CHEMISTRY
THEORETICAL CHEMISTRY
PHYSICAL CHEMISTRY

Blocks 1 - 10

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Block - 1

ATOMIC STRUCTURE

Matter is made up of tiny particles called molecules. The simplest part of a substance is atom. Molecules have independent existence while atoms may or may not have independent existence. Molecules may be monoatomic (ex: sodium, potassium, calcium etc.), diatomic (O_2, H_2, N_2, Cl_2 etc) or polyatomic (CO_2, SO_2, NH_3 etc). All elementary gases are diatomic in nature except inert gases (He, Ne, Ar, Kr, Xe, Rn). Atoms of the same element are similar while atoms of different elements are dissimilar. Atoms combine in a simple whole number ratio to form compounds.

Atoms are indivisible during chemical reactions. But under-special experimental conditions they divide into three main particles called subatomic particles viz; electron, proton and neutron. The discovery of these, their properties and arrangement in an atom are discussed in this Block.

UNIT - 1 RUTHERFORD MODEL OF ATOM

Contents

1.1 AIMS AND OBJECTIVES

The purpose of this unit is to describe about the model of the atom developed by Rutherford for the structure of the atom. By the end of this unit you will be able to understand that

- An atom is made up of the fundamental particles - electron, proton and neutron.
- The number of particles of each type in an atom depends on atomic number and atomic mass of the atom.
- Every atom has a specific arrangement of the fundamental particles in it.
- α-ray scattering experiment of Rutherford.
- The concept of nucleus and the arrangement of electrons around the nucleus.
- The inadequacy of the model to explain some important experimental facts.
- The need for a new look at the atomic model suggested by Rutherford.

1.2 INTRODUCTION

1. What are the fundamental particles called subatomic particles?
2. How many particles of each type are present in an atom?
3. How are they arranged in an atom?

The answers to the above questions are the basis for the earlier views on the modern structure of the atom.

1.3 DISCOVERY OF ELECTRON, PROTON AND NEUTRON

A gas at low pressure was confined in a discharge tube and subjected to a high potential. As a result of this, cathode rays are produced and these travel away from the cathode at right angles to it. The cathode rays are invisible to the naked eye but cause fluorescence when they impinge on a glass surface. They cast sharp shadows of opaque objects, rotate a paddle wheel kept in their path and are deflected by magnetic and electric fields. These indicate that cathode rays are made up of negatively charged material particles travelling in straight lines. **J.J. Thomson** produced cathode rays by taking different gases or vapours in the discharge tube and found that the charge to mass (e/m) ratio of the cathode ray particle remains the same for all these substances. Thus the fundamental particle constituting the cathode rays is found to be universal constituent of all forms of matter and it is named *electron*. It has an electric charge equal to -1 and mass equal to 1/1840 amu (negligible mass).

The discovery of electron as a subatomic particle led for the search of its counterpart positive particle since atom is neutral. The positive rays (stream of positive particles) are later identified in the discharge tube experiment using a perfect cathode. It was established that the charge to mass ratio (e/m) of a positive ray particle is not constant for different substances. The lightest positive ray particle is obtained when hydrogen gas (the lightest atoms) was used in the discharge tube. This is named *'proton* and the electric charge on the proton is found equal to +1 and mass equal to 1 amu.

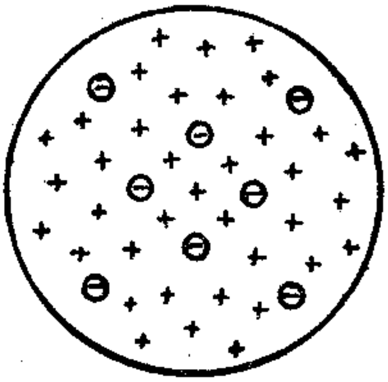
The assumption that an atom is made up of an equal number of electrons and protons only was not in agreement with certain known facts. So Rutherford proposed in 1920 that there must exist another fundamental particle with charge zero and mass 1 amu. In 1932 **Chadwick** obtained a stream of neutral particles by bombarding light elements like boron or beryllium with α-rays. The particle carried a mass of 1 amu. This particle is called *neutron*.

Check your progress - 1

How do you establish that an atom is made up of electrons, protons and neutrons ?

1.4 THOMSON'S MODEL OF THE ATOM

Thus by the beginning of 20th century it was established that electrons, protons (in equal numbers)



1.1 Thomson's model of atom

and neutrons are present in an atom. The arrangement of these subatomic particles in an atom is pictured by atomic models. **J.J. Thomson**, a leading scientist of the period proposed one such model. According to him, the negatively charged electrons are embedded in a sphere of positive electrification. Thus an atom may be visualised as a 'water melon' in which the "seeds" represent electrons and the fibrous material the massive protons. But this model lacked experimental proof and so it was not acceptable.

1.5 RUTHERFORD'S MODEL OF THE ATOM

E. Rutherford, an eminent scientist suggested an alternate model based on experimental work. Naturally, Rutherford model of an atom was found to be superior. To understand Rutherford model, first, let us look at his experiment. Before describing his experiment, we will discuss a simple experience that you can visualise easily.

Suppose you sit in a room with a toy gun and try to shoot at the wall with a fairly large number, say 1000, of glass marbles using it. In the first trial, you hit the wall with the 1000 marbles one after another.

How many of them will pass through the wall and reach the other side? ....
None!

Reason: A wall is a solid obstruction through which a material particle like a glass marble can not pass through.

As the next trial, try to shoot the marbles at the wall fitted with a window or fitted with iron bars or a grill.

What happens?

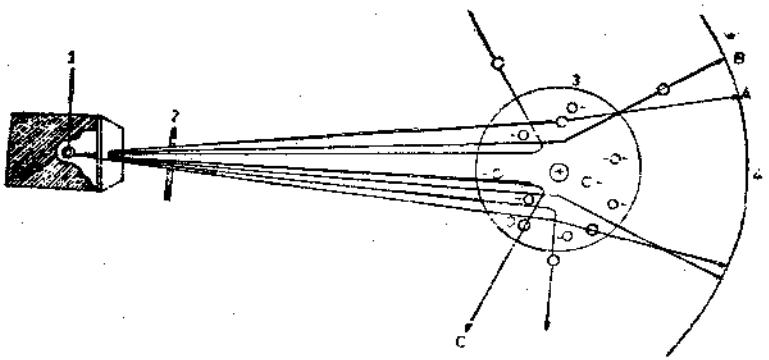
Those marbles whose path lies in between the bars, pass through without changing their path. And those which hit the bars are deflected from their paths through various angles. Occassionally, a marble which encouunters a head-on-collision with the bar is returned in the same path or is scattered through a large angle.

1.5.1 Rutherford's α-ray Scattering Experiment

Now let us consider the famous experiment conducted by **Rutherford.** He used α-ray particles as projectiles (marbles) and a thin gold foil as the target (wall with grill).

A radioactive substance like polonium kept in a lead box acts as the source of α-particles. A narrow beam of α-particles escapes through a small hole and impinge on the thin gold foil kept in their path.

Each α-particle has a mass of 4 amu and an electrical charge of +2. A fluorescent screen is set up at a distance around the fold. When an α-particle hits the screen, a flash of light (called scintillation) can be seen. Thus the path taken by an α-particle can be observed.



1.2 α-ray scattering experiment

1. Radioactive substance 2. Slit 3. Gold Foil 4. Fluorescent screen 5. Deflected α-rays

1.5.2 Observations and conclusions drawn by Rutherford

(i) Most of the α-particles passed almost straight through the foil and hit the fluorescent screen. This indicates that these α-particles did not encounter any obstruction in their passage through the metal foil. Remember! the metal foil is made up of atoms and if the atoms are solid throughout their volume, every α-particle aimed at them would have bounced back (like the marbles striking the solid wall). But here most of the α-particles which are material particles passed through gold foil undeflected. This indicates that most of the space in atom is empty.

(ii) A few α-particles are scattered through various angles as in the figure 1.2. Occassionally an α-particle was deflected through a very large angle. We know that like charges repel and this must have been the cause for the deflection of an α-particle. So the positively charged α-particle must have encountered a collision with another positively charged region in the atom. The fact that the number of scattered α-particles is small indicates that this region is small but massive. That means there exists a small region in an atom where all its mass and positive charge are concentrated. Unless it is highly massive and strongly positive, it can't scatter α-particles through large angles. This small region which is possibly at the centre of the atom is called its *nucleus*. The electrons which are negatively charged are outside the nucleus.

Check your progress - 2

What is the experimental proof that an atom has mostly an empty space?

1.6 DRAWBACKS IN RUTHERFORD MODEL

The nuclear atom of Rutherford model explained the experimental facts of the scattering of α-particles. But this model was not in agreement with a number of experiments dealing with electric charges. It is known that like charges repel and unlike charges attract each other. As a result of this attraction, the oppositely charged bodies must move towards each other and finally come in contact or merge together. Then their electric charges are neutralised. In the Rutherford model negatively charged electrons and a strong positively charged nucleus are present. If in this process all the electrons merge with the nucleus, the nucleus is no longer positively charged. And then it could not be able to scatter α-particles. But nucleus does scatter α-particles as is evidenced in Rutherford's experiment. There is no doubt about it. To explain this established fact we must assume that somehow electrons do not fall into the nucleus in spite of the electrostatic attraction of the electrons by the nucleus.

What is that unseen force which prevents the electrons from falling into the nucleus even though they are attracted by the nucleus?

1.6.1 Rutherford's suggestion

Rutherford came forward with a new idea. An electron revolves round the nucleus (Fig. 1.3) as a planet revolves round the sun. This is the essence of the so called planetary model. The centrifugal force thus developed by the electron, balances the nuclear attraction. The electron is thus prevented from falling into the nucleus. But this suggestion does not stand to logical reasoning. When a charged body moves changing its direction it is accelerated. According to classical electromagnetic theory, an accelerating electric charge must lose some of its energy. It is obvious an accelerating electric charge must emit radiation continuously. The electron would then trace a spiral path and finally merge with the nucleus (Fig 1.4).

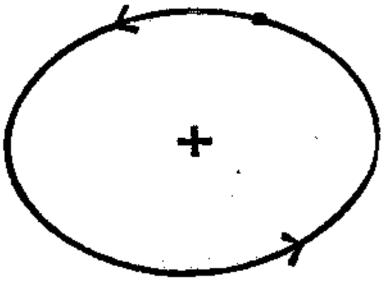


Fig. 1.3 Rutherford's Model of atom

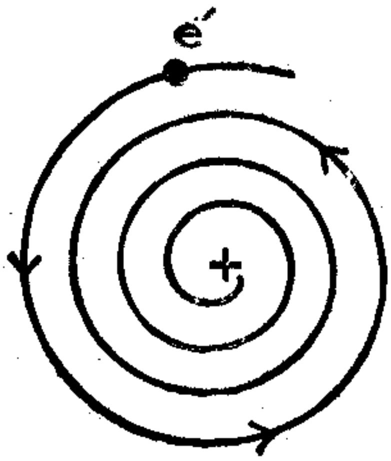


Fig. 1.4 Continuous emission of radiation and spiral path of electron

As a consequence of the continuous emission of radiation by an electron, the spectrum obtained from an atom must be a continuous spectrum. But it is an established fact that the spectra of the atoms are line spectra. So Rutherford model of an atom fails to explain the origin of line spectra. Thus it becomes necessary to modify the atomic model suggested by Rutherford. The Bohr model of atom which replaced the Rutherford model successfully explains most of the experimental phenomena.

1.7 SUMMARY

In this unit we briefly studied about (i) discovery of electron, proton and neutrons. (ii) Thompsons model of the atom, Rutherford's model of the atom (iii) An experiment by Rutherford's which has clearly dealt about α-ray scattering was also studied in this unit (iv) certain observations drawn by Rutherd has been studied, like positive charge in the centre of the atom is called nucleus. (v) The electrons which are negatively charged are outside the nucleus. (vi) Finally we read in this unit drawbacks of Rutherford model and suggestions made by him.

1.8 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines

1. What are cathode rays? Describe their properties.
2. DescribeRutherford's model of the atom.

II. Answer the following in 30 lines

1. How do the atomic spectra point out the drawbacks of Rutherford model?
2. Discuss critically the drawbacks of Rutherford model.

1.9 MODEL ANSWERS TO CHECK YOUR PROGRESS

1: Any gas in a discharge tube experiment was found to release negatively charged rays called cathode rays that move a paddle wheel. This establishes the presence of electrons in an atom. Neutrality of an atom suggests the presence of protons. As the atomic mass is more than the mass of the constitutent protons and electrons, neutrons also should be present in any atom.

2: Deflection of very few α-particles in Rutherford's Gold Foil is the experimental proof that an atom has mostly empty space.

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UNIT - 2 : PLANCK'S QUANTUM THEORY

Contents

2.1 AIMS AND OBJECTIVES

The aim of this unit is to describe in brief the quantum theory of radiation and make you to understand the nature and behaviour of the different regions in the electromagnetic spectrum. After completing this unit you must able to understand:

- Corpuscular theory
- Wave theory of light
- Wave characteristics
- Black body radiation
- Planck's quantum theory
- Quantum theory and atomic structure

2.2 INTRODUCTION

With the help of a small lens, focus bright sun's rays on to a piece of paper or cotton. After sometime the papers or cotton becomes very hot and finally burns into a flame. These observations suggest that rays (light) travelling from the sun are reaching the paper or cotton and increasing the thermal energy of the object (paper or cotton) as indicated by the rise in temperature of the object. When the temperature reaches the ignition temperature of the object, the paper or cotton burns into a flame. It will also be observed that the rays cast well defined shadows of the opaque. Objects placed in the path of the rays. These observations make you conclude that sun's rays (a form of light) travels through space in straight lines. The fact that these rays are increasing the energy (thermal) of paper or cotton, when the former falls continuously for some time on the latter suggests that light is a form of energy. It is also evident that the light is travelling from sun to the cotton. Then the question is, what is it that travels and carries energy with it.

Check Your Progress - 1

What is the nature of light?

2.3 CORPUSCULAR THEORY OF LIGHT

According to Newton, light is composed of minute particles or corpuscles. The streams of these corpuscular sort out from the light source and travel in all directions in straight lines. This concept eventhough could explain the observations recorded in Fig. 3.1, could not successfully explain all phenomena of *diffraction* and *intereference* of light. It also could not explain why the velocity of light varies with the medium in which it travels. For example velocity of light in water is less than the velocity in air.

2.4 WAVE THEORY OF LIGHT

Hugens proposed this wave theory of light. According to this theory light is considered as electro-magnetic radiation and is assumed to travel in the form of waves in all directions. The theory could successfully explain the phenomena of diffraction and intereference.

2.5 CHARACTERISTICS OF WAVE

You are familiar with different types of waves. One such type are the water waves. You stand on a raised tankbund and look at the surface of the moving water below. You observe water waves. The experience is similar when you look at the ocean from a mountain cliff nearby. The waves reach the shore at regular intervals and the entire wave motion is very systematic and follows a rythm. Water waves repeatedly dash agasinst tankbund or the sea shore. In due course there is erosion of tankbund or the sea shore. This is similar to burning of paper or cotton by sun's rays focussed on them. This suggests that water waves to carry energy with them. It is thus evident that light waves or water waves carry energy with them. A wave possesses the following characteristics.

i) Wavepossess energy and carries it during propogation.
ii) Wave possess characteristic dimensions represented by wavelength.
iii) Wave propogation occurs with characteristic frequency.
iv) Wave moves with characteristic velocity.

Some of these characteristics of a wave are depicted schematically in figure 2.1

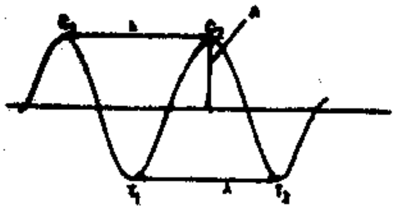

Fig 2.1 Characteristics of wave C_1, C_2 = Crests; T_1, T_2 = Troughs; A= Amplitude

2.5.1. Wave Length (λ)

It is the distance between any two successive crests (C_1 & C_2) or troughs (T_1 & T_2) of the wave and is represented by (Lamda). The points of maximum are called crests and the points of minimum are named troughs. The wave-length is measured in Angstroms, A° (1A°= 10^{-8}cm) or in nanometers, nm (nm = 10^{-9}cm).

2.5.2. Wave Frequency (υ)

The number of waves that travel past a given point in one second is called the wave frequency. It is designated by the letter υ (nue) and is expressed in cycles per second.

2.5.3 Velocity (c)

The distance travelled by a wave in one second is called its velocity. It is designated by the letter 'c' and is expressed in centimeters per sec. the velocity of light in air is 3×10^{10} cm. per second. All forms of light (ultra violet, visible or infrared) travel with the same velocity. But they differ from one another in their wave length or frequency or energy.

2.5.4 Wave number ($\bar{\upsilon}$)

Frequency of light is very often expressed in terms of wave number. This is designated by the symbol (µue bar). It is defined as the number of waves (or wavelength) per centimetre, wave number thus is the reciprocal of wavelength expressed in centimeters.

$$\bar{\upsilon} = 1/\lambda$$

But frequency of light ($\bar{\upsilon}$) is related to the velocity (c) and wavelngth λ) by the equation $\upsilon = c/\lambda$

Therefore we can write $\upsilon = c\ \bar{\upsilon}$

2.6 BLACK BODY RADIATION

When a radiation is incident on the surface of a body there are three possibilities. A part of the radiant energy is reflected, some of it is absorbed and yet another position is transmitted. All the incident energy is thus not absorbed, because ordinary bodies are not perfect absorbers of radiation. But a blackbody behaves in a different way. By definition a blackbody is one which is a perfect absorber of energy or radiation and which retains any energy that strikes it. An ideal example for a black body is a hollow metallic sphere with small hole made into it and blackened inside. Any radiation that enters the sphere through the hole falls on the black surface and most of it is absorbed. Any part of it which is reflected is again incident on the inner black surface. This repeats itself till all the energy is absorbed finally. A black body is not only a perfect absorber or radiant energy but also a perfect radiator. It is in thermal equilibrium with its surroundings. The energy radiated by a heated perfect black body is maximum compared to other bodies heated to the same temperature. The energy is not emitted with a single frequency. It is also not uniformly distributed at all wavelengths. For each temperature the energy radiated is maximum at a certain wavelength (Fig. 2.2). The position of this maximum shifts towards lower wavelength with increase of temperature. The phenomenon of black body radiation could not be explained on the basis of classical theory of continuous emission of radiation.

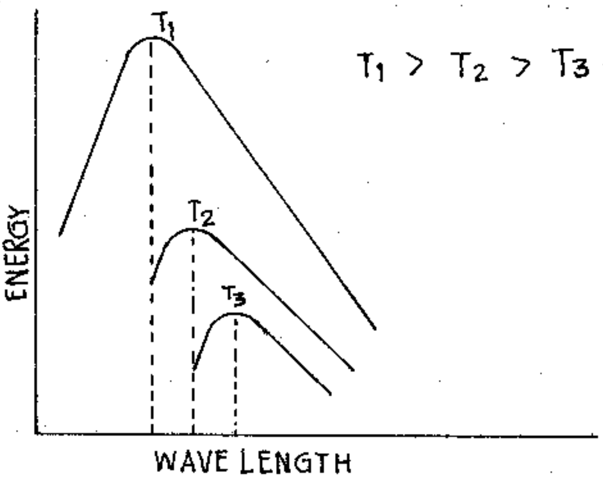

Fig 2.2 Specteral distribution of radiation from a Black body at various temperatures

2.7 PLANCK'S QUANTUM THEORY

To explain the phenomenon of black body radiation, Planck proposed the quantum theory of radiation. This states that black bodies radiate energy not continuously, but discontinuously in energy packets called 'quanta'. The energy E associated each quantum for a radiation of particular frequency is given by the relation.

$$E = h\upsilon$$

Where ' h' is universal constant called Planck's constant

$$h = 6.63 \times 10^{-27} \text{ erg sec.}$$

Check Your Progress - 2

How do you explain black body radiation?

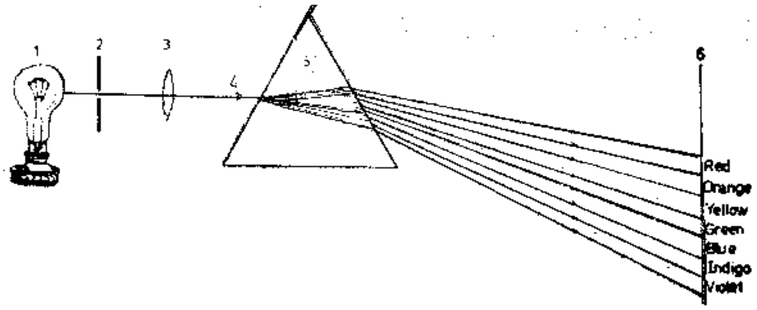

Fig. 3.1 Spectrum of white light

1. Filament lamp 2. Slit 3 . Lens 4. White light beam 5. Glass Prism 6. Screen

Each colour corresponds to a light radiation or a band of radiations with specific characteristics. The array of colours can be caught on a white screen or recorded on a photographic film. All the seven colours in the form of bands can be seen when the white light coming from the sun or emitted by an electric bulb (filament lamp) is passed through the glass prism. There are no gaps in between the colour bands and the bands are continuous. Such a spectrum is called continuous

3.3 LINE SPECTRA

In the experiment discribed in 3.1 the source of light is a tungsten filament electric bulb and the filament is made incandescent at high temperatures. Similar to incandescent tungsten filament many metals or their compounds emit light when they are made incandescent by raising their temperature to high values. For example we can introduce sodium chloride into a bunsen flame and raise its temperature to high values. The salt at this high temperature imparts a bright yellow colour is characteristic of the light emitted by sodium chloride when raised to high temperatures. The yellow light when passed through a glass prism is split into two distinct yellow lines separated by a dark space (Fig. 3.1). This system of two distinct yellow lines separated by dark space is due to the light emitted by sodium at high temperatures and is called sodium spectrum. Such a spectrum consisting of distinct lines separated by dark spaces (or gaps) is called a line spectrum. Each line has specific characteristics. Note the difference between this spectrum and the spectrum obtained from sun rays (solar spectrum) mentioned above in figure 3.1. The latter contains continuous bands in contrast to the distinct lines in the former.

