



NATIONAL OPEN UNIVERSITY OF NIGERIA

SCHOOL OF SCIENCE AND TECHNOLOGY

COURSE CODE: CHM 201

COURSE TITLE: GENERAL CHEMISTRY

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National Open University of Nigeria 2006

First Printed 2006

ISBN

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Printed by

For

National Open University of Nigeria

TABLE OF CONTENTS **PAGE****UNIT 1 ELECTRONIC STRUCTURE OF ATOMS**

- 1.1 Introduction
- 1.2 Discovery of Sub-atomic Particles
- 1.3 Earlier Atom Models
- 1.4 Light as Electromagnetic Wave
- 1.5 Failures of Classical Physics
- 1.6 Planck's Quantum Theory, Black Body Radiation and Heat Capacity Variation
- 1.7 Einstein's Theory of Photoelectric Effect
- 1.8 Bohr Atom Model
- 1.9 Calculation of Radius of Orbits
- 1.10 Energy of an Electron in an Orbit
- 1.11 Atomic Spectra and Bohr's Theory
- 1.12 Critical Analysis of Bohr's Theory
- 1.13 Refinements in the Atomic Spectra Theory
- 1.14 Summary
- 1.15 Terminal Questions
- 1.16 Answers

UNIT 4 MOLECULAR PROPERTIES

- 4.1 Introduction
 - 4.2 Polar and Non-polar molecules
 - 4.3 Dielectric Constant
 - 4.4 Dipole Moment – An explanation
 - 4.5 Determination of Dipole Moment
 - 4.6 Applications of Dipole Moment Studies
 - 4.7 Magnetic Properties of Matter
 - 4.8 Paramagnetism
 - 4.9 Diamagnetism
 - 4.10 Optical Activity
 - 4.11 Summary
 - 4.12 Terminal Questions
 - 4.13 Answers
- Appendix

UNIT 1 ELECTRONIC STRUCTURE OF ATOMS

Structure

- 1.1 Introduction
 - Objectives
- 1.2 Discovery of Sub-atomic Particles
- 1.3 Earlier Atom Models
- 1.4 Light as Electromagnetic Wave
- 1.5 Failures of Classical Physics
 - Black Body Radiation
 - Heat Capacity Variation
 - Photoelectric Effect
 - Atomic Spectra
- 1.6 Planck's Quantum Theory, Black Body Radiation and Heat Capacity Variation
- 1.7 Einstein's Theory of Photoelectric Effect
- 1.8 Bohr Atom Model
- 1.9 Calculation of Radius of Orbits
- 1.10 Energy of an Electron in an Orbit
- 1.11 Atomic Spectra and Bohr's Theory
- 1.12 Critical Analysis of Bohr's Theory
- 1.13 Refinements in the Atomic Spectra Theory
- 1.14 Summary
- 1.15 Terminal Questions
- 1.16 Answers

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.

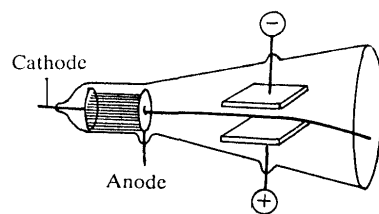


Fig. 1.1: Deflection of Cathode Rays towards a Positive plate in an Electrostatic Field proving their Negative Charge.

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 positive ions pass through them, as shown in Fig. 1.2.

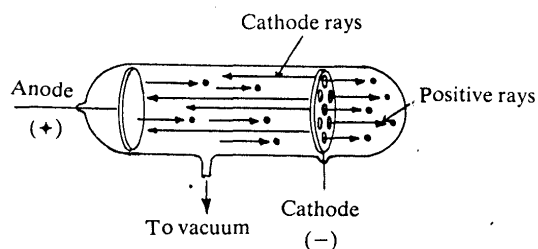


Fig. 1.2: Positive rays.

These streams of positive ions, called positive rays, were first observed by Goldstein (1886). The charge to mass ratios of positive ions depends 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. Charge of the proton is equal in magnitude but opposite in sign to that of the electron.

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 '*prates*' 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.

Table 1.1: Sub-atomic Particles

Particle	Mass/kg	Charge/C
Electron	9.109×10^{-31}	$- 1.602 \times 10^{-19}$
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.

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

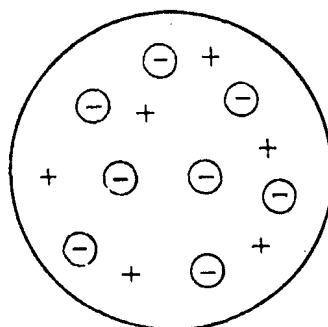


Fig. 1.3: Thomson's "plum pudding" model for the atom.

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.

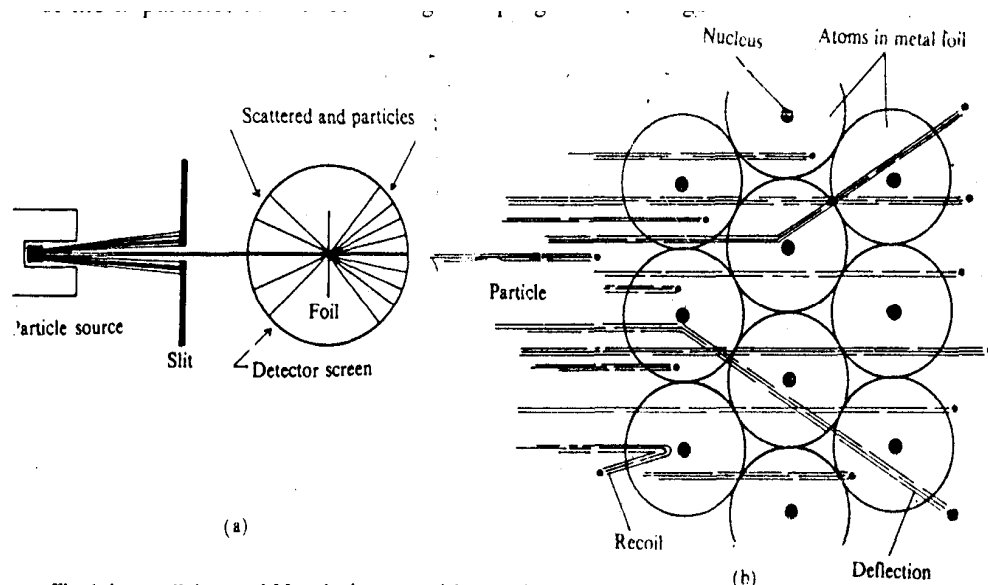


Fig. 1.4: (a) Geiger and Marsden's α -particle experiment.

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

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.

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.



Ernest

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?

1.4 LIGHT AS ELECTROMAGNETIC WAVE

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.....

A wave is a traveling disturbance that transports energy.

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.

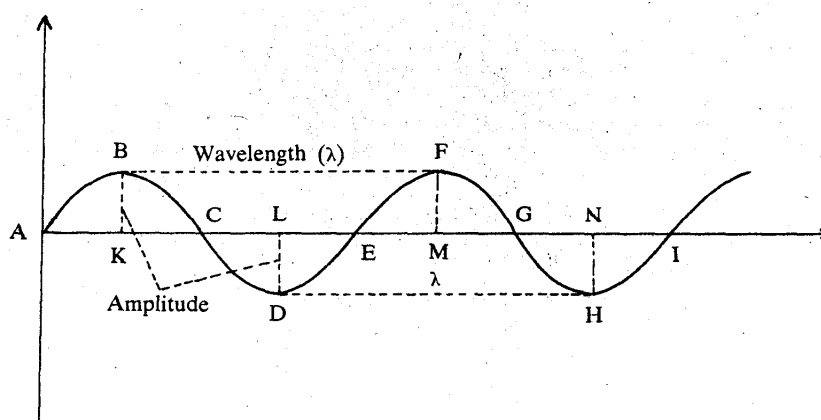


Fig. 1.5: Wave Propagation.

