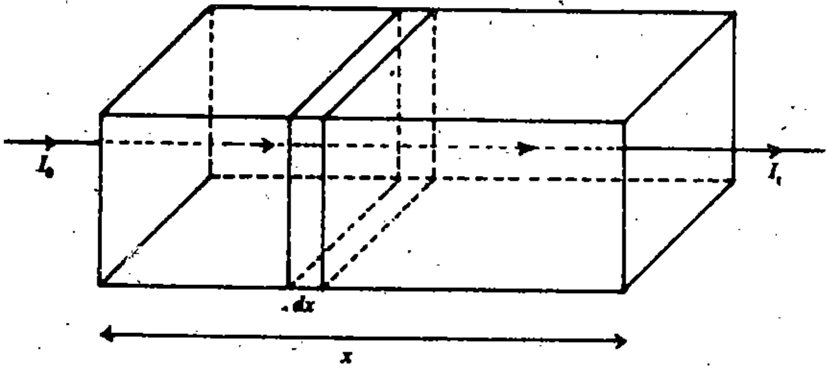


Fig. 8.19 : Illustration of Lambert's Law.

Let us consider that the light enters the sample with the intensity I_0. When it goes out of the sample, the intensity of transmitted light is I_t. Somewhere in the sample, let us consider a small section of thickness dx. The light here enters with intensity I and goes out with intensity $I - dI$. The change in intensity,

$$I - dI - I = -dI \quad ...(8.9)$$

According to this law, this should be proportional to the thickness dx and the intensity I at that part, i.e.,

$$-dI = kIdx$$

or $$-\frac{dI}{I} = kdx \quad ...(8.10)$$

where k is the proportionality constant. Now we can integrate it, knowing that the intensity varies from I_0 to I_t and the thickness of the sample varies from 0 to x.

Then we have,

$$-\int_{I_0}^{I_t} \frac{dI}{I} = k\int_0^x dx$$

or

$$\ln\frac{I_t}{I_0} = -kx$$

or

$$\frac{I_t}{I_0} = e^{-kx}$$

$$I_t = I_0 e^{-kx} \quad ...(8.11)$$

The intensity of light absorbed by the sample,

$$I_{abs} = I_0 - I_t = I_0 - I_0 e^{-kx}$$

$$= I_0(1 - e^{-kx}) \quad ...(8.12)$$

Here 'k' is the proportionality constant. It is obvious that larger the value of k, greater is the absorption.

Beer's Law

Beer extended Lambert's law to solutions. According to this law, the value of k in Eq. 8.12 is proportional to the concentration of the solution.

$$k = k'c \qquad \text{...(8.13)}$$

where k' is another proportionality constant and c is the concentration of the solution. In the combined form, these laws are known as Beer-Lambert law. It can be written by substitution of Eq. 8.13 in Eq. 8.11.

$$I_t = I_0 e^{-k'cx}$$

$$= I_0\, 10^{-k'cx/2.303}$$

$$= I_0 10^{-acx} \qquad \text{...(8.14)}$$

where $a = \frac{k'}{2.303}$ is known as the **absorption** coefficient or extinction coefficient of the solute.

$$\text{Also, } \log \frac{I_0}{I_t} = acx \qquad \text{...(8.15)}$$

where the term log I_0/I_t is commonly called the **absorbance** and given the symbol A.

Thus, Eq. 8.15 becomes,

$$A = acx \qquad \text{...(8.16)}$$

Eq. 8.14 and Eq. 8.15 are termed as mathematical statements of **Beer-Lambert law**.

8.11.2 Molar Extinction Coefficient

The numerical value of the extinction coefficient, a, depends on the units used for expressing the concentration of the absorbing solution. Concentration units such as molality, parts per million (ppm) (which is milligram per dm^3), grams per 100 cm^3, etc. are often used.

If x mg of a substance is present in 1 dm^3 of a solution, then the solution is said to have x ppm (x parts per million) of the substance. But if x μg is present in 1 dm^3 of a solution, then the concentration of the solution is referred to as x ppb (x parts per billion).

1 mg = 10^{-3} g
1 μg = 10^{-6} g

However, a different symbol, ε (epsilon), is used in place of a when the concentration is expressed as mol m^{-3}. Eq. 8.16 may then be written as,

$$A = \varepsilon cx$$

$$\text{or } \varepsilon = \frac{A}{cx} \qquad \text{...(8.17)}$$

If x and c are in units m and mol m^{-3}, then ε is in m^2 mol^{-1} and is described as the **molar decadic absorptivity** or **molar extinction coefficient**. The ε value is characteristic of a particular compound at a given wavelength. Usually for the wavelength of maximum absorbance (λ_{max}), molar decadic absorptivity, ε, is most commonly expressed as ε_{max}. Some typical values for ε_{max} of organic compounds are already listed in Table 8.3.

Using Eq. 8.17 we can calculate ε for a compound, if x and c are known, and if A is experimentally determined. It is important to realise that, once ε has been determined, it is possible to estimate the concentration, c_i, of a solution of unknown concentration by measuring its absorbance, A_i, using the same cell. This behaviour is the basis of the quantitative application of Beer-Lambert law. Therefore,

$$c_i = \frac{A_i}{x\varepsilon} \qquad \text{...(8.18)}$$

We generally make measurements in cells of 1 cm thickness; for a compound, ε is constant for a particular wavelength. In such a condition, Beer-Lambert law may be written

$$A \propto c$$

Hence, by measuring the values of A for different concentration values of the solution of a substance in the same cell and plotting the curve A vs. c, a straight line will be obtained and this would pass through the origin as evident from Fig. 8.20. This **calibration line** may then be used to determine unknown concentration of a solution of the same material in the same solvent, after measurement of the absorbance. For example, for a solution of absorbance, A_i, the concentration c_i is given by the interpolation of the curve in Fig. 8.20.

Quantitative measurements based on Beer-Lambert law are extensively used for ultraviolet and visible spectra and less in the case of infrared spectra. The reason is that ε value for the molecules are larger in the ultraviolet and visible regions, whereas it is smaller in the infrared region.

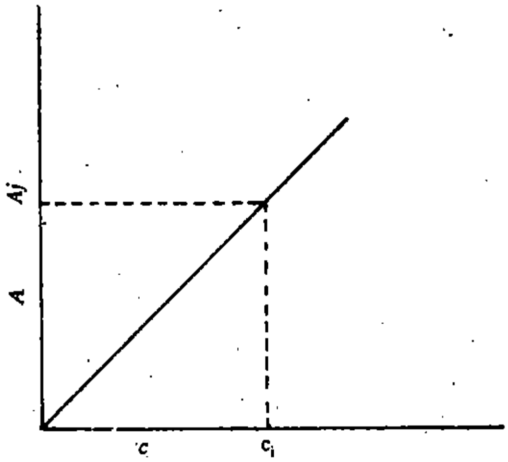


Fig. 8.20 : A calibration line showing the relationship between absorbance and concentration.

8.11.3 Deviation From Beer-Lambert Law

As mentioned earlier, when Beer-Lambert law is obeyed, calibration plot will be obtained as a straight line passing through the origin. If there are deviations from Beer-Lambert law, the calibration plot will curve either upward (positive deviation) or downward (negative deviation) as indicated by OP and OR, represented in Fig. 8.21. The ideal curve is represented by OQ. The reasons for such deviations are both instrumental and chemical. To avoid deviation, we generally prefer dilute solutions.

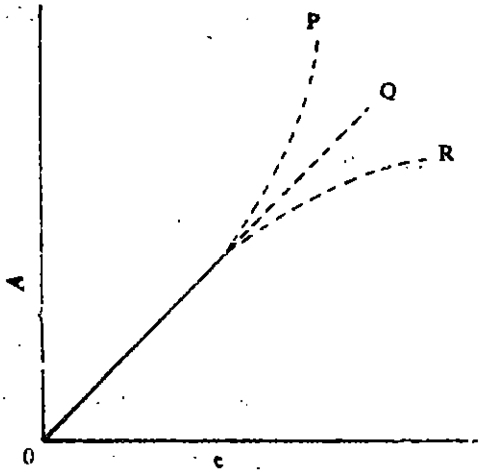


Fig. 8.21 : Deviation from Beer-Lambert Law.

Why don't you try the following SAQ to test your "grip" of Beer-Lambert law?

SAQ 7

An organic compound has $\lambda_{max} = 400$ nm. The absorbance of its solution ($c = 132$ mg cm^{-3}) was found to be 0.465. If a test solution of this compound gave an absorbance of 0.501, calculate its concentration. (Do not change the concentration units.)

....

....

....

8.12 SUMMARY

In this unit we have described the infrared, ultraviolet and visible spectra. We are summarising below what we have studied so far :

- Vibrational transitions are active in the infrared region of electromagnetic spectrum. We observe vibrational band only if a particular vibration produces a change in dipole moment.
- Functional groups in organic compounds can be identified on the basis of characteristic group frequencies.
- Electronic transitions are observed in the ultraviolet and visible region ; they are generally due to the transitions involving electrons of σ, π or n orbitals.
- Beer-Lambert law relates absorbance with concentration and the thickness of the sample through which the light travels.

8.13 TERMINAL QUESTIONS

1. Calculate the frequency of O–H band, if the force constant and reduced mass of the atom pair are 770 N m^{-1} and 1.563×10^{-27} kg, respectively.
2. How many normal vibrational modes are possible for ethane and benzene ?
3. Characteristic group frequencies (in cm^{-1}) and functional groups are given below. Match the pairs.

i) 1650	a) $-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}-$
ii) 2100	b) $-\underset{|}{\overset{|}{C}}-H$
iii) 2960	c) $-\overset{|}{C}=\overset{|}{C}-$
iv) 900	d) $-C \equiv N$

4. Of each pair of transitions, which would require radiation of lesser energy ?
   a) $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ in $CH_3-C \equiv N$
   b) Stretching or rotational transition in ICl
   c) $\pi \rightarrow \pi^*$ or N = 0 stretching in $CH_3-N=0$
   d) $-C \equiv C-$ stretching or $-\overset{|}{C}=\overset{|}{C}-$ stretching.
5. For each of the following molecules indicate the possible electronic excitations :
   a) $CH_3CH_2CH_3$ b) $CH_2CH=CH_2$
   c) $CH_3CH=0$ d) $CH_3-CH=CH-CH=CH-CH_3$
6. State Beer-Lambert law.
7. Compound X exhibits molar extinction coefficient of 245 m^2 mol^{-1} at 450 nm. What concentration of X in a solution will cause a 25% decrease in the intensity of 450 nm radiation, when the solution is placed in a 0.01 m absorption cell ?

8.14 ANSWERS

Self-assessment Questions

1. The force constant can be calculated using the equation,

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

This can be rearranged as,

$$k = 4\pi^2 c^2 \bar{\nu}^2 \mu$$

$$= 4 \times 3.142^2 \times [2.998 \times 10^8 \,(m\,s^{-1})]^2 \times [2.143 \times 10^5 \,(m^{-1})]^2 \times 1.139 \times 10^{-26} \,(kg)$$

$$= 1857 \,(kg\,m^2\,s^{-2})\,(m^{-2})$$

$$= 1857 \,(kg\,m\,s^{-2})\,(m^{-1})$$

$$= 1857 \text{ N m}^{-1} \qquad \{\because 1 \text{ kg m s}^{-2} = 1 \text{ N}\}$$

2. The expected modes of vibration are :

CO_2 : linear ; $(3 \times 3 - 5) = 4$

SO_2 : Nonlinear ; $(3 \times 3 - 6) = 3$

$CHCl_3$: Nonlinear ; $(3 \times 5 - 6) = 9$

3.

Functional group	**Wave number/cm^{-1}**
$-\overset{\vert}{C}=O$	1700
$-\overset{\vert}{N}-H$	3350
$=\overset{\vert}{C}-H$	3020
$-C\equiv C-$	2050
$-O-H$	3400

4. This infrared spectrum has peaks at 3300, 2100 and 1640 cm^{-1}, indicating the presence of $\equiv C-H$, $-C\equiv C-$ and $-\overset{|}{C}=\overset{|}{C}-$ groups. (In fact, this is the infrared spectrum of 1-methoxy-but-1-en-3-yne).

5. a) $n \rightarrow \sigma^*$ b) $n \rightarrow \sigma^*$ c) $\pi \rightarrow \pi^*$ d) $\pi \rightarrow \pi^*$.

6. $CH_3-CH=CH-CH=CH-CH_3$ will have higher λ_{max} than $CH_3-CH=CH_2$ because of conjugation.