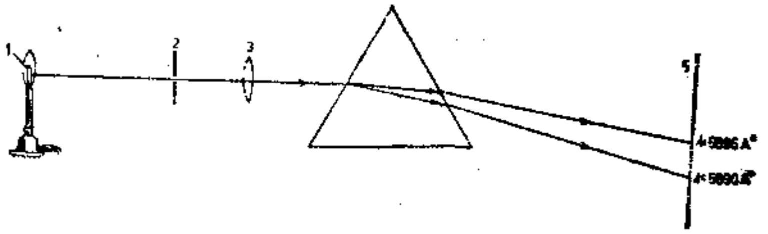

Fig. 3.2 Line Spectrum of sodium atom

1. Bunsen Flame containing NaCl 2. Slit 3. Lens 4. Glass prism 5. Screen

Check Your Progress - 1

What is meant by the term 'line spectrum'?

3.4 HYDROGEN SPECTRUM

We can repeat the experiments described in 3.1 or 3.2 with some changes. The tungston filament lamp (electric bulb) or bunsen flame containing sodium chloride can be replaced by a hydrogen lamp which contains hydrogen gas raised to high temperatures and acts as a source of hydrogen atoms.

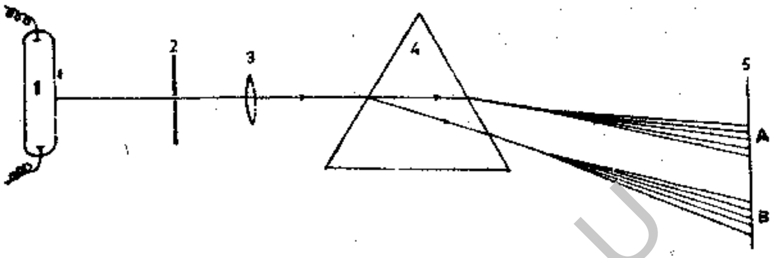

Fig. 3.3 (a) Hydrogen Spectrum
1. Hydrogen lamp 2. Slit 3. Lens 4. Quartz prism 5. Screen

When an electric current is passed through hydrogen gas at low pressures in the hydrogen lamp, red light is emitted by the hot hydrogen atoms. The light when passed through a prism made up of quartz, splits into a series of sharp but distinct lines (Fig. 3.3 [a]) Each line is distinct by characteristic properties. The array of these lines is called hydrogen spectrum. Based on the magnitude of energy associated with light responsible for the appearence of each of the lines. The lines are grouped into different regions and are called *ultraviolet, visible* and *infrared regions.* Like hydrogen atom, atoms of other elements also exhibit line spectra. However the simplest line spectrum is given by atomic hydrogen. Because of its simplicity and the characteristic pattern, the hydrogen spectrum attracted the attention of many scientists. Does the spectrum of hydrogen atom depend on the structure of hydrogen atom? Do the lines in the spectrum provide clues to the structure of the atom? are some of the questions worrying the many scientists. You recollect the problem "Atoms do not collapse even though the positively charged nucleus attracts the electrons revolving around it and even a moving charged body is expected to lose continuously its energy".

Many scientists believed that explanation for the line spectrum of hydrogen leads to a proper understanding of the structure of hydrogen atom. Therefore scientists began searching for simple mathematical relationships if any existing, to explain the position of lines in the spectrum. In 1885, Balmer proposed a simple mathematical equation to express typical characteristic namely the frequency of the lines in the visible region of the hydrogen spectrum. The series of lines in this visible region is therefore regarded as Balmer series. The frequency ($\bar{\upsilon}$) of the lines (or the wave number υ), is expressed by the equation

$$\bar{\upsilon} = 109677\ (1/2^2 - 1/n^2)$$

Where 'n' is an integer equal to or greater than 3 i.e n = 3,4,5,6,...............

The wave number $\bar{\upsilon}$, of the spectral lines are thus calculated from the emperical equation. The equation is in agreement with the experimental facts. The excellent agreement between the wave numbers calculated and the experimentally determined values surprised the scientists.

The series of lines which lie in the ultraviolet region is known as *Lyman series.*

These wave numbers of these lines are expressed by the equation

$$\bar{\upsilon} = 109677 (1/n^2_2 - 1/n^2_1)$$

Covers all the observed spectral lines of the hydrogen atom.

n_1 and n_2 are integers and $n_1 > n_2$. The constant 109677 ($3.289 \times 10^{15/s}$) is characteristic of the hydrogen atom is called *Rydberg constant.* It has the units cm^{-1} (reciprocal cm). For a given spectral series n_2 remains constant while n_1 varies for line to line in any series. The different equations proposed to represent the various series are given below.

Lyman series in the ultraviolet region $n_2 = 1$, $n_1 = 2,3,4,$ ....
Balmer series in the visible region $n_2 = 2$, $n_1 = 3,4,5,$ ...,............
Paschen series in the infrared region $n_2 = 3$, $n_1 = 4,5,6,7$ ....
Brackett series in the infrared region $n_2 = 4$, $n_1 = 5,6,7,8,$ ....
Pfund series in the infrared region $n_2 = 5$, $n_1 = 6$.

The above equations are purely emperical. But the experimental data satisfactorly fitted into these equations. It is therefore evident that a satisfactory model of hydrogen atom should provide a rational basis for these emperical equations.

Check Your Progress - 2

How do you calculate the wave length of the first line of the Balmer series?

3.4.1 Bohr's model of hydrogen atom

In 1913, Niels Bohr proposed a model for hydrogen atom to explain the observations mentioned above. He showed a way out of the dilemma posed by Rutherford model. For example he not only explained why atoms do not collapse but also succeeded in explaining the origin of the line spectra. The atomic model proposed explained quite well the line spectra of elements. Hydrogen atom contains one electron and a nucleus that consists of a single proton. Bohr thus retained the nuclear model of the atom proposed by Rutherford because it was based on experiment. He also agreed that the negatively charged electron revolves round the nucleus. But he took the bold step by applying Planck's quantum theory to the electron revolving round the nucleus. The electron of the hydrogen atom can exist only in certain spherical orbits. These are also called energy levels or shells. These shells are arranged concentrically around the nucleus. He also envisaged that the electron in the atom has certain specified energies and angular momenta. In other words Bohr thus proposed the concept of stationary orbits. There will be no change in the energy of the electron moving in such orbits (Stationary orbits). The angular momentum (mur) of electron is given by $mur = n.\ h/2\pi$. (Cm = mass of electron, υ = vilocity of electron, r = radius of orbt).

Where 'n' is an integer 1,2,3 etc 'n' is called Principal quantum number. 'h' is Planck's constant.

This condition leads us to include that the energy of an electron can have only certain discrete values but not continuous values. It can be shown that the permitted energy values (or levels) are given by the equation

$E_n = 2\pi^2 me^4/n^2h^2$

Substituting the numerical values for π, m_1, e and h, in the above equation, it can be rewritten as

$E_n = -(2.179 \times 10^{-8}\ j)/n^2$

Where n = 1,2,3 etc.

The radius of the circular orbit is given by the equation : $r = n^2h^2/4\pi^2 me^2$

3.4.2 Bohr's postulates

i) The concept of 'nucleus' possesing the positive charge and practically all mass of the atom concentrated at the centre given in Rutherford's model of atom is retained.

ii) The electrons revolve round the nucleus with high speeds in specified orbits each associated with a definite energy. Each of these orbits as mentioned earlier is called stationary orbit or stationary state, because the energy of the electron in this orbit is constant as long as it remains in this orbit. In otherwords, with nucleus at the centre and with increasing radius, a series of concentric spherical surfaces (orbits) are proposed. They are numbered as n = 1,2,3,4 .... Starting from the one nearest to the nucleus (Fig. 3.4 (a). 'n' is called the principal quantum number. They are also named as shells or quantum levels and designated as K,L,M,N .... orbits or shells. The electron cannot have an energy that would place it between the permissable orbits.

iii) When an electron jumps from an outer orbit into an inner orbit energy is radiated by the atom. This emitted energy manifests itself in the form of a spectral line in the atomic spectrum.

$\Delta E = E_2 - E_1 = h\upsilon$

E_1 = Energy of inner orbit

E_2 = Energy of outer orbit

υ = frequency of the spectral line in the atomic spectrum.

h = Planck's constant.

iv) The angular momentum of electron moving round the nucleus is quantized and governed by the equation.

$mur = n.\ h/2\pi$

m = mass of electron

u = Velocity of electron

r = radius of the orbit

3.4.3 Explanation of hydrogen spectrum

Bohr's model of hydrogen atom successfully explains as to why atoms do not collapse even though the revolving electron is expected to lose energy continuously. The lowest possible quantum state for the electron to occupy is n = 1 quantum state. So long as the electron revolves round the nucleus in any specified orbit, there is no change in the energy or angular momentum of the electron so the question of an electron losing energy during its motion (as required by electrodynamics) and hence falling into the nucleus and consequential collapse of the atom does not arise.

Bohr attributes the lines in the hydrogen spectrum to the possible electronic transitions and the energy changes accompanying them (Fig. 3.4 a & b).

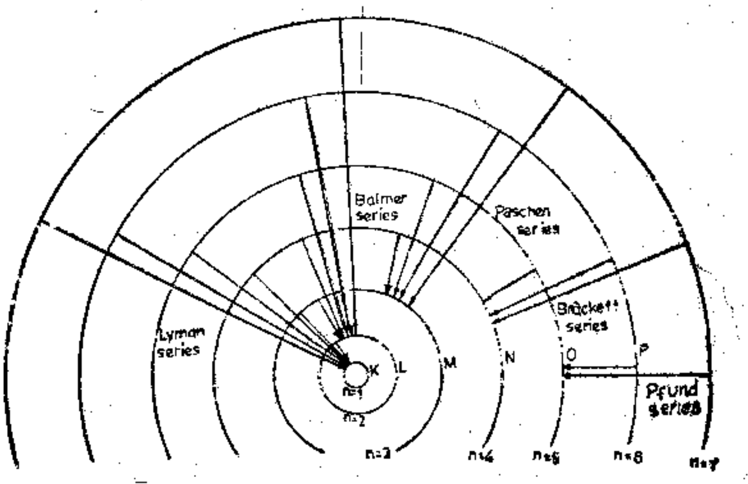

Fig. 3.4 (a) Electron transitions in hydrogen atom

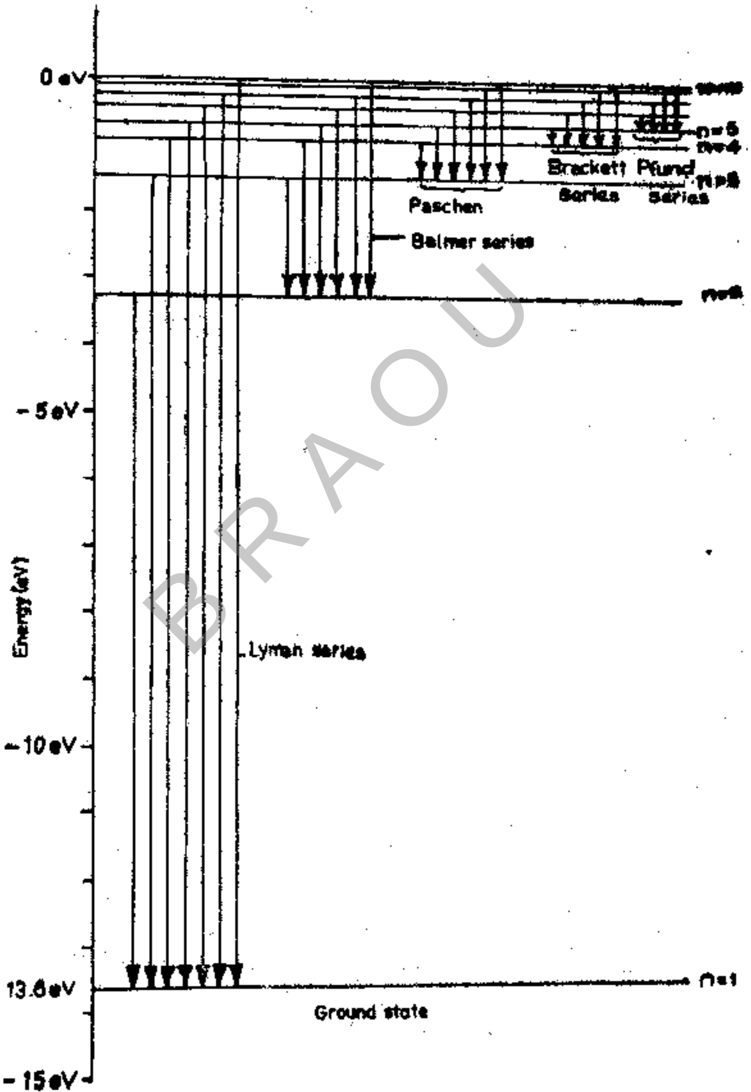

Fig. 3.4. (b) Electron transtions in hydrogen atom

The electronic transitions in the hydrogen atom and the corresponding spectral lines (or series of lines) is shown in figure 3.4 (b). The electronic transitions to n=1 (Lyman series) release more energy than those to n=2 (Balmer series). Therefore the wavelengths of the lines of the Lyman series are shorter than those of Balmer series and the lines of the Lyman series occur in the ultraviolet region (high energy or low wavelength region). On the other hand the lines of the Paschen series which represents transitions to n=3 level occur low energy or longer wavelength. The Paschen series therefore appears in the infrared region (low energy region).

The Bohr theory is thus successfully in interpreting the spectum of hydrogen. It however fails to explain the spectra of atoms that contain more than one electron.

3.5 SUMMARY

In this unit we have studied about

i) The charactedristic features of a continuous spectrum and a line spectrum.

ii) The lines in the hydrogen spectrum and the mathematical expressions, relations the wave number of the radiation with Rydberg constant.

iii) The different spectral series in the hydrogen spectrum.

iv). The Bohr model of hydrogen atom as an acceptable atomic model.

v) The logical explanation of the origin of line spectra given by Bohr atomic model.

3.6 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines.

1. State Bohr's Postulates.

2. How does Bohr's theory explain the origin of atomic spectrum of hydrogen?

3. What is principal quantum number? and what does it denote?

II. Answer the following in 30 lines.

1. How do atomic spectra arise? How are these theoritically explained?

2. Discuss critically Bohr's model of the atom.

3.7 MODEL ANSWERS TO CHECK YOUR PROGRESS

1 When energy is supplied to atoms their electrons to go higher energy states. Definite quanta of energy will be emitted by these electrons when they come back to their original orbits. This energy will effect a photographic plate & called line spectrum. Atomic spectrum is called line spectrum.

2 $\bar{\upsilon} = 109677\ (1/2^2 - 1/3^2)$ Balmer's formula
$1/\lambda = 109677\ \text{X}\ 5/36$
$1/\lambda = 36/548385 = 6.564\ \text{X}\ 10^{-5}$ cms.
$\lambda = 6564$ A (visible region)

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Revised by: Prof. S. Brahmaji Rao.

UNIT - 4 : QUANTUM NUMBERS

Contents

4.1 AIMS AND OBJECTIVES

This unit is to make you understand the significance of the quantum numbers and use them in identifying an electron with reference to it's energy and position in an atom. By the end of this unit you must be able to understand:

- Limitations of Bohr's theory.
- Inadequacy of the principal quantum number, 'n' to completely describe the energy of electron.
- Azimuthal quantum number 'l', and explaining the energy sublevels in atoms.
- Magnetic quantum number,'m' and its significance.
- Spin of an electron and spin quantum number 's'.
- Pauli's exclusion principle

4.2 INTRODUCTION

The emission of spectra of hydrogen was successfully explained by Bohr. But Bohr's theory could not explain the occurence of fine structures in the spectrum. Introduction of quantum mechanics to hydrogen and other atoms yields different quantum numbers known as Principal quantum number, Azimuthal quantum number, Magnetic quantum number and Spin quantum number.

4.3 PRINCIPAL QUANTUM NUMBER 'n'

Bohr's theory of hydrogen atom enables us to calculate the radius and energy associated with each possible orbit in the hydrogen atom. The basic principle of Bohr's theory is that only specified energy levels are possible for electrons in atoms. These energy levels are numbered starting with the lowest as 1, the next one as 2, the next higer as 3 etc., The number of the energy level denoted by 'n' is called the ***principal quantum number***. The energies calculated from Bohr's theory were in good agreement with the experimental values. Also Bohr's theory could successfully explain the origin of the series of lines in hydrogen spectrum. So far the theory was a tremendous success. Quantum mechanics deals with the study of laws of motion that govern the behaviour of small particles such as electrons. An important consequence of the application of quantum mechanics to the motion of electrons in an atom is that the maximum number of electrons in any shell (energy level) is limited to $2n^2$. This means that the first shell contains a maximum of $2 \times 1^2 = 2$ electrons. The second shell has a maximum of $2 \times 2^2 = 8$ electrons and so on. There is an implied suggestion in Bohr's theory hat all the electrons in a given shell are of the same energy. This may not be true always.

Check Your Progress - 1

What does principal quantum number signify?

4.4 AZIMUTHAL QUANTUM NUMBER 'l'

The experimental basis for Bohr's theory was the presence of lines in the emission spectrum of hydrogen. Each line in the spectrum corresponds to an emitted radiation characterised by its frequency and wave length. However, a few years later, spectroscopes of high resolving power were used to study the hydrogen spectrum. This revealed that a line in the hydrogen spectrum was not a single line but a collection of groups of very fine lines. This phenomenon points out that all the electrons in a given shell need not necessarily be of the same energy. Bohr's theory was incapable of explaining the presence of these finer lines. In view of this, Bohr's mnodel has been slightly modified by Sommerfeld. The latter proposed that the orbits are elliptical but not circular as envisaged by Bohr. This predicts that the energy of electrons in the same orbit (shell) differs from electron to electron, Azimuthal quantum number 'k' has been introduced to explain the fact. Although Sommerfeld's azimuthal quantum number is modified and designated as 'l'. Each energy level thus actually consists of a certain number of energy sub levels closely bunched together. Technically we describe this by saying that a main shell (main energy level) is composed of one or more sub shells more energy sub levels. The energy difference between the various sub levels in a given main level may not be too high but it is significant. The number of sub levels in any main level is equal to its principal quantum number, 'n'. Thus K shell consists of only one energy level. The L shell (n = 2) consists of two energy sub levels. This amounts to saying that all the electrons in the second shell do not possess the same energy. They fall into two groups. One group has an energy slightly higher than the other group. Similarly the M shell (n = 3) has three energy sub levels and so on. The sub shells or sub levels as they are often called can be distinguished from one another by various notations.

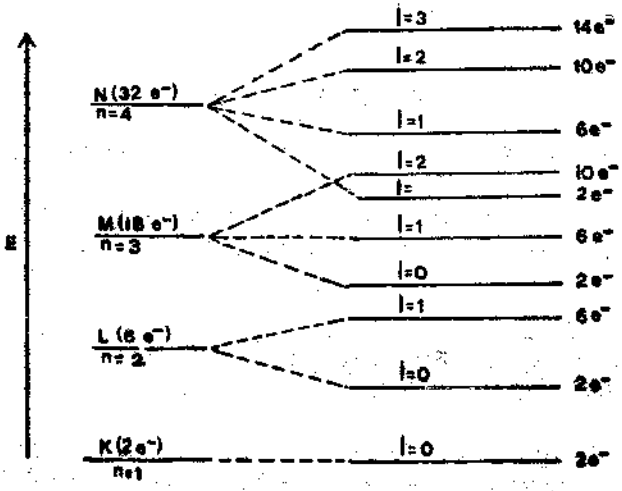

Fig. 4.1 Main energy and sub energy levels

It was stated earlier that the electron in a hydrogen atom has an angular momentum which is also quantised. The quantised values of angular momentum can be specified in terms of another quantum number besides 'n'. This is the azimuthal quantum number 'l'. It is also called angular momentum quantum number. It may be interesting to note that this quantum number 'l' is a device to distinguish the various sub levels in a main level. The permitted values of 'l' are again positive and integral. They re O,1,2,.................. (n-1). For exampl.e 'L' shell (n = 2) has two sub shells denoted by 1=O, 1=1, 1=2. The sub shell with 1=O represents the lowest energy sub shell. The next higher energy subshell is represented by 1=1 sub shell 1=2, represents the next higher. The energy level diagram (fig. 4.1) must now be redrawn to accommodate the sub levels (sub shells).

The main levels are indicated by the leters K,L,M,N etc., corresponding to the principal quantum number n = 1,2,3,4 etc. The sub levels are marked by the azimuthal quantum numbers 1=O,1,2,3. It is significant that the (1=2) sub level in n=3 level has a higher energy than the 1=O sub level in n=4 level. Thus there is the possibility of overlapping of the sub levels at times.