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.

$$\lambda = \frac{c}{\nu}$$

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

$\bar{\nu}$ pronounced as "nu bar".

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 ($\bar{\nu}$: nu tilde). Wave number is related to frequency and wavelength as per Eq. 1.2.

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$$

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

The SI unit of ν 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}
Radio waves	3×10^6	3.33×10^6	10^5	3.98×10^{-8}
Microwave	0.30m	0.0333	10^9	3.98×10^{-4}
Far infrared	0.0006 m (600 μm)	16.6	4.98×10^{11}	0.191
Near infrared	30 μm	333	10^{13}	3.98
Visible	80 μm (800 nm)	1.25×10^4	3.75×10^{14}	149.8
Ultraviolet	400 nm	2.5×10^4	7.5×10^{14}	299.2

	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 nm	10^{11}	3×10^{21}	1.19×10^9

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, $\lambda = \frac{c}{\nu}$.

$$\begin{aligned}
 &= \frac{2.998 \times 10^8}{10^{15}} = 2.998 \times 10^{-7} \text{ m} \\
 &= 2.998 \times 10^8 \text{ nm.}
 \end{aligned}$$

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

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

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.

SAQ2

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

.....

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

Calculation of energy in Table 1.2 is done using Eq. 1.2 is done using Eq. 1.6 given in sec 1.6, where n is equal to Avogadro number (6.022×10^{23})

b) In **VIBGYOR**, relate the frequencies 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.

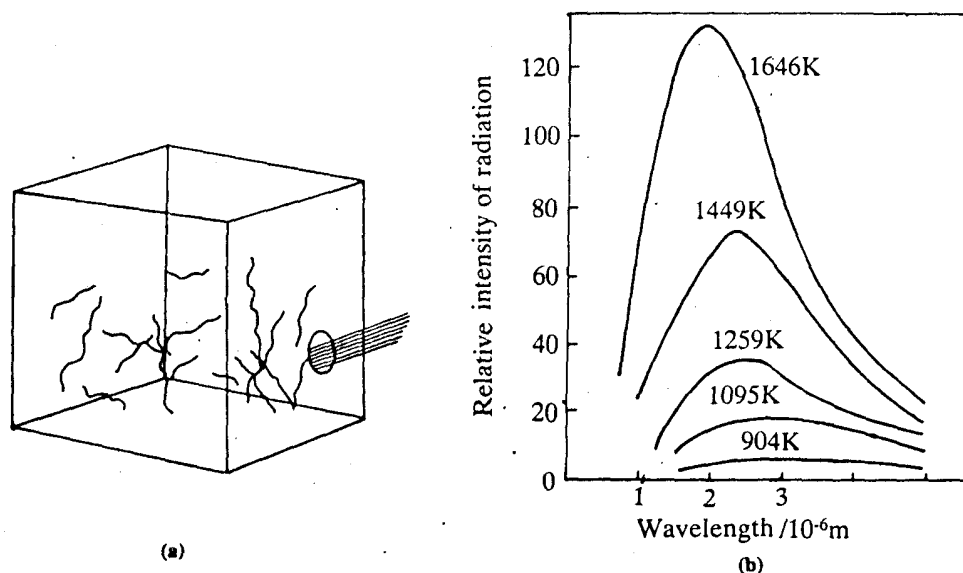


Fig. 1.6: (a) Black body radiation. The walls reflect and absorb light, entering the cavity; (b) Distribution of energy in black body radiation.

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

- i) At shorter wavelength region, which 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 $24.93 \text{ J mol}^{-1} \text{ K}^{-1}$ 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 $24.93 \text{ J mol}^{-1} \text{ K}^{-1}$ at low temperatures and (lie 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 a 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 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.

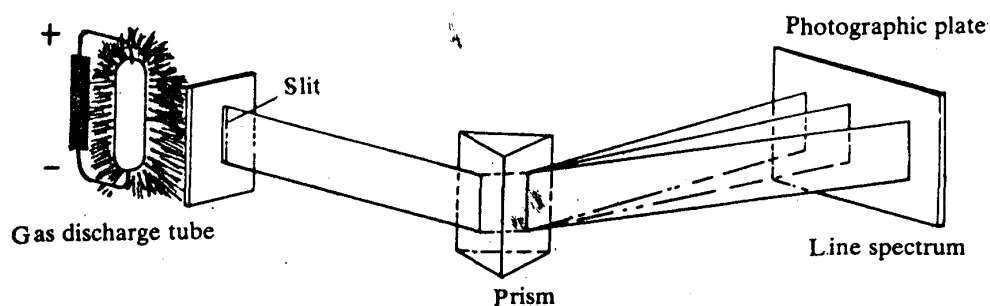


Fig. 1.7: Apparatus for atomic spectra.

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).