7. According to Beer-Lambert law, $A \propto c$. If A_1 and A_2 are the absorbance values of a substance in solutions of concentrations, c_1 and c_2, then $A_1 \propto c_1$ and $A_2 \propto c_2$.

$$\text{or } \frac{A_1}{c_1} = \frac{A_2}{c_2}$$

$A_1 = 0.465$, $c_1 = 132$ mg cm^{-3}

$A_2 = 0.501$, $c_2 = ?$ mg cm^{-3}

$$c_2 = c_1 \frac{A_2}{A_1} = 132\ (\text{mg cm}^{-3}) \times \frac{0.501}{0.465}$$

$$= 142 \text{ mg cm}^{-3}.$$

Terminal Questions

1. $k = 770$ N m^{-1}

$\mu = 1.563 \times 10^{-27}$ kg

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$= \frac{1}{2 \times 3.142} \times \sqrt{\frac{770\ (\text{N m}^{-1})}{1.563 \times 10^{-27} (\text{kg})}}$$

$$= 1.117 \times 10^{14} \text{ Hz}$$

$$\bar{\nu} = \frac{\nu}{c} = 3.726 \times 10^5 \text{ m}^{-1}$$

$$= 3726 \text{ cm}^{-1}.$$

2. Ethane has $3 \times 8 - 6 = 18$ normal vibration modes; benzene has $3 \times 12 - 6 = 30$ normal vibration modes.

3. (i) c (ii) d (iii) b (iv) a

4. a) $n \rightarrow \pi^*$ b) rotational c) N=O stretching d) $-\overset{|}{C}=\overset{|}{C}-$ stretching.

5. a) $\sigma \rightarrow \sigma^*$ b) $\pi \rightarrow \pi^*$, $\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ c) $n \rightarrow \pi^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \sigma^*$ d) $\pi \rightarrow \pi^*$, $\pi \rightarrow \sigma^*$ and $\sigma - \sigma^*$.

6. As given in Sec. 8.11.

7. If the intensity of the incident light (I_0) is assumed to be 100%, then the intensity of the light transmitted (I_t) after passing through the solution of concentration c is 75% (since there is 25% reduction in the intensity).

i.e., $\frac{I_0}{I_t} = \frac{100}{75}$

According to Beer-Lambert law,

$$\log \frac{I_0}{I_t} = \varepsilon c x$$

$\varepsilon = 245 \text{ m}^2 \text{ mol}^{-1}$

$x = 10^{-2} \text{ m}$

$c = ? \text{ mol m}^{-3}$

$$c = \frac{\log I_0/I_t}{\varepsilon x}$$

$$= \frac{\log 100/75}{245 \text{ (m}^2 \text{ mol}^{-1}) \times 10^{-2} \text{ (m)}}$$

$$= 0.0510 \text{ mol m}^{-3}.$$

UNIT 9 NUCLEAR CHEMISTRY

Structure

9.1 INTRODUCTION

In Block 1, we studied the arrangement of electrons in atoms and molecules in detail. In Units 6, 7 and 8 of this block, the application of physical methods in determining the structure of molecules is discussed. While studying the structure of molecules using physical methods, importance was given to electronic arrangement around the constituent atoms, as chemical reactivity depends mainly on the electron configuration of the elements. In chemical reactions, valence electrons are lent, borrowed or shared between combining atoms. The atomic nucleus remains unchanged. In nuclear reactions on the other hand, the nucleus of an atom of one element is changed into the nucleus of an atom of another element. The energy changes accompanying nuclear reactions are much larger as compared to chemical reactions. The vast amount of energy trapped in atomic nucleus, which is released during nuclear transformations can be used for the betterment of the society or for its total destruction. Nuclear chemistry deals with different types of nuclear reactions, their rates and the energy changes accompanying them.

In this unit, we will explain nuclear structure and its influence on nuclear reactions. After describing atomic nucleus and binding energy, we will discuss nuclear stability in terms of the number of protons and neutrons in a nucleus. Next, we will discuss various types of radioactive decay by which nuclei spontaneously emit particles and radiation. Then we will discuss transmutation reactions which can be used to produce new elements. We will conclude by describing the role of nuclear chemistry in power generation, archaeological dating and warfare.

Objectives

After studying this unit, you should be able to:

- define the terms, isotope, isobar and isotone,
- explain the terms, mass defect and binding energy,
- describe various types of radioactive decay and calculate radioactive decay constant,
- explain the principle of artificial transmutation,
- compare nuclear fission and fusion reactions and state their utility,

- describe the role of nuclear chemistry in warfare, power generation, dating, medicines and study of reaction mechanism, and
- state the harmful effects of radiation.

9.2 EARLY DEVELOPMENTS IN NUCLEAR CHEMISTRY

Studies in nuclear chemistry began with the accidental detection of the emission of energy from a uranium salt. In 1896 in France, Becquerel found that uranium compounds emitted some highly energetic rays which penetrated the protective black paper covering and affected the photographic plates. Marie Curie suggested the name **"radioactivity"** for this **spontaneous emission of radiation.**

Over the next few years after this discovery, Marie Curie and her husband, Pierie Curie, discovered two more radioactive elements, polonium (named after 'Poland' the country from which Marie Curie originally hailed) and radium (which means ray giver). In 1903, the Curies shared the Nobel Prize in Physics with Henri Becquerel for their discoveries. Meanwhile in England, Rutherford, from the study of radioactive materials, identified two main types of radiation, which he called alpha (α) rays and beta (β) rays. His experiments also showed that these two types of nuclear radiations are accompanied by the emission of particles from the nucleus. From the deflection in the electric field, Rutherford was able to show that α rays are helium nuclei and β rays are stream of electrons.

Villard demonstrated the existence of a third type of radiation, which is not associated with particle emission. This radiation was called gamma radiation or γ rays. Gamma rays are electromagnetic radiation, somewhat like X rays in character, but have higher energies and shorter wavelengths. An experimental setup that distinguishes these three types of radiation is shown in Fig. 9.1.

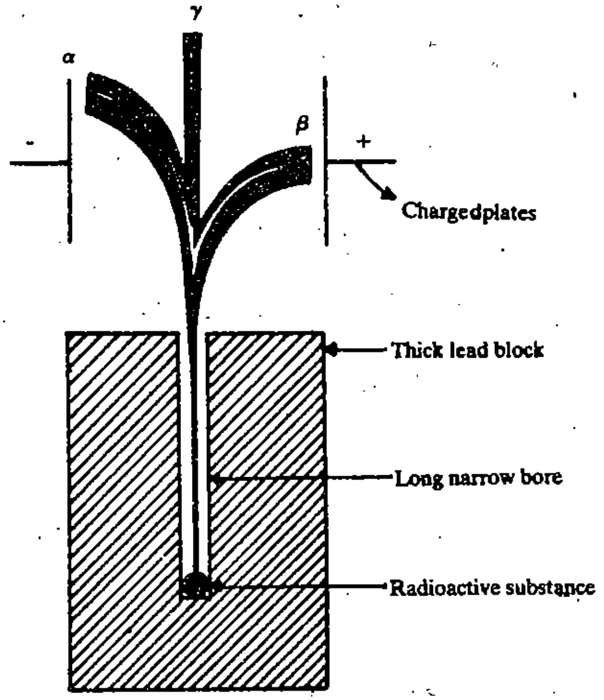


Fig. 9.1: The behaviour of α, β and γ radiations in an electric field

You can see that when a beam of nuclear radiation is passed between electric or magnetic poles, it is split into three separate beams. Two beams called α and β rays, bend towards negative and positive plates, respectively. The third beam called γ rays, is unaffected by the electric poles and passes along its path without any deflection. Thus the positive, negative and neutral characteristics of α, β and γ rays, respectively are brought out clearly.

Alpha rays, beta rays and gamma rays are emitted by the naturally-occurring radioactive substances. Apart from these three radiations, there are also two more types of particles called positrons and neutrons which are emitted by man-made radioactive elements. The symbols and properties of these five types of radiations are given in Table 9.1.

Table 9.1: Characteristics of Common Types of Radioactive Radiations

Name	Symbols	Identity	Charge	Relative mass (u)	Penetrating power	Ionisation effect
Alpha rays or alpha particles	α, ${}^{4}_{2}He$, He^{++}	Helium nucleus	2+	4.00150	Low	High
Beta rays or beta particles	β, β^{-}, ${}^{0}_{-1}e$	Electron	1–	0.000585	Low & Moderate	Moderate
Gamma rays	γ, ${}^{0}_{0}\gamma$	High energy electro-magnetic radiation	0	0	Very High	Very Low
Positron	β^{+}, ${}^{0}_{+1}e$	Positively charged electron	1+	0.000585	Low	Moderate
Neutron	n, ${}^{1}_{0}n$	Neutral	0	1.00867	High	None

9.3 NUCLEAR STRUCTURE AND STABILITY

We have stated earlier that nuclear chemistry is concerned with changes in the nuclei of atoms. You are naturally interested to know the different aspects of nuclear chemistry like natural radioactivity, artificial transmutation and tracer techniques. Before analysing these aspects, we begin with a brief review of the nucleus.

9.3.1 Atomic Nucleus

In Unit 1, you have seen that atomic nucleus is composed of protons and neutrons. These fundamental particles are called **nucleons**. The number of protons in the nucleus is called its **atomic number** (Z). Sum of the number of protons and neutrons is called **mass number** (A). In the notation that has been developed to describe atomic nuclei, we write the mass number (A) as a superscript and the atomic number (Z) as a subscript to the left of the symbol of the element X, such as ${}^{A}_{Z}X$.

The constituents of the nucleus are collectively called nucleons.

Examples : ${}^{1}_{1}H$, ${}^{14}_{7}N$, ${}^{16}_{8}O$, etc.

Different atomic species with the same number of protons but different number of neutrons are said to be **isotopes** of the same chemical element. Thus, ${}^{16}_{8}O$, ${}^{17}_{8}O$ and ${}^{18}_{8}O$ represent three isotopes of oxygen. In other words, isotopes are atoms which have same nuclear charge but different mass number. The word isotopes is generally used when two or more different nuclear species are discussed. But when we are talking about a single nuclear species with a given value of A and Z, the term **nuclide** is preferred. Thus, we can say that the two isotopes of oxygen, ${}^{16}_{8}O$ and ${}^{18}_{8}O$ are individually called nuclides.

Isobars are nuclides with the same A but different Z; ${}^{235}_{92}U$, ${}^{235}_{93}Np$ and ${}^{235}_{94}Pu$ are isobars.

Isotones are nuclides with the same number of neutrons but with different Z. For example, ${}^{14}_{6}C$, ${}^{15}_{7}N$ and ${}^{16}_{8}O$ are isotones, since each nucleus contains eight neutrons.

So far we have considered fundamental particles of the nucleus and classified the nuclides on the basis of Z and A values of the nuclei. Now let us see how these particles affect the size of nucleus. Then we shall study the forces which are responsible for packing these particles closely together. Before that, try to answer the following SAQs using the ideas discussed above.

SAQ 1

Indicate the number of neutrons and protons in each of the following nuclides: ${}^{7}_{3}Li$, ${}^{22}_{10}Ne$, ${}^{239}_{94}Pu$ and ${}^{194}_{78}Pt$.

SAQ 2

We are giving below some nuclides. You name them as isotopes or isobars or isotones. Write your answer in the space given below:

a) ${}^{14}_{7}N$, ${}^{15}_{7}N$, ${}^{16}_{7}N$

b) ${}^{233}_{90}Th$, ${}^{233}_{91}Pa$, ${}^{233}_{92}U$

c) ${}^{32}_{16}S$, ${}^{33}_{16}S$, ${}^{34}_{16}S$

d) ${}^{30}_{14}Si$, ${}^{31}_{15}P$, ${}^{32}_{16}S$

9.3.2 Nuclear Size

The first indications of the size of the nucleus were obtained from Rutherford's α particle scattering experiment, which we discussed in Unit 1. From this experiment, Rutherford concluded that almost the whole mass of the atom is concentrated in the nucleus, which is quite small compared to the size of the whole atom. He postulated nucleus as a sphere. Rutherford also calculated the radius of the nucleus and atom to be of the order of 10^{-14} and 10^{-10} m, respectively. More accurate information has now been obtained from experiments on the scattering of neutrons. The results can be summarised by the equation.

Neutron scattering is preferred, because a neutron is unchanged. It experiences no coulomb repulsion when it approaches a nucleus and it reaches nearer to the nuclear surface.

$$R = r_0 A^{1/3}$$

where R is the radius of the nucleus, A its mass number and r_0 the proportionality constant. The numerical value of r_0 is approximately about 1.3×10^{-15}m. Thus, you see that nuclear radius, R is directly proportional to the cube root of A.

9.3.3 Binding Energy

You know that atomic nucleus consists of protons and neutrons, which are positively charged and neutral, respectively. Is it not interesting to note that protons are confined within the small dimensions of the nucleus, in spite of mutual repulsion ? This suggests that there must be some attractive forces operating in the nucleus which must be stronger than the repulsive forces among the protons.