4.5 MAGNETIC QUANTUM NUMBER 'm'

An electron has an angular momentum and thus revolves round the atomic nucleus. In doing so, it behaves like an electric current circulating in a loop of wire. As a result of this, the electron in motion produces a magnetic field. The observed magnetism is also quantised and this is denoted by the third quantum number called magnetic quantum number, 'm'. Naturally we expect the values of 'm' to depend on the value of 'l'. The possible values of m are -1..........to .... +1

4.6 SPIN QUANTUM NUMBER 's'

Besides this, an electron spins on its own axis. This also contributes to the magnetic property of the electron. It is expressed by the spin quantum number 's'. There are only two possible spins for an electron, clockwise and anticlockwise. (Fig. 4.2)

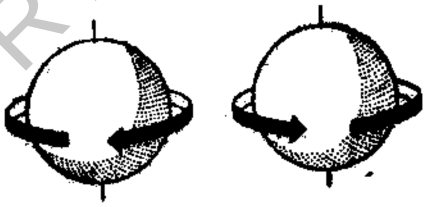

Fig. 4.2 Electron spin

One of the spins is denoted by spin quantum number $s = +1/2$ and the other by $s = -1/2$.

Thus an electron has four quantum numbers n,l,m, and s. Complete description of an electron in terms of its energy and placement in the atom is possible only when all the four quantum numbers are notified.

4.7. PAULI'S EXCLUSION PRINCIPLE

To explain the observed experimental results in respect of spectra of atoms, Pauli enunciated a principle called "no two electrons in an atom can have all the four quantum numbers the same. They must differ in atleast one of the four quantum numbers n,l,m, or s". It is necessary to follow Pauli's principle while assigning quantum numbers to various electrons in atom.

Check Your Progress - 2

Write the significance of spin quantum number?

4.8. SUMMARY

In this unit we have studied about

i) The inadequacies of Bohr's theory resulting in the application of quantum mechanics to the study of electron.

ii) Inability of Bohr model to explain the fine lines in hydrogen spectrum.

iii) The consequent need to introduce Azimuthal quantum number.

iv) The magnetic quantum number and spin quantum number.

v) Pauli's exclusion principle.

4.9 MODEL EXAMINATION QUESTIONS

I Answer the following in 10 lines.

1. How are elections in an atom described in respect of their energies and position?
2. What are the reason for modifying Bohr's model of the atom? What are these modifications?

II Answer the following in 30 lines.

1. Discuss about the quantum numbers and their significance?
2. How was hydrogen spectrum responsible for the introduction of quantum numbers?

4.10 MODEL ANSWERS TO CHECK YOUR PROGRESS

1 Principal quantum number signifies -
a) main energy level to which an electron belongs.
b) energy of an electron
c) size of an orbital

2 This quantum number indictes the spin of an electron i.e. clockwise or anticlockwise spin.
These are also indicated by +1/2 (or ↑) and -1/2 (or ↓).

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UNIT - 5 : WAVE NATURE OF ELECTRON

Contents

5.1 AIMS AND OBJECTIVES

This Unit mainly aims at introducing the wve nature and particle nature of electron (dual nature) and the consequential uncertainity in position and momentum of an electron simultaneously. The concept of orbital model of an atom in place of Bohr's orbit and the drawbacks of the model are also discussed. After completing this unit you should understand:

- Bohr's model broke with classical mechanics.
- It is not possible to determine simultaneously the exact position and velocity of an electron around the nucleus in an atom.
- Modern theory of atomic structure is based on the wave nature of the electron.
- The wave length λ of the waves associated with particulate motion is given by the equation $\lambda = h/mv$.
- The special description of the motion of electron called 'orbital'.
- Orbitals have definite shapes and are designated as s,p,d and f orbitals.

5.2 INTRODUCTION

As seen already, the Bohr's theory was successful in explaining the spectrum of the hydrogen atom and the spectra of hydrogen like atoms. But it failed to explain the observed energy levels in the case of many electrons in atoms. Though Bohr's theory broke with classical mechanics in assuming that electrons could occupy only orbits having a radius such that the angular momentum is equal to some integral multiple of $h/2\pi$ this was only of an adhoc nature. At that time this was assumed there was no justification. Another unsatisfactory aspect of the theory was the attempt to determine, simultaneously, the exact position and the velocity of an electron around the nucleus in an atom. It is now a well established fact that such determination is impossible for microparticles such as electrons. The modern theory of atomic structure is essentially based on the wave nature of the electron. This theory is more satisfactory than the old classical theory in many ways, and is the result of the work of deBroglie, Schrodinger, Hisenberg and others.

5.3 WAVE NATURE OF LIGHT

Properties of light, such as interference, diffraction, are explained successfully by assuming it to be made of waves. On the other hand the study of atomic spectra has established the fact that light is emitted or absorbed in "quanta", or descrete packets of energy, called "photons". This fact supports particle nature of light. It is now clearly established that light, or to be more general, any radiation had duel characteristics i.e, of waves and of particles. This means that some properties of light can be explained by assuming it to be made of waves, whereas other properties are explained on the basis of the assumption that light is made of particles (photons). Scientists say there is no contradiction in this.

5.4 DUAL CHARACTER OF LIGHT

The dual characteristics of light can be illustrated with the help of Planck's equation and Einstein's equation.

According to Planck, the energy E of light (radiation) of frequency υ is given by

$$E = h\upsilon \qquad (1)$$

Where 'h' is a universal constant, called Planck's constant and has the units of ergsecond ($h=6.625 \times 10^{-27}$ erg. sec).

The Einstein equation for mass and energy equivalance of a photon is

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

Where 'm' is the mass of a photon and 'c' is the velocity of light. Thus combining equations 1 and 2, we have $h\upsilon = mc^2$ (3)

Wavelength, λ is related to the frequency, by the equation

$$\lambda = c/\upsilon \text{ or } \upsilon = c/\lambda \qquad (4)$$

Hence equation (3) can be written as $hc/\lambda = mc^2$ or $\lambda = hc/mc^2$

Therefore $\lambda = h/mc$ or h/p (5)

Where p = momentum = mc

Thus the wavelength λ associated with photons of mass 'm' and velocity 'c' (or momentum $p = mc$) is given by equation (5). These relations clearly establish the dual nature of light. This was further confirmed by Compton in his famous experiment on X-ray scattering.

These observations led deBroglie to argue that if radiation like light behaves both as waves as well as particles, then it should be possible for matter (particles) too to exhibit the dual characteristics as particle and waves. He thus suggested that an electron of mass 'm' and moving with a velocity 'u' should have a wavelength λ given by equation (6)

$$\lambda = h/mu \qquad (6)$$

Experimental confirmation of the wave nature of the electron was provided by *Davisson* and

Germer by their work on the diffraction of electron beams by crystal lattices. It is now a well recognised concept that every form of matter has associated with it a wave character. But in the case of large masses the wave character is more or less totally masked, while it is quite perceptible in the realm of subatomic systems like electrons. Equation (6), known as the de Broglie equation, has an important conseqence. From this the existence of stationary states, or the states of constant energy proposed by Bohr (against all known laws at that time) follows naturally.

5.4 THE UNCERTAINTY PRINCIPLE

One important drawback of Bohr's theory was its attempt to determine simultaneously the **position** as well as the **momentum** of an electron moving around the atomic nucleus. In 1927, *Werner Heisenberg showed that it is impossible to determine, simultaneously and accurately, the velocity or any related properties (energy or momentum) of a particle, as well as its position.* This statement, known as Heisenberg's Uncertainty principle, is one of the most fundamental principles of modern science. According to this, any attempt at determining the exact position of a particle, will introduce a measure of uncertainty about its velocity (or momentum) and vice versa. This uncertainty inaccuracy is in no way dependent on the accuracy of the measuring device or the method of measurement. It is simply inherent in the very scheme of things in nature. Basically the inaccuracy is the result of the interaction, of the particles under observation with the measuring device. In the case of a very small particle like the electron, its interaction with energy, (of the measuring source) during the process of observing it, will produce a perceptible change in momentum.

The meaning of all this is that any attempt to determine the exact location of an electron around the nucleus in an atom will be futile exercise, as it will lead to considerable inaccuracy about the momentum (or energy) of the electron. Rather this attempt must be to determine the momentum (or energy) accurately and to think in terms of the probability (in the case of position) of finding the electron in a volume of space around the atomic nucleus. This is evidently sensible, because exact determination of energy changes in physico-chemical processes is a matter of great importance. Thus we shift from the deterministic principle to the probability principle, (in respect of position) which is the edifice of modern thought on atomic structure.

The *Uncertainty Principle* may be expressed by the equation

$$\Delta q \times \Delta p = h \qquad (7)$$

Where Δp is the uncertainty in momentum and Δq the uncertainty in position and h, is the Planck constant. In any experiment in which p is determined accurately, Δq will be large (ie, the uncertainty regarding position is large). Under these conditions the experiment is regarded as a particle experiment. On the other hand in an experiment in which 'q' is precise, then Δp is correspondingly large and the uncertainty of momentum is high. Under these circumstances the observation is regarded as an experiment in waves. This means that behaviour of an electron, proton or any other micro particle form of matter cannot be explained by the concept of a particle and wave simultaneously.

Since $p = mu$ or $\Delta p = m\Delta u$

equation (7) can be expressed as : $\Delta q \times m\Delta u \approx h$

$$\Delta q \times \Delta u = h/m \qquad (8)$$

For particles of large mass, (m is ~~very~~ large) h/m will become very small and will be almost zero. For such macroscopic particles there will be no uncertainty about either position or momentum. But for subatomic particles like electrons, protons, etc, the uncertainty is relatively large since 'm' is small.

Check Your Progress - 1

Why it is not possible to determine accurately the position and energy of an electron simultaneously?

5.6 WAVE NATURE OF ELECTRON

It is now an accepted fact that the electron behaves as a wave too. It is only natural that a wave equation should describe the motion of the electron. Schrodinger developed a wave equation to describe the behaviour of electrons in atoms. The treatment is highly mathematical and need not be considered here. But the results that follow from this mathematical treatment are highly interesting and describe with considerable precision, the behaviour of electrons in atoms. But a limitation needs to be mentioned. Precise calculations have been possible only in the case of one electron system like the hydrogen atom, and of hydrogen like atoms. Only approximate solutions are available in the case of many electron systems. Even then the conclusions are successfully used in the description of atomic structure.

5.7 WAVE EQUATION

The equation for wave motion has been developed by Schrodinger and is known as Schrodinger's wave equation. The equation (9) derived for the movement in the three principal mutually perpendicular directions is given below.

$$\delta^2\psi/\delta x^2 + \delta^2\psi/\delta y^2 + \delta^2\psi/\delta z^2 = 4\pi^2/\lambda^2 \quad \psi \tag{9}$$

ψ = Wave function and λ = Wave length

Introducing de Broglie's relationship $\lambda = h/mu$ into equation (9)

We have $$\delta^2\psi/\delta x^2 + \delta^2\psi/\delta y^2 + \delta^2\psi/\delta z^2 = 4\pi^2 m^2 u^2/h^2 \quad \psi \tag{10}$$

But kinetic energy $1/2\ mu^2 = (E\text{-}U)$ where E = total energy and U = potential energy. Therefore equation (10) can be written as equation (11)

We have $$\delta^2\psi/\delta x^2 + \delta^2\psi/\delta y^2 + \delta^2\psi/\delta z^2 = 8\pi^2 m/h^2\ (E-U) \quad \psi \tag{11}$$

Schrodinger originally suggested that for an electron the value of ψ^2 at any point could be interpretted as the electrical charge density at that point. According to his view the electron has regarded as cloud of electricity, the denisity of which varies from place to place. *Born* however proposed that ψ^2 at any point is supposed to represent the probability of the electron being found at that point at a given instant. In a sense, therefore the quantity ψ^2 is regarded as the wave mechanical equivalent of the electron orbit in the classical theory. It is for this reason the electron wave function ψ is referred to as an **orbital** or as an **orbital wave function.** The wave equation is useful to determine the probability of finding the electron in the volume of space around the nucleus in the atom.

5.8. WAVE MECHANICS

This new treatment, known as wave mechanics, provides a basis for Bohr's assumptions regarding the existence of *Stationary states or Energy levels.* But in the place of the Bohr orbits describing the motion of an electron around the atomic nucleus, we now have a picture describing the probability of finding an electron in a volume of space around the nucleus. This *Spatial description of the motion of an electron is called an "orbital".*

Various types of atomic orbitals are possible. Each of them corresponds to a definite set of combination of the quantum numbers (Unit - 4). Orbitals can be classified in accordance with values of the principal quantum number, 'n' and the angular momentum quantum number, l. As discussed already, l can have value 0,1,2, etc. The orbital corresponding to $l = 0$ is called 's' electrons. The electrons in the orbital for which $l = 0$ called 's' electrons. When n=1, l can have only one value, zero, and the corresponding orbital is called ls orbital. 1 indicates the values of Principal quantum number n, and 's' gives the value of 1 (which is zero). When n=2, 'l' can have two possible values, zero and one. Once again, when l '=0, the orbital is called the 's' orbital, but it is now designated as 2s orbital, as it corresponds the principal quantum number 2(n=2). The other value of l (when n=2) is one. The orbitals corresponding to l =1 'p' orbitals correspond to the three values of the magnetic quantum number, 'm'. These are designated as '2p' orbitals since the principal quantum number is 2 (n=2). When n=3, three values of l are possible. These are 0, 1 and 2. The orbitals corresponding to l =0 and 1 (n=3) are known, as usual, 3s and 3p orbitals. Those corresponding to l =2 are called 'd' orbitals and are designated '3d' in the case of n=3. There are five 'd' orbitals (corresponding to five 'm' values when l =2).

When the principal quantum number is 4(n=4), we have one 's', three 'p', five 'd' and seven 'f' orbitals (corresponding to l =0,1,2 and 3 respectively). These orbitals are designated 4s 4p, 4d and 4 f respectively.

5.9. THE SHAPES OF THE ATOMIC ORBITALS

The modern treatment of the problems of atomic structure is essentially mathematical in character. But for a chemist, more interested in moleculer shape and geometry, a physical or pictorial model is essential. Irrespective of the principal quantum number, all orbitals with l =0, i.e, the 's' orbitals are spherical in shape. The size of 's' orbital depends on the value of n. The shapes of orbitals are shown in figure 5.1. The orbital corresponding to l =1, i.e, p orbitals has a shape which somewhat resembles a dumbbell (Fig. 5.1). There are three 'p' orbitals. The three p orbitals are identical in shape except for the direction or orientation in space. They are directed along the three mutually perpendicular co-ordinates. For this reason they re known as p_x,p_y, and p_z orbitals to emphasise their directional character. The shape of the orbitals plays a very important role in determining molecular geometry.

Check Your Progress - 2

What is meant by 'orbital'?

The 'd' and 'f' orbitals are even more complex in shape. The approximate shapes of the 'd' orbitals are shown in the figure 5.1. There are five 'd' orbitals. These are designed as dxy, dyz, dxz, $dx^2 - y^2$ and dz^2. It is not necessary, at this stage, to discuss the 'f' orbitals.

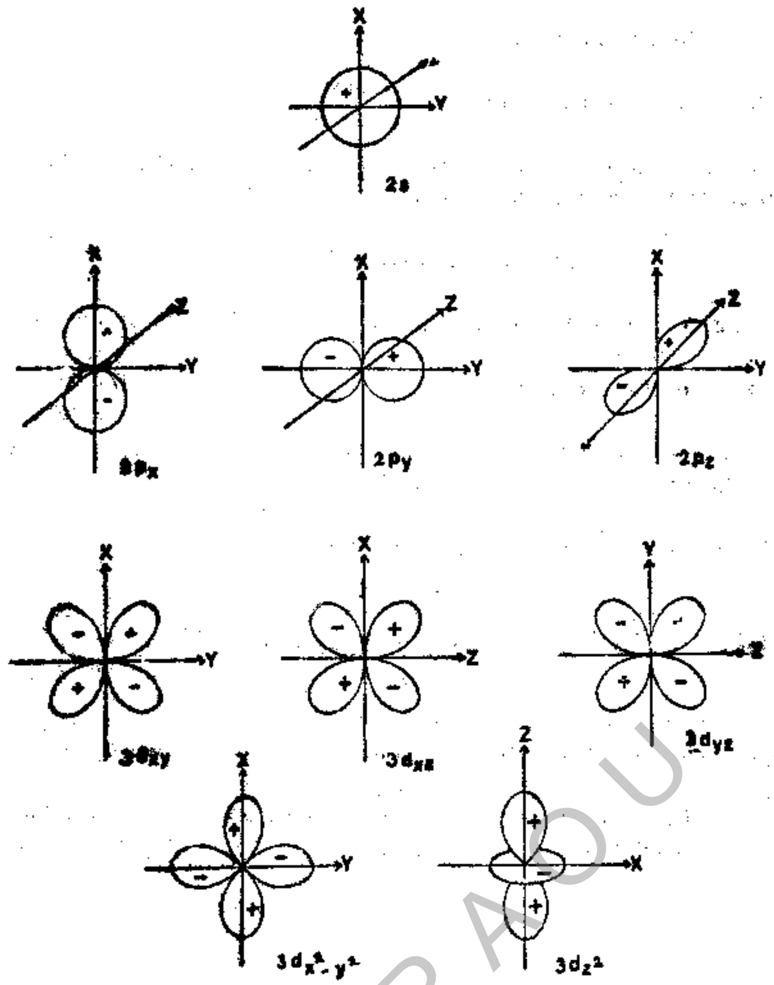


Fig. 5.1 Shapes of orbitals

We now have the necessary background for discussing the arrangement of electrons in atoms. This arrangement of electrons in atoms known as *electronic configuration of atoms,* is discussed in unit 6.

5.10 SUMMARY

In This unit we have studied about

i) The failure of Bohr's atomic model to explain spectra of many electron systems.

ii) The contradiction of Bohr model with the established Heisenberg uncertainty principle.

iii) Dual character of light (radiation in general) leading to de Broglie relation between λ and mu.

iv) The wave mechanical model of atom.

v) The shapes of atomic orbitals.

5.11 EXAMINATIONS QUESTIONS:

I. Answer the following in 10 lines.

1. Discuss the dual nature of ight
2. Derive the equation used to calculate the wavelength associated with the motion of a particle from Planck and Einstein equations.
3. Discuss Heisenberg's Uncertainty principle.
4. Bringout the relation between the values of 'l ' and the shapes of orbitals.

II. Answer the following in 30 lines.

1. Discuss the dual nature of electron. How is this useful to describe the motion of electrons in atoms?
2. Discuss about the orbital model of the atom.

5.12 MODEL ANSWERS TO CHECK YOUR PROGRESS

1 Energy and position of electron in the atom are conjugative properties. Determination of one property accurately introduces uncertainty in the measurement of the other.

2 Orbital is electon cloud in an atom. It is the atmoic space where there is maximum probability of finding an electron. Orbital is proposed as a result of the wave nature of electrons.

UNIT - 6 ELECTRONIC CONFIGURATION OF ATOMS

Contents :

6.1 AIMS & OBJECTIVES

In this unit we explain you the principles underlying the method of arriving at the electronic configuration of atoms and illustrate the same with suitable examples. When you have finished to read this unit you should be able to understand that

- The orbitals have definite energies associated with them.
- The relative order of the energies for each type of orbital is approximately as $1s< 2s< 2p<3s< 3p< 4sr \cong 3d$.
- The guidelines and the rules involved in the filling up of atoms with electrons, is referred to as **Aufbau principle.**
- Electronic configuration of different atoms

6.2 INTRODUCTION

In the last unit we discussed about the wave nature of the electron. the definitive electron *orbits* have been replaced by the wave mechanical probability (orbitals) or determining the motion of the electron. This should not be construed, however, to mean that the electron is not a particle anymore nor should be talked exclusively in terms of electron waves. What needs to be emphasised is that the electron shows the properties of both a particle and a wave. That is, the behaviour of the electron in an atom can be best described by treating it as a particle in some respects and as a wave in certain others. Except in situations where precise mathematical descriptions of electronic energies in atoms and molecules are concerned, electrons are still treated, and will continue to be treated, as particles in ordinary chemical reactions.

In atomic and molecular systems, and in processes, whether physical or chemical, precise calculations of energy are of utmost importance. And in the context of the uncertainty principle we may be satisfied with only the probability of the charge of the electron being found in a certain region of space around the atomic nucleus. This probability description may be regarded as the atomic *orbital*.

The nuclear model of the atom is still the basis of all descriptions of the structure of the atom. The atomic nucleus consists of protons and neutrons, which together account,, almost entirely, for the mass of the atom. Both protons and neutrons are particles of unit mass. While the proton carries unit positive charge, the neutron is electrically neutral; it carries no charge. The number of positive charges (i.e. the protons) in the nucleus is called the "atomic number" of the element concerned. The positive charge of the proton is exactly balanced by the negative charge of an electron moving around the nucleus. Thus, in a neutral atom, the number of protons (atomic number) is equal to the number of electrons outside the nucleus. The atomic number is a characteristic and fundamental property of an element.

The atom of each element has a *build up* (configuration), characteristic of the element. The manner in which electrons are distributed in the various energy levels (or orbitals) is known as the electronic configuration of the atom. According to the quantum theory, electrons in an atom cannot have all possible values of energy, but can exist only in certain discrete energy levels. With the help of the quantum numbers, it is possible to get a clear idea of the electronic configuration of the elements.

For each value of the principle quantum number, n, there will be a total of n^2 different orbitals. For example when $n=1$, we have only *one orbital* ($l=0$) and, as already discussed it is called the 's' orbital (for $n = 1, l = 0$ the orbital concerned is the '1s orbital). For $n=2$, there are 2^2 (4) four orbitals and *one* of them is the '2s' orbital ($n = 2, l = 0$). The *other three* are the '2p' orbitals ($n = 2, l = 1$) which are directed along the three coordinate axes.