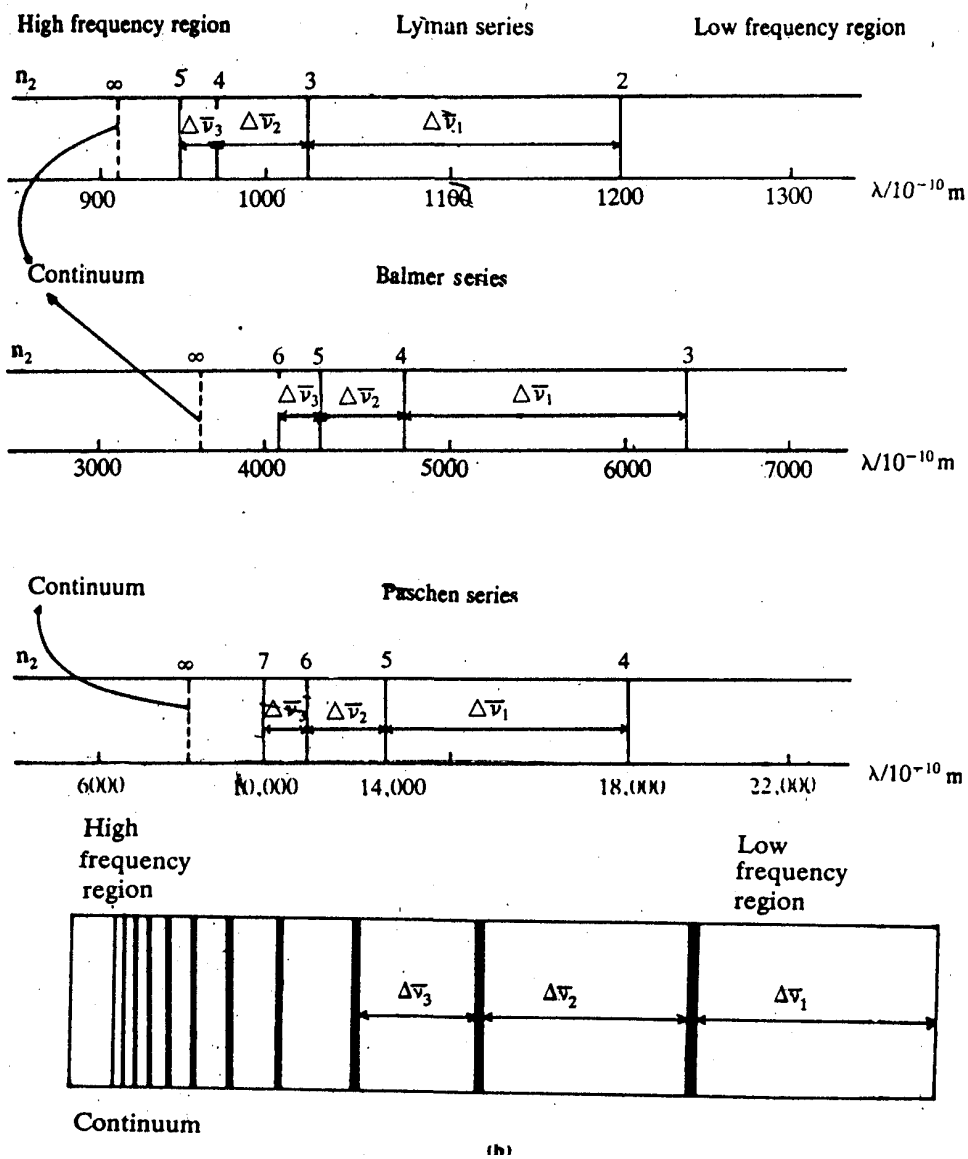


Fig. 1.8: (a) Atomic Spectra of Hydrogen. Only a few discrete lines followed by a continuum in the three series shown. Note the spacing $\Delta \nu$ decreases as frequency increases in each series; that is, in each series, $\Delta \nu_1 > \Delta \nu_2 > \Delta \nu_3$. (b) Discrete lines followed by a continuum in Balmer series. Reproduced from the actual spectrum.

$$\bar{\nu} = 1 = R \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \quad \dots(1.3)$$

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:

$$\bar{\nu} = \nu_{\infty} - \frac{R}{(n-d)^2} \quad \dots(1.4)$$

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:

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

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 continuous spectra at higher frequencies. On the basis of classical physics, the atomic spectra were 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.

1.6 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.

$$E = nh\nu = n \epsilon \dots (1.6)$$

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 $6.626 \times 10^{-34} \text{ J s}$. 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 x 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,

$$\Delta\epsilon = E_2 - E_1 = (n + 1) h\nu - nh\nu = h\nu \quad \dots (1.7)$$

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

Unit of $h = \text{J s}$

$$= \text{kg m}^2 \text{ s}^{-2} \cdot \text{s}$$

$$= \text{kg m}^2 \text{ s}^{-1} = (\text{kgms}^{-1}) \text{ m}$$

= (Unit of mass x unit of velocity) x unit of length

= (Unit of linear momentum) x 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 quantized 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, $e^{-\epsilon/kT}$, and 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, $e^{-\epsilon/kT}$. The term $e^{-\epsilon/kT}$ is in fact equal to $\frac{1}{e^{\epsilon/kT}}$

and hence is a fraction. As ϵ increases, the value of the fraction $e^{-\epsilon/kT}$ 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 $E/h\nu$.

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

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 $\lambda = 560 \text{ nm}$. 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 value 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:

$$h\nu - h\nu_0 = mv^2/2 \quad \dots (1.8)$$

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 $9 \times 10^5 \text{ ms}^{-1}$ from sodium metal surface, having a threshold frequency of $4.61 \times 10^{14} \text{ Hz}$ (mass of the photoelectron = $9.109 \times 10^{-31} \text{ kg}$).

.....

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.

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

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:

$$\Delta E = h\nu - hc\bar{\nu} \quad \dots (1.10)$$

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 $+e$.

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.

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

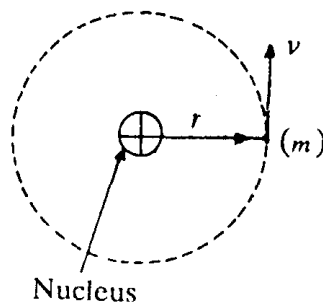


Fig. 1.9: Bohr model for the hydrogen atom. An electron of mass m moves with the velocity v in an orbit with radius r from the centre

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.

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

$$f_a = \frac{-Ze^2}{(4\pi\epsilon_0)r^2} \quad \dots (1.12)$$

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 $8.854 \times 10^{-12} \text{C}^2 \text{N}^{-1} \text{m}^{-2}$. The terms e and r have coulomb (C) and metre (m) units, respectively while Z is unitless.

The centrifugal force, $f_c = mv^2$ (1.13)

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

$$\frac{-Ze^2}{4\pi\epsilon_0 r^2} = \frac{-mv^2}{r} \quad \dots(1.14)$$

Rearranging Eq. 1.9, we can write, $v = \frac{nh}{4\pi mr}$

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

Multiplying both sides by m ,

$$mv^2 = \frac{n^2 h^2}{4\pi^2 m r^2} \quad \dots (1.15)$$

Substituting Eq. 1.14 in Eq. 1.15 we get,

$$\frac{mv^2}{4\pi\epsilon_0 r} = \frac{n^2 h^2}{4\pi^2 m r^2}$$

$$r = \frac{n^2 \epsilon_0 h^2}{\pi m Z e^2} \quad \dots(1.16)$$

Is pronounced as "epsilon zero".

Unit of f_a = unit of

$$\frac{-Ze^2}{(4\pi\epsilon_0)r^2}; \pi \text{ and } Z \text{ are unitless.}$$

$$\text{Unit of } f_a = \frac{\text{C}^2}{\text{C}^2 \text{N}^{-1} \text{m}^2 \text{m}^2} = \text{N}$$

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 ($n = 1, Z = 1$).

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

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

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

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

$$r = 53 n^2 \text{ pm} \quad \dots (1.17)$$

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.

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

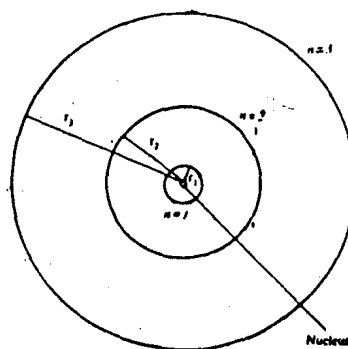


Fig. 1.10: The radius of the orbits in hydrogen atom is proportional to n^2 values. First three orbits only = 1:4:9.

SAQ5

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.,

$$E_n = \text{P.E.} + \text{K.E.} \quad \dots (1.18)$$

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_r) 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:

$$\begin{aligned} \text{P.E.} &= \int_r^\infty f_a \cdot dr \\ &= \int_r^\infty \frac{-Ze^2}{4\pi\epsilon_0 r^2} \cdot dr \\ &= \frac{-Ze^2}{4\pi\epsilon_0} \int_r^\infty \frac{dr}{r^2} \\ &= \frac{-Ze^2}{4\pi\epsilon_0} \left[-\frac{1}{r} \right]_r^\infty \\ \text{P.E.} &= \frac{-Ze^2}{4\pi\epsilon_0 r} ; \text{ also, K.E.} = \frac{mv^2}{2} \end{aligned}$$

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,

$$E_n = \frac{mv^2}{2} - \frac{Ze^2}{4\pi\epsilon_0 r} \quad \dots(1.19)$$

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

Substituting Eq. 1.20 in Eq. 1.19,

$$\begin{aligned} E_n &= \frac{Ze^2}{8\pi\epsilon_0 r} - \frac{Ze^2}{4\pi\epsilon_0 r} \\ &= \frac{-Ze^2}{8\pi\epsilon_0 r} \quad \dots(1.21) \end{aligned}$$

Substituting for r from Eq. 1.16,

$$\begin{aligned} E_n &= \frac{-Ze^2}{8\pi\epsilon_0} \cdot \frac{\pi m Ze^2}{n^2 \epsilon_0 h^2} \\ &= \frac{-Z^2 e^4 m}{8\epsilon_0^2 h^2 n^2} \quad \dots(1.22) \end{aligned}$$

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 n th orbit of hydrogen atom is obtained as,

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

$$E_n = \frac{-2.178 \times 10^{-18}}{n^2} \quad \dots(1.23)$$

You must remember that $Z = 1$ for hydrogen atom. In the first orbit, $n=1$ 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 it 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,

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

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

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 ,

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

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

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

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

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

You can see that Eq. 1.28 is similar in form to Eqs. 1.3, 1.4 or 1.5 given in Subsec. 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.