Yukawa (1935) suggested that a rapid exchange of nuclear particles called π mesons results in an attractive force between nucleons in a manner analogous to the sharing of electrons between nuclei in covalent bonds. The closely packed protons and neutrons rapidly exchange π mesons, which may be π^+, π^- or π° and have a mass of about 275 times that of the electron.

Some of the exchange processes are given below:

$$p \underset{\pi^+}{\overset{\pi^-}{\rightleftharpoons}} n\ ;\ p \underset{\pi^\circ}{\overset{\pi^\circ}{\rightleftharpoons}} p;\ n \underset{\pi^\circ}{\overset{\pi^\circ}{\rightleftharpoons}} n$$

Where symbols, n and p stands for neutron and proton, respectively.

Forces of attraction between nucleons are very strong at short distances but decrease rapidly as distance increases.

Stability of nuclei can be viewed from energy considerations also. Careful measurements of relative atomic masses show that their values are slightly less than the sum of the masses of the nucleons. This difference is called **mass defect** (Δm).

$$\Delta m = \text{sum of the mass of nucleons (or calculated mass)} - \text{measured nuclear mass} \quad ...(9.1)$$

The energy equivalent of mass defect is called **binding energy** (ΔE). It can be regarded as the amount of energy liberated when nucleons are brought together in the nucleus. Binding energy can also be defined as the amount of energy needed to break a given nucleus into its constituent nucleons. We can find the magnitude of the binding energy from the mass defect using Einstein equation;

$$\Delta E = \Delta mc^2 \quad ...(9.2)$$

where ΔE is the binding energy, Δm is the mass defect and c is the speed of light. A convenient unit of energy to use on the nuclear scale is the **million electron volt, MeV**, the magnitude of which is approximately equal to 1.602×10^{-13} J. The unit of mass is atomic mass unit (u), which is exactly one-twelfth the mass of a carbon atom.

SI Unit of energy is J (joule), but in nuclear chemistry, we customarily use MeV (million electron volt) as a unit of nuclear energy.

$$1 \text{ Atomic mass unit (u)} = 1.661 \times 10^{-27} \text{ kg} \qquad \text{...(9.3)}$$

Let us illustrate the calculation of mass defect and binding energy taking helium nucleus, as an example. The measured mass of helium nucleus is 4.00150 u. The calculated mass of helium nucleus is given by adding the relative masses of two protons and two neutrons.

Mass of two protons = 2×1.00728 u = 2.01456 u

Mass of two neutrons = 2×1.00867 u = 2.01734 u

$\therefore$ calculated mass of helium nucleus = 4.03190 u

Using Eq. 9.1, the mass defect of helium nucleus is,

$$\Delta m = 4.03190 \text{ u} - 4.00150 \text{ u}$$
$$= 0.03040 \text{ u}.$$

To calculate the binding energy of helium nucleus, mass defect is to be calculated in kg. Using Eq. 9.2,

Mass defect of helium in kg = $0.03040 \times 1.661 \times 10^{-27}$ kg = 5.04944×10^{-29} kg.

Substituting this value in Eq. 9.2, the binding energy of a single helium nucleus is,

$$\Delta E = 5.04944 \times 10^{-29} (\text{kg}) \times [2.998 \times 10^{8} (\text{m s}^{-1})]^2$$
$$= 4.53844 \times 10^{-12} \text{ kg m}^2\text{s}^{-2}$$
$$= 4.53844 \times 10^{-12} \text{ J} \qquad (\because 1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2})$$

1u = 931.9 MeV nucleus^{-1}
= 1.493×10^{-10} J nucleus^{-1}
= 8.990×10^{10} kJ mol^{-1}

In MeV units,

$$\Delta E = \frac{4.53844 \times 10^{-12} (\text{J}) \times 1 (\text{MeV})}{1.602 \times 10^{-13} (\text{J})}$$
$$= 28.3 \text{ MeV}. \qquad (\because 1 \text{ MeV} = 1.602 \times 10^{-13} \text{ J})$$

What we have calculated so far is the binding energy of a single helium nucleus.

The binding energy in nuclear structure has the same significance as bond energy (discussed in Unit 3) in molecular structure. The binding energy is the energy evolved during the formation of a nucleus from the constituent nucleons; the bond energy is the energy evolved in the formation of a bond from the constituent atoms. High bond energy values signify the stability of chemical bonds whereas high binding energy values point out the stability of nuclei. A comparison of a nuclear reaction with a chemical reaction based on the relative amounts of binding energy and bond energy values can clearly indicate the importance of nuclear reactions in the energy sector which is again discussed in Section 9.5.

We can compare the relative amounts of binding energy and bond energy, once we get binding energy in molar quantities as we do for bond energy. To obtain binding energy of one mole nuclei of helium, for example, we have to multiply the value obtained above, by Avogadro number (6.022×10^{23}). The binding energy of one mole nuclei of helium

$$= 6.022 \times 10^{23} \times 4.53844 \times 10^{-12} \text{ J mol}^{-1}$$

$$= 2.733 \times 10^{9} \text{kJ mol}^{-1}$$

From Table 3.9 of Unit 3, we note that the chemical bond energy values roughly range between 100 – 950 kJ mol^{-1}. Thus, it is evident that nuclear binding energies are at least $10^6 - 10^7$ times larger than the chemical bond energies.

Bond energy is a measure of the stability of a bond in a molecule; binding energy is a measure of the stability of a nucleus in an atom.

Among the nuclides, the binding energy values are more readily compared as binding energy per nucleon, which is obtained by dividing the binding energy of a nucleus by the number of nucleons in that nucleus. Since helium nucleus contains 4 nucleons (2 protons and 2 neutrons), the binding energy per nucleon for this nuclide is 1.13461×10^{-12} J or 7.08 MeV. In Fig. 9.2, binding energy per nucleon is plotted against mass number for some nuclides.

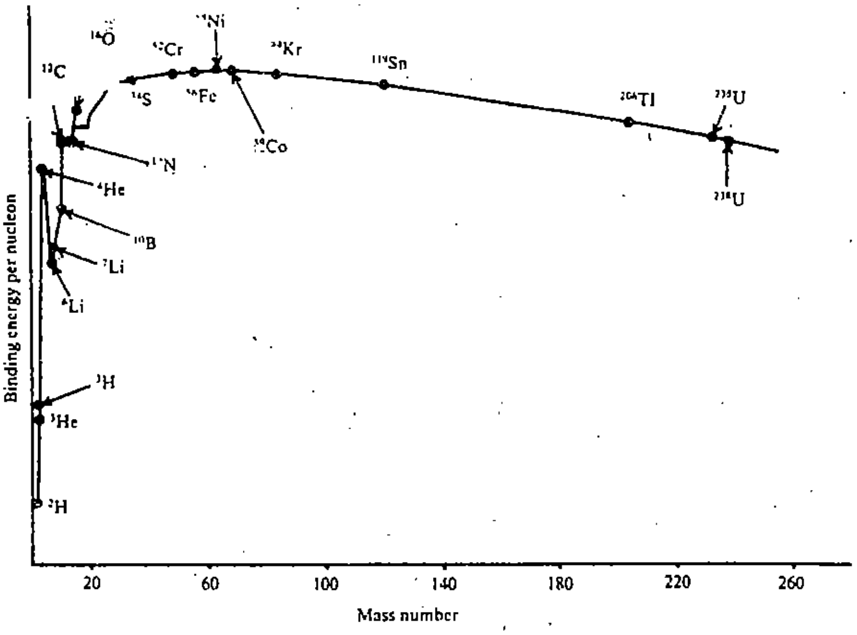
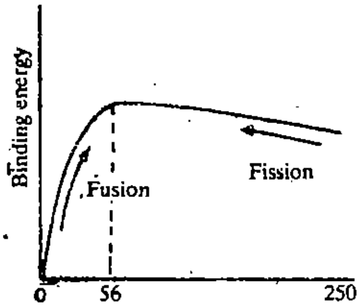


Fig. 9.2 : Plot of binding energy per nucleon versus mass number.



Mass number

Fig. 9.3: Regions in which fusion and fission are theoretically possible.

At the beginning of the curve, the binding energy per nucleon rises rapidly. This means that an increase in the number of nucleons causes them to be held together more strongly. The curve reaches a maximum around iron, cobalt and nickel. These nuclei are the most stable ones. After the maximum is reached, the curve falls off gradually, showing that the heavier nuclei are not as stable as the intermediate ones. This variation in average binding energy is responsible for the lighter nuclei undergoing fusion reaction and heavier nuclei undergoing fission reaction, see Fig. 9.3. We will discuss the fission and fusion reactions in detail in sub-sections 9.4.6 and 9.4.7, respectively.

Both fusion and fission are exothermic reactions, in which mass is converted into energy.

SAQ 3

Using the data given below, calculate the binding energy per nucleon in J and in MeV for $^{6}_{3}$Li.

Mass of proton = 1.00728 u; Mass of neutron = 1.00867 u; Actual atomic mass of $^{6}_{3}$Li = 6.01348 u;

....

....

9.3.4 Nuclear Stability

A number of factors contribute towards the stability of a nucleus. A major factor is the nuclear composition, i.e., number of protons and neutrons. The relationship between nuclear stability and nuclear composition can be conveniently represented through a plot of the number of protons versus the number of neutrons (Fig. 9.4). This diagram shows that the stable isotopes fall into a narrow band, which is called the **band of stability**. It also indicates that in general the lighter stable nuclei have equal number of protons and neutrons. Heavier stable nuclei, however, have slightly more neutrons than protons. For example, $^{16}_{8}$O nuclide has 8 neutrons and 8 protons; $^{207}_{82}$Pb has 125 neutrons and 82 protons. In the $^{207}_{82}$Pb nuclide, the neutron to proton ratio (*n*/*p*) is approximately equal to 1.5.

We can understand why the ratio of neutrons to protons increases with atomic number in order to have nuclear stability if we consider that as the number of protons in the nucleus increases, there must be more and more neutrons present to help overcome the strong repulsive forces among the protons.Experimentally it is observed that the stable nuclides end atZ=83, i.e.,there is an upperlimit to the number ofprotons that can exist in a stable nucleus.

Relative stability of a nucleus can be predicted from its location relative to the band of stability. The isotopes that fall to the left or to the right of the band of stability have unstable nuclei and are radioactive. Note that all isotopes with atomic numbers above 83 are radioactive. Radioactive nuclei change spontaneously to other nuclei that fall either in or closer to the band of stability. The exact nature of these changes to give more stable nuclei will be discussed in subsequent sections.

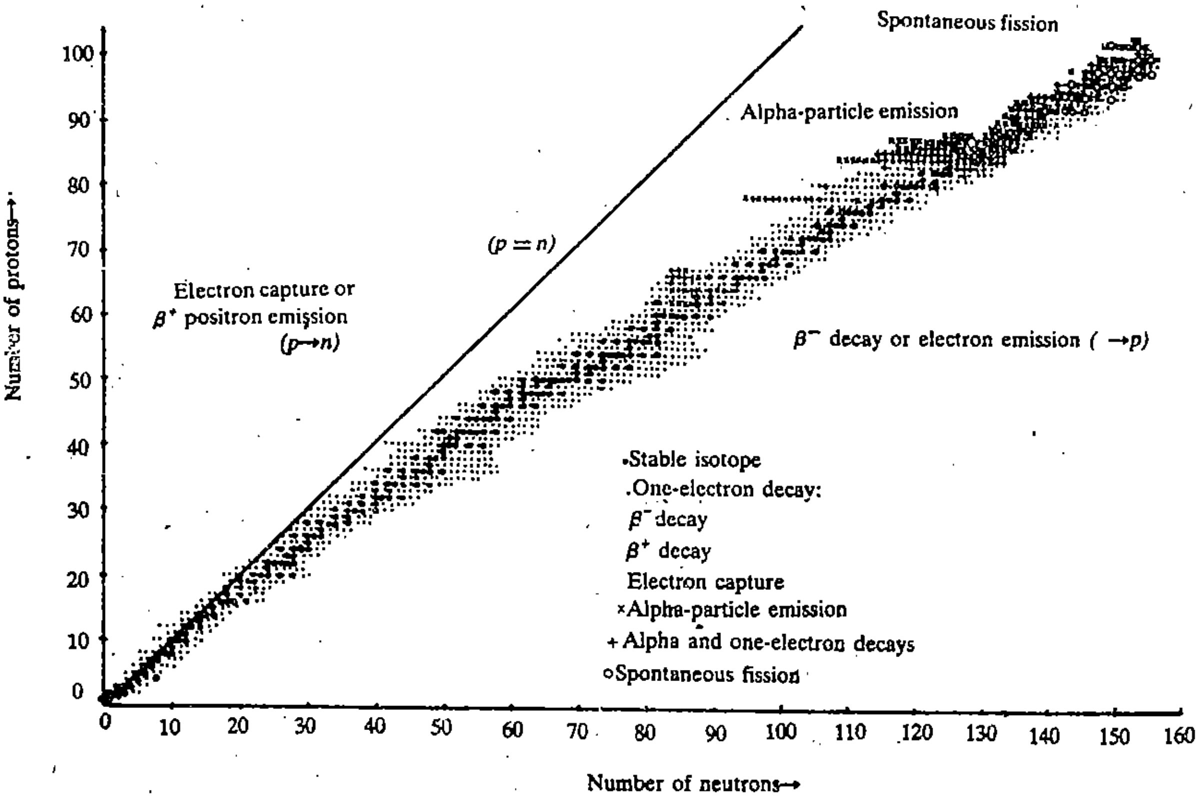


Fig. 9.4: The number of protons as a function of the number of neutrons for the stable nuclei.