Check Your Progress - 1

How is the number of electrons in atom inferred?

6.3 ORBITAL ENERGIES

Each atomic orbital possesses a characteristic energy, whose value can be calculated. For the higher atoms the relative order of the energies for each type of orbital 's' approximately as follows

1s < 2s< 2p< 3s< 3p< 4s ≅ 3d.

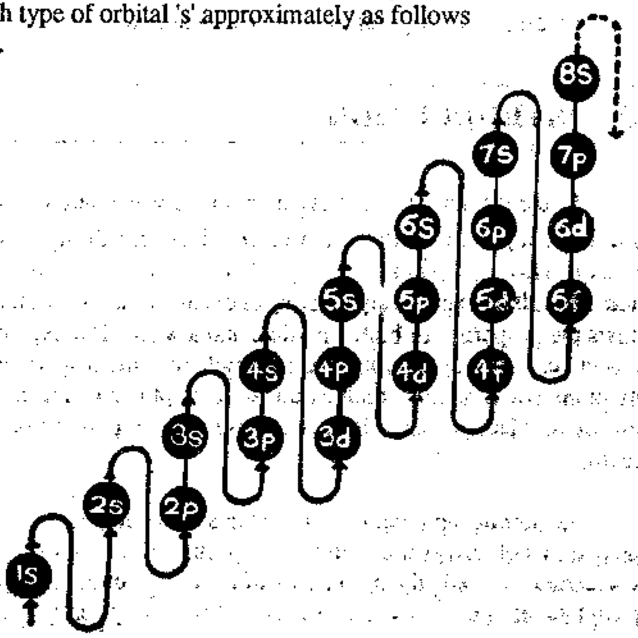


Fig 6.1. The schematic diagram showing the energy levels of atomic orbitals.

Check Your Progress - 2

Which orbital of 3d and 4s has higher energy.

6.3.1 Aufbau Principle

With the help of the energy level diagram it is possible to write the electronic configuration of elements. Certain guidelines have been worked out for this purpose, and these are very helpful to arrive at the configuration. These are (i) Atoms in the lowest energy state are said to be in the *Ground State* (ii) The building up of the electronic configuration of the elements begins by adding electrons to the appropriate orbitals, starting with the lowest energy atomic orbital (Fig. 6.1). This procedure is known as the "Aufbau" (building up) process.

6.3.2 Pauli's Exclusion Principle

Another important guideline is the one known as 'Pauli's exclusion principle', about which mention has already been made (Unit-4). According to this principle *no two electrons in the same atom can have all the four quantum numbers the same.* Each atomic orbital can accommodate a maximum of two electrons only. In terms of the exclusion principle, an orbital can have these electrons only if the two electrons have *Opposite spins.*

6.4 BUILDING UP OF ELECTRONIC CONFIGURATION

With these two guidelines, let us begin the process of deriving, the electronic configuration of a few atoms, starting with the hydrogen atom. The atomic orbital of lowest energy is the 1s orbital. As mentioned already, '1' refers to the principal quantum number, (n=1). The simplest of all atoms, the hydrogen atom (atomic number-1), has a nucleus which is simply a bare proton and an electron occupying the 1s orbital. Thus the configuration of the hydrogen would be $1s^1$.

$$H \rightarrow 1s_2$$

Next is the helium atom with atomic number, 2. The two electrons in the atom can both go into the 1s orbital, provided they have opposite spins. Therefore the configuration of the helium atom would be $1s^2$.

$$He \rightarrow 1s^2$$

The third element, lithium, has an atomic number 3. The 1s orbital can take in only two electrons. The third electron should, therefore, go into the orbital of next higher energy, ie., the 2s orbital. Accordingly, the configuration of lithium could be $1s^2\ 2s^1$. In a similar manner, the configuration of beryllium (atomic number, 4) can be writtenas $1s^2 2s^2$.

$$Li \rightarrow 1s^2 2s^1$$

$$Be \rightarrow 1s^2 2s^2$$

Now the 2s orbital is also filled. The orbitals of next higher energy are the 2p orbitals, of which there are three. These *three* orbitals are of the same energy. Orbitals of the same energy are said to be "degenerate". Since there are three such degenerate orbitals, the 'p' orbitals are said to possess a three-fold degeneracy. In the element Boron (atomic number, 5) the fifth electron would go into one of the 'p' orbitals. Hence its configuration would be $1s^2 2s^2 2p^1$

$$B \rightarrow 1s^2 2s^2 2p^1$$

In the next element *carbon* (atomic number,6), two possibilities can arise. The fifth and sixth electrons can go into the same 2p orbitals, such as $2p_x$, or they can go into separate (but degenerate) 2p orbitals, such as $2p_x$ and $2p_y$. According to Hund's rule, ***the number of unpaired electrons in a given energy level is maximum.*** In otherwords, whenever degenerate orbitals are available, electrons first go into totally vacant orbitals. Pairing up commences only after each of the degenerate orbitals is half-filled. This is because, as far as possible, negatively charged electrons tend to keep away from one another. Thus, in the ground state of carbon the two electrons in the p orbitals remain unpaired; they occupy separate p orbitals. They are said to have 'parellel spins' (electrons which are paired, and occupy the same orbital have 'antiparallel' spins). The configuration of carbon can, therefore, be written as $1s^2 2s^2 2p^1_x 2p^1_y$ (or $1s^2$ $2s^2$ $2p^2$, with the understanding that the 2p electrons are in separate 2p orbitals). Likewise, in nitrogen (atomic number, 7) the three 2p electrons are also unpaired. The configuration of nitrogen would be $1s^2 2s^2 2p^1_x 2p^1_y 2p^1_z$ (or $1s^2$ $2s^2$ $2p^3$).

$$C \rightarrow 1s^2 2s^2 2p^1_x 2p^1_y$$

$$N \rightarrow 1s^2 2s^2 2p^1_x 2p^1_y 2p^1_z$$

The next element Oxygen (atomic number 8) has eight electrons. The fifth, sixth and seventh electrons occupy separate 2p orbitals (Remember that all electrons are identical, numbering them is only a matter of convenience). The eighth electron would now pair up with one of the unpaired 2p electrons. The configuration of oxygen can be written as $1s^2\ 2s^2\ 2p^2_x\ 2p^1_y\ 2p^1_z$ (or $1s^2\ 2s^2\ 2p^4$). Following, similar procedure the configuration of the next two elements Fluorine (atomic number, 9) and Neon (atomic number, 10) can be written as follows

$$O \rightarrow 1s^2\ 2s^2\ 2p^2_x\ 2p^1_y\ 2p^1_z\ (1s^2\ 2s^2\ 2p^4)$$

$$F \rightarrow 1s^2\ 2s^2\ 2p^2_x\ 2p^2_y\ 2p^1_z\ (1s^2\ 2s^2\ 2p^5)$$

$$Ne \rightarrow 1s^2\ 2s^2\ 2p^2_x\ 2p^2_y\ 2p^2_z\ (1s^2\ 2s^2\ 2p^6)$$

In Neon, all orbitals corresponding to the principal quantum number 2 are completely filled. (just as in helium atom, the single 1s rbital corresponding to $n=1$ is completely filled). This makes the atoms remarkably stable, and correspondingly remain unreactive in relation to other elements. This would be true too of the other noble gas elements that follow.

Sodium (At. No. 11), the next element after neon, would have an electron in the 3s orbital. The configuration would be $1s^2\ 2s^2\ 2p^6\ 3s^1$. The configuration of the other elements follow in a natural way. The following table shows the electronic configurations of the first 20 elements, starting with hydrogen.

6.4.1 Electronic Configuration of elements with atomic numbers ranging from 1 to 20

At No.	Element	Configuration
1.	H	$1s^1$
2.	He	$1s^2$
3.	Li	$1s^2 2s^1$
4.	Be	$1s^2 2s^2$
5.	B	$1s^2 2s^2 2p^1$
6.	C	$1s^2 2s^2 2p^2$
7.	N	$1s^2 2s^2 2p^3$
8.	O	$1s^2 2s^2 2p^4$
9.	F	$1s^2 2s^2 2p^5$
10.	Ne	$1s^2 2s^2 2p^6$
11.	Na	$1s^2 2s^2 2p^6 3s^1$
12.	Mg	$1s^2 2s^2 2p^6 3s^2$
13.	Al	$1s^2 2s^2 2p^6 3s^2 3p^1$
14.	Si	$1s^2 2s^2 2p^6 3s^2 3p^2$
15.	P	$1s^2 2s^2 2p^6 3s^2 3p^3$
16.	S	$1s^2 2s^2 2p^6 3s^2 3p^4$
17.	Cl	$1s^2 2s^2 2p^6 3s^2 3p^5$
18.	Ar	$1s^2 2s^2 2p^6 3s^2 3p^6$
19.	K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
20.	Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

Note that in potassium (K) and calcium (Ca) it is the 4s orbital that takes in the electrons, but not the 3rd orbital. Calculations show that the 4s orbital is of a slightly lower energy than the 3d orbital.

With scandium (At No. 21), a new series of elements begins, in which the 3d orbitals get filled up. As there are five 'd' orbitals, there would be a total of 10 elements in which the 3d orbitals are occupied. These 10 elements are known as the 'transition elements' (or rather the first transition series of elements). They have properties characteristic of themselves.

The configuration of the transition elements, beginning with scandium (At No. 21) and ending with zinc (At. No. 30) is given below.

6.4.2 Electronic configuration of atoms with atomic numbers ranging from 21 to 30.

At no	Element	Configuration
21.	Sc	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$
22.	Ti	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$
23.	V	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$
24.	Cr	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$
25.	Mn	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$

26.	Fe	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6$
27.	Co	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^7$
28.	Ni	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^8$
29.	Cu	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$
30.	Zn	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}$

It should be noted that in the case of chromium (Cr) and copper, (Cu) one of the 4s electrons moves into the 3d orbitals. This happens because of the additional stability imparted when the 'd' orbitals are exactly half filled (i.e. contain 5 'd' electrons) or completely filled (i.e. contain 10 'd' electrons).

Following the general principles described above the electronic configuration of all the known elements have been derived. These configurations agree in most cases satisfactorily with the configurations arrived at experimentally from spectroscopic studies.

6.5 SUMMARY :

In this Unit we have studied about :

i) The orbitals having definite energies associated with them.

ii) The relative order of the energies for each type of orbital

iii) The Aufbau principle as the guidelines to be followed in filling up the atomic orbitals with electrons.

iv) The electronic configurations of the atoms.

6.6 MODEL EXAMINATION QUESTIONS:

I **Answer the following in 10 lines.**

1. Explain the meaning of 'Aufbau' Principle.

2. State and explain Pauli's exclusion principle.

3. State 'Hund's rule' and bring out its significance in arriving at electronic configuration of atoms.

4. Comment critically on the configuration of chromium and copper.

5. Write the electronic configurations of atoms with atomic numbers 2,10,18. What do these signify?

II. **Answer the following in 30 lines.**

1. Give a critical account of the nature and energies of the different atomic orbitals.

2. Discuss critically with illustrations the 'Aufbau' principle of atoms.

6.7 MODEL ANSWERS TO CHECK YOUR PROGRESS:

1 Number of electrons in an atom is inferred based on its atomic number. Atomic number of an atom is equal to the number of electrons that it contains. It is also equal to the number of protons present in it.

2 During the filling up of orbitals of an atom with electrons, energy of 4s orbital is less than the energy of 3d orbital. But once these orbitals get filled with electrons, energy of 4s orbital will be more than the energy of 3d orbital.

6.8 GLOSSARY

Angular momentum	:	Momentum associated with the rotation of a body. It is a vectorial quantity like linear momentum. For a body of mass 'm' moving with a linear velocity 'v' and having a position vector 'r' with respect to fixed coordinate origin the angular momentum is mvr.
amu (atomic mass unit)	:	Atomic mass unit is an arbitrarily defined unit in terms of which the mass of an individual atom is expressed. It is defined as 1/12 the mass of carbon atom with mass number 12. It is also known as Dalton.
Cathode rays	:	A stream of electrons emitted from the negatively charged electrode or cathode when an electric discharge takes place in a discharge tube.
Corpuscle	:	A minute particle. A particle of light in corpuscular theory of light.
Diffraction	:	The bending of light waves or other waves, into the region of the geometrical shadow of an obstacle.
Discharge tube	:	An evacuated enclosure containing a gas at low pressure through which current can flow when sufficient voltage is applied between metal electrodes in the tube.
Fluorescent screen	:	A screen coated with special chemical substance called fluorescent substance, enabling it to emit visible light when struck by high energy radiations such as γ-rays, X-rays or electron beams.
Hydrogen like atom	:	The ion having a single electron in the outer mostg orbit. It resembles hydrogen atom in structure. Li^+ and Be^{++} are examples.
Interference	:	The addition or combination of waves. If the crest of one wave meets the trough of another of equal amplitude, the wave is destroyed at that point; conversely, superposition of one crest upon another leads to an increased effect.
Pobability distribution function	:	A statical representation (through an expression or graph) of the chance of occurence of an event or a phenomenon. For example the chance of an electron being found in the space around nucleus in an atom is given by the atomic orbital or electron wave function.
Quantum	:	The smallest unit or the indivisible amount of energy. The quantum of light is referred to as Photon.
Spectrum	:	A series of radiant energies arranged in order of wavelength or frequency. Based on the frequency range or wavelength range, the electromagnetic spectrum is divided into radio frequency, infrared, visible, ultraviolet and X-ray regions.
α-rays	:	The positively charged rays emanating from a radioactive element. it consists of fast moving particles, with mass number 4 and charge +2 (helium nuclei)

Block - 2

CHEMICAL BOND

What are Molecules?

Atoms combine to form molecules both of elements and compounds. *Molecules are thus aggregate of atoms, held together in such a way that each molecule behaves as if it were a single entity.* We have molecules of varying complexity, starting with simple diatomic molecules like hydrogen (H_2), oxygen (O_2), chlorine (Cl_2), hydrogen chloride (HCl) etc., and ending with huge macro molecules comprising thousands and thousands of atoms (proteins). We have, ofcourse, the 'monoatomic' molecules of the noble gases - helium, neon, argon etc., which are, in effect, single atoms only. Each compound has distinct and characteristic properties, depending not only on the molecular composition of the compound, but also on the manner which the atoms are arranged.

The atoms in a molecule are held together by *forces* which constitute the *"Chemical Bond"*. A chemical reaction is a process in which one bonding arrangement is replaced by another. Atoms can combine with one another in a variety of ways to form, literally, thousands and thousands of compounds.

How do Atoms Combine?

Why and how do atoms combine to form chemical compounds? In the formation of chemical bonds, atoms follow the general pattern of behaviour of material systems, namely, one of acquiring a state of lowest energy which, in turn, is associated with a state of maximum stability. When a pair of atoms combine to form a bond, a certain amount of energy, characteristic of the bond formed, is *released*, and the chemical species so formed relatively much more stable than the component atoms. This same *amount* is to be *supplied* to break the particular bond. Formation and cleavage of chemical bonds and the energy changes accompanying these processes are matters of particular interest to chemists. The present discussion is, however, restricted only to qualitative aspects of bond formation.

The manner in which atoms combine and the type of bond that is formed depends on many factors. Among these factors are atomic size, nuclear charge and electron distribution around the nucleus. These factors evidently differ for atoms of different elements. Strictly, the bonding process is a very complex one. In the main, the atoms of one element differ from those of all other elements in the manner in which they combine with atoms of other elements. Quantitative treatment requires a mathematical background of a high order. But for a basic, qualitative understanding, of bonding, we use simplified concepts, which enable us to classify bonding processes into a few simple categories.

Types of Chemical Bonds

Chemical bonds can be devided into three distinct types - the *ionic bond*, the *covalent bond* and the *metallic bond*. But it should be emphasised that this classification is an arbitrary one, as no single bond can be said to belong exclusively to either one type or the other. This is more true of first two types of bonds, i.e., the ionic bond and the covalent bond. Yet the classification is extremely useful for a basic understanding of the manner of formation of the chemical bond.

UNIT - 7 THE IONIC BOND

Contents:

7.1 AIMS AND OBJECTIVES

This unit aims to describe formation of ionic bond and to explain the different shapes of compounds in the solid state (crystal) containing these ionic bonds. After completing this unit you will able to understand that

- Why do atoms combine to give molecules?
- How do atoms combine to form ionic compounds?
- The size of the atom is altered by the addition or removal of electrons.
- Oppositely charged ions are held by electrostatic forces in ionic compounds.
- The co-ordination number of ionic solids and the geometry of ionic crystal vary with the ratio of the ionic radii.
- Lattice energy of an ionic compound is the energy required to separate one mole of its ions by infinite distances.
- Born-Haber cycle relates lattice energy and other thermochemical quantities involved in the formation of an ionic compound.
- Lattice energy of ionic solids can be calculated using these thermo-chemical data with the help of Born-Haber cycle.

7.2 INTRODUCTION

The elements belonging to the 'Zero' group of the periodic table, the inert gases (also known as the noble gases) are noted for their extreme lack of chemical reactivity. These elements are helium, neon, argon, krypton and xenon. They do not normally show any tendency to react with other elements. Their molecules, as mentioned already, are monoatomic, that, they contain only one atom. From their lack of reactivity, we may conclude that these atoms are extremely stable.

An examination of the electronic configuration of the inert gases, reveals the fact that the atoms of these gases contain an arrangement of eight electrons in their outermost shell. (The exception, of course, is helium, which is having an atomic number 2, can have only one electronic shell that can accommodate a maximum of two electrons only). This fact, coupled with the lack of reactivity of these elements, led to conclusion that an arrangement of eight electrons in the outermost shell (and two in the case of helium) represents a very stable arrangement. Other elements react with one another to acquire this stable configuration of electron 'octet'. Though this view is no more entirely valid, it was the first meaningful attempt to explain bond formation.

7.3 FORMATION OF IONIC BOND

How do atoms attain the electron 'octet' in their outermost shells? One way of explaining it is as follows.

Consider, for instance, the sodium atom (atomic number 11) which has the electronic configuration $1s^2 2s^2 2p^6 3s^1$. The first and second shells are full, but the third shell has only one electron. When sodium reacts with other atoms it would do so in such a way as to lose the single outermost electron and acquire a configuration resembling the nearest inert gas atom, *neon*, which has the configuration $1s^2 2s^2 2p^6$. As a result a sodium ion, Na^+, is formed, having a net charge of +1.

$$Na \rightarrow Na^+ + e^-$$

Now let us consider the chlorine atom (atomic number 17). It has the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^5$. Its outermost shell is short of one electron for the octet. If the chlorine atom were to gain an electron, the octer would be complete, and the chloride ion, Cl^-, would have the configuration resembling that of *argon*, the inert gas nearest to chlorine in the periodic table. The chloride ion has a net charge of -1.

$$Cl + e^- \rightarrow Cl^-$$

When sodium and chlorine react with each other, the single outermost electron of the sodium atom is transferred to chlorine atom and the sodium ion Na^+ and the chloride ion, Cl^-, are produced. These two oppositely charged ions attract each other and are held together. Since both sodium and chlorine atoms acquire a stable inert gas configuration, such a process would tend to take place readily and sodium chloride, $Na^+ Cl^-$, is formed. Showing only the outermost (the valence) electrons, the process can be indicated as follows.

$$Na + Cl \rightarrow Na^+ \; Cl^-$$

The bond formed thus, as a result of the electrostatic attraction between two oppositely charged ions, is called "Ionic Bond", (also known orginally as electrovalent bond).

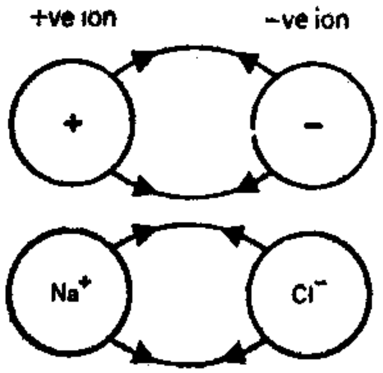
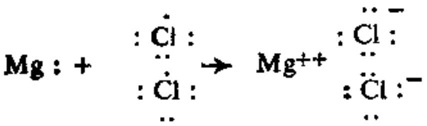


Fig. 7.1 Electrostatic attraction.

Let us consider another example, - the formation of magnesium chloride. magnesium has the configuration $1s^2 2s^2 2p^6 3s^2$, with two more electrons than the nearest gas *neon*. By losing these two electrons magnesium is changed to magnesium ion, Mg^{++}.

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

If these two electrons are transferred to two chlorine atoms, one to each, magnesium chloride can be formed.



$$Mg : + \begin{array}{c} :\dot{Cl}: \\ :\ddot{Cl}: \end{array} \rightarrow Mg^{++} \begin{array}{c} :\ddot{Cl}:^- \\ :\ddot{Cl}:^- \end{array}$$

Thus ionic bonds are formed as a result of electron transfer from one atom to another. The atom losing the electron(s) is called **electron donor** and the atom gaining them is called **electron acceptor.** Justify what sort of atoms can form ionic bonds? The elements immediately preceeding the inert gases in the periodic table are the halogens (group VII). These are highly 'electronegative', i.e., they have a tendency to gain electrons rather readily. The elements immediately following the inert gases are the alkali metals (group I) and the alkaline earth metals (group II). The atoms of these elements have a tendency to lose electrons rather readily and are thus called "electro positive". Ionic bonds are formed when electropositive elements react with electronegative elements. Besides the halogen's oxygen, sulphur, and nitrogen are highly electronegative. The halogen compounds of the alkali and alkaline earth metals are predominantly ionic in character.