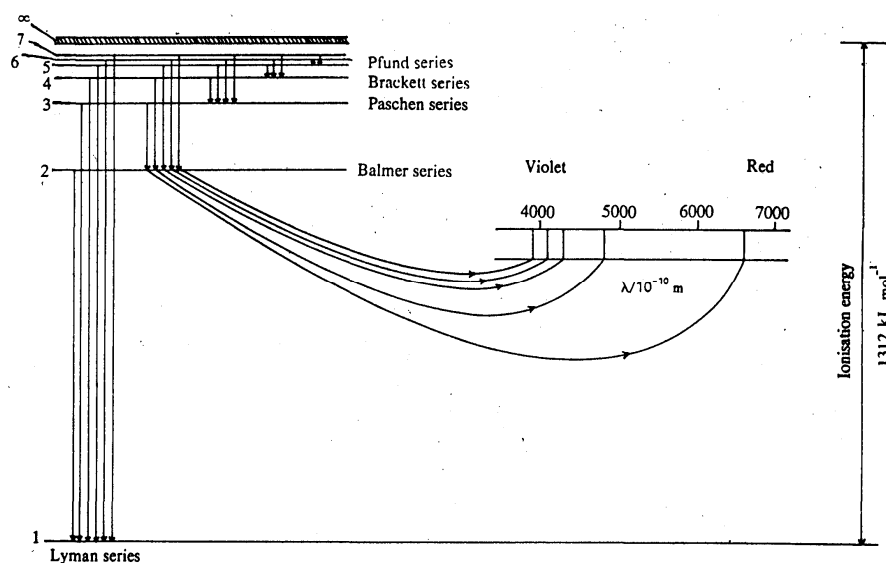


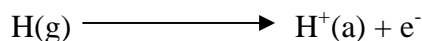
Fig. 1.11: Spectral Transitions among Different Energy Levels. Note, for Balmer series, the Corresponding Spectral Lines are shown.

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 spacing 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	$\frac{\tilde{\nu}_n}{\text{m}^{-1}} = 1.097 \times 10^7 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$	Spacing $(\tilde{\nu}_n - \tilde{\nu}_{n-1})/\text{m}^{-1}$
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:



The energy difference between the ground state of hydrogen atom, and the excited state that corresponds to convergence limit of the spectral lines, $n_2 = \infty$, is called the ionisation energy of hydrogen 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 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 of hydrogen atom is defined as the minimum energy necessary to remove the electron from $n = 1$ state to infinite distance ($n_2 = \infty$) leaving it without any kinetic energy and it can be calculated using Eq. 1.28 For hydrogen atom, the ionisation energy in the wave number unit.

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

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

$$\begin{aligned} &= 6.022 \times 10^{23} \text{ } hc\bar{\nu} \text{ J mol}^{-1} \\ &= 6.022 \times 10^{23} \times 6.626 \times 10^{-34} \times 2.998 \times 10^8 \times 1.097 \times 10^7 \text{ J mol}^{-1} \\ &= 1.312 \times 10^6 \text{ J mol}^{-1} \\ &= 1312 \times 10^3 \text{ J mol}^{-1} \\ &= 1312 \text{ kJ mol}^{-1}. \end{aligned}$$

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 the electron can never be zero. However, Bohr on, wave mechanics (Unit 2) shows that in $n = J$ 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 $0, 1, \dots, (n-1)$ 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 n th 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, $R_H = \frac{Z^2 e^2 m}{8\epsilon_0^2 h^3 c}$ 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.

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

$$\text{b) } \nu_R < \nu_O < \nu_V < \nu_G < \nu_B < \nu_I < \nu_V.$$

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

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

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

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

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

- 5) $r_2 = 53 n \text{ pm} = 53 \times 2^2 \text{ pm} = 212 \text{ pm.}$
 6) $E_\infty = 0.$
 7) The electron in an outer orbit has higher energy than one 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) $m_l = +2, +1, 0, -1, -2.$

While working out problems, value of λ should be used in metre unit.

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) $\nu = 9.993 \times 10^{14} \text{ Hz}$; $\bar{\nu} = 3.333 \times 10^6 \text{ m}^{-1}$;
 $\epsilon = 6.621 \times 10^{-19} \text{ J}$; $E = 398.8 \text{ kJ mol}^{-1}$.
- 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) $\frac{hc}{\lambda} = h\nu_0 + mv^2/2$
 $= [(6.626 \times 10^{-34} \times 4.55 \times 10^{14}) + 2.0 \times 10^{-19}] \text{ J}$
 $\lambda = 396.1 \text{ nm}$.
- 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) $r_3 = 9r_1 = 477 \text{ pm}$.
- 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) $-2.42 \times 10^{-19} \text{ J}$; $-1.361 \times 10^{-19} \text{ J}$.

- 16) a) Substitution of the values of the various parameters gives

$$R_H = 1.097 \times 10^7 \text{ m}^{-1},$$

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

- 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 4 MOLECULAR PROPERTIES

Structure

- 4.1 Introduction
Objective
- 4.2 Polar and Non-polar molecules
- 4.3 Dielectric Constant
- 4.4 Dipole Moment – An explanation
- 4.5 Determination of Dipole Moment
Polar and Non polar Molecules Redefined.
Percentage Ionic Character
Structure Elucidation
- 4.6 Applications of Dipole Moment Studies
Polar and Non polar Molecules Redefined.
Percentage Ionic Character
Structure Elucidation
- 4.7 Magnetic Properties of Matter
- 4.8 Paramagnetism
- 4.9 Diamagnetism
- 4.10 Optical Activity
- 4.11 Summary
- 4.12 Terminal Questions
- 4.13 Answers
Appendix

4.1 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 will discuss three 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. 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

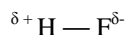
dipole in an electric field and a magnetic dipole in a magnetic field. In order to help you understand this treatment without breaking the continuity in the unit, electric and magnetic parameters along with SI units are explained in the Appendix. **You are advised to get familiarised with these-parameters 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.

Polarity in a chemical bond is due to the difference in electronegativity between the atoms forming the bond.



4.2 POLAR AND NONPOLAR MOLECULES

IN CHE 101 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.

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. 4.6.1. It is better to introduce the property of matter called dielectric constant in order to help you understand the dipole moment concept.

4.3 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.f.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.

$$\epsilon_r = \frac{C}{C_0} \quad \dots (4.1)$$

The unit for capacitance is farad (F). $1 \text{ F} = 1 \text{ CV}^{-1}$

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 4.1: 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 Subsec. 4.5.2 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.4.1).

4.4 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. 4.1).

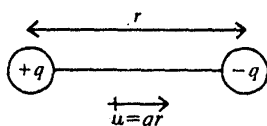


Fig. 6.1: Representation of a Dipole.

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 p ., and is given by

$$\mu = q r \quad \dots 4.2)$$

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,

$$\begin{aligned} \mu &= 1.602 \times 10^{-19} \text{ (C)} \times 1 \times 10^{-10} \text{ (m)} \\ &= 16.02 \times 10^{-30} \text{ C m} \end{aligned}$$

In literature, the dipole moment values are given in debye (D) units.

$$1 \text{ D} = 3.336 \times 10^{-30} \text{ C m}$$

In the next section, we study how dipole moment is estimated for polar molecules. You try the following SAQ, using Eq. 4.2. It would help you in understanding Sec. 4.6.2.