Another factor also has a major effect on the stability. The nuclei with even number of protons and neutrons are apparently more stable than those containing an odd number of these particles. For example, of the known stable nuclides 157 are even-even, 52 are even-odd, 50 are odd-even and only 5 are odd-odd.

Protons Neutrons	Even Even	Even Odd	Odd Even	Odd Odd
Stable nuclei	157	52	50	5

An analogy can be made between the pairing of electrons and the pairing of nucleons. Just as increased stability is associated with pairs of electrons of opposite spin, increased stability is associated with pairs of like nucleons.

Nuclei with certain "magic numbers" of protons or neutrons seem to be especially stable. Stability is associated with 2, 8, 20, 28, 50, 82 and 126 of either protons or neutrons. For example, the $^{4}_{2}He$ nucleus, with two protons and two neutrons, is exceptionally stable. So are the $^{16}_{8}O$ nucleus (eight protons, eight neutrons) and the $^{40}_{20}Ca$ nucleus (20 protons, 20 neutrons).

The nuclear shell model was developed in 1949 to explain the existence of magic numbers. These numbers may have a significance similar to that of the total numbers of electrons in the noble gases: 2, 10, 18, 36, 54, 86.

Before proceeding further, answer the following SAQ.

SAQ 4

Among the nuclei given below, mark YES for those falling within the band of stability and NO for the rest. Make use of Fig. 9.4.

i) $^{17}_{7}N$ ☐

ii) $^{12}_{6}C$ ☐

iii) $^{35}_{16}S$ ☐

iv) $^{1}_{1}H$ ☐

v) $^{31}_{15}P$ ☐

vi) $^{39}_{20}Ca$ ☐

vii) $^{233}_{90}Th$ ☐

9.4 NUCLEAR REACTIONS

In this section, we describe reactions of nuclei that cause changes in their atomic numbers, mass numbers and energy states. Such reactions are called nuclear reactions. Nuclear reactions are of the following types:

1) spontaneous decay of naturally occurring or artificially produced radioactive nuclei
2) fission of unstable heavy nuclei
3) fusion of light nuclei
4) nuclear reactions by bombardment of nuclei with other nuclei or with other fast moving particles.

Before going into details of the nuclear reactions, we would like to give you some idea about the way, equations for nuclear reactions are generally written.

Similar to chemical reactions, all types of nuclear reactions are accompanied by either the absorption of energy (endoergic reaction) or release of energy (exoergic reaction). The amount of energy absorbed or released in a nuclear reaction is generally called Q value of nuclear reaction (as ΔH in chemical reactions). Q value is calculated from the change in mass between the reactants and the products of the nuclear reactions, similar to the binding energy calculation.
Q value = change in mass × c^2 J

9.4.1 Writing Equations for Nuclear Reactions

Equation for nuclear reaction has to be written in such a way that both sides are balanced with respect to mass number and atomic number. That is, the sum of the mass numbers of the reactants must be equal to the sum of the mass numbers of the products; similarly, the sum of the atomic numbers of the reactants must be equal to that of the products. If the atomic number and the mass number of all but one of the particles in a nuclear reaction are known, the remaining particle can be identified by balancing the equation. Consider the following example:

The reaction of an α particle with magnesium ($^{25}_{12}Mg$) produces a proton ($^{1}_{1}H$) and a nuclide of another element. Let us identify the nuclide produced.

The nuclear reaction may be written as;

$$^{25}_{12}Mg + ^{4}_{2}He \longrightarrow ^{A}_{Z}X + ^{1}_{1}H$$

where A is the mass number and Z is the atomic number of the new nuclide, X.

Since, the sum of the mass numbers of the reactants must be equal to the sum of the mass numbers of the products. $25 + 4 = A + 1$, or $A = 28$. Similarly, by balancing the atomic numbers, we can write, $12 + 2 = Z + 1$ and so, $Z = 13$. The element with atomic number 13 is aluminium. Thus, the product is $^{28}_{13}Al$.

Let us see whether you can work out the following SAQ using the above principle.

SAQ 5

Complete the following nuclear equations:

a) $^{135}_{53}I \longrightarrow ^{135}_{54}Xe + ?$

b) $^{245}_{97}Bk \longrightarrow ^{4}_{2}He + ?$

c) $^{238}_{92}U + ^{12}_{6}C \longrightarrow ^{246}_{98}Cf + ?$

d) $^{96}_{42}\text{Mo} + ^{2}_{1}\text{H} \longrightarrow ^{1}_{0}n + ?$

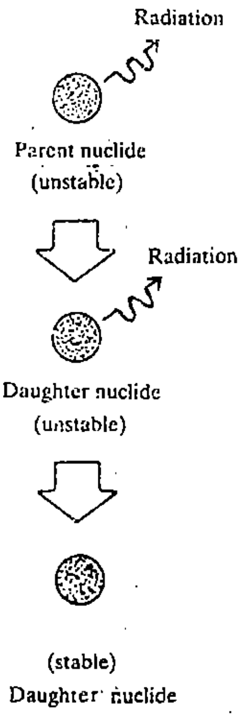
e) $^{20}_{8}\text{O} \longrightarrow ^{20}_{9}\text{F} + ?$

9.4.2 Radioactive Decay

We have already defined radioactivity as the spontaneous emission of radiation from the unstable nuclei. Radioactivity is also known as radioactive decay. The unstable nucleus is often called the **parent nuclide** and the nucleus, that results from the decay, is called the **daughter nuclide**. The daughter nuclide may be stable or it may decay further.

Some simple rules for predicting the occurrence and nature of radioactivity can be formulated by referring to the stability band of Fig. 9.4. Unstable nuclei decay in such a fashion so as to yield daughter nuclei which are closer to the band of stability than the parent nuclide. Different types of radioactive decay are given below:

Radioactivity is the term used to describe the spontaneous emission of radiation from an unstable nucleus.



i) **α decay:** The loss of an α particle by a radioactive nuclide, known as α decay, occurs primarily in heavy nuclei (A>200; Z>83). Loss of an α particle gives a daughter nuclide with a mass number that is 4 units smaller and an atomic number that is 2 units smaller as compared to the parent nuclide. Consequently, the daughter nuclide has a larger neutron to proton ratio than the parent nuclide and if the parent nuclide lies below the band of stability, the daughter nuclide will lie closer to the band. A typical α decay can be represented by an equation such as,

$$^{232}_{90}\text{Th} \longrightarrow ^{228}_{88}\text{Ra} + ^{4}_{2}\text{He}$$

$n/p = 1.57 \qquad n/p = 1.59$

ii) **β decay:** A nuclide with large neutron to proton ratio (one that lies above the band of stability) can reduce this ratio by electron emission or β decay. In this transformation, a neutron splits into a proton and an electron, with the emission of latter.

$$^{1}_{0}n \longrightarrow ^{1}_{1}\text{H} + ^{0}_{-1}e$$

Thus, electron emission does not change the mass number of the nuclide but increases the number of proton(s) and decreases the number of neutron(s). An example is the decay of $^{14}_{6}$C to $^{14}_{7}$N.

$$^{14}_{6}\text{C} \longrightarrow ^{14}_{7}\text{N} + ^{0}_{-1}e$$

$n/p = 1.33 \qquad n/p = 1$

iii) **β⁺ decay:** Certain artificially produced nuclides in which the neutron to proton ratio is low, i.e., nuclides which lie below the band of stability, decay by the emission of a positron (β^+or$^{0}_{+1}e$). During the course of β⁺ decay, a proton is converted into a neutron with the emission of a positron. The neutron to proton ratio increases and the daughter nuclide lies closer to the band of stability than the parent nuclide. Decay of $^{11}_{6}$C to $^{11}_{5}$B is an example of $^{0}_{+1}$e decay.

Energy is released during radioactive decay because the products are more stable than the reactants.

$$^{11}_{6}\text{C} \longrightarrow ^{11}_{5}\text{B} + ^{0}_{-1}e$$

$n/p = 0.83 \qquad n/p = 1.2$

iv) **Electron Capture:** A proton is converted into a neutron when one of the orbital electrons in an atom is captured by the nucleus. This capture is called K electron capture and it leads to a decrease in atomic number by one unit.

The electrons are captured from 1s (K shell) orbitals (being nearest to the nucleus).

$$^{1}_{1}\text{H} + ^{0}_{-1}e \longrightarrow ^{1}_{0}n$$

An example for this type is the decay of $^{7}_{4}$Be to $^{7}_{3}$Li

$$^{7}_{4}\text{Be} + ^{0}_{-1}e \longrightarrow ^{7}_{3}\text{Li}$$

$n/p = 0.75 \longrightarrow n/p = 1.33$

Electron capture has the same effect on the nucleus as that of positron emission. It increases the neutron to proton ratio and like positron decay, electron capture occurs when the neutron to proton ratio is low.

v) **γ ray emission:** A daughter nuclide is not always produced in its ground state; it may be formed in an excited state and then it may decay to its ground state with the emission of γ rays. Fig. 9.5 illustrates three different ways by which $^{233}_{92}U$ may be transformed into $^{229}_{90}Th$. Two paths give excited states of the $^{229}_{90}Th$ nuclide, which decay into the ground state by emission of γ rays.

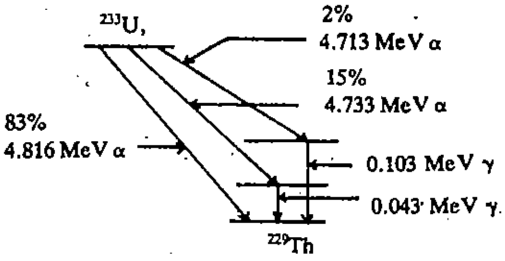


Fig. 9.5: The decay of $^{233}_{92}U$ to $^{229}_{90}Th$.

Note that there is no change of mass number or atomic number during emission of the γ rays. The γ ray emission is observed only when a nuclear reaction produces a daughter nuclide in an excited state.

The radioactive decay processes so far discussed are summarised in Table 9.2.

Table 9.2: Radioactive Decay Processes

Process	Nuclear Condition	Emitted radiation	Change in		
			A	Z	$N^a = A-Z$
α decay	Heavy nuclei	^4_2He (α particles)	–4	–2	–2
β decay	neutron to proton ratio too high	$^0_{-1}e$ (electrons)	0	+1	–1
β^+ decay	neutron to proton ratio too low	$^0_{+1}e$ (positron)	0	–1	+1
Electron capture	neutron to proton ratio too low	none	0	–1	+1
γ emission	excited nuclear state	γ rays	0	0	0

a – Here N represents change in number of neutrons.

See if you can do the following SAQ.

SAQ 6

For each of the nuclear conditions given below, indicate the type of radioactive decay which you expect :

a) neutron to proton ratio too low

....

b) neutron to proton ratio too high

....

c) heavy nuclei

....

d) excited nuclear state

....

9.4.3 Kinetics of Radioactive Decay

Like chemical reactions, nuclear reactions also proceed at certain specific rates. The rate depends on the nature of the nuclide. The radioactive decay follows first order kinetics. This means that the total number of nuclei that decay in a given time interval is proportional to the total number of nuclei initially present. If the number of nuclei at a particular time is N, and if the change in this number is dN during a time dt, then the rate of decay is proportional to N and can be represented by,

$$\frac{-dN}{dt} \propto N \qquad \text{which means}$$

$$\frac{-dN}{dt} = kN \qquad \text{...(9.4)}$$

The left hand side of the above expression represents rate of nuclear decay; the negative sign indicates that as time proceeds, the number of remaining nuclei decreases. The constant k is the first order decay constant. To be able to calculate the number of nuclei remaining after a particular time interval t, Eq. 9.4 is integrated, assuming that at the start of radioactive decay ($t = 0$), the number of nuclei is N_0, and after time t, it is equal to N_t.