7.4 IONIC RADIUS

The size of an atom is altered by the addition or removal of electrons. During these changes the nuclear charge, however, remains unchanged. Hence, the change in the size resulting from the conversion of an atom to an ion is attributable to the number of electrons added or removed. When as atom loses an electron, a positive ion is formed. Now the positive charge of the nucleus is one unit more than the electronic charge around it. As a result, the remaining electrons are pulled inwards by the excess nuclear charge-owing to the greater attraction exerted by it. Hence, the positive ion becomes smaller in size than the neutral atom. Removal of a second electron would be even more difficult, as the second electron would have pulled out against the attraction of excess positive charge in the nucleus. And a doubly charged cation would be smaller even than a single charged ion. The opposite would occur when a neutral atom is converted to a negative ion by the addition of one or more electrons. The electrostatic force exerted by the nucleus is now distributed over a larger number of electrons than in the neutral atom. Therefore, there is an expansion of volume to accommodate the extra electrons added.

Two oppositely charged ions approach each other as a result of the electrostatic attraction between them. But as they come closer and closer, the electrostatic attraction is countered by repulsive force. At some point these two forces just balance each other. This distance is called the "Interionic distance", i.e., the distance between the nuclei of the two oppositely charged particles.

The 'radius' of a given ion is not constant but varies with the number of ions of opposite charge around it. By methods of X-ray analysis the distance between the centres of the two oppositely charged ions can be estimated. In crystals ions are so packed that we can assume that they are more or less spheres of characteristic size. Hence we can assign "ionic radius" values of these ions. But it should be noted that these ionic radii in a crystal. Thus the ionic radii of two oppositely charged ions are such that the sum of these two radii is equal to the distance between two adjacent ions in contact with one another in the crystal.

X-ray measurements provide a method for finding the distance between two adjacent ions, as for example, the distance between sodium ions and chloride ions in sodium chloride. But it is not possible to determine from this, to say, what part of this distance is to be considered as the ionic radius of sodium, and what part of this is the chloride ion. However, as a rule, positive ions are much smaller in size compared to negative ions that surround them. Thus a small central cation may be considered as being surrounded by four large anions, as indicated in Fig. 7.2.

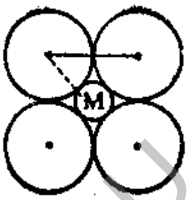


Fig. 7.2 Packing of anions and cation

Assuming that the anions are in contact with one another, it can be seen that the radius of the anion is half the distance between the two anions. The radius of the cation is then obtained by substracting the radius of the cation from the distance between the cation and anion. By this and other methods, the radii of many ions have been estimated. The radii of some ions with the inert gas configurations are mentioned below.

7.4.1 Ionic radii of some atoms

Cation	*Radius (A)°*	*Anion*	*Radius (A)°*
Li$^+$	0.61	H$^-$	1.54
Na$^+$	0.94	F$^-$	1.36
K$^+$	1.33	Cl$^-$	1.81
Mg^{++}	0.65	Br$^-$	1.95
Ca	0.99	I$^-$	2.16
Ba^{++}	1.35	O^{--}	1.40
Al^{+++}	0.50	S^{--}	1.84

It should be noted that many cations, especially those with high positive charges do not exist as simple ions. Because of their relatively small size, they are invariably associated with water molecules in aqueous solution, owing to the interaction between the cation and the dipole (water). This interaction produces the phenomenon of "hydration". Cations are invariably hydrated. In principle anions also could be hydrated, but because of their larger size, they are hydrated, if at all, to an extremely small extent or none at all.

Check Your Progress - 1

How ion size is related to its charge?

7.4.2 Ionic Radius and Crystal Structure

In an ionic soild, positive ions are surrounded by negative ions and vice versa. Most inorganic crystals are exceedingly ionic in character. The sizes of the component ions are the important factors in determining the structure of crystals. In an ionic crystal each ion tends to surround itself with as many ions of possible charges as possible. The number of nearest possible neighbours (i.e., ions of opposite charge) is known as the *co-ordination number* of a given ion. The co-ordination number is mainly dependent on the radii of the ions as well as the radius ratio of the two ions.

Considering ions to be rigid spheres it is possible to determine the structure of an ionic crystal formed by two different ions. Mathematical calculations show that when the cation radius to anion radius, r_c/r_a is greater than 0.15, three anions would be in contact with a central cation.

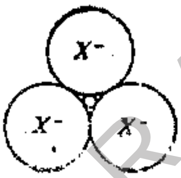


Fig. 7.3 Packing of ions when the ionic ratio is 0.15

The coordination number of the cation is 3

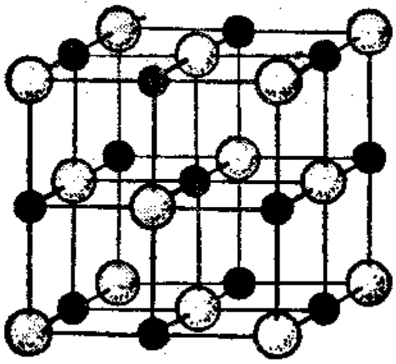
The following table gives the co-ordination number and the geometry of an ionic crystal from a knowledge of the r_c/r_a ratio.

Table 7.4.3 Ionic radius ratio r_c/r_a and crystal shape

Ratio	*Co-ordination number*	*Shape*
0.155	3	Planar traingle
0.225	4	Tetrahedral
0.414	4	Square planar
0.414	6	Octahedral
0.732	8	Body-centred cubic

Ionic compounds are divided into three main groups AX$_1$ > AX$_2$ and AX$_3$ depending on the relative numbers of positive and negative ions. It is not possible here to present a detailed description of all the three groups. We shall discuss briefly the first group of crystal structure, namely the AX group.

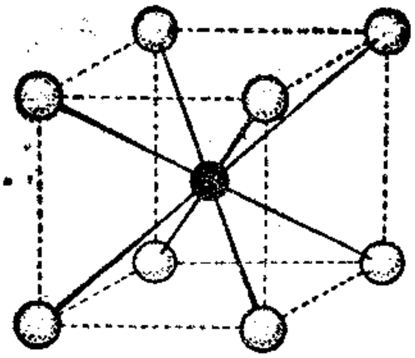
Three different crystal structures are possible for the AX group of ionic compounds. Each structural arrangement is named after the most familiar formula AX and having the cesium chloride (CsCl) structure and the four fold coordination is known as the zinc sulphide (ZnS) structure. The CsCl structure and the NaCl structure and the mosst common. In the crystal of NaCl, a sodium ion is surrounded by six chloride ions arranged in an octahedron. Like-wise, a chloride is surrounded by sodium ions. The arrangement of the ions in sodium chloride (crystal pattern) is shown below.



NaCl

Fig. 7.4 Arrangement of ions in a sodium chloride crystal

The compactness of any crystal structure depends greatly on the effective radii of the ions present. At the same time; ions of the same type are kept separated to the extent possible by interspersing ions of opposite charge. Thus, in the crystal pattern of sodium chloride the sodium ions are found to be located at the corners of a cube, while another sodium ion is located at the centre of each face. Such a crystal pattern is known as *face-centred cubic lattice*. In cesium chloride a different type of packing is to be found. This is because the ionic radius ratio (0.93) in CsCl is different from that in NaCl (0.53). Around each ion of a particular sign, eight ions of opposite sign are arranged. This produces an arrangement known as body-centred cubic lattice. The arrangement is shown in figure 7.5.



CsCl

Fig. 7.5 Arrangement of ions in a cesium chloride crystal

What we have discussed is only a very simplified and also a very small part of the structure of ionic crystals. There are many other types of crystals. Actually there are seven different crystal systems.

7.5 LATTICE ENERGY

The crystal or lattice energy of an ionic compound is the energy required to separate one formula weight (mole) or its ions by infinite distances. It is also the *energy released when the crystal (MX) lattice of ionic compound is formed from free gaseous cations and anions* (of the compound) *separated from each other by infinite distances.*

Direct determination of lattice energy has been possible in the case of only a few compounds. An indirect method, which relates the lattice energy to other thermochemical quantities, has been devised, and is known-the *Born-Haber Cycle*. In cases where the energy of formation of a crystalline compound (ionic) from its constitutent elements is available, it may be considered as the sum of the energies of the various intermediate steps involved in the formation of the compound. From such knowledge it is possible to calculate theoretically the lattice energy of a crystal.

7.5.1 Born Haber Cycle

The formation of sodium chloride from sodium and chlorine may be taken as an example to illustrate the principle of Born-Haber Cycle. The various steps, and the energy changes involved, may be indicated as follows.

(i) Sublimation of sodium metal
$Na (s) \rightarrow Na)g)$; sublimation energy, $S = 26.0$ K.Cals/mole

ii) Dissociation of molecular chlorine into atoms
$Cl_2 (g) \rightarrow 1/2\ Cl_2 (g)$; Dissociation energy, $1/2\ D. = 28.6$ K.Cals/mole

(iii) Ionization of sodium atom
$Na (g) \rightarrow Na^+ (g) + e^-$; ionization energy; $I = 118.0$ K.Cals/mole

(iv) Electron affinity (E) of chlorine atom,
$Cl (g) + e^- \rightarrow Cl^- (g)$; $E = -86.5$ K.Cals/mole.

(v) Lattice energy (U) of sodium chloride
$Na^+ (g) + Cl^- (g) \rightarrow Na^+Cl^- (s) - U$

(vi) The heat of formation (ΔH) of sodium chloride from its constituent atoms;
$Na(s) + 1/2\ Cl_2 (g) \rightarrow Na^+ Cl^- (s)\ \ \Delta H = 98.2$ K.Cals/mole

This last head quantity, ΔH is the algebraic sum of the first five.
$- \Delta H = S + 1/2\ D + 1 - E - U$

From this, the lattice energy, U, can be obtained as:
$U = S + 1/2\ D + L - E + \Delta H = 184.3$ K.Cals/mole

The Born-Haber Cycle for ionic soild (MX) can be diagrammatically indicated as shown in Fig. 7.6

$$\begin{tikzcd}
MX(s) & & M^+ (g) + X^- (g) \arrow[ll, "U^0 (-)"'] \\
M (s) + 1/2X_2(g) \arrow[u, "\Delta Hf (-)"] \arrow[rr, "S + 1/2D"] & & M(g) + X(g) \arrow[u, "I + E (-)"']
\end{tikzcd}$$

Fig 7.6 Born-Haber cycle

Check Your Progress - 2

Mention the different steps in Born-Haber cycle.

7.6 PROPERTIES OF IONIC COMPOUNDS

In Ionic solids the component ions, are held together by strong electrostatic forces. It would need relatively large quantities of energy to tear these ions apart. Consequently ionic compounds have fairly high melting points and boiling points. Ionic solids are hard and brittle and cleared only along certain planes. They do not conduct electricity in the solid state, but when melted or dissolved in solvents like water, they conduct electricity. This is because in the solid the ions are held rigidly in their equilibrium positions, while in the molten state or in aqueous solution the crystal lattice breaks down and the ions are free to move about. Thus when a potential is applied, they conduct electricity.

As a rule ionic compounds are soluble in polar solvents (eg., water) and are insoluble in non polar solvents (eg., carbon tetrachloride).

7.7 SUMMARY

In this unit we have studied about

i) The formation of molecules by the combination of atoms

ii) The manner in which atoms combine and the type of bond formed.

iii) The formation of an ionic bond as a result of electron (s) transfer from one atom to another.

iv) Radius ratio of ions and the crystal shape

v) The face centred cubic lattice (Na Cl) and body centred cubic lattice (Cs Cl).

vi) The lattice energy which is the energy released when the crystal lattice in ionic compound is formed from its component ions in the gaseous state.

vii) Born-Haber cycle which is a thermodynamic cycle of energy changes relating to sublimation, dissociation, ionisation, electron affinity, lattice energy and the heat of formation.

viii) The properties of ionic compounds.

7.8. MODEL EXAMINATION QUESTIONS:

I. Answer the following in 10 lines each.

1 Explain the formation of ionic bond in terms of electron octet.

2 Describe briefly the packing of ions in crystal.

3 Write a concise account of Born-Haber cycle.

4 How are ionic radii determined?

II. Answer the following in 30 lines each.

1 Write critically about the nature and formation of ionic bond.

2 Discuss Born-Haber cycle and describe its use in the elucidation of lattice energy.

3 Explain clearly the change in the shape of crystal with the change in the ratio of the radii of the ions in the crystal.

7.9 MODEL ANSWERS TO CHECK YOUR PROGRESS

1 An atom and its ions possess the same number of protons but they differ in the number of electrons. More are the number of electrons in such a species bigger will be its size. Therefore a negative ion is bigger than its atom, which in turn is bigger than its positive ion.

2 These steps are -

a) Sublimation of electropositive element.

b) Ionisation.

c) Dissociation of electronegative element.

d) Electron affinity.

e) Lattice energy of the ionic bond.

f) Heat of formation of the ionic bond.

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UNIT - 8 : THE COVALENT BOND

Contents :

8.1 AIMS AND OBJECTIVES

The purpose of this unit is to describe you in brief the mode of formation, the nature of covalent bond and the shapes of molecules.

- By the end of this unit you should be able to understand that
- The bond formed by mutual sharing of two electrons between two combining atoms is known as covalent bond.
- Homo-atomic molecules such as H_2, Cl_2, N_2 and heteroatomic molecules such as HCl, H_2O, NH_3 are some examples of molecules containing covalent bonds.
- It is possible that both the electrons responsible for the covalent bond formation are donated by one atom and accepted by the other atom is called co-ordinate covalent bond or simply co-ordinate bond.
- Basing on the type of overlap (end to end or lateral), the covalent bond formed is termed sigma (σ) or pi (π) bond.
- The extent of overlap can be taken as a measure of the strength of bond formed, σ bond involving greater overlap is a stronger bond than π bond involving lesser overlap.
- The average distance between the nuclei of the two bonding atoms is known as the *bond length or bond distance.*
- The angle of intersection between the lines drawn through the nucleus of an atom to the nuclei of atoms bonded to it is called bond angle.

PREFACE

This course deals with the topics in **Theoretical Chemistry** and **Physical Chemistry** include in the syllabus for the Second year of the B.Sc. course offered by the Andhra Pradesh Open University. These topics cover the 'core area' of Chemistry to be studied in the Second Year of the **Three Year Degree Course in Science.** The syllabus is for the sake of convenience divided into Blocks, each of which comprises a number of Units. Each Block generally covers a specific area of the subject. The Units are prepared by specialists in accordance with a format so designed as to enable the student read and understand them without much difficulty. Each Unit begins with a statement of its aims and objectives and has at its end Model examination questions intended to test the student's comprehension of its subject matter. Generally technical terms with which the student may not be familiar are given at the end of each Block under the head, **Glossary** if necessary.

In the first section of the course dealing with Theoretical Chemistry, it is attempted to explain the basic theoretical principles underlying atomic structure, chemical bond and molecular structure. It is hoped that this section will help the student to acquire the necessary theoretical knowledge to understand the properties and behaviour of matter.

In the other section of the course, dealing with Physical Chemistry, efforts are made to describe the behaviour of matter in its gaseous and solution states. One of the objectives of physical chemistry is to be able to apply measurements of physical properties to the elucidation of molecular structure. Hence this aspect has been stressed to the extent required.

The University hopes that this course material will help the student to get acquainted with the concepts and principles of chemistry in general and of Theoretical Chemistry and Physical Chemistry in particular.

UNIT - 3 : ATOMIC SPECTRA

Contents

3.1 AIMS AND OBJECTIVES

To make you understand the behaviour of atoms in normal atom and excited states, the process of arriving at it by Bohr. After completing this unit you will be able to understand:

- Origin and types of optical spectra
- Study of hydrogen spectrum
- Bohrs nuclear model of atom
- Quantization of energy of electrons in atoms
- Introduction of principal quantum number
- Explanation of hydrogen spectrum

3.2 INTRODUCTION

You are familiar with day light coming from the Sun as soon as there is day break. You are also equally aware of the light from an electric bulb in the nights. This light is bright and white. But this white light in reality is not a single coloured light. It is made up of seven colours. These colours are the so called rainbow colours (violet, indigo, blue, green, yellow, orange, and red). If you paint cardboard disc with these seven colours in the order mentioned and rotate the disc vigorously, you observe that these seven colours merge into one single colour namely white. In a similar way on a cloudy day, you observe on the sky that sun's light is split into these seven colours and the array of these colours observed in the sky is called rainbow. You are also familiar with the fact that a beam of light is bent (refracted) while passing through a glass prism. But the extent of this bending varies with the colour of the light beam. So when a beam of white light (a mixture of seven colours) from an electric bulb is passed through a glass prism the constituent coloured rays are bent through different angles resulting in the formation of an array of colours similar to a rainbow. This phenomenon is illustrated in figure 3.1 and is called dispersion of light. The resulting array of colours seen on a screen is called the spectrum.

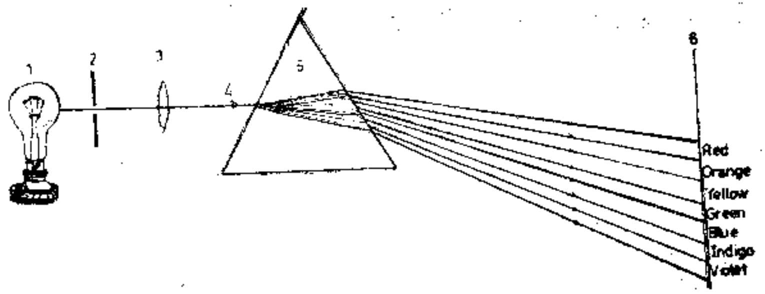


Fig. 3.1 Spectrum of white light

1. Filament lamp 2. Slit 3 . Lens 4. White light beam 5. Glass Prism 6. Screen

Each colour corresponds to a light radiation or a band of radiations with specific characteristics. The array of colours can be caught on a white screen or recorded on a photographic film. All the seven colours in the form of bands can be seen when the white light coming from the sun or emitted by an electric bulb (filament lamp) is passed through the glass prism. There are no gaps in between the colour bands and the bands are continuous. Such a spectrum is called continuous

3.3 LINE SPECTRA

In the experiment discribed in 3.1 the source of light is a tungsten filament electric bulb and the filament is made incandescent at high temperatures. Similar to incandescent tungsten filament many metals or their compounds emit light when they are made incandescent by raising their temperature to high values. For example we can introduce sodium chloride into a bunsen flame and raise its temperature to high values. The salt at this high temperature imparts a bright yellow colour is characteristic of the light emitted by sodium chloride when raised to high temperatures. The yellow light when passed through a glass prism is split into two distinct yellow lines separated by a dark space (Fig. 3.1). This system of two distinct yellow lines separated by dark space is due to the light emitted by sodium at high temperatures and is called sodium spectrum. Such a spectrum consisting of distinct lines separated by dark spaces (or gaps) is called a line spectrum. Each line has specific characteristics. Note the difference between this spectrum and the spectrum obtained from sun rays (solar spectrum) mentioned above in figure 3.1. The latter contains continuous bands in contrast to the distinct lines in the former.

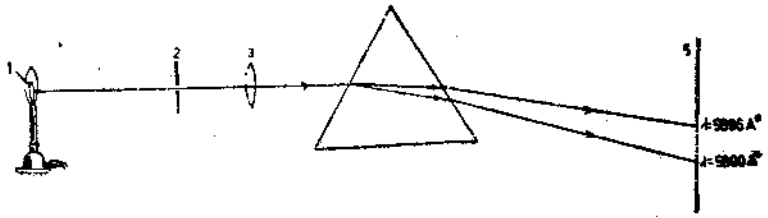


Fig. 3.2 Line Spectrum of sodium atom

1. Bunsen Flame containing NaCl 2. Slit 3. Lens 4. Glass prism 5. Screen

- The enthalpy change that takes place when a molecule in gaseous state dissociates into atoms along a bond is called bond dissociation energy of that bond.
- Bond energy is an average of bond dissociation energies of all similar bonds in the molecule.
- Hybrid orbitals are formed by the combination of two or more atomic orbitals of similar energy.

8.2 INTRODUCTION

In ionic compounds the bond between two combining atoms is formed as a result of transfer of electrons from one atom to another. Consequently, we have two ions of opposite charges and the two are then held together by electrostatic attraction. It has already been pointed out that the elements of the first and second groups of the periodic table, namely, the alkali and alkaline earth metals are electropositive and can readily form positive ions. The halogens, on the other hand, are electronegative and form negative ions by gaining electrons. So do, oxygen and sulphur.

As we move to the centre of the periodic table, we find that it becomes increasingly difficult for atoms to be converted to trivalent ions, whether positive or negative. For cations, extremely large amounts of energy will be required to remove the third and subsequent electrons. Likewise to add a third or fourth extra-electron to an atom will be more or less impossiblé, as this would imply adding these electrons against the extreme repulsion of the already existing excess negative charge. Another aspect is that when two electronegative atoms react, ionic bonds cannot be formed as both the atoms have a tendency to gain electrons.

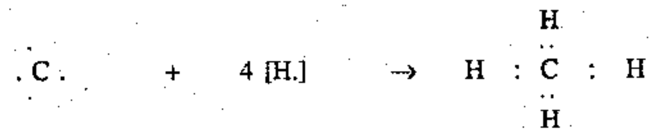
8.3 COVALENT BOND FORMATION

How then does bonding occur in the instances mentioned above? In these and similar cases, inert gas configuration may be attained by sharing electrons. Let us consider the formation of the chlorine molecule, Cl_2, from a reaction between to chlorine atoms. Showing only the electrons in the outermost shells, the reaciton may be visualized as follows.

$$:\underset{\cdot}{\ddot{Cl}}\,\cdot \quad + \quad \cdot\,\underset{\cdot\cdot}{\ddot{Cl}}\,: \quad \rightarrow \quad :\underset{\cdot\cdot}{\ddot{Cl}}\,:\,\underset{\cdot\cdot}{\ddot{Cl}}\,:$$

Each chlorine atom has seven electrons in its outermost shell. Each atom can acquire the electron octet by sharing an electron with the other.