SAQ 2

The dipole moment and the bond distance in hydrogen chloride are 3.57×10^{-31} 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.

4.5 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.

4.5.1 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_o , for one mole (called **molar orientation polarisation**) is given by,

$$P_o = \frac{N_A \mu^2}{9 \epsilon_0 k T} \quad \dots (4.3)$$

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.

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_t). 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

$$P_D = \frac{N_A \alpha_e}{3 \epsilon_0} \quad \dots (4.4)$$

Polarisability, α_e , of a molecule speaks of its "willingness" to get its electron cloud deformed by an applied electric field.

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,

$$P_v = \frac{N_A \alpha_v}{3 \epsilon_0} \quad \dots (4.5)$$

Distortion polarisation measures the disturbance in the electronic distribution in the molecules whereas vibrational polarisation indicates the dislocation of the nuclei.

The total molar polarisation (P_M) of a substance is the sum of P_0 , P_D and P_v . Thus, we have,

$$P_v = \frac{N_A \alpha_v}{3 \epsilon_0} \left(\alpha_e + \alpha_v + 3 k T \right) \quad \dots (4.5)$$

This equation is useful in the calculation of dipole moment

The unit of total molar polarisation is $\text{m}^3 \text{mol}^{-1}$.

4.5.2 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,

$$P_M = \frac{\epsilon_r - 1}{\epsilon_r + 2} \frac{M}{\rho} \quad \dots (4.7)$$

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. 4.6. The slope of this straight line is equal to $\frac{N_A \mu^2}{9 \epsilon_0 k}$

Hence,

$$\mu = \sqrt{\frac{9 \epsilon_0 k \times \text{slope}}{N_A}} \quad \dots (4.8)$$

The slope of P_M against $1/T$ plot is to be substituted in Eq.4.8 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. 4.7, the molar polarisation of the solution has to be found out from which the molar polarisation of the substance can be calculated, after subtracting 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. 4.3, show that molar orientation polarisation has the unit, $\text{m}^3 \text{mol}^{-1}$

4.6 APPLICATIONS OF DIPOLE MOMENT STUDIES

First let us see how dipole moment studies help us redefine polar and nonpolar molecules.

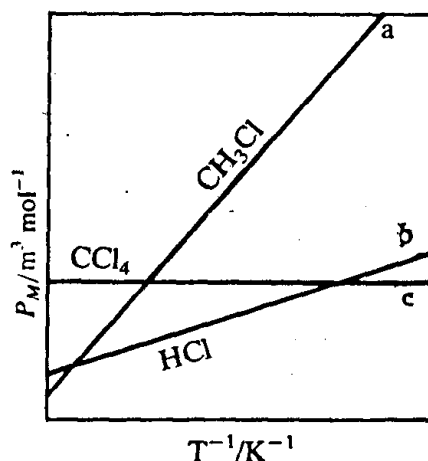


Fig. 4.2: P_M against $1/T$ plot for CH_3Cl (a), HCl (b) and CCl_4 (c)

4.6.1 Polar and Nonpolar Molecules Redefined

In Sec. 4.2, we defined polar and nonpolar molecules based on electronegativity. Now let us define them in a different way. In Fig. 4.2 the P_M vs $1/T$ curves a, b and c are drawn for CH_3Cl , HCl and CCl_4 molecules, respectively.

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 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. 4.8. 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.

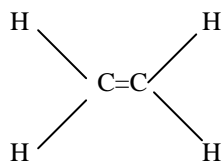
4.6.2 Percentage Ionic Character

A polar molecule has a permanent dipole moment and for a nonpolar molecule, $\mu = 0$.

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 (μ_{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. 4.2 and represented as $\mu_{\text{calculated}}$.

$$\begin{aligned}\mu_{\text{calculated}} &= 1.602 \times 10^{-19} \text{ (C)} \times 127.5 \times 10^{-12} \text{ (m)} \\ &= 20.42 \times 10^{-30} \text{ C (m)}\end{aligned}$$

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: centre of symmetry indicated as a dot in the middle of the double bond.

We can estimate the % ionic character using the relationship,

$$\text{Ionic character} = \frac{\mu_{\text{observed}} \times 100}{\mu_{\text{calculated}}} \%$$

$$\text{Hence, ionic character in HCl} = \frac{3.57 \times 10^{-30} \text{ (C m)} \times 100}{20.42 \times 10^{-30} \text{ (C m)}} = 17.5\%$$

4.6.3 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.

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 (at least after seeing their serious faces, although in royal dress) ?

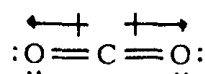
i) Carbon monoxide

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 \equiv 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:

$$\begin{aligned}
 \cos \theta &= \frac{\mu_{\text{CO}_2}^2}{2 \mu_{\text{C=O}}^2} - 1 \\
 &= \frac{[0(\text{C m})]^2}{2[7.67 \times 10^{-30} (\text{C m})]^2} - 1 \\
 &= -1 \\
 \theta &= \cos^{-1}(-1) = 180^\circ \quad \dots (4.10)
 \end{aligned}$$

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 CO₂, the carbon atom is at the centre of symmetry.

iii) Let us now study the structure of water. The bond moment, $\mu_{\text{O-H}}$ and the dipole moment $\mu_{\text{H}_2\text{O}}$ are reported to be $5.02 \times 10^{-30} \text{ C m}$ and $6.14 \times 10^{-30} \text{ C m}$, respectively.

Again using the parallelogram law of bond moments, we can calculate the bond angle θ .

$$\begin{aligned}
 \cos \theta &= \frac{\mu_{\text{H}_2\text{O}}^2}{2 \mu_{\text{O-H}}^2} - 1 \\
 \cos \theta &= \frac{[6.14 \times 10^{-30} (\text{C m})]^2}{2 \times [5.02 \times 10^{-30} (\text{C m})]^2} - 1 \\
 &= -0.2520 \\
 \theta &= \cos^{-1}(-0.2520) = 104^\circ 36'
 \end{aligned}$$

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 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 $4.871 \times 10^{-30} \text{ C m}$, 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 CHE 101)

4.7 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). $1 \text{ T} = 1 \text{ N A}^{-1} \text{ mT}^{-1}$

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 numbers 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. 4.3. 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.

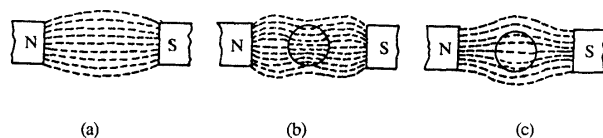


Fig. 4.3: Magnetic lines of force: (a) in free space, (b) in paramagnetic substance and (c) in diamagnetic substance.

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 4.2. It should be understood that the **susceptibility** (%) measures the ease of magnetisation of a material. It is a dimensionless quantity.

Table 4.2: Magnetic Characteristics of Materials

Type	Magnetic induction (B)	Susceptibility (X)

Paramagnetic	$B > B_0$	small positive value
Diamagnetic	$B < B_0$	small negative value
Ferromagnetic	$B \gg B_0$	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,

$$\chi_M = \frac{\chi^M}{P} \quad \dots (4.11)$$

where χ , M and p refer to the magnetic susceptibility, molecular mass (kg mol^{-1}) and density (kg m^{-3}), respectively. Evidently, χ_M has the unit, $\text{m}^3 \text{mol}^{-1}$. Susceptibility measurements are made using Goay 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.