The number of nuclei that decay in a unit time is proportional to the total number of nuclei present.

$$\int_{N_0}^{N_t} \frac{dN}{N} = \int_0^t k dt$$

$$\text{or } \ln \frac{N_0}{N_t} = kt \qquad \text{...(9.5)}$$

'ln' stands for logarithm to the base e and 'log' stands for logarithm to the base 10. To convert the former into latter, the following formula is used. $\ln x = 2.303 \log x$.

On changing the logarithmic base to 10, we get,

$$2.303 \log \frac{N_0}{N_t} = kt \qquad \text{.... (9.6)}$$

which is the rate equation for a first order reaction.

An important property of radioactive decay, like any other first order reaction, is that the time required for 50% of a particular material to decay is constant. This time interval is denoted as the **half-life period**, or $t_{1/2}$. It is independent of the amount of the material taken initially.

At $t_{1/2}$, $N_t = N_0/2$. Using this expression in Eq. 9.6,

$$2.303 \log \frac{N_0}{N_0/2} = kt_{1/2}$$

$$2.303 \log 2 = kt_{1/2}$$

$$\text{or } t_{1/2} = \frac{0.693}{k} \qquad \text{...(9.7)}$$

The half-life period of a radioactive isotope is the time in which the number of radioactive nuclei decreases by half.

If either the half-life period or the first order rate constant is known, the other can be calculated. You can make use of Table 9.3 to calculate the amount of the radioactive material left after different number of half-life periods.

Table 9.3: Reactant Amounts After Different Time Intervals

Number of half-life period(s)	Fraction of radioactive material remaining
0	1
1	1/2
2	1/4
3	1/8
4	1/16
5	1/32
n	$(\frac{1}{2})^n$

SAQ7

Calculate the rate constant for the radioactive disintegration of $^{60}_{27}Co$, an isotope used in cancer treatment. It decays with a half-life of 5.26 year to produce $^{60}_{28}$ Ni.

....

....

9.4.4 Natural Radioactivity

Cosmic rays are a natural source of ionising radiation. Cosmic rays are atomic particles (electrons, neutrons positrons, protons, α particles and other heavier nuclei) moving at almost the speed of light. The original source of cosmic rays appears to have been huge explosive reactions in our galaxy.

The radioactive nuclides that occur naturally on earth can be divided into three categories. The first category of nuclides, of which $^{14}_{6}C$ is an important member, are formed by the action of cosmic rays. For example, the formation of $^{14}_{6}C$ from $^{14}_{7}N$ can be explained as follows:

$$^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{14}_{6}C + ^{1}_{1}H \qquad .... (9.8)$$

A second group consists of nuclides with half-life periods of the magnitude of the life of the earth. The examples are, $^{87}_{37}Rb$ ($t_{1/2} = 5 \times 10^{11}$ y), $^{232}_{90}Th$ ($t_{1/2} = 1.39 \times 10^{10}$ y) and $^{235}_{92}U$ ($t_{1/2} = 7.13 \times 10^{8}$ y). The symbol 'y' stands for the unit year.

The third category of radioactive nuclides have shorter half-life periods. They are formed by the radioactive decay of the long lived nuclides. Such decay process results in what is called a radioactive family, or series. Three radioactive series are found in nature. In Table 9.4, we summarise the starting and ending nuclei in these three series.

Fajans — Soddy — Russell summarised α and β decay in the form of **Group Displacement Law**. This law states that whenever a parent nucleus emits an α particle, its atomic number is decreased by two units and the new element is shifted two positions to its left in the Periodic Table from that of the parent element. On the other hand, when the parent nucleus emits a β particle, the atomic number is increased by one and hence the product is shifted one place to its right in the Periodic Table.

Table 9.4: Natural Radioactive Decay Series

Parent	Half-Life y	End product	Name
$^{238}_{92}U$	4.51×10^{9}	$^{206}_{82}Pb$	Uranium series
$^{235}_{92}U$	7.31×10^{8}	$^{207}_{82}Pb$	Actinium series
$^{232}_{90}Th$	1.39×10^{10}	$^{208}_{82}Pb$	Thorium series

To illustrate the multiple stages in the radioactive series, uranium and actinium series have been shown in Fig. 9.6.

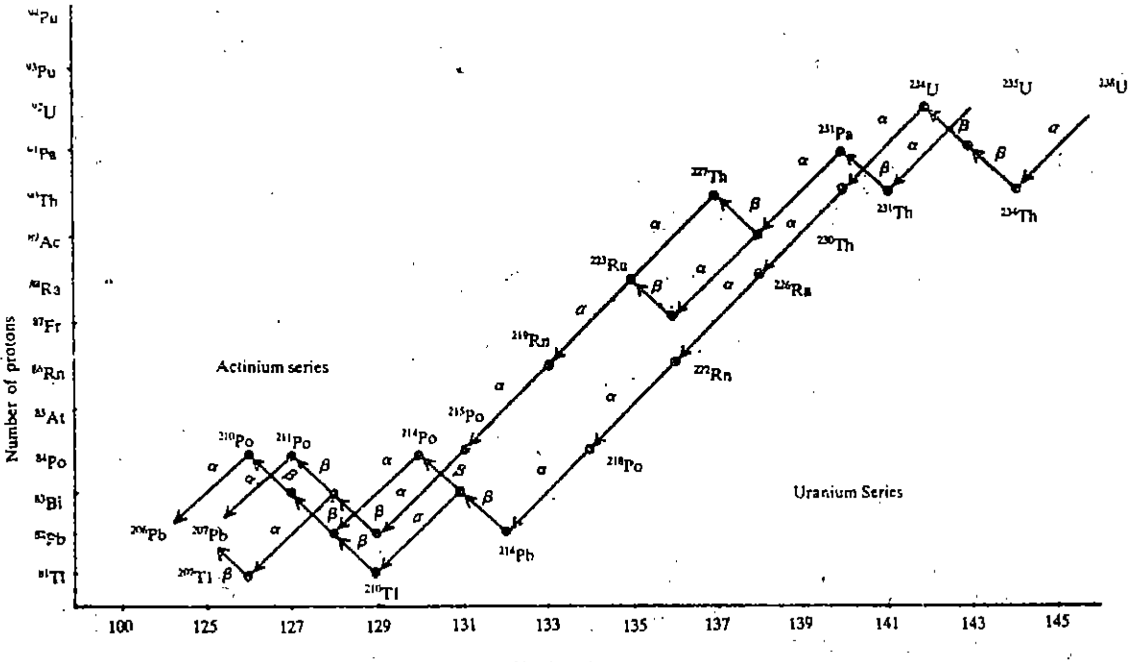


Fig. 9.6: Uranium series and actinium series.

In the next sub-section, we shall define nuclear transformation and study its different types.

9.4.5 Nuclear Transformation

A nuclear transformation is a nuclear reaction in which a bombarding particle causes a nucleus of an element to change into a nucleus of another element. It is also known as **transmutation** reaction. The first such nuclear transformation was carried out by Rutherford (1919). He prepared oxygen from nitrogen by bombardment with α particles. This reaction can be represented as,

$$^{14}_{7}N + ^{4}_{2}He \longrightarrow ^{17}_{8}O + ^{1}_{1}H \qquad ...(9.9)$$

Alchemists tried in vain to transmute lead into gold.

The nucleus of deuterium is known as deutron and is represented as $^{2}_{1}H$.

The bombardment of beryllium by α particles led to the discovery of neutrons by Chadwick in 1932.
$^{9}_{4}Be + ^{4}_{2}He \longrightarrow ^{12}_{6}C + ^{1}_{0}n$

Types of Nuclear Transformation

Nuclear reactions have been initiated using electrons, neutrons and by a series of positively charged particles with low masses, such as protons, deutrons and α particles. The development of high energy accelerators has also made it possible to use heavy nuclei with positive charges, such as $^{10}_{5}B$, $^{12}_{6}C$, $^{16}_{8}O$, or even heavier nuclides as bombarding particles.

Accelerators are employed to impart the required velocity to the bombarding positive particles to have successful reaction with a given nucleus, overcoming mutual repulsion. The emission in nuclear reactions includes X rays, neutrons, protons and different nuclides.

There is a simple notation for representing a nuclear reaction. The symbols of the bombarding particle and of the emitted particle are placed in parentheses between the symbols of the reactant and the product nuclei. For example, the reaction in which nitrogen is transformed into oxygen by bombardment with α particles is represented as,

$$^{14}_{7}N\ (\alpha,\ p)\ ^{17}_{8}O$$

The corresponding equation is given by Eq. 9.9. Examples of the more common type of transformation varieties are listed in Table 9.5. The symbols used in this Table include *n* for neutron, *p* for proton, *d* for deutron, α for alpha particle, and γ for gamma rays.

Table 9.5: Types of Nuclear Transformation

Type	Example	Representation
(α, n)	$^{75}_{33}As + ^{4}_{2}He \longrightarrow ^{78}_{35}Br + ^{1}_{0}n$	$^{75}_{33}As\ (\alpha, n)\ ^{78}_{35}Br$
(α, p)	$^{106}_{46}Pd + ^{4}_{2}He \longrightarrow ^{109}_{47}Ag + ^{1}_{1}H$	$^{106}_{46}Pd\ (\alpha, p)\ ^{109}_{47}Ag$
(p, n)	$^{7}_{3}Li + ^{1}_{1}H \longrightarrow ^{7}_{4}Be + ^{1}_{0}n$	$^{7}_{3}Li\ (p, n)\ ^{7}_{4}Be$
(p, γ)	$^{14}_{7}N + ^{1}_{1}H \longrightarrow ^{15}_{8}O + \gamma$	$^{14}_{7}N\ (p, \gamma)\ ^{15}_{8}O$
(p, α)	$^{9}_{4}Be + ^{1}_{1}H \longrightarrow ^{6}_{3}Li + ^{4}_{2}He$	$^{9}_{4}Be\ (p, \alpha)\ ^{6}_{3}Li$
(d, p)	$^{31}_{15}P + ^{2}_{1}H \longrightarrow ^{32}_{15}P + ^{1}_{1}H$	$^{31}_{15}P\ (d, p)\ ^{32}_{15}P$
(d, n)	$^{209}_{83}Bi + ^{2}_{1}H \longrightarrow ^{210}_{84}Po + ^{1}_{0}n$	$^{209}_{83}Bi\ (d, n)\ ^{210}_{84}Po$
(n, γ)	$^{59}_{27}Co + ^{1}_{0}n \longrightarrow ^{60}_{27}Co + \gamma$	$^{59}_{27}Co\ (n, \gamma)\ ^{60}_{27}Co$
(n, p)	$^{45}_{21}Sc + ^{1}_{0}n \longrightarrow ^{45}_{20}Ca + ^{1}_{1}H$	$^{45}_{21}Sc\ (n, p)\ ^{45}_{20}Ca$
(n, α)	$^{27}_{13}Al + ^{1}_{0}n \longrightarrow ^{24}_{11}Na + ^{4}_{2}He$	$^{27}_{13}Al\ (n, \alpha)\ ^{24}_{11}Na$

There are many transformation reactions in which the product nucleus is unstable and hence decays spontaneously like naturally occurring radioactive nuclides. We call this process of artificial production of radioactive substances as artificial radioactivity. The first such nuclide was produced by the (α, n) reaction:

$$^{27}_{13}Al + ^{4}_{2}He \longrightarrow ^{30}_{15}P + ^{1}_{0}n$$

The product, $^{30}_{15}P$ decays by positron emission.

$$^{30}_{15}P \longrightarrow ^{30}_{14}Si + ^{0}_{+1}e$$

Nuclear transformation reactions have also been used to prepare elements that are not found on earth. Synthesis of transuranium elements with atomic numbers greater than 92, are the examples of such nuclear reactions. A list containing such bombardment reactions and the elements produced is shown in Table 9.6. Attempts to prepare heavier elements continue even today.