The formation of a more complex molecule like methane can be visualised as follows



$$\cdot\underset{\cdot}{\dot{C}}\cdot \quad + \quad 4\,[H.] \quad \rightarrow \quad H : \overset{\displaystyle H}{\underset{\displaystyle H}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}}}} : H$$

The carbon atom has four electrons in its outermost shell, and is thus four short of the octet. On the other hand each of the hydrogen atoms has only one electron in its shell and is one short of the electron 'duplet' (resembling the configuration of the nearest inert gas, helium, which can have a maximum of two electrons in its shell). Thus, if each of the four hydrogen atoms shares its one electron with the carbon atom, each would acquire the duplet, and the carbon would, in turn, acquire the octet. Thus a stable molecule can be formed.

A bond formed by mutual sharing of electrons between two combining atoms (each atom contributing one electron) is known as a covalent bond. It was also called by G.N. Lewis as electron-pair bond. Most organic compounds, and quite a few inorganic compounds are covalent in character.

electrons of the combining atoms are no more associated with their original nuclei. Instead there is an equal chance of each electron being associated with either atom. In turn, each nucleus may be associated with the two electrons.

In addition to these factors, Pauli's exclusion principle also will be operative. The formation of a stable covalent bond will be favoured only if the two electrons involved in the bonding process have opposite spins.

8.5.1 Overlap of Orbitals

A crude representation would be to describe the bonding process in terms of the *'overlap' of the atomic orbitals.* In the two separated hydrogen atoms, the respective electrons will be in the 1s atomic orbitals. When the two hydrogen atoms approach each other, the two 1s atomic orbitals, having electrons with opposite spins, will tend to overlap and form the bond. The greater the overlap the stronger is the bond. The overlap of the atomic orbitals would lead to a lowering of the energy of the system. The overlap would be greatest at the optimum internuclear distance, and the molecule would be most stable under these conditions. If the two electrons possess the same spin, the energy of the system would be far greater than the sum of the separate atoms. When such atoms approach one another, there will be considerable repulsion which prevents the formation of a stable bond.

When the two atoms approach each other there will be an increase in the electronic charge density when the overlapping of the atomic orbitals (containing electrons with opposite spins) takes place. The charge density will be maximum at the point midway between the two nuclei. Thus has the effect of reducing the repulsion between the nuclei as well as producing an attraction of the nuclei for the accumulated charge between them. Both these conditions favour the formation of a stable bond. What we have attempted is a qualitative description of a theory which is basically mathematical in concept and treatment. Nevertheless even this description provides a sufficient understanding of the formation of the covalent bond.

An important point needs to be mentioned. In order to produce effective overlap, the atomic orbitals involved should have more or less the same energy. Of course, in the case of the hydrogen molecules, the two atomic orbitals of both hydrogen atoms are identical in all respects, including energy. So the formation of bond is easy. On the other hand, if we consider the formation of a molecule from two different atoms. The same type may not be used. For example, in the case of the HCl molecule, the 1s orbital of the chlorine atom has much smaller energy than 1s orbital of the hydrogen atom. In fact, it is found that the 2s, 2p or even the 3s orbitals are ruled out, as their energies are far too low. The 3p orbitals are of comparable energy. Hence we can postulate the combination of the 1s atomic orbital of hydrogen with one of the three 3p orbitals of chlorine. Considering the electronic configuration of the chlorine atom, viz., $1s^2$, $2s^2$,$2p^6$, $3s^2$, $3p^6$, $3p^2_x$, $3p^2_y$, $3p^1_z$.

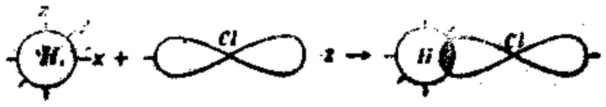


Fig. 8.1 Formation of HCl

We can visualise the overlap of the hydrogen '1s' atomic orbital with one of the 3p orbitals of chlorine; in this case we may choose the $3p_z$ orbital, as it contains one electron only. The overlap will be maximum if it takes place among the internucleus axis.

8.5.2 Sigma σ and Pi π bonds

A bond thus formed, by the end to end overlap of atomic orbitals is known as a " σ bond. This happens when two 3p orbitals of the chlorine atoms (one from each) overlap end on to end on, as follows

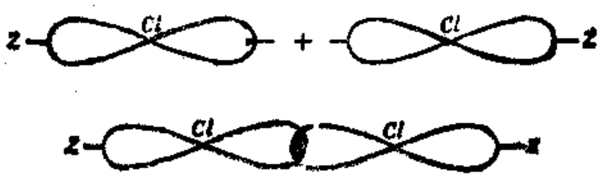


Fig. 8.2 Formation of σ bond

Under certain conditions, two 'p' orbitals may overlap laterally as follows

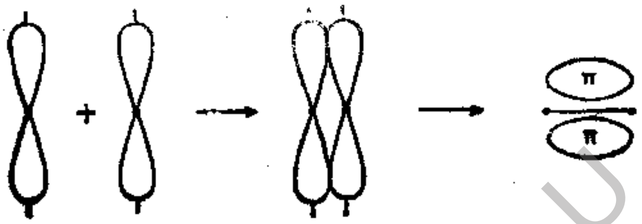


Fig. 8.3 Formation of π bond

This lateral overlap leads to a comparatively weaker interaction and the bond so formed is correspondingly weaker than a σ bond. Such a bond formed by the lateral overlap of 'p' orbitals known as a 'π' (pi) bond.

In many compounds more than one bond can be formed between two atoms. These are known as 'multiple' bonds. In a multiple bond one is σ bond and the rest π bonds. A π bond cannot be formed before a σ bond. It is always formed only after a σ bond is first formed.

8.6 BOND LENGTHS

We have already discussed that two atoms can form a stable bond when their nuclei are at certain optimum distance from each other under the given conditions, such that their energy is minimised and stability maximised. *This well defined average distance between the nuclei of the two bonding atoms is known as the* **bond length** or **bond distance.** On the other hand, it has to be noted that the atoms in a molecule are not static. They are always vibrating with respect to one another, about their mean positions. As such it is rather difficult to talk of a single fixed distance between any two atoms. Within this limitation, however, bond lengths can and have been determined and found to be reasonably constant for a bond between two specific atoms. Most bond distances have been obtained from X-ray data and molecular spectra. Experiments show that, by and large, bond lengths are independent of the molecule in which the particular bond occurs. From this it may be concluded that bond lengths (and, as indeed other properties of a bond) are largely determined by the nature of the bonding atoms. Table 8.6. gives some data for bond lengths in a few diatomic molecules.

Check Your Progress - 2

Explain the terms "bond length", bond angle, and 'bond energy'.

8.9 HYBRID ORBITALS

In many molecules the shape of the molecule and strength of the bonds could not be correctly predicted from the nature of the pure atomic orbitals involved in the bond formation. For example, oxygen forms with hydrogen, water molecule in which one oxygen atom combines with two hydrogen atoms. The electronic configuration of oxygen is $1s^2$, $2s^2$, $2p^2x$, $2p^1y$, $2p^1z$. From this configuration it has to be inferred that the two 'p' orbitals (p_y, p_z) containing the unpaired electrons overlap with the 1s orbitals of the two hydrogen atoms. If this were to be true the bond angle in water is expected to be 90^0 since the two p-orbitlals are perpendicular to each other. However the measured angle is about 105^0. In a similar way carbon with electronic configuration $1s^2$, $2s^2$, $2p^2x$, $2p^1y$, $2p^0z$, combines with four hydrogen atoms to give methane (CH_4). Since there are only two p -orbitals containing unpaired electrons carbon is expected to combine with only two hydrogen atoms. So to account for its ability to combine with four hydrogens, it is therefore to be assumed that the two electrons in 2s orbital get unpaired and one of these will be promoted to empty p_z orbital before carbon combines with four hydrogen atoms. In such an event, the four bonds formed are not expected to have the same strength since one bond is formed by the overlap of 1s orbital of hydrogen ion 2s orbital of carbon, while the other three hydrogen atoms with the three p orbitals of carbon. But in methane all the four bonds are of equal strength. Therefore to account for correct bond strengths in the molecule and the shape of the molecule a process of combination of atomic orbitals of different symmetries is envisaged before they take part in the bond formation. This process is called *hybridization*. It must be noted that it is a valuable concept in predicting and describing the shape of a molecule.

The combination may take place between two or three types of atomic orbitals and the number of orbitals involved can vary from two to seven. However, the number of hybridized orbitals is always equal to the number of atomic orbitals involved in the combination of hybridization. The type of hybridization is named after the symmetry or spacial distribution of the hybridized orbitals formed. It is also named on the basis of the type of atomic orbitals involved in the hybridization.

The number of outer atomic orbitals and commonly occuring shapes and types of hybridization are summarized in table 8.9.1

Table 8.9.1 Shapes and Types of Hybridization

Number of atomic orbitals	Shapes (symmetry)	Hybridization (type of atomic orbitals)
2	Linear	Sp
3	Plane triangle	Sp^2
4	Tetrahedron	Sp^3
4	Square planar	$d\ sp^2$
5	Trigonal bipyramid	$Sp^3\ d$
6	Octahedron	$Sp^3\ d^2$
7	Pentagonal bipyramid	$Sp^3\ d^3$

The shapes of water molecule, ammonia molecule and methane molecule are predicted from the nature of hybridized orbitals, involved in the bond formation as angular, pryramidal, and tetrahedral. The shapes are illustrated in figure 8.5.

Long shaded portion indicates lone pair, (hybridization is tetrahedral)

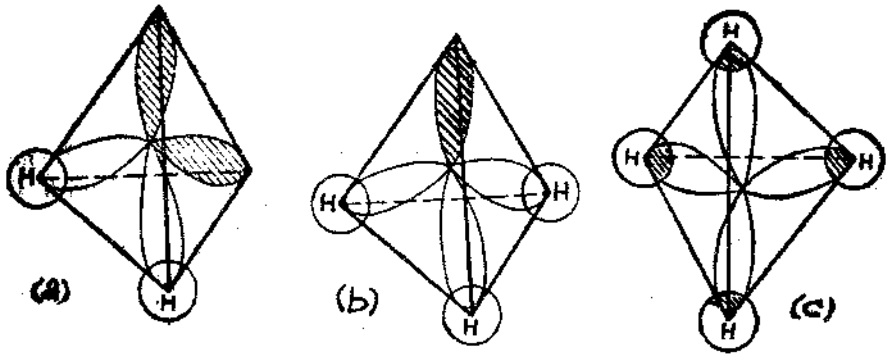
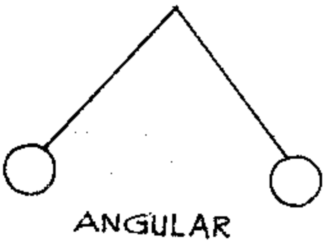
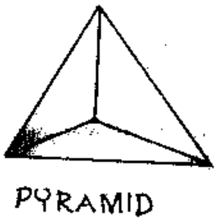


Fig. 8.5 Shapes of a) H_2O, b) NH_3, and c) CH_4 molecules.





The discussion prescribed in this section thus clearly signifies the importance of the hybrid orbitals in the formationof covalent molecules.

8.10 SUMMARY

In this unit we have studied about

i) The bond formed by mutual sharing of a pair of electrons between two combining atoms (covalent bond).

ii) Some specific examples of molecules having covalent bonds H_2, Cl_2, N_2, HCl, H_2O, NH_3, CH_4 etc.

iii) Homoatomic and heteroatomic molecules.

iv) A special case of a covalent bond where in the shared electron pair is contributed by one species (coordinate covalent bond).

v) The two basic approaches to the study of chemical bonding valence bond theory and the molecular orbital theory.

vi) The valence bond theory which supposes that the combining atoms largely maintain their identity and the bond arises due to interaction of the valence electrons of the combining atoms.

vii) The valene bond theory describes the bonding process in terms of the overlap of atomic orbitals.

viii) The bond formed by the end to end overlap of atomic orbitals; bond formed by lateral overlap of atomic orbitals.

ix) The average distance between the nuclei of the two bonding atoms being termed as bond length.

x) Bond angle and bond energy and the other important characteristics of a bond.

xi) The concept of hybridisation which is valuable in predictions and determining the shape of a molecule.

8.12 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines each.

1. Describe briefly the mode of formation of the chemical bonds in H_2, HCl, NH_3 and NH_4^+.

2. Illustrate the formation of σ and π bonds.

3. Give the shapes of Sp^3, Sp^3d^2 and Sp^3d^3 hybrid orbitals.

4. Distinguish clearly between bond dissociation energy and bond energy.

II. Answer the following in 30 lines each.

1. Discuss critically the formation of covalent bond.

2. Write a concise account of valence bond theory of covalent bond.

3. Discuss the concept of hybrid orbitals and their need to explain the shapes of molecules.

8.12 MODEL ANSWERS TO CHECK YOUR PROGRESS

1 They differ in their formation. Electron transfer between atoms results in ionic bond. Electron sharing results in covalent bond. Ionic bonding is non-directional whereas covalent bond is directional.

2 Bond Length :- Equilbrium distance between the centres of the nuclei of bonded atoms is bond length.

Bond angle :- The angle made at the junction of two covalent bonds is bond angle.

Bond energy :- It is the average of the bond dissociation energies of identical bonds of a substance.

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UNIT - 9 OTHER CHEMICAL BONDS

Contents

9.1 AIMS AND OBJECTIVES

We explain you in this unit the nature of bonds other than ionic and covalent bonds present in some compounds, metals and associated molecules.

- At the end of this unit you should be able to understand that
- The bonds present in electron deficient compounds, metals and associated molecules can not be completely described by the concept of ionic bond or covalent bond.
- Diborane is a typical example of electron deficient compound.
- The chemical bond presnt between the atoms in a solid metal is called *metallic bond.*
- *'Electron Sea'* theory and *'band'* theory are introduced to explain the nature of metallic bond.
- Water, liquid ammonia and liquid hydrogen fluoride show abnormal physical properties. These are attributed to the presence of a special bond called *hydrogen bond* in these substances.
- Hydrogen atom bridges two electronagative elements through hydrogen bond.
- The hydrogen bond formed between two discrete molecules is called *intermolecular* hydrogen bond and the hydrogen bond formed within the same molecule is called *intramolecular* hydrogen bond.
- Hydrogen bond energy lies in the range 3 to 10 K.Cals/mole.
- Presence of hydrogen bond in molecules can be established by infrared spectroscopy.

two oxygen atoms as shown in figure 9.4. The hydrogen bond formed in such an instance is known as *intramolecular hydrogen bond.* It is for this reason that intramolecularly hydrogen bonded substances (ortho) are more soluble in organic solvents and have lower melting and boiling points than their intermolecularly hydrogen bonded isomers (meta and para isomers).

Hydrogen bond is larger than the corresponding covalent bond. It is for this reason the hydrogen bond is weaker than the corresponding covelant bond. The energy of hydrogen bond varies from about 3 K.Cals/mole to 10 K.Cals/mole depending on the two electronegative atoms between which the bond is formed. Typical values of bond energy are present in table 9.6.1

Check Your Progress - 2

Distinguish between intramolecular and intermolecular hydrogen bonds.

Table 9.6.1 Energies of some hydrogen bonds formed by neutral molecules.

H.Bond	K.Cals/mole
F-H.....O	10
F-H.....F	6.8
O-H.....O	4.5 - 7.0
O-H.....F	3.0
O-H.....S	4.0
N-H.....N	3.5 - 6.0
N-H.....O	4 - 6.0

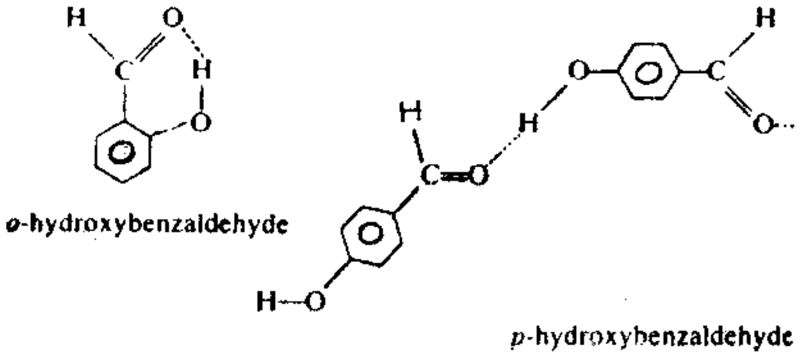
9.6.2 Nature of Hydrogen Bond

Hydrogen atom with only one stable orbitals (1s) containing one electron can form only one covalent bond and further according to Pauli's principle, a hydrogen atom cannot be associated with more than two electrons. It is therefore not possible for the hydrogen to form two covalent bonds with the two electronegative atoms. The experimental results also suggest that the two atoms between which hydrogen bond is formed must be strongly electronegative. Thus the hydrogen bond is largely to be electrostatic or ionic in nature. The bond energy of hydrogen bond (3 to 10 K.Cals) is also very small compared to the expected value for covalent bond. The difference between intramolecular hydrogen bonded compounds and intermolecular hydrogen bonded compounds are illustrated by the melting and boiling points of the isomers of hydroxy benzaldehyde presented in table 9.6.3.

9.6.3 Melting and Boiling points of hydrogen bonded substances

Substance	Nature of hydrogen bond	Melting point (°C)	Boiling point (°C)
0-hydroxy benzaldehyde	inter	-7	126.5
m-hydroxy benzaldehyde	inter	106.7	240
p-hydroxy benzaldehyde	inter	116	----

These differences in properties are readily understood on the basis of ortho hydroxy benzaldehyde acting as a discrete molecular unit due to intramolecular hydrogen bonding but meta and para isomers behaving as polymeric units.


o-hydroxybenzaldehyde

p-hydroxybenzaldehyde

Fig. 9.4. Hydrogen bonding in ortho and para hydroxy benzaldehyde

From the brief discussion presented earlier, it is obvious that a hydrogen bond can be present in the same molecule (between two adjacent groups) or between two discrete molecules. The former is called intramolecular hydrogen bond and the latter intermolecular hydrogen bond as mentioned earlier. In either case, it is observed that hydrogen atom bridges the two electronegative elements (F, O, N). Hydrogen is bound to one of these atoms by *covalent bond* (solid line) and to the other atom by *hydrogen bond* (broken line). The presence of hydrogen bond in a compound can be identified by recording the infrared spectrum of the compound. The vibrational frequency of O-H, or N-H, as the case may be, is very much effected if the hydrogen of the bond is involved in the hydrogen bond formation. The abnormal physical properties of the compounds also indicate the presence of hydrogen bond. Hydrogen bond present in protein molecules is known to play a vital and significant role in the biological processes.

9.7 SUMMARY

In this unit we have studied about

i) The bonds present in electron deficient molecules such as diborane.

ii) The metallic bond which satisfactorily explains the characteristic properties of metals.

iii) The free electron theory according to which the metal atoms are present as cations and form a lattice of rigid spheres; this is embedded in a sea of free valency electrons which could move in the interstices.

iv) The valence bond approach which envisages a structure involving delocalised bonds and the time picture is a resonance hybrid of many possible bonding form.

v) The Band theory or molecular orbital theory which successfully explains the high thermal and electrical conductivity of metals.

vi) The intermolecular hydrogen bond and the intramolecular hydrogen bond with examples.

9.8. MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines each.

1. Explain the bonding in diborane.
2. Describe briefly the free electron theory of metals?
3. How is valence bond theory inadequate to explain completely the characteristic properties of metals?
4. Give an account of the structures of liquid HF, liquid H_2O with special reference to hydrogen bond.

II. Answer the following in 30 lines each.

1. Give a critical account of the bonding in electron deficient molecules.
2. Discuss the different theories of metallic bond.
3. Explain with examples the need to propose the concept of hydrogen bond

9.9 MODEL ANSWERS TO CHECK YOUR PROGRESS

1 Boron and hydrogen atoms donate two electrons for bond formation. These two electrons bind hydrogen atoms and two boron atoms. This is a special type of bond called 3 centered bond. Two such bonds bind the two BH_3 units of diborane

2 Hydrogen bond present within the molecule is called intramolecular hydrogen bond. eg:- O - nitrophenol - Hydrogen bond present between the molecules is called intermolecular hydrogen bond. eg:- ethnol.

9.10 GLOSSARY

Octet :	An outer electron configuration of eight electrons found in the atoms of rare gas elements (except helium).
Valence bond theory :	Theory of chemical bond invoking the participation or overlap of atomic orbitals.
Valence electrons :	Electrons in the outermost orbit of an atom.

Block - 3

MOLECULAR STRUCTURE

The chemist hopes to answer the following questions in the case of any new compound that is prepared.

1. What are its constituent elements? (Molecular composition)

2. How many atoms of each element are bound in a molecule of the compound? (Molecular formula)

3. How are these atoms arranged (bound) in the molecule? (Molecular structure)

The first two questions concern the study of the composition and molecular formula of the compound and the third the structural formula of the compound. It is quite possible that there can be more than one compound with the same molecular formula. They are called 'isomers'. These are distinguished from one another by their strucutral formula. This means that the arrangement of atoms within the molecule is an important aspect of every compound. The nature of 'bonding' between the atoms and the related aspects such as bond length, bond angle and the shape of the molecule are some of the structural features which are of interest to any chemist.