4.8 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 result 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 $1.381 \times 10^{-23} \text{ J K}^{-1}$), then it is possible to derive the relationship between the molar paramagnetic susceptibility and temperature as given by,

$$\chi_M = \frac{\mu_0 N_A m^2}{3 k T} \quad \dots (4.12)$$

In this expression, μ_0 stands for the permeability of free space and it is equal to $4\pi \times 10^{-7} \text{ T m A}^{-1}$. N_A stands for Avogadro constant.

Eq. 4.12 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,

$$\chi_M \propto 1/T \quad \dots (4.13)$$

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).

$$\mu_B = \frac{e h}{4 \pi m_e} \quad \dots (4.14)$$

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?

In this expression, e and m_e stand for the charge and mass of the electron, respectively.

$$\begin{aligned} \therefore \mu_B &= \frac{1.602 \times 10^{-19} \text{ (C)} \times 6.626 \times 10^{-34} \text{ (J s)}}{4 \times 3.142 \times 9.109 \times 10^{-31} \text{ (kg)}} \\ &= 9.274 \times 10^{-24} \frac{\text{C J s}}{\text{kg}} \end{aligned}$$

but $1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$ and

$$1 \text{ C} = 1 \text{ A s}$$

$$\begin{aligned} \text{Hence, } \mu_B &= 9.274 \times 10^{-24} \frac{\text{A s kg m}^2 \text{ s}^{-2}}{\text{kg}} \\ &= 9.274 \times 10^{-24} \text{ A m}^2 \end{aligned}$$

The magnetic moment due to n unpaired electrons is given by the expression,

$$m = \sqrt{n(n+2)} \mu_B \quad \dots (4.15)$$

Number of unpaired electrons (n)	(Magnetic moment)	(Magnetic moment)
	μ_B	10^{-23} A m^2
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.		
4	4.899	4.543
5	5.916	5.486

In this equation, the magnetic moment due to electron spin alone is considered, since the orbital contribution is much less.

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. 4.15.

Table 4.3: Magnetic Moment (m) Values for Different n Values

It is more useful to combine Eqs. 4.12 and 4.15, to get,

$$\chi_M = \frac{\mu_0 N_A n (n+2) \mu_B^2}{3 k T} \quad \dots (6.16)$$

It is interesting to see how Eq. 4.16 can be used to predict the number of unpaired electrons in a molecule or ion. The support for 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. 4.16. In CHE 221 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

4.9 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 4.4 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.

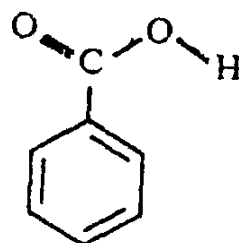
Table 4.4: Atomic and Bond Contributions to Molar Diamagnetic Susceptibility; $10^{12} X_M/m^3 \text{ mol}^{-1}$

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 X_M for benzoic acid using Table 4.4. 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.

$$\begin{array}{llll}
 7 \text{ C} & = 7 (-6.00 \times 10^{-12}) & = -42.00 \times 10^{-12} & \text{m}^3 \text{ mol}^{-1} \\
 6 \text{ H} & = 6 (-2.93 \times 10^{-12}) & = -17.58 \times 10^{-12} & \text{m}^3 \text{ mol}^{-1} \\
 1 \text{ C-O} & = 1 (-4.61 \times 10^{-12}) & = -4.61 \times 10^{-12} & \text{m}^3 \text{ mol}^{-1} \\
 \text{(same as R-OH)} & & & \\
 1 \text{ C=O} & = 1 (-3.36 \times 10^{-12}) & = -3.36 \times 10^{-12} & \text{m}^3 \text{ mol}^{-1} \\
 1 \text{ Benzene} & = 1 (-1.4 \times 10^{-12}) & = \frac{-1.4 \times 10^{-12}}{-68.95 \times 10^{-12}} & \text{m}^3 \text{ mol}^{-1} \\
 & & & \text{m}^3 \text{ mol}^{-1}
 \end{array}$$



Benzoic acid

It is close to the observed value of $-70.3 \times 10^{-12} \text{ m}^3 \text{ mol}^{-1}$.

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) $\text{H}_4\text{P}_2\text{O}_6$ iii) $\text{H}_6\text{P}_3\text{O}_9$

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4.10 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. A4.

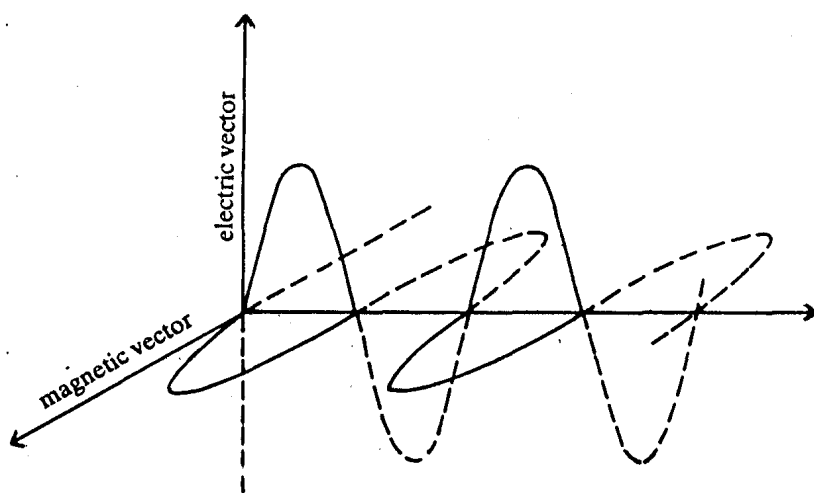


Fig. 4.4: Oscillating electric and magnetic fields in light.

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 out coming 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. 4.5), whose odd faces are inclined in the opposite direction, rotate the plane of the polarised light in the opposite direction.

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.

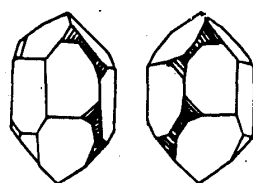


Fig. 4.5: Quartz Crystals having Mirror Image Relationship.

Quartz is the most stable crystalline form of silica.

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. 4.6 as I and II.

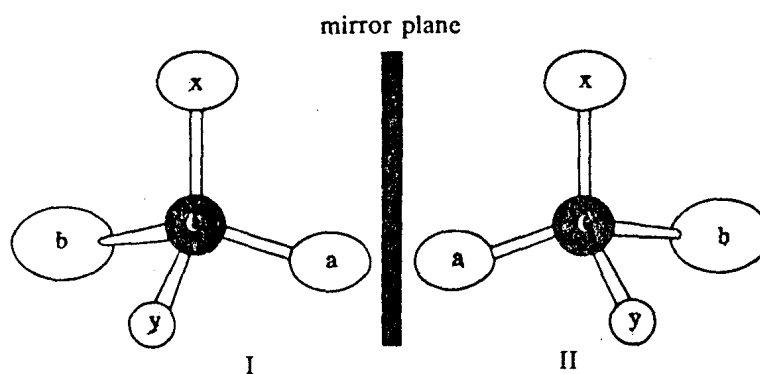
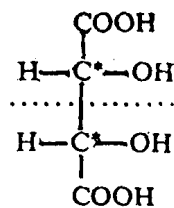
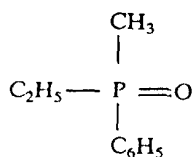


Fig. 4.6: Mirror Image Relationship between Enantiomers.

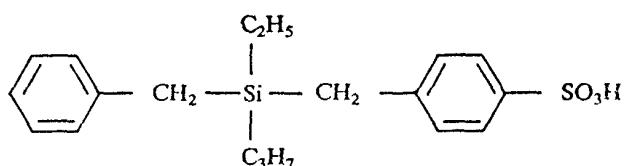


VIII

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.