Table 9.6: The Reactions Involved in the Preparation of the Transuranium Elements

Name	Symbol	Atomic Number	Reaction
Neptunium	Np	93	$^{238}_{92}U + ^{1}_{0}n \longrightarrow ^{239}_{93}Np + ^{0}_{-1}e$
Plutonium	Pu	94	$^{238}_{93}Np \longrightarrow ^{238}_{94}Pu + ^{0}_{-1}e$
Americium	Am	95	$^{239}_{94}Pu + ^{1}_{0}n \longrightarrow ^{240}_{95}Am + ^{0}_{-1}e$
Curium	Cm	96	$^{239}_{94}Pu + ^{4}_{2}He \longrightarrow ^{242}_{96}Cm + ^{1}_{0}n$
Berkelium	Bk	97	$^{241}_{95}Am + ^{4}_{2}He \longrightarrow ^{243}_{97}Bk + 2\,^{1}_{0}n$
Californium	Cf	98	$^{242}_{96}Cm + ^{4}_{2}He \longrightarrow ^{245}_{98}Cf + ^{1}_{0}n$
Einsteinium	Es	99	$^{238}_{92}U + 15\,^{1}_{0}n \longrightarrow ^{253}_{99}Es + 7\,^{0}_{-1}n$
Fermium	Fm	100	$^{239}_{94}Pu + 15\,^{1}_{0}n \longrightarrow ^{254}_{100}Fm + 6\,^{0}_{-1}e$
Mendelevium	Md	101	$^{253}_{99}Es + ^{4}_{2}He \longrightarrow ^{256}_{101}Md + ^{1}_{0}n$
Nobelium	No	102	$^{246}_{96}Cm + ^{12}_{6}C \longrightarrow ^{254}_{102}No + 4\,^{1}_{0}n$
Lawrencium	Lr	103	$^{250}_{98}Cf + ^{11}_{5}B \longrightarrow ^{257}_{103}Lr + 4\,^{1}_{0}n$
Unnilquadium	Unq	104	$^{249}_{98}Cf + ^{12}_{6}C \longrightarrow ^{257}_{104}Unq + 4\,^{1}_{0}n$
Unnilpentium	Unp	105	$^{249}_{98}Cf + ^{15}_{7}N \longrightarrow ^{260}_{105}Unp + 4\,^{1}_{0}n$
Unnilhexium	Unh	106	$^{206}_{82}Pb + ^{54}_{24}Cr \longrightarrow ^{257}_{106}Unh + 3\,^{1}_{0}n$
			$^{249}_{98}Cf + ^{19}_{8}O \longrightarrow ^{263}_{106}Unh + 4\,^{1}_{0}n$

By now, you are familiar with some of the nuclear transformations. In most of these reactions, we have to bombard the atoms with high-velocity particles. It is worthwhile to know some principles of transmutation reactions.

In sub-section 9.3.3, we have mentioned that nuclear forces are powerful at short ranges. Therefore, for the nuclear transformation of a nucleus, it is necessary that the bombarding particle should come close to a nucleus so that it comes under its nuclear force and is "fused" with it. Generally, this fusion forms an unstable intermediate nuclear particle that ejects some other particles like α or β or neutrons during the formation of the new element. To understand more clearly, let us first take neutron bombardment which is a very effective means to bring about a nuclear change. Unlike positively charged particles which are repelled by the positive nucleus of an atom, the uncharged neutron does not require a high velocity in order to come close to a nucleus. Indeed a slow moving neutron passing close to a nucleus has a greater chance of being attracted into the nucleus than does a high speed neutron which might just pass by it.

Now consider the bombardment by positive particles. Experiments indicate that highly charged positive nuclei repel incoming slow positive particles thereby preventing effective collision with these nuclei. Calculations show that an alpha particle needs 27 MeV of energy in order to push it close enough to a nucleus like radon so that short range nuclear forces become effective and a radium nucleus can be formed (see Fig. 9.7).

$${}^{4}_{2}He + {}^{222}_{86}Rn \longrightarrow {}^{226}_{88}Ra$$

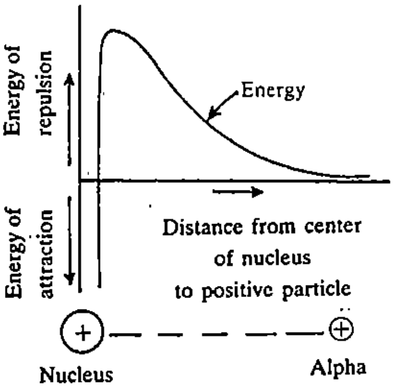


Fig 9.7: If an alpha particle has enough energy to overcome the coulombic repulsion of a nucleus, it can penetrate close enough to the positive nucleus to come under the effective control of the powerful short range nuclear attraction and to join the nucleus.

9.4.6 Fission

The kind of nuclear reaction most often in the news is **nuclear fission**. Nuclear fission is the process by which a large nucleus breaks into two or more nuclei of medium size. The fission process begins when a slow moving neutron hits an atom of a fissionable nuclide – one that has a tendency to split apart. The only naturally occurring fissionable nuclide is ${}^{235}_{92}U$. There are many ways by which ${}^{235}_{92}U$ can break apart. One of them is,

In nuclear fission, a heavy nucleus of an atom splits into two or more smaller nuclei, which are more tightly bound than the parent nucleus. The fission process is accompanied by the evolution of enormous amounts of energy.

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

Energy evolved during this process is 1.9×10^{10} kJ mol^{-1}.

All the fission reactions of ${}^{235}_{92}U$ have three common characteristics:

- each reaction produces one nuclide with mass number near 90-95 and another with a mass number near 135-140. (see Fig. 9.8),
- each reaction generates a large amount of energy, and
- each reaction produces more than one neutron.

The production of excess neutrons allows the fission process to be self-sustaining. This means that the neutrons formed in the fission process initiate additional fission reactions, as we can see in Fig. 9.9. Such reactions are called **chain reactions**.

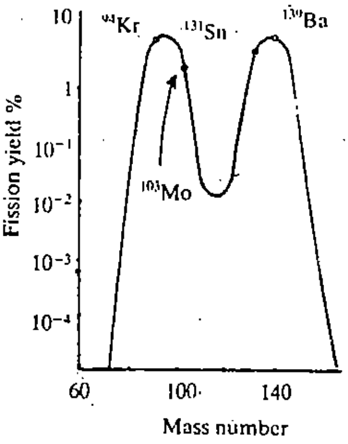


Fig 9.8 : The percentage of nuclides of different mass numbers formed by the fission of uranium ${}^{235}_{92}U$. The most common fission produces one nucleus with a mass of about 95 and another of about 138.

We have already explained in sub-section 9.3.3 why a fission reaction is accompanied by the release of a large amount of energy. A fission reaction results in the formation of nuclei having larger average binding energy than the original nucleus. Now, if we know the average binding energy of the reactant and the product nuclei, we can calculate the energy released during the fission reaction for example, the average binding energy of ${}^{235}_{92}U$ is around 7.6 MeV/nucleon, whereas for the products of fission, ${}^{141}_{56}Ba$ and ${}^{92}_{36}Kr$, the same is around 8.5 MeV/nucleon. This means that while the formation of uranium nucleus from its nucleons can release 235 × 7.6 MeV of energy, the formation of nuclei of products of fission can release about (141 × 8.5 + 92 × 8.5) MeV of energy. Hence the energy released by the fission is,

$$\Delta E = (141 \times 8.5 + 92 \times 8.5) - 235 \times 7.6 \text{ MeV}$$

$$= (1198.5 + 782) - 1786 \text{ MeV}$$

$$= 194.5 \text{ MeV.}$$

Depending on the binding energy of the product and the reactant nuclei, the energy of fission varies. As a practical average value, 200 MeV per fission is used.

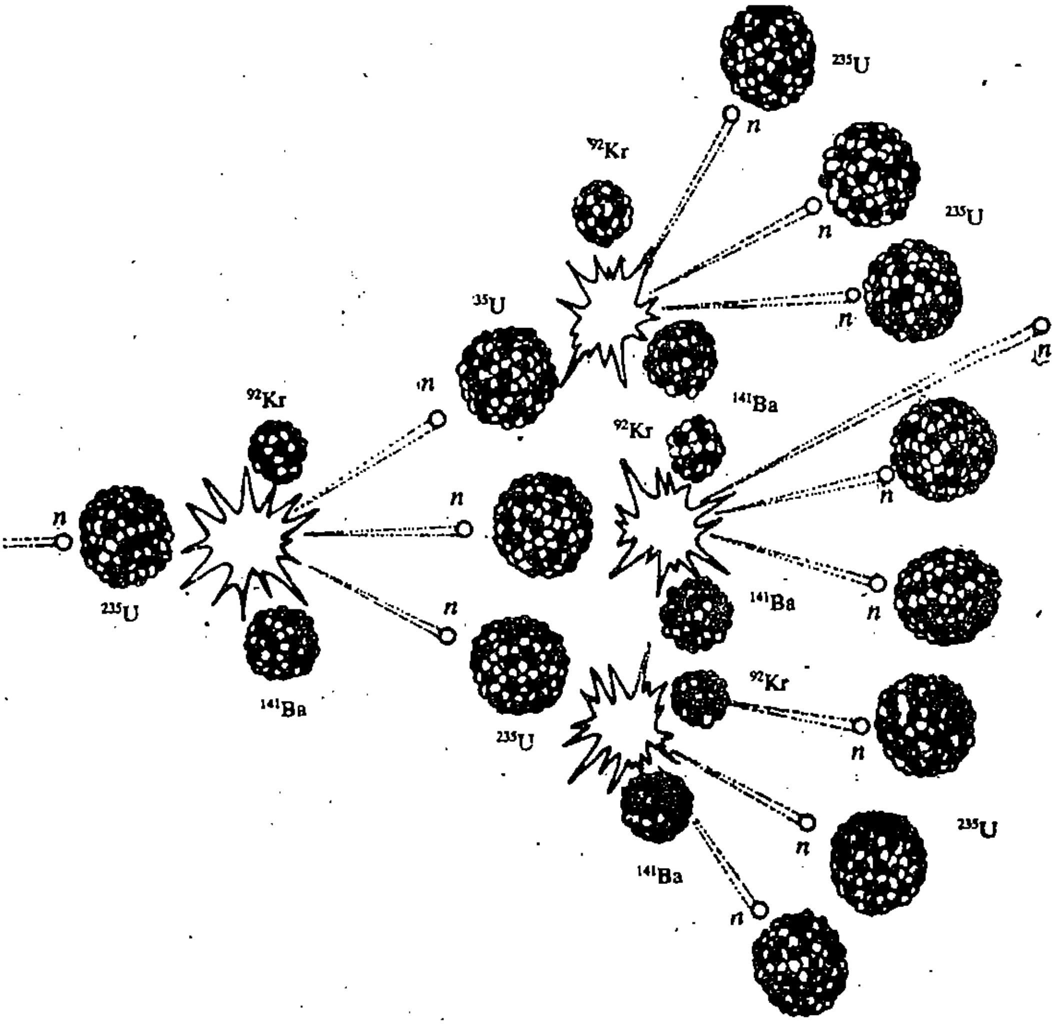


Fig. 9.9 : A nuclear chain reaction. When a nucleus undergoes fission, two or three neutrons are produced that are capable of reacting with other nuclei. If a critical mass of fissionable nuclei is present, a chain reaction will occur.

We also arrive at the fission energy from a different consideration. In fact, the value of mass loss in nuclear fission comes to around 0.22 u per uranium atom. Using Eqs. 9.2 and 9.3,

$$\Delta E = 0.22 \times 1.661 \times 10^{-27}\ \text{kg} \times (2.998 \times 10^{8}\ \text{m s}^{-1})^{2}$$

$$= 3.284 \times 10^{-11}\ \text{J}$$

$$= \frac{3.284 \times 10^{-11}\ \text{J} \times 1\ \text{MeV}}{1.602 \times 10^{-13}\ \text{J}} \qquad (\because 1\ \text{MeV} = 1.602 \times 10^{-13}\ \text{J})$$

$$= 205\ \text{MeV}.$$

The fission energy calculated above is per uranium atom. In molar quantities, the fission energy is,

$$\Delta E = 3.284 \times 10^{-11} \times 6.022 \times 10^{23}\ \text{J mol}^{-1}$$

$$= 1.978 \times 10^{13}\ \text{J mol}^{-1}$$

Although $^{235}_{92}U$ is the only naturally occurring fissionable nuclide, others can be synthesised. One such is $^{239}_{92}Pu$, produced by the reaction of $^{238}_{92}U$, quite an abundant isotope of uranium, with a neutron. At the first instance, $^{239}_{92}U$ is formed which, in turn, decays in two steps to form $^{239}_{94}Pu$.

$$^{238}_{92}U + ^{1}_{0}n \longrightarrow ^{239}_{92}U$$

$$^{239}_{92}\text{U} \longrightarrow\ ^{239}_{93}\text{Np} + ^{0}_{-1}e,\ t_{1/2} = 23.5 \text{ minute}$$

$$^{239}_{93}\text{Np} \longrightarrow\ ^{239}_{94}\text{Pu} + ^{0}_{-1}e;\ t_{1/2} = 2.35 \text{ day}$$

Like $^{235}_{92}U$ nuclide, $^{239}_{94}Pu$ can also supply large amounts of energy through nuclear fission.

Another synthetic fissionable nuclide is $^{233}_{92}U$, formed from $^{232}_{90}Th$ which is also rather abundant.

80% of the world's thorium is located in India as monazite sand on the sea coast of Kerala state.

$$^{232}_{90}\text{Th} + ^{1}_{0}n \longrightarrow\ ^{233}_{90}\text{Th} \xrightarrow{^{0}_{-1}e}\ ^{233}_{91}\text{Pa} \xrightarrow{^{0}_{-1}e}\ ^{233}_{92}\text{U}$$

A chain reaction as indicated in Fig. 9.9 is possible only if each of the fission reaction gives rise to another fission reaction. The minimum mass of fissionable material needed for such a process is known as critical mass.