The objective of this block is to explain how these structural aspects are established. the discussion is limited to only a few physical methods. The physical methods are used to determine some physical properties of the compounds under investigation for the purpose of making out the molecular structure. The properties considered in this block are i) dipole moment and ii) molecular spectral characteristics.

UNIT - 10 DIPOLE MOMENTS

Contents

10.1 AIMS AND OBJECTIVES

The purpose of this unit is to explain you the meaning of dipole moment of a compound and to enable you to use the values of dipole moment to arrive at the molecular structure. After completing this unit you must be able to understand that

- Molecules are classified as polar and non-polar.
- Polarity of molecule is dependent on the symmetry and the polarity of bonds in the molecule.
- The dipole moment is a property of the polar molecule.
- The dipole moment is a vector quantity.
- The dipole moment of a molecule is a 'vector sum' of the individual bond moments in the molecule.
- The dipole moments of molecules provide an insight into the structure of molecules.

10.2 INTRODUCTION

A covalent bond is formed when two electrons are shared between two atoms of the same element or between two atoms of different elements. This sharing of the electrons can take place in two ways.

Equal sharing of bonded electron pair

The electron pair is shared equally by two bonding atoms when the electronegativities of the two atoms are equal. This is observed mostly in homodiatomic molecules (hydrogen and chlorine)

Fig. 10.1 Equal sharing of bonded electron pair

The bonded electron pair in each molecule is equally attracted by the two nuclei of the bonding atoms and lies at the centre of the molecule. This means that the electron pair is shared by both the atoms equally. In the language of wave mechanics, it can be said that the probability of locating the electron pair in the vicinity of any nucleus is the same. The molecule is symmetrical in the distribution of mass as well as electrical charge. Because of this uniform distribution, the molecule is symmetrical and the bond fomed between the atoms is called **non-polar** covalent bond, the molecule is referred to as non-polar. Thus hydrogen and chlorine are classified as non-polar molecules.

Unequal sharing of bonded electron pair

The bonded electron pair can as well be shared unequally between the bonding atoms when the electronegativities of the two atoms widely differ. Heteroatomic molecules (HF and H_2O) are examples of such unequal sharing. The bonded electron pair is attracted more towards the nucleus of one atom than to that of the other. For example, the fluorine atom in HF and the oxygen atom in H_2O exert a greater pull on the bonded pair than the hydrogen atom. The bonded pair does not lie at the centre of the line joining the nuclei of the bonded atoms. In the first example (HF), the bonded pair is pulled nearer to the nucleus of fluorine atom as it has a greater electronegativity than hydrogen. As a result, the *fluorine end* of the molecule acquires a partial negative charge (δ-) and as a consequence a partial positive charge (δ +) developes at the *hydrogen end*.

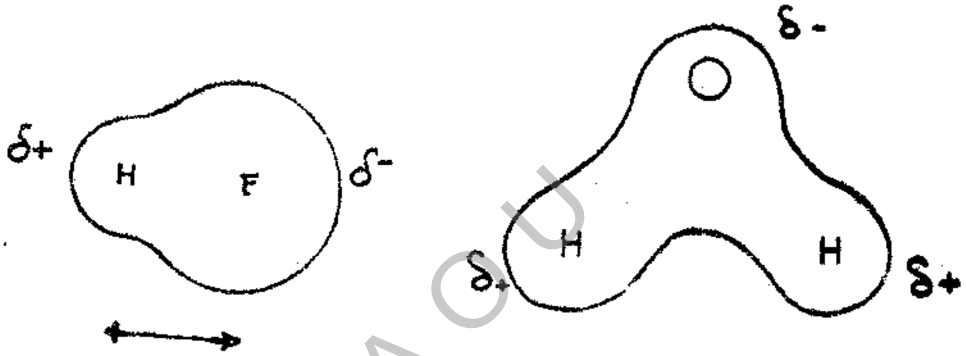


Fig. 10.2 Unequal sharing of bonded electron pair.

The two ends of HF molecule thus act as the two electrical poles of opposite charges. It is, therefore, called a *dipole*. The molecule is referred to as *polar molecule*. Similarly, in a water molecule the oxygen atom acquires a partial negative charge (δ-) and the hydrogen atoms a partial (δ+) positive charge. This polarity in the molecule is inherently due to the partial ionic character of the covalent bond in the molecule. However, in the case of water molecules and such other polyatomic molecules, not only the polarity of the bonds but also the symmetry of the molecule (geometrical shape) play a significant role. This aspect is discussed in more detail in a later section of this unit. The examples (HF& H_2O) illustrate the permanent polar molecules or permanent dipoles. But even non-polar molecules such as H_2 and Cl_2 under the influence of a strong electric field can temporarily suffer deformation in their shape and become polar. such a type of polarity is called *'induced polarity'* and the molecules manifesting it are called *'induced dipoles'*.

10.3 DIPOLE MOMENT

The polarity of a molecule is expressed in terms of its *dipole moment*. a diatomic molecule such as H-F or H-Cl as explained earlier, has partial positive and negative charges at the hydrogen and halogen ends, respectively. These molecules can, therefore, be taken to be simple systems of two point electrical charges (equal) of opposite singns separated by a rigid link or rod. The electrical dipole moment is expressed as *the product of the magnitude of charge and the distance separating the charges*.

$$^{\delta+}\mathrm{O} \overset{d}{-} \mathrm{O}^{\delta-}$$

The dipole moment is represented by the symbol μ (mu) and expressed by equation (1).
Dipole Moment $\mu = e \times d$ .... (1)
e = charge
d = distance separating the positive and negative charges.

The dipole moment is similar to waht is known as the *'Moment of a force'* in Physics with which you are familiar. The dipole moment is a *vector* quantity, it has magnitude as well as direction.

The dipole moment is the product of the electric charge and the distance separating the charges. The electric charge is expressed in electrostatic units (esu) and is of the order of 10^{-10} e.s. units. The distance (bond length) is expressed in centimetres (or angstrom units, A°) and is of the order of 10^{-8} cm (or 1A°). thus the dipole moment is of the order $10^{-10} \times 10^{-8} = 10^{-18}$ electrostatic centimetres. This quantity is called 'Debye Unit' denoted by the symbol *D* and is used to express the magnitude of dipole moment.

1 Debye unit = D = 10^{-18} e.s. cm.

The dipole moment is a vector quantity and, therefore, its magnitude as well as its direction have to be indicated. For example, the dipole moment of HCl is 1.03 D. The partial negative charge (δ^{-1}) is on the chlorine atom and the partial positive charge (δ^{+}) is on the hydrogen atom. The direction is indicated by an arrow mark from the positive end, to the negative end. Thus HCl is represented as H → Cl. In the case of the water molecule containing two polar bonds, the directions are represented in each case as shown below Dipole moments of some simple molecules and some bonds are given in table 10.3.1

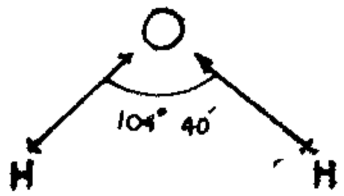


Table 10.3.1 Dipole moments of some simple molecules or bonds

Molecule / Bond	Dipole moment (D)	Molecule / Bond	Dipole moment (D)
HCN	2.93	CH_4	0
HF	1.90	CCl_4	0
HCl	1.03	O-H	1.6
HBr	0.78	N-H	1.3
HI	0.38	C-Cl	1.5
H_2O	1.85	C-Br	1.4
H_2S	1.10	C-I	1.2
CO_2	0	C-O	0.7
CS_2	0	C-H	0.4
CH_3Cl	1.86	C-N	0.2
NH_3	1.46	C=O	2.3

Check Your Progress - 1

How is dipole moment expressed?

10.4 EXPERIMENTAL DETERMINATION OF THE DIPOLE MOMENT

The dipole moment is usually determined for a substance in the vapour state or in the solution condition and the methods used in this regard are discussed in this section.

10.4.1 Vapour-Temperature method

The dipole moment is determined by measuring the dielectric constant (D) and the density (ρ) of the vapour of the substance at different temperatures. If the substance decomposes on heating, the observations are made under reduced pressures. The value of total polarization (P) of the molecule is calculated with the equation $P = \frac{D-1}{D+2} \times \frac{M}{\rho}$ ...... (2)

(where M = molecular weight of the substance) and is plotted against $\frac{I}{T}$.

A linear plot will be obtained and the slope (b) of the plot is given by the equation:

$$b = \frac{4}{3} \pi N \left(\frac{\mu^2}{3k}\right) \qquad (3)$$

Where N = Avogadro number
k = Boltzman constant
μ = Dipole moment

From the value of slope (b), the dipole moment (μ) is calculated from the equation (3) mentioned above.

10.4.2 Dilute Solution method

The solution method is generally used in the case of substances which cannot be converted into their vapours easily without their suffering decomposition. In this method the substance is dissolved in a non-polar solvent and dielectric constants (D_1 and $D_{1,2}$) and the densities of the solvent and the dilute solution (P_1 and $P_{1,2}$) are measured. From the respective values of dielectric constant and density, the molar polarization of the solvent (P_1) and of the solution ($P_{1,2}$) are calculated from the equations 4 and 5.

$$P = \frac{D_1-1}{D_1+2} \times \frac{M_1}{P_1} \qquad ...... \quad (4)$$

$$P_{1,2} = \frac{D_{1,2}-1}{D_{1,2}+2} \times \frac{x_1M_1 + x_2M_2}{P_{1,2}} \qquad .... \quad (5)$$

The molar polarization (P_2) of the substance is obtained from the values of P_1 and $P_{1,2}$ with the help of the equation, (6).

$$P_{1,2} = x_1P_1 + x_2P_2 \qquad ... (6)$$

$$P_2 = \frac{P_{1,2} - x_1 P_1}{x_2} \qquad .....(7)$$

In the equations (4, 5 & 6) given

D_1 and $D_{1,2}$ represent dielectric constants of solvent and solution

M_1 and M_2, represent the molecular weights of solvent and substance and x_1 and x_2 represent the molefractions of solvent and substance in the solution.

P_1 $P_{1,2}$ molar polarizations and ρ_1 $\rho_{1,2}$ densities of solvent and solution.

The P_2 values are plotted against x_2 and the value of P_2 corresponding to the dilute solution ($x_2 =$ o) is obtained by extrapolation. The dipole moment of the substance is obtained from the value of P_2 at $x_2 =$ o by substituting the same in the equation (7)

$$\mu = 0.0128 \sqrt{(P_2 - P_D)T} \qquad ...... (8)$$

Where T is temperature and P_D distortion polarization which is equal to the molar refraction for the D-line approximately.

10.5 APPLICATIONS OF DIPOLE MOMENTS : ELUCIDATION OF MOLECULAR STRUCTURE

The geometry of the molecule or the shape of the molecule can be established with the help of dipolemoment data of the molecule. By comparison of the experimentally determined dipole moment and theoretically anticipated value, structural information such as the molecular resonance and molecular symmetry can be ascertained. In this section the use of dipole moment in this regard is discussed in brief in respect to diatomic, triatomic, and polyatomic molecules, besides disubstituted aromatic compounds.

10.5.1. Diatomic molecules

A diatomic molecule is linear or rod-like in shape. If it is a homodiatomic molecule like H_2, C_2, N_2 etc., it will have only zero dipole moment as discussed earlier. In the case of heterodiatomic molecules such as HCl. HF it will have a measurable value. This as mentioned earlier, is due to the polarity of the covalent bond between the atoms and hence polarity can be evaluated from the value of dielectric constant.

10.5.2 Triatomic molecules

Triatomic molecules are of utmost importance because there could be two possibilities concerning the arrangement of atoms in such molecules. These are linear and non-linear (or bent) arrangements. For example, a triatomic molecule like H_2O can have either of the following two structures.

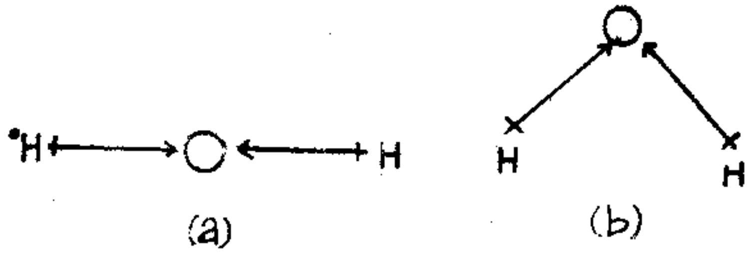


Fig. 10.3 Possible shapes of water molecule
(a) linear shape (b) bent shape

As mentioned earlier, the dipole moment of a molecule arises because of the polarity of the covalent bond or bonds in the molecule and the observed net diploment is a vector sum of dipole moments of all such individual bonds. The term 'vector sum', stresses the importance of magnitude and direction. In structure I (linear) the two OH bond moments are equal and unlike (direction wise) and are acting in a straight line. Thus they cancel out each other and the net moment of the molecule would be 'zero'. But experiments show that the dipole moment of water is 1.84 D. This experimental value, therefore, rules out structure 1 for water. Structure II (angular or bent) does not allow the two OH bond moments to mutually cancel out each other. Each OH bond moment is equal to 1.6 D and direction-wise they act at an angle of less than 1800 (non-linear). The dipole moment of a molecule containing two polar bonds is evaluated by adding graphically or with the help of the equation. The value of μ calculated from the experimental value of 105^0 D for H_2O is approximately 1.84 D. This shows that structure II (bent structure) is acceptable for the water molecule. The carbondioxide (CO_2) molecule has zero dipole moment. This shows that that molecule is symmetrical and hence linear. Similar is the structure of carbon-disulphide (CS_2). Sulphur dioxide, on the other hand, has a dipole moment of 1.6 D. This suggests that the molecule is angular.

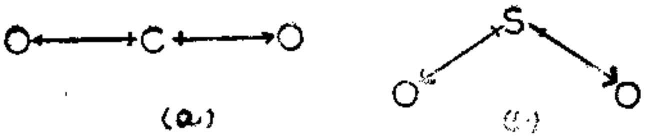


Fig. 10.4 Shapes of a) carbondioxide b) carbondisulfide c) sulphur dioxide molecules

Check Your Progress - 2

What is the reason for water not having zero dipole moment?

10.5.3 Tetraatmoic Molecules

The ammonia molecule (NH_3) is an example of tetraatomic molecule. The important possible structures are traingular planar or traigonal pyramidal.

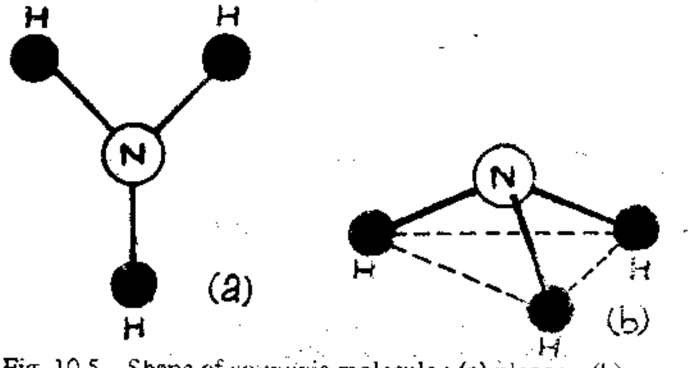


Fig. 10.5 Shape of ammonia molecule : (a) planar (b) pyramidal

The ammonia molecule has a dipole moment of 1.46 D. This suggests that the molecule has no planar structure, since in a symmetrical traingular planar structure the vector sum of the dipole moments of N-H bonds is 'zero'. This confirms that the ammonia molecule has a pyramidal structure (b). Boron trichloride (BCl_3), on the other hand, has a zero dipole moment. It suggests that BCl_3 has a triangular planar structure as shown below:

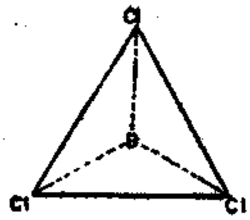


Fig. 10.6 Shape of boron trichloride molecule.

10.5.4 Polyatomic molecules

Methane (CH_4), chloroform ($CHCl_3$) and carbontetrachloride (CCl_4) are some of the polyatomic molecules. The dipole moments of these compounds are $CH_4 \rightarrow 0$, $CHCl_3 \rightarrow 1.5$ and $CCl_4 \rightarrow 0$. The zero values suggest a symmetrical tetrahedral structure with carbon at the centre and hydrogen and chlorine atoms at the four corners in the case of CH_4 and CCl_4. In the case of methane, each C - H bond has a dipole moment of 0.4 D. If the methane molecule is tetrahedral the bond moment of the four bonds cancel out one another and leave zero dipole moment for methane. Similar arguments apply to CCl_4 molecule also. In fact, all molecules possessing a centre of symmetry are non-polar. If three of the hydrogen atoms are replaced by chlorine atoms ($CHCl_3$) the resulting chloroform molecule loses its symmetry and possesses a net dipole moment 1.15 D.

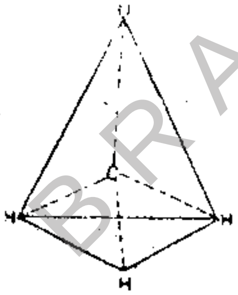


Fig. 10.7 Shape of methane molecule

10.5.5 Disubstituted aromatic compounds

It is convenient to consider the resultant moment of a functional group in benzene compounds rather than those of the individual bonds. The values derived for some important groups by **J.W. Williams** from measurements in solution on the assumption that C - H linkage in benzene has no dipole moment and that benzene ring is planar are given below:

NO_2	CN	OH	Cl	H	CH_3	NH_2
-3.9	-3.8	-1.7	-1.5	0	+0.4	+1.5 D

The sign preceeding the value indicates the direction in which the moment operates (remember that the moment is a vector quantity). Nitro group, strangely is electronegative and is presumably negatively charged with respect to the benzene ring. The group moment is, therefore, given negative sign. For similar reasons, methyl and amine groups have positive signs.

UNIT - 11 MOLECULAR SPECTRA

Contents

11.1 AIMS AND OBJECTIVES

This unit is mainly to describe you the wave length and energies of different regions of the electromagnetic spectrum and explain the different types of molecular spectra.

When you have finished this unit you must be able to understand that

- There are apparently several different regions of electromagnetic spectrum
- The regions are referred to γ-ray, x-ray, ultraviolet, visible, infrared, microwave and radio wave regions.
- The spectra exhibited by molecules are called *'molecular spectra'* and contain *bands and not* lines (as in spectra exhibited by atoms)
- Molecular spectra are broadly classified as *rotation* (microwave), *rotation-vibration* (infrared) and *electronic* (ultraviolet - visible) spectra.
- The energy of molecules is quantized just like the energy of atoms.
- Energy levels are referred to as electronic, vibrational and rotational depending upon the type of transition.
- The magnitude of energy involved in electronic, vibrational and rotational transitions is 5.0, 0.1 and 0.005 electron volts respectively.

11.2 INTRODUCTION

Energy is absorbed or emitted by atoms in discrete amounts corresponding to the precise transitions of electrons in the atoms. This is a fundamental postulate of the *quantum theory* (see unit 2). In a similar way the energy is absorbed or emitted by *molecules* also in *quanta* corresponding to the precise transitions in the molecules. It is possible to verify how this behaviour occurs, and to measure the amounts of energy absorbed or emitted, since energy change manifests itself as electromagnetic radiation of a precise frequency.

It will be seen in the next unit that molecules (or even atoms) absorb only certain frequencies but not all frequencies. In a similar way, the excited molecules emit energy of discrete frequencies belonging to specific regions of electromagnetic spectrum.

11.3 Electromagnetic Spectrum

Visible light is just one of the possible forms of energy. It is a part of electromagnetic spectrum. This electromagnetic spectrum is a manifestation of energy of different values. The electromagnetic radiation is wave-like in nature. All forms of radiation are characterised by their *frequency* (and hence *wavelength)* and their *energy*. Electromagnetic radiation consists of oscillating electric and magnetic fields, which can be transmitted through space with a specific velocity. The velocity in vaccuum is 3×10^{10} cms/sec. But the wavelength or the frequency of the electromagnetic spectrum varies from region to region in the spectrum. The velocity, wavelength and frequency or radiation are related by the equation $c = \upsilon\lambda$ where c = velocity, λ = wavelength, υ = frequency. λ has units of length (normally mm or A^0) and υ has units of reciprocal time (sec^{-1}).

Based on the apparent apprearence or some characteristic property (frequency or energy), the different regions of the electromagnetic spectrum named are as radio waves, micro waves, infrared rays, visible rays, ultra-violet rays, X-rays and α-rays. The complete range of these rays is referred to (as mentioned earlier) as electromagnetic spectrum. Each region is characterised by a specific energy or frequency range. The electromagnetic spectrum is presented in Fig. 11.1

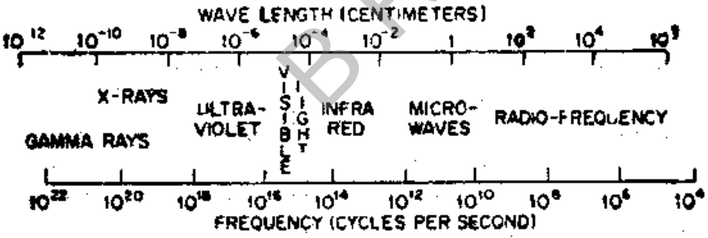


Fig. 11.1 Electromagnetic spectrum

Check Your Progress - 1

Name the different regions of the electromagnetic spectrum.