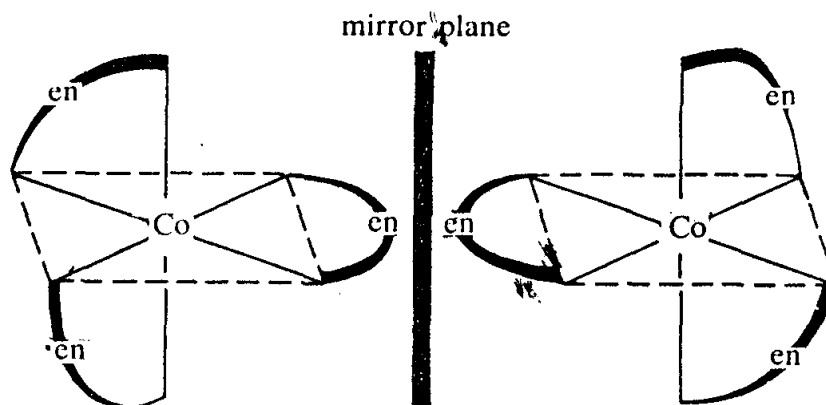


IX



X

Many co-ordination complexes, having ligands such as ethylenediamine (en), have optical activity and the enantiomers have been isolated. An example is $\text{Co}(\text{en})_3^{3+}$ (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 $[\alpha]$, 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,

$$[\alpha]_{\lambda}^t = \frac{\text{Observed rotation (degree)}}{\text{length (dm)} \times \text{concentration (kg dm}^{-3}\text{)}}$$

The specific rotation depends on the temperature (t) and the wavelength (λ) of the light used for measurement. Thus $[\alpha]_{\text{D}}^{20}$ indicates that the rotation is measured at 20°C with the D line of sodium having $\lambda = 589.3$ nm.

4.11 SUMMARY

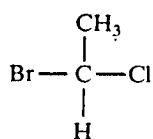
In this unit, you have studied the interaction of matter with the electric field, magnetic field and electromagnetic radiation. The contents of this unit can be summarised as follows:

- 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.

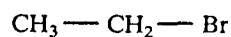
4.12 TERMINAL QUESTIONS

- 1) Calculate the dipole moment of sodium chloride molecule at an internuclear separation of 500pm.
(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 m³.
 - 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 Mn²⁺ ion in μ_B units (Assume high spin Molecular Properties state)?

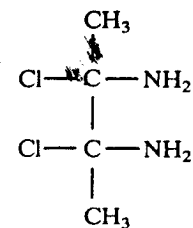
- 4) Which of the following can exhibit optical activity?



(i)



(ii)



(iii)

4.13 ANSWERS

Self-Assessment Questions

- 1) Dielectric constant of the material is given by the ratio,

$$\frac{80.1 \times 10^{-12} (\text{F})}{8.9 \times 10^{-12} (\text{F})} ; \text{ it is equal}$$

- 2) The charge on chlorine or hydrogen (q) = n/r

$$= \frac{3.57 \times 10^{-30} (\text{C m})}{127.5 \times 10^{-12} (\text{m})}$$

$$= 2.8 \times 10^{-20} \text{C}$$

Compared to the magnitude of the charge of an electron ($1.602 \times 10^{-19} \text{C}$), the negative charge on chlorine of HCl is less, indicating that charge separation in HCl is not complete. See Sub-section 4.6.2 also.

- 3) The units of N_A , μ , ϵ_0 , k and T are mol^{-1} , C m , $\text{C}^2 \text{m}^{-2} \text{N}^{-1}$, J K^{-1} and K , respectively. Substituting only the relevant units in Eq.4.3, we get,

$$\begin{aligned} \text{Unit of } P_0 &= \frac{\text{mol}^{-1} \text{C}^2 \text{m}^2}{\text{C}^2 \text{m}^{-2} \text{N}^{-1} \text{J K}^{-1} \text{K}} \\ &= \frac{\text{mol}^{-1} \text{m}^4}{\text{N}^{-1} \text{J}} = \frac{\text{mol}^{-1} \text{m}^4}{\text{N}^{-1} \text{N m}} \quad \{ \because 1 \text{ J} = 1 \text{ N m} \} \\ &= \text{m}^3 \text{mol}^{-1} \end{aligned}$$

- 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 $\text{H}_4\text{P}_2\text{O}_6$ and $\text{H}_6\text{P}_3\text{O}_9$ are 50 and 75, respectively. Since hypophosphoric acid is diamagnetic, it must have even number of electrons. Hence, the possible formula is $\text{H}_4\text{P}_2\text{O}_6$.

Terminal Questions

$$1) \quad \mu = q \cdot r = 1.602 \times 10^{-19} \text{ (C)} \times 500 \times 10^{-12} \text{ (m)} \\ = 8.010 \times 10^{-29} \text{ Cm.}$$

$$2) \quad \text{i) Its molecular mass is } 0.154 \text{ kg mol}^{-1}.$$

$$P_M = \frac{\epsilon_0 - 1}{\epsilon_r + 2} \cdot \frac{M}{P} = \frac{(2.238 - 1)}{(2.238 + 2)} \cdot \frac{0.154 \text{ (kg mol}^{-1})}{1.595 \times 10^3 \text{ (kg mol}^{-1})}$$

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 4.3, $m = 5.916 \mu_B$.

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 4.3 -4.6).

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).

$$1 \text{ C} = 1 \text{ As}$$

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^1) 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.

$$\text{Hence, } F = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{d^2} \quad \dots(\text{A.1})$$

The SI units of force, charge and distance are newton (N), coulomb (C) and metre (m), respectively. Therefore, ϵ_0 has the unit, $\text{C}^2 \text{N}^{-1} \text{m}^{-2}$. The value of ϵ_0 is equal to $8.854 \times 10^{-12} \text{C}^2 \text{N}^{-1} \text{m}^{-2}$. 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.

$$V = \frac{w}{q} \quad \dots (\text{A.2})$$

The units for electrical energy, charge and potential difference are joule (J), coulomb (C) and volt (V), respectively.

$$\text{Hence, } 1 \text{ volt} = 1 \text{ joule}/1 \text{ coulomb} \dots (\text{A.3})$$

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).

$$\text{i.e., } E = F/q \quad \dots \text{ (A.4)}$$

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).

$$E = V/d \quad \dots \text{ (A.5)}$$

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:

$$1 \text{ joule} = 1 \text{ volt coulomb} = 1 \text{ newton metre}$$

(electrical energy) (mechanical energy)

$$\text{i.e., } 1 \text{ J} = 1 \text{ V C} = 1 \text{ N m}$$

$$\text{Or } 1 \text{ V m}^{-1} = 1 \text{ N C}^{-1} \quad \dots \text{ (A.6)}$$

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.

$$E_0 = k \frac{q}{A} \quad \dots \text{ (A.7)}$$

The proportionality constant k , has been found to be equal to $(1/\epsilon_0)$, ϵ_0 being the permittivity of the vacuum.

$$\text{Hence, } E_0 = \frac{1}{\epsilon_0} \frac{q}{A} \quad \dots \text{ (A.8)}$$

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,

$$E_0 = \frac{1}{\epsilon_r \epsilon_0} \frac{q}{A} \quad \dots \text{ (A.9)}$$

where ϵ_r is the relative **permittivity or dielectric constant** of the material. Using Eqs. A.5 and A.9 we can write,

$$q = \frac{\epsilon_r \epsilon_0 A}{d} \cdot V$$

The term $\frac{\epsilon_r \epsilon_0 A}{d}$ can be represented by the letter C . Hence Eq. A. 10 can be written as,

$$q = C V \quad \dots \text{(A.11)}$$

$$\text{or } C = \frac{q}{V} = \frac{\epsilon_r \epsilon_0 A}{d} \quad \dots \text{(A.12)}$$