The actual critical mass depends on several factors including the purity of the fissionable material, the shape of the fissioning material, the presence and absence of a casing to reflect neutrons etc. Fission reaction generates enormous amounts of energy which can be used in atom bombs or in nuclear reactors. Details of the applications of nuclear energy will be discussed in sub-section 9.5.1.

9.4.7 Fusion

The process in which two small nuclides come together to form one large, more stable nuclide is called nuclear fusion. This is the opposite of fission process. Some examples of fusion reactions are:

$$^{2}_{1}\text{H} + ^{2}_{1}\text{H} \longrightarrow\ ^{3}_{2}\text{He} + ^{1}_{0}n$$

$$^{2}_{1}\text{H} + ^{6}_{3}\text{Li} \longrightarrow 2\ ^{4}_{2}\text{He}$$

$$4\ ^{1}_{1}\text{H} \longrightarrow\ ^{4}_{2}\text{He} + 2\ ^{0}_{+1}e$$

Our principal source of energy is the sun. The solar energy is produced by the fusion of four hydrogen nuclei into a helium nucleus. Like fission reaction, fusion reaction is also accompanied by liberation of large amounts of energy. Fusion reactions have a much higher energy/mass ratio than fission reaction, because greater proportion of mass of the reactants is converted into energy. We can calculate the energy changes in a fusion reaction from the mass defect and binding energy methods, similar to the fission reaction. For example, let us consider the mass defect method for the following fission reaction:

Everyday about 6.3×10^{18} kJ of energy from the sun reaches the surface of the earth.

$$^{2}_{1}\text{H} + ^{6}_{3}\text{Li} \longrightarrow 2\ ^{4}_{2}\text{He}$$

The calculations indicate that the mass defect in this case is 0.0243 u. We can obtain the energy change for this reaction from Eq. 9.2.

$$\Delta E = 0.0243 \times 1.661 \times 10^{-27}\ (\text{kg}) \times (2.998 \times 10^{8}\ (\text{m s}^{-1}))^{2}$$

$$= 3.6278 \times 10^{-12}\ \text{J}$$

This energy change is for the formation of 2 nuclides of $^{4}_{2}He$; for 1 mole of helium it would be

$$\Delta E = \frac{3.6278 \times 10^{-12}\ (\text{J}) \times 6.022 \times 10^{23}\ (\text{mol}^{-1})}{2}$$

$$= 1.0923 \times 10^{12}\ \text{J mol}^{-1}$$

Although fusion reactions are highly exothermic, they require high activation energy because two positively charged particles must come together. The electrostatic repulsion must be overcome before the particles can get close enough to be fused together. The high activation energy needed for this process causes serious problems. It has been estimated that a temperature of at least several million kelvin is necessary to supply the energy needed thermally to start a fusion reaction.

Such a high temperature can be obtained from only fission reaction. Thus, we can fuse deuterium and tritium in a fission bomb. This typical process is used in hydrogen bomb.

$${}_{1}^{2}H + {}_{1}^{3}H \longrightarrow {}_{2}^{4}He + {}_{0}^{1}n$$

Such a bomb is several times more powerful than a fission bomb.

So far we have discussed the nucleus and the nuclear reactions. In the next section, we will discuss the applications of nuclear chemistry.

9.5 APPLICATIONS OF NUCLEAR CHEMISTRY

You have studied that fission reactions can release a large amount of energy. This energy can be used in an atom bomb or for the production of electricity by means of a nuclear reactor. The nuclear reactor controls the fission process. Apart from this, it has been realised that radioactive isotopes of common elements are uniquely valuable. A radioactive atom acts as a label or tag: it can be added at one point in a reaction and followed thereafter, to unravel the complex course of chemical reactions. Radioisotopes have also given us a means of accurately dating past events, both historical and geological. Nuclear chemistry helps us even in developing theories regarding the origin and the evolution of the universe. Now we will take up these applications of nuclear chemistry in detail.

9.5.1 Atom Bomb

It is, of course, ironical to project atom bomb as an application of nuclear chemistry. It is, however, a historical fact that the nuclear energy was first used, as a military weapon.

An atom bomb consists of two sections, each containing ${}_{92}^{235}U$ or ${}_{94}^{239}Pu$. Each section is below the critical mass; the two are kept separately from each other. The sum of the two pieces, however, exceeds the critical mass. Just before the explosion, the two pieces are brought together by the force of conventional explosive. The weapon dropped on Hiroshima, Japan, near the end of World War II, was a ${}_{92}^{235}U$ fission bomb of this type. You are perhaps curious to have an estimate of the energy that devastated Hiroshima. Work out the following SAQ to find it out.

SAQ 8

The loss of mass about 0.22 u per ${}_{92}^{235}U$ atom occurs in its fission reaction. Calculate the amount of energy released in kJ during the bomb explosion of Hiroshima in World War II. Remember, 0.45 kg of ${}_{92}^{235}U$ was used and $1 \text{ u} = 1.661 \times 1^{-27}$ kg.

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9.5.2 Nuclear Reactors

In a nuclear reactor, fission reaction takes place but at a controlled rate, slow enough to avoid an explosion but fast enough to produce usable heat. Fission reactions are controlled by the use of control rods made of materials such as cadmium or boron which absorb neutrons and thus prohibit the chain from progressing too rapidly (see Fig. 9.10) and also by the slowing down of energetic neutrons. As said earlier, slow moving neutron has a greater chance of being attracted into the nucleus than a high speed (high energy) neutron. In the case of neutron reactors, a **moderator** is incorporated in the design to slow the neutrons emitted on fission so that they are more readily captured by another fissionable nucleus. Different moderators as heavy water, water, graphite and beryllium are commonly used. The moderator qualities decrease in the order $D_2O > C > Be > H_2O$.

The large quantity of energy generated in the controlled nuclear reaction appears primarily as heat, and hence, nuclear reactors must be cooled. One of the main applications of the released thermal energy is in the production of electricity. The heat removed from the reactor is used to convert water to steam, which is then used to turn steam turbines that generate electricity (Fig. 9.11).

Energy produced by 1 kg of uranium or by 2.5 × 10^{6} kg of coal of best quality or by 20 kilotonnes of TNT (2, 4, 6–trinitrotoluene) =8.4×10^{13} J.

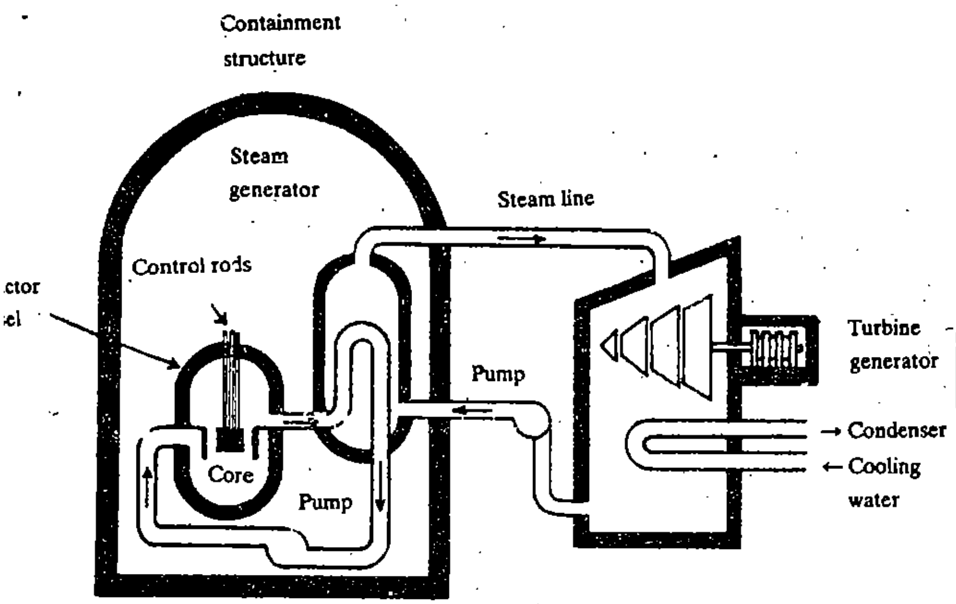


Fig. 9.11: Schematic diagram of a nuclear electric generating station.

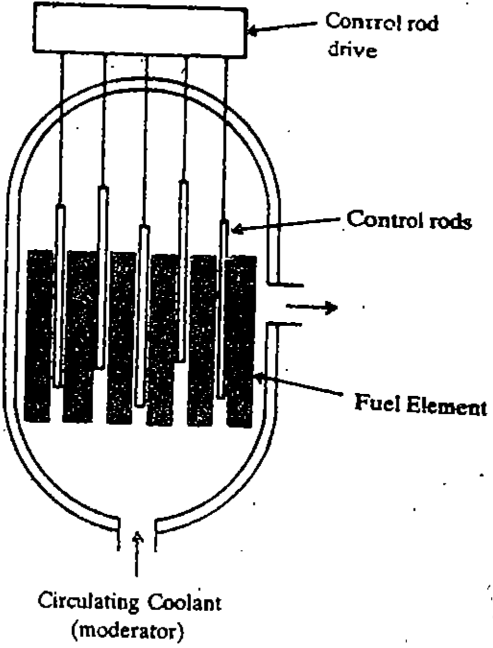


Fig. 9.10: Schematic diagram of a fission reactor.

Like petroleum and coal, there is only a limited supply of the fissionable $^{235}_{92}$U and the nuclear reactors would face a somewhat uncertain future if it is not possible to generate other fissionable isotopes. In a **breeder reactor** some of the control rods are replaced with rods containing $^{238}_{92}$U. Some of the neutrons produced in the fission reaction of $^{235}_{92}$U are absorbed by $^{238}_{92}$U and give the nuclide $^{239}_{92}$U, which changes to fissionable nuclide $^{239}_{94}$Pu as shown earlier in sub-section 9.4.6. Breeder reactors have the useful property that they produce more fissionable isotopes then they consume. Besides uranium, thorium can also be used as control rods in breeder reactors to produce fissionable $^{233}_{92}$U. India has very rich deposits of the thorium ore, monazite.

At present, worldwide, 114 nuclear plants are operating in 26 countries, generating 298,000 megawatts of electricity, accounting for 16% of the world's total generating capacity.

Certain implications of the use of nuclear energy, however, must be considered. Nuclear fission reactors, in general, have the undesirable effect of producing highly radioactive by-products – some with extremely long half-lives, that are very difficult to dispose of safely. Furthermore, the disasters in the power generating reactors, in the three mile island in Pennsylvania, U.S.A (1979) and Chernobyl, U.S.S.R (1986) pose a question to the safety of nuclear reactors. Therefore, increased use of nuclear power will require intensified efforts to avoid accidents.

Nuclear physicists are trying to find a way to develop fusion reactor. Deuterium is the principal fuel proposed for power generation through fusion. You will be surprised to know that even if only a small fraction of all the deuterium present in the oceans could be separated and recovered, the energy that could be supplied by fusion reaction is hundreds of thousands of times larger than all the energy contained in all the fossil fuels in the world. Still another advantage is that fusion reactions are relatively clean, in the sense that the products are generally not radioactive; so the waste disposal problem posed by fission reactors is avoided.

Despite these advantages, there are some major technical obstacles that must be overcome before fusion energy becomes a commercial reality. One of them is that the fusion reaction has high activation energy as mentioned earlier. Recently, high energy lasers are being developed to provide the necessary activation energy. An equally important problem is the lack of a suitable container for conducting a fusion reaction at a temperature of several million degrees kelvin (10^8 K). At this temperature, all reaction molecules dissociate into atoms, and the atoms ionise, forming a state of matter called **plasma**. One approach, that is being tested, is to suspend the reactants in the form of plasma of the mass of ions in a strong magnetic field (a magnetic bottle).

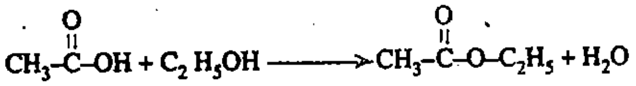
9.5.3 Tracers

One of the chemical applications of nuclear chemistry is the study of reaction mechanisms wherein the radioactive isotopes are used as tracers. The radioactive isotopes can be "traced" by using a detection device known as **Geiger Muller counter** and hence this method is known as tracer or labelling technique. Thus, by tagging a molecule with a radioisotope, its fate in chemical or biochemical change can be traced. For example, the several steps and intermediates occurring during the buildup of glucose from carbon dioxide in photosynthesis were uncovered by Calvin by using carbon dioxide containing labelled carbon isotope, ${}^{14}_{6}C$.