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.

$$C_0 = \frac{\epsilon_0 A}{d} \quad \dots \text{(A.13)}$$

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,

$$\epsilon_r = C/C_0 \quad \dots \text{(A. 14)}$$

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,

$$\begin{aligned}
 C_0 &= \frac{\epsilon_0 A}{d} \\
 &= \frac{8.854 \times 10^{-12} (\text{C}^2 \text{N}^{-1} \text{m}^{-2}) \times 0.01 (\text{m}^2)}{0.01 (\text{m})} \\
 &= 8.854 \times 10^{-12} \text{C}^2 \text{N}^{-1} \text{m}^{-1} \\
 &= 8.854 \times 10^{-12} \text{F} \\
 &= 8.854 \text{ pF}
 \end{aligned}$$

The capacitance of the capacitor (C) filled with mica is found to be 47.81 pF. The dielectric constant of mica is,

$$\begin{aligned}
 \epsilon_r &= \frac{C}{C_0} = \frac{47.81 \times 10^{-12} (\text{F})}{8.854 \times 10^{-12} (\text{F})} \\
 &= 5.4
 \end{aligned}$$

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, \mathbf{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 μ_1 and μ_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, μ , of this molecule XYZ is the resultant DY (diagonal of the parallelogram) of the two bond moments and is equal to $\mu_1 + \mu_2$

Hence, $\mu = DY = \mu_1 + \mu_2$

Let μ_1 , μ_2 and μ represent the magnitude of the vectors μ_1 , μ_2 and μ , 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.

From Fig. A. 1, $\angle DXE = \angle ZYX = \theta$

In the right angled $\triangle DYE$,

$$\begin{aligned} DY^2 &= DE^2 + EY^2 \\ &= DE^2 + (EX + XY)^2 \\ &= DE^2 + EX^2 + 2EX \cdot XY + XY^2 \end{aligned}$$

$$= DX^2 + 2 \cdot DX \cos \theta \cdot XY + XY^2$$

$$\left[\begin{array}{l} \frac{EX}{DX} = \cos \theta \\ \text{and } DE^2 + EX^2 = DX^2 \end{array} \right]$$

$$DY^2 = ZY^2 + 2ZY \cdot XY \cos \theta + XY^2$$

[DX = ZY; opposite sides of a parallelogram]

$$\left\{ \begin{array}{l} DY = \mu \\ ZY = \mu_2 \\ \text{and } XY = \mu_1 \end{array} \right\}$$

$$\therefore \cos \theta = \frac{\mu^2 - (\mu_1^2 + \mu_2^2)}{2 \mu_1 \mu_2}$$

... (A.15)

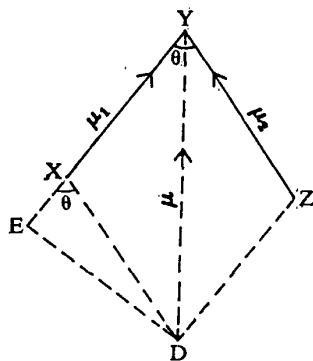


Fig A.1: Dipole Vectors for the Bond Moments and the Resultant Moment of the Molecule XYZ.

Let us use Eq. A.15 to calculate the bond angle in water and carbon dioxide.

For water: $\mu_1 = \mu_2 = \mu_{\text{O-H}}$ = The O-H bond moment

$$\mu = \mu_{\text{H}_2\text{O}} = \text{Dipole moment of water}$$

Using Eq. A.15

$$\cos \theta = \frac{\mu^2 - (\mu_1^2 + \mu_2^2)}{2 \mu_1 \mu_2}$$

$$\text{i.e. } \cos \theta = \frac{\mu_{\text{H}_2\text{O}}^2}{2\mu_{\text{O-H}}^2} - 1$$

For carbon dioxide: $\mu_1 = \mu_2 = \mu_{\text{C=O}}$ = The C=O bond moment and
 $\mu = \mu_{\text{CO}_2}$ = Dipole moment of carbon dioxide

$$\text{Hence, } \cos \theta = \frac{\mu_{\text{CO}_2}^2 - 2\mu_{\text{C=O}}^2}{2\mu_{\text{C=O}}^2} = \frac{\mu_{\text{CO}_2}^2}{2\mu_{\text{C=O}}^2} - 1$$

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.

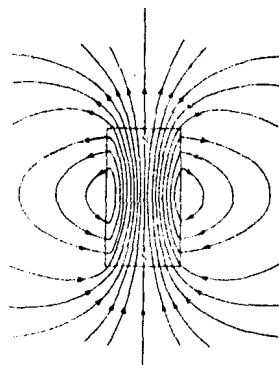


Fig. A.2: Magnetic Field Lines directed from North Pole to South Pole.

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.

$$F = q v B \quad \dots \text{(A.16)}$$

The parameter B is often called magnetic induction. Rearranging Eq. A. 16,

$$B = F/q v \quad \dots \text{(A.17)}$$

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,

$$\begin{aligned} 1 \text{ T} &= 1 \text{ N (Cms}^{-1}\text{)}^{-1} \\ &= 1 \text{ N (A s ms}^{-1}\text{)}^{-1} \\ 1 \text{ T} &= 1 \text{ N A}^{-1} \text{ m}^{-1} \quad \dots \text{(A.18)} \end{aligned}$$

Torque is the rotational effect of a force. The unit of torque is N m or J.

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,

$$\begin{aligned}\tau &= I N A B \\ &= m B\end{aligned}\quad \dots \text{(A.19)}$$

The product $I N A$ is called the magnetic moment (m) of the coil and evidently its unit is A m^2 (since V 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 $I = 20 \text{ A}$.

$$\begin{aligned}m &= I N A \text{ [Area of a rectangular coil, } A = \text{length of the coil} \times \text{its width]} \\ &= 20 \text{ (A)} \times 100 \times 0.1 \text{ (m)} \times 0.05 \text{ (m)} = 10 \text{ Am}\end{aligned}$$

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,

$$B_0 = \frac{\mu_0 N I}{l} \quad \dots \text{(A.20)}$$

Here μ_0 is the permeability of free space or air and is equal to $4\pi \times 10^{-7} \text{ TmA}^{-1}$. 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.

$$B = \frac{\mu N I}{l} \quad \dots \text{(A.21)}$$

where μ is the permeability of the core material and it has the same units as μ_0 , namely, 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 A m^{-1} since magnetic moment and volume have A m^2 and 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.

$$H = B_0/\mu_0 \quad \dots \text{(A.22)}$$

$$= B/\mu \quad \dots \text{(A.23)}$$

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,

$$H = \frac{NI}{l} \quad \dots \text{(A.24)}$$

The unit of H is 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 $\mu_0 M$.

$$\text{Hence } B = B_0 + \mu_0 M \quad \dots \text{(A.25)}$$

$$\text{Using Eq. A.22, we get, } B = \mu_0 H + \mu_0 M = \mu_0 (H + M) \quad \dots \text{(A.26)}$$

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.

$$\chi = M/H \quad \dots(\text{A.27})$$

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,

$$B = \mu_0 (H + \chi H)$$

$$= \mu_0 (1 + \chi) H$$

$$\text{or } B = \mu H \quad \dots(\text{A.28})$$

$$\text{where } \mu = \mu_0 (1 + \chi) \quad \dots(\text{A.29})$$

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.