We use a star to indicate radioactive isotope.

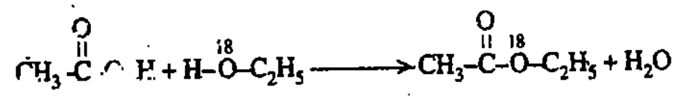
$$6\overset{*}{C}O_2 + 6H_2O \longrightarrow \overset{*}{C}_6H_{12}O_6 + 6O_2$$

Besides radioisotopes, sometimes the less abundantly occurring stable isotopes are also used as tracers, e.g. ${}^{2}_{1}H$, ${}^{18}_{8}O$. In such cases the detection of the isotope is done by mass spectrometry. We can predict the correct mechanism of a reaction using such tracers. For example, consider the formation of ester from alcohol and acid.



$$CH_3-\overset{\overset{O}{\|}}{C}-OH + C_2H_5OH \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-O-C_2H_5 + H_2O$$

There is a question about the source of oxygen atom of the water molecules produced. Does it come from the hydroxyl group of the alcohol or from that of the acid ? This question can be answered by carrying out the reaction with alcohol or acid containing labelled oxygen ${}^{18}_{8}O$. in the hydroxyl group. It is seen that if the alcohol is labelled with ${}^{18}_{8}O$, all the labelled ${}^{18}_{8}O$. becomes incorporated into ester. It is clear, therefore, that the reaction involves the removal of the OH group from the acid and the H from the alcohol.



$$CH_3-\overset{\overset{O}{\|}}{C}-OH + H-\overset{18}{O}-C_2H_5 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-\overset{18}{O}-C_2H_5 + H_2O$$

Radioactive tracers such as ${}^{32}_{15}P$ and ${}^{35}_{16}S$ have been particularly useful in studying biochemical reactions.

A number of medical diagnostic procedures employ tracers. The rates of some body functions are determined by detecting the rate of passage of a tracer, as in the measurement of blood flow through the heart by following blood serum labelled with ${}^{131}_{53}I$. Several tracers tend to become accumulated in specific organs. Take for example, ${}^{131}_{53}I$ in the thyroid and ${}^{201}_{81}Tl$ in the heart; detection of their radiation from the normal and diseased tissues can aid in locating disorders. In Table 9.7 we are giving the list of tracers, which are commonly used for the purpose of medical diagnosis.

Table 9.7 : Tracers and their application in medical diagnosis

Tracers	Application
${}^{51}_{24}Cr$, chromium	blood volume, red blood cell life time
${}^{59}_{26}Fe$, iron	iron turnover
${}^{85}_{38}Sr$, strontium	bone scan
${}^{99}_{43}Tc$, technetium	brain scan
${}^{131}_{53}I$, iodine	thyroid function
${}^{198}_{79}Au$, gold	liver scan

9.5.4 Radioactive Dating

An estimate of the age of materials can be had by measuring the activity of radioactive isotopes present in them. Such a technique is known as dating and now we take up two illustrations for this technique.

Age of Minerals

It is quite interesting to calculate the probable age of the earth based on the activity of radioactive isotopes in the minerals. An assumption is made that the earth must be at least as old as the rocks and minerals in its crust. One method is to measure the relative amounts of ${}^{238}_{92}U$ and ${}^{206}_{82}Pb$ in the rock. For the decay of ${}^{238}_{92}U$ to ${}^{206}_{82}Pb$ the half-life period is 4.51×10^{9}year. Suppose that we want to calculate the age of a rock that contains 2.77×10^{-4} kg of ${}^{206}_{82}Pb$, for every 1.667×10^{-3} kg of ${}^{238}_{92}U$.

First we assume that all the ${}^{206}_{82}Pb$ resulted from the decay of ${}^{238}_{92}U$. Then, the weight of ${}^{238}_{92}U$ that has changed to ${}^{206}_{82}Pb$ is,

$$\frac{238}{206} \times 2.77 \times 10^{-4}\,\text{kg} = 3.2 \times 10^{-4}\,\text{kg}$$

The weight of ${}^{238}_{92}Pb$ originally present

$$= (1.667 \times 10^{-3} + 3.2 \times 10^{-4})\,\text{kg}$$

$$= 1.987 \times 10^{-3}\,\text{kg}$$

The age of the rock (i.e., the earth) is equal to the time required for the decay of 1.987×10^{-3} kg of ${}^{238}_{92}U$ to 1.667×10^{-3} kg. Since $t_{1/2}$ for ${}^{238}_{92}U$ is 4.51×10^{9}year, its decay constant can be calculated using Eq. 9.7.

$$k = \frac{0.693}{4.51 \times 10^{9}\,\text{year}} = 1.54 \times 10^{-10}\,\text{year}^{-1}$$

Using this k value in Eq. 9.6, the age of the rock can be calculated.

N_0 = Initial amount of ${}^{238}_{92}U$ in the rock

$= 1.987 \times 10^{-3}$ kg

N_t = Amount of ${}^{238}_{92}U$ in the rock at present

$= 1.667 \times 10^{-3}$ kg

$$k = 1.54 \times 10^{-10}\,\text{year}^{-1} = \frac{2.303}{t} \log \frac{1.987 \times 10^{-3}\,(\text{kg})}{1.667 \times 10^{-3}\,(\text{kg})}$$

$$t = 1.14 \times 10^{9}\,\text{year.}$$

Hence, the age of the earth is also equal to 1.14×10^{9} year, since it is assumed to be equal to the time required for the decay of ${}^{238}_{92}U$ from 1.987×10^{-3} kg to 1.667×10^{-3} kg, as given above.

Age of the Organic Materials

An interesting method of dating ancient objects of organic source is based on the fact that the preserved object, if not too old, contains a measurable amount of radioactive ${}^{14}_{6}C$. In atmosphere, ${}^{14}_{6}C$ is formed by the reaction of cosmic neutrons with nitrogen.

$${}^{14}_{7}N + {}^{1}_{0}n \longrightarrow {}^{14}_{6}C + {}^{1}_{1}H$$

The radioactive ${}^{14}_{6}C$ formed by the above process is eventually incorporated into the carbon dioxide of the air. A constant concentration, amounting to about one atom of ${}^{14}_{6}C$ to every

10^{12} atoms of ${}^{12}_{6}C$ is established in atmospheric carbon dioxide. A living plant, taking in carbon dioxide, has the same ${}^{14}_{6}C/{}^{12}_{6}C$ ratio, as the plant-eating animals or human beings.

When a plant or an animal dies, the intake of radioactive carbon stops. Consequently the radioactive decay of ${}^{14}_{6}C$ takes place and the ratio, ${}^{14}_{6}C/{}^{12}_{6}C$ drops.

$${}^{14}_{6}C \xrightarrow{\qquad} {}^{14}_{7}N + {}^{0}_{-1}e \ (t_{1/2} = 5720 \text{ year})$$

Let the ${}^{14}_{6}C/{}^{12}_{6}C$ ratio values in living and dead organic materials be r_1 and r_2, respectively.
Then the age of the dead organic material.

$$t = \frac{2.303 \times 5720}{0.693} \log \frac{r_1}{r_2} \text{ year}$$

By measuring the ratio ${}^{14}_{6}C/{}^{12}_{6}C$ in the organic material and comparing it to that of the living cells, one can estimate the time at which the plant or animal (the source of the organic material) died.

As an illustration, let us calculate the age of a piece of wood for which the ratio ${}^{14}_{6}C/{}^{12}_{6}C$ is 0.4 times that of a living plant. Since $t_{1/2}$ = 5720 year, the value of k, using Eq. 9.7 is,

$$k = \frac{0.693}{5720 \text{ year}} = 1.212 \times 10^{-4} \text{ year}^{-1}$$

$$\text{since } N_t = 0.4\, N_0, \ \frac{N_0}{N_t} = \frac{1}{0.4} = 2.5$$

Substituting these values in Eq. 9.6,

$$k = 1.212 \times 10^{-4} \text{ year}^{-1} = \frac{2.303}{t} \log \frac{N_0}{N_t}$$

$$= \frac{2.303}{t} \log 2.5$$

$$= \frac{2.303}{t} \times 0.3979$$

$$t = \frac{2.303 \times 0.3979}{1.212 \times 10^{-4}} \text{ year}$$

$$t = 7564 \text{ year.}$$

It means that the wood belonged to a tree which was alive before 7564 years. Try the following SAQ yourself, to check your understanding of the calculations given above

SAQ 9
A tiny piece of organic material taken from the sea was found to have ${}^{14}_{6}C/{}^{12}_{6}C$ ratio 0.795 times that in a plant living today. The half-life period of ${}^{14}_{6}C$ is 5720 year. Estimate the age of that piece.

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9.5.5 Other Applications

Apart from the above mentioned applications, nuclear chemistry is also used in the fields of medicine and agriculture. We have already seen some diagnostic uses of radioactive isotopes in sub-section 9.5.3.

${}^{60}_{27}Co$ is produced in a nuclear reactor.

The high energy radiation given off by radium was used for many years in the treatment of cancer. Nowadays, ${}^{60}_{27}Co$ which is cheaper than radium and gives off even more powerful radiation, is used for this purpose. Certain types of cancer can be treated internally with radioactive isotopes.

By using ${}^{32}_{15}P$ isotopes as tracers, we can predict at what time during the growth of the plant, phosphatic fertiliser is needed. The Green Revolution of our country was essentially due to improved quality of seeds and one of the contributing factors was seed protection through radiation with γ rays. However, excess doses are lethal.

9.6 BIOLOGICAL EFFECTS OF RADIATION

So far we have discussed some applications of nuclear chemistry. Casual use of radioisotopes has harmful side effects. There is always the danger of exposure of radiation from radioactive substances. Here we will discuss how these radiations are harmful to us.

Like Xrays, the higher energy radiation emitted by radioactive nuclides has great penetrating power. When such a radiation is absorbed by molecules, it can result in the breakage of covalent bonds. The large amount of water in living cells makes this molecule a likely target for attack by radiation. Water molecules are known to undergo dissociation into hydroxyl radicals and hydrogen radicals on absorption of radiation (denoted by the energy term, $h\nu$).

$$H_2O \xrightarrow{h\nu} HO + H$$

The extremely energetic hydroxyl radicals can react with many of the molecules in the living cells, disrupting bonds in them. The potential biological effects of these radiation-induced bond ruptures were not appreciated by early workers in the nuclear field. This resulted in some serious health problems, some of which proved fatal. If bonds are broken in molecules that govern genetic pattern, mutations can result, so that future generation may have features different from parents. Thus, concern must be raised about any situation leading to higher levels of radiation.

A well-known example of the careless handling of radioactive substances resulting in many deaths was provided by Swiss workers whose occupation was painting radium dial watches. It was their practice to sharpen the tips of their brushes by licking them and as a result, over a period of time they accumulated considerable amounts of radium in their bodies which led to cancer.

The effect of radiation on biological cells also include changes that modify the immediate reproduction of these cells. Cells may be killed or may become modified so that they become malignant, reproducing wildly in a cancerous manner. Radiation is used to control tumors but also may cause noncancer cells to become malignant. Clearly, we must exercise judgment regarding exposure to all radiation, sunlight and X rays included, balancing benefits against potential dangers. But, we can minimise the danger of radiation by proper precautions and safety measures in much the same way as the danger accompanying the use of chemicals in the chemistry laboratory is minimised.

9.7 SUMMARY

In this unit, we first explained briefly the different features of atomic nucleus. We noted that the atomic nucleus contains two kinds of particles, positively charged protons and electrically neutral neutrons. We defined isotopes, isobars and isotones on the basis of mass number and atomic number. After that, we defined binding energy and mass defect, and explained how nuclear binding energies are much larger than the chemical bond energies. We mentioned that the stability of nuclei is dependent on n/p ratio. Then we described different types of nuclear decay.

We discussed the kinetics of radioactive decay and we described different types of transmutation reactions and their utility in the preparation of new elements. Different features of fission and fusion reactions were also explained. Finally, the applications of nuclear chemistry in different fields were discussed.

9.8 TERMINAL QUESTIONS

1. Calculate the energy in kJ mol^{-1} liberated in the following fusion reaction:

   $${}^{2}_{1}H + {}^{2}_{1}H \longrightarrow {}^{4}_{2}He$$

   The accurate atomic masses of ${}^{2}_{1}He$ and ${}^{4}_{2}He$ are 2.014 102 and 4.002 6034 u, respectively and $1\ u = 1.661 \times 10^{-27}$ kg.

2. Comment on the stability of each of the following nuclides and also predict the mode of decay, if any.

   a) ${}^{27}_{12}Mg$; b) ${}^{35}_{17}Cl$; c) ${}^{212}_{83}Bi$; d) ${}^{56}_{26}Fe$