11.4 MOLECULAR SPECTROSCOPY

It is the study of the absorption or emission of electromagnetic radiation by molecules. When a substance is subjected to the impact of electromagnetic radiation, a part of it is absorbed, a part of it is transimitted and yet another part is scattered. The intensity and the region of the radiation absorbed by a substance depend on the chemical nature and the structure of the molecules of which the substance is composed. Therefore, useful information about the molecular structure of the substance can be obtained from the examination of the intensity and the frequencies of the radiation absorbed or emitted by the molecule. This type of examination or analysis is called **absorption or emission spectral study.** An absorption spectrum is obtained by placing the substance between the source of the radiation and the measuring device called 'spectrometer' and exposing it gradually to the different frequencies of electromagnetic radiation. In recording the absorption spectrum the percentage transmission at any specified frequency of the incident radiation is plotted against the corresponding frequency (or wavelength). A reading of cent per cent transmission means that all of the incident radiation is transmitted by the substance, without any of it being absorbed. The frequency at which transmission is less than cent per cent is the one which is absorbed to greater or lesser extent. These absorptions are the responses of the molecule to the impact of incident radiation. The spectra of molecules are called *'band spectra'* to distinguish them from the *'line spectra'* of atoms. Molecular spectra consist of *bands* while atomic spectra consists of *lines.* However, a close examination of the *bands* in molecular spectra reveals that they consist of large number of *closely spaced lines.* A molecule also (like an atom) can exist in a number of energy states. A change from one particular state to another occurs when the molecule absorbs energy. A molecule in its lowest energy state is said to be in the *ground state.* When a substance is exposed to electromagnetic radiation, it is likely to absorb radiations belonging to certain regions (frequencies) of the electromagnetic spectrum depending on the nature of the molecule. This absorption puts the molecules of that substance into higher, energy states. Molecules in such higher energy states are called 'excited molecules'. These excited molecules return to the lower energy state or to the ground state and emit characteristic radiation. Finally, it is the radiation of the origin of a particular frequency (or wavelength) or radiation absorbed (or emitted) which provides detailed structural information about the molecules. This information in turn is helpful to the investigation of molecular structure. So let us examine the different types of transitions with the attendant energy changes that are likely to take place in the molecules of a substance when the substance absorbs electromagnetic radiation.

11.5 TYPES OF ABSORPTION : MOLECULAR SPECTRA

A molecule can store energy in different ways. First the electrons in molecules occupy molecular orbitals with precise energy (like those of atoms in atomic orbitals). The energy state of the molecule is dictated by the total energy of the molecule. It will have a component to the translational motion, a component due to the rotational motion about the centre of gravity of the molecule and a component due to the vibrational motion of the atoms of the molecule against one another. A molecule is the basic structural unit of matter containing two or more atoms bound by chemical bonds (covalent bonds).

11.5.1 Translational motion

A molecule like a particle moves through space. This is known as *'Translational motion'.* A molecule is free to move in the *three* mutually perpendicular directions (x, y, and z axes). It has thus *three* degrees of freedom for its translational motion.

11.5.2 Rotational motion

A molecule can as well rotate about the three axes that pass through the centre of gravity of the molecule and are mutually perpendicular. Thus molecules (non-linear) will have *three* degrees of freedom for rotational motion. A linear molecule will have only *two* degrees of freedom as rotation on *its own axis* is not possible.

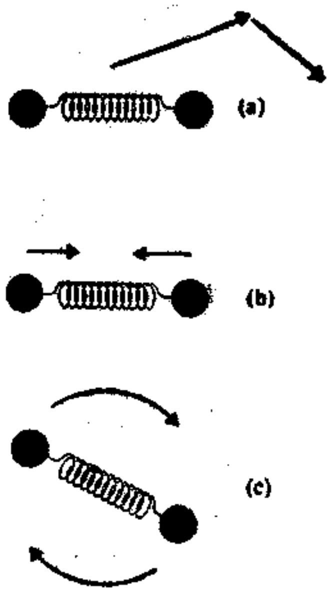


Fig. 11.2 Types of molecular motion
(a) Translation (b) Vibration (c) Rotation

11.5.3 Vibrational motion

A molecule is not a rigid body, since the chemical bonds in molecules can stretch or bend. The motion relating to this *stretching or bending* is referred to as *vibration*. There will be 3n-6 vibrational degrees of freedom to a molecule (non-linear) composed of 'n' atoms. The number of degrees of freedom for a linear molecule however is 3n-5.

Check Your Progress - 2

How many vibrational degrees are there for a six atom non-linear molecule?

11.5.4 Electronic motion

The molecule too (like the atom) has electrons occupying orbitals of different but definite energies. These orbitals are referred to as *'molecular orbitals'*. The electrons in a molecule can undergo transitions from one molecular orbital to another and such transitions are called 'electronic transitions' or 'electronic motions'.

Depending on the environment in which a molecule is placed it can have some or all types of motions mentioned above. Each one of the transitions or motions manifests in the form of a line or a group of lines in the molecular spectrum. The molecular spectra are accordingly classified as *electronic spectra* (ultraviolet visible spectra) *vibration-rotation spectra* (infrared spectra) and pure *rotation spectra* (microwave spectra).

11.6 SUMMARY

In this unit we have studied about

i) The electromagnetic spectrum and its various regions.

ii) The study of absorption of radiation by molecules; and the useful information about the molecular structure of a substance obtained from the examination of the intensity and frequencies of the radiation absorbed.

iii) The types of absorption due to the energy state of the molecule.

iv) The various components of the total energy of a molecule namely translational, rotational, vibrational and the electronic motions.

11.7 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines each.

1. Explain the difference between an atomic spectrum and a molecular spectrum.
2. Distinguish between an absorption spectrum and emission spectrum.
3. How is a spectrum represented?

II. Answer the following in 30 lines each.

1. Describe with a neat sketch the different regions of the electro-magnetic spectrum giving the frequency range of each region.

11.8 MODEL ANSWERS TO CHECK YOUR PROGRESS

1 Different regions of the electromagnetic spectrum are :

(a) α–rays (b) X-rays (c) U.V. rays (d) Visible rays
(e) Infrared rays (f) Micro waves (j) Radio waves

2 The vibrational degrees of freedom of a non-linear molecule = 3n-6 (n = No. of atoms).

$$= (3 \times 6) - 6 = 12.$$

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UNIT - 12 SIMPLE APPLICATIONS OF MOLECULAR SPECTRA (QUALITATIVE)

Contents

12.1 AIMS AND OBJECTIVES

The main purpose of this unit is to discuss the applications of molecular spectra in the elucidation of molecular structure.

By the end of this unit you will be able to understand:

Absorption spectroscopy is a useful tool to get to know the structural features of molecules.

Rotation, Vibration-rotation and electronic spectra provide information about bond lengths, bond strengths and the functional groups in organic molecules.

- Rotation spectra are exhibited by *polar* molecules only. The spectra are called *microwave spectra.* Rotational changes in the molecule manifest such spectra.

- Rotation quantum number (J) changes by one unit ($\Delta J = +1$) when molecule absorbs microwave radiation.

- Vibration-rotation spectra are exhibited by molecules possessing *oscillating dipole moments.* The spectra are referred to as *infrared spectra*. Vibrational and rotational changes in the molecule are responsible for the spectra.

- Vibrational quantum number (v) changes by one Unit ($\Delta v = +1$ when the molecule absorbs infrared radiation.

- Infrared spectroscopy helps to identify the functional groups and the structural features of organic molecules.

- Electronic spectra result from *electronic transitions* in the molecules. The spectra are also referred to as *ultraviolet-visible* spectra.

- The electronic transitions involved in the ultraviolet-visible absorptions are $\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$

  The energies associated with these transitions are in the order.
  $\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$

12.2 INTRODUCTION

A good number of physical methods are available for the elucidation of molecular structure. Spectroscopy in general, and absorption spectroscopy in particular, is one such physical method which is widely employed for the purpose of determining the molecular structure. 'Molecular Structure' is quite a complex term which covers several aspects (both qualitative and quantitative) of molecules. The term 'Molecular Structure', however, in the present unit is used in a very restricted sense and is meant to establish the bond lengths, bond strengths and bond angles of simple covalent molecules, besides the identification of the functional groups in organic molecules. The spectra considered here are *rotation* (micro-wave) *spectra, vibration-rotation* (infratred) *spectra* and *electronic spectra* (ultraviolet-visible) in which the mathematical analysis is deliberately simplified or omitted completely.

12.3 ROTATION SPECTRA (MICROWAVE SPECTRA)

12.3.1 Theoretical principles

A molecule exposed to electromagnetic radiation absorbs microwave region of the radiation if it is a *popular molecule.* A molecule such as HCl, HBr possessing permanent dipole moment, interacts with the oscillating electric field associated with the electromagnetic radiation and exhibits a *microwave* spectrum or *rotation* spectrum. Non-polar molecules like H_2, N_2, CO_2 will not absorb microwave radiation and, therefore, the rotation spectrum cannot be recorded. Polar molecules absorbing the microwave radiation undergo rotational changes subject to the condition that $\Delta J = +1$ (where J = rotation quantum number). This suggests that transitions, J = 0 to J = 1, J = 1 to J = 2 to J = 3, J = 3 to J = 4, etc., are only allowed when a polar molecule absorbs the electromagnetic radiation in the microwave region. These transitions are shown in figure 12.1. This condition is classified under the *selection rule.*

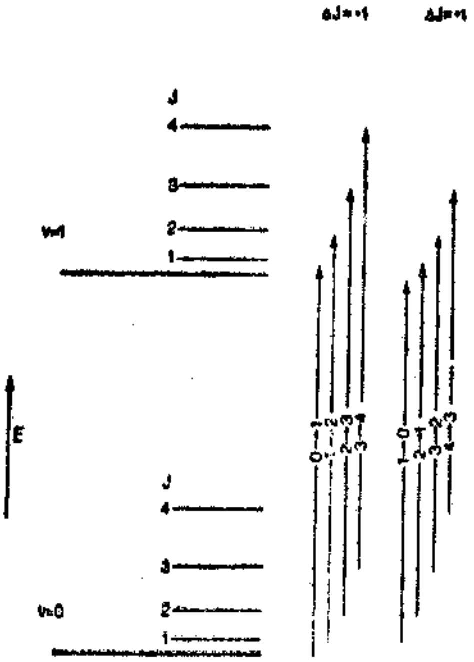


Fig. 12.1 Allowed rotational transitions in diatomic molecules

The rotational energy-E_J of a diatomic molecule in the gaseous state around an axis perpendicular to the line joining the nuclei is given by equation (1)

$$E_J = \frac{h^2 J (J+1)}{8 \pi^2 I} \qquad \text{.... (1)}$$

Where 'I' is the moment of the inertia of the molecule about the axis of rotation, 'J' is the rotational quantum number which may be zero or an integer, 1, 2, 3 etc., and 'h' is the Planck's constant.

The energy $(\Delta E)_r$ absorbed in the transition of the molecule from a lower rotational quantum state (J') to a upper rotational quantum state (J") is given by equation (2)

$$E_{J''} - E_{J'} = \frac{h^2}{8 \Pi^2 I} [J'' (J'' + a) - J' (J' + 1)] \qquad \text{.... (2)}$$

Where J" = Upper rotational quantum number and
J' = Lower rotational quantum number

The energy absorbed in the transitions

$J_0 \rightarrow 1$, $J_1 \rightarrow 2$, $J_2 \rightarrow 3$, $J_3 \rightarrow 4$ .... is, therefore, given by the equations 3, 4, 5 etc., respectively.

$$J_0 \rightarrow 1 \qquad E_1 - E_0 = \frac{h^2}{8 \pi^2 I} [1 (1+1) - 0 (0+1)] \qquad \text{... (3)}$$

$$= \frac{h^2}{8 \pi^2 I} \times 2$$

$$J_1 \rightarrow 2 \qquad E_2 - E_1 = \frac{h^2}{8 \pi^2 I} [2 (2+1) - 1 (1+1)] \qquad \text{... (4)}$$

$$= \frac{h^2}{8\pi^2 I} \times 4$$

$$J_2 \rightarrow 3 \qquad E_3 - E_2 = [\,3\,(3+1) - 2\,(2+1)\,] \qquad \dots (5)$$

$$= \frac{h^2}{8\pi^2 I} \times 6$$

According to quantum theory

$$E_j'' - E_j' = \Delta E = hc\upsilon \qquad \dots (6)$$

(refer to unit 2). Equations 3, 4, 5 can therefore be written as

$$hc\upsilon_1 = \frac{h^2}{8\pi^2 I} \times 2 \text{ or } \upsilon_1 = \frac{h^2}{8\pi^2 I} \times 2 \qquad \dots (7)$$

$$hc\upsilon_2 = \frac{h^2}{8\pi^2 I} \times 4 \text{ or } \upsilon_2 = \frac{h^2}{8\pi^2 I} \times 4 \qquad \dots (8)$$

$$hc\upsilon_3 = \frac{h^2}{8\pi^2 I} \times 6 \text{ or } \upsilon_3 = \frac{h^2}{8\pi^2 I} \times 6 \qquad \dots (9)$$

Where c is velocity of light and υ_1, υ_2, υ_3 are wave numbers. Equation (7, 8, 9) can be represented by the general equation (10)

$$\upsilon = \frac{h^2}{8\pi^2 I} \times 2m \qquad \dots (10)$$

Where 'm' is an integar 1, 2, 3, etc.,

Euqation (10) is rewritten for convenience as equation (11)

$$\upsilon = B \times 2m = 2Bm \qquad \dots (11)$$

Where $B = h/8\,\Pi^2 I c$ cm^{-1} and 'm' is 1, 2, 3, etc., the wave number υ (or frequency) of successive lines in a rotational spectrum is thus equal to 2B, 4B, 6B, etc., The spacing between any two successive lines is therefore 2B. For a diatomic molecule of the type under consideration, I the moment of inertia is given as equation (12)

$$I = \upsilon r^2 \qquad \dots (12)$$

Where υ = reduced mass of the molecule; r = distance between the atoms (bond distance).

Check your Progress - 1

Write the expression for the rotational energy and explain the terms.

12.3.2 Applications

A measure of the spacing (2B) between any two successive lines in the rotation spectrum, therefore, makes it possible to determine B and hence the moment of inertia I. The rotational spectra obtained for simple diatomic molecules hydrogen fluoride and carbon monoxide are presented in figures 12.2 (a) and 12.2 (b) respectively

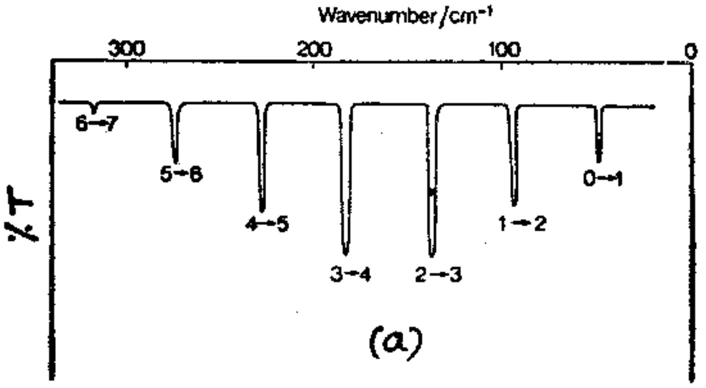


Fig. 12.2 (a) Rotational absorption spectrum of gaseous hydrogen fluoride.

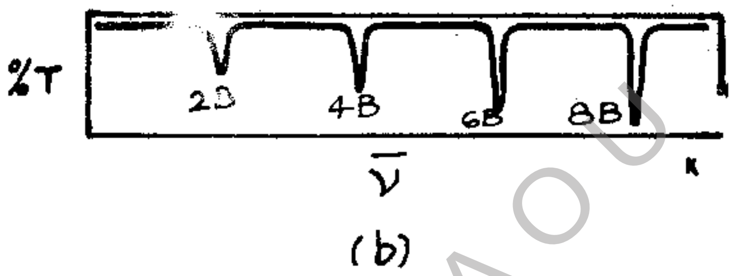


Fig. 12.2 (b) Rotational absorption spectrum of gaseous carbon monoxide.

From the spectrum for CO it is found that the spacing (2B) between any two successive lines is 7.6 X 10^{-17} erg.

$$B = \frac{h}{8\pi^2 I} \text{ cm}^{-1} \text{ or } \frac{h^2}{8\pi^2 I} \text{ ergs.}$$

Therefore $$2B = \frac{2h^2}{8\pi^2 I} = 7.6 \times 10^{-17} \text{ ergs.}$$

$$I = \frac{2h^2}{8\pi^2 \times 7.6 \times 10^{-17}} = \frac{2 \times (6.6 \times 10^{-27})^2}{8\pi^2 \times 7.6 \times 10^{-17}}$$

$$= 1.45 \times 10^{-39} \text{ g.cm}^2$$

$$\mu = \frac{m_c \times m_o}{(m_c \times m_o) N} = \frac{12 \times 16}{28 \times 6.2 \times 10^{23}} = 1.14 \times 10^{-23}$$

$$r = \sqrt{I/\mu} = \sqrt{1.45 \times 10^{-39}/1.14 \times 10^{-23}} = 1.13 \times 10^{-8} \text{ cm} = 1.13 \text{ A}^0$$

The bond distance of carbon monoxide is, therefore, 1.13 A°. Thus it is possible to determine moments of inertia and bond distances of molecules sufficiently accurately with the help of the rotation spectrum.

12.3.3 Limitations of microwave spectroscopy

1. Molecules with permanent dipole moment can only be suited.
2. Molecule should be in its gaseous form, since rotation energy equation $E_j = h^2/8\pi^2 Ix\ J(J+1)$ is applicable in this state only.

12.4 VIBRATION - ROTATION SPECTRA (INFRARED SPECTRA)

12.4.1 Utility

Infrared spectroscopy has now become an asset of almost incomparable value of all chemists interested in structural problems in organic chemistry. It offers great facility and certainty in establishing the presence or absence of a large number of structural features in a molecule. Moreover, the light in the infrared region can cause the molecular vibrations of atomic groupings which are devoid of useful chemical activity. Even though vibrational spectroscopy has become almost universal in its application to carbon compounds, it is also widely used for the determination of structure of inorganic compounds.

12.4.2 Origin of vibrational spectra

The infrared spectra, as described earlier, arise due to vibrational and rotational transitions that take place in a molecule when the molecule interacts with electromagnetic radiation and absorbs the radiation in the Infrared region. Before we consider the vibrations in a molecule let us examine a simple model consisting of two balls of different masses connected by a light spring (Fig. 12.3)

Fig. 12.3 A simple model of a harmonic oscillator

If we stretch the spring and release it, the balls in the model vibrate with a constant frequency. The frequency of vibration is related to the strength of the spring and the masses of the balls as expressed by the following equation:

$$f = 1/2\pi \sqrt{k/\mu}$$

$$\text{or } \upsilon_0 = 1/2\pi \sqrt{k/\mu} \quad \ldots \quad (13)$$

Where f or υ_0 = Vibrational frequency; k = force constant; μ *reduced mass* of the system. Reduced mass μ is equal to $m_1 \times m_2/(m_1 + m_2) \times N$. The system that obeys equation (13) is said to be in simple harmonic motion. The energy of vibration can be expressed by the equation $E = h\upsilon_0$ from quantum theory. This energy manifests as a band in the vibration spectrum. However, certain modifications need to be considered in order to describe the vibration of real molecules.

12.4.3 Vibration in a molecule

In the case of vibrating molecules only certain energies are allowed. This means that vibrational energy is quantised and it can take only specified values. These are given by the equation (14).

$$E_{vib} = (v + 1/2)\, h\upsilon_0 \qquad \text{... (14)}$$

Where υ_0 is vibrational quantum number and υ_0 the *fundamental frequency.* According to the selection rule, the vibrational transitions take place in such a way that $\Delta v = + 1$. V can take values 0, 1, 2, 3, etc., But now the question is, can all molecules absorb electromagnetic radiation (infrared radiation) ? and induce transitions among the vibrational energy levels? It is deduced from quantum theoretical principles that electromagnetic radiation can induce such vibrational transitions which lead to an *oscillating dipole moment* (change in dipole moment) of the molecule. This condition is called the *second selection rule.* According to this condition non-polar molecules like H_2, O_2 are not expected to be infrared active since their vibrations do not lead to change in dipole moment of the molecule. But this does not mean that all non-polar molecules are infrared inactive. In the case of non-polar molecules containing more than two atoms, some bonds can attain temporary polarity during vibration and produce oscillating dipole moment. Such molecules even though they are non-polar show infrared activity due to the vibration of these bonds. For example, carbon dioxide, even though non-polar, has some infrared active vibrations. The vibrational energy changes in the case of infrared active molecules, when the molecule interacts with infrared radiation and absorbs the same. The change (Δ E) is calculated using the equation 15.

$$E_{vib} = (v + 1/2)\, h\, \upsilon_0 \qquad \text{... (15)}$$

Where v = vibration quantum number; υ_0 = fundamental frequency. For a vibrational transition v = 0 to v = 1, the energy change is

$$E_1 - E_0 = [\, (V_1 + 1/2) + h\, \upsilon_0 - (V_0 + 1/2)\, h\, \upsilon_0 \,] \qquad \text{... (16)}$$

$$\Delta E = h\, \upsilon_0\, [\, (1 + 1/2) - (0 + 1/2)\,] \qquad \text{... (17)}$$

$$\Delta E = h\, \upsilon_0 \times 1 \qquad \text{... (18)}$$

For a vibrational transition from v_1 to v_2

$$E_2 - E_1 = [\, (v_2 + 1/2)\ h\, \upsilon_0 - (v_1 + 1/2)\ h\, \upsilon_0 \,] \qquad \text{... (19)}$$

$$\Delta E = h\, \upsilon_0\, [\, (2 + 1/2) - (1 + 1/2)\,] \qquad \text{... (20)}$$

$$\Delta E = h\, \upsilon_0 \times 1 \qquad \text{... (21)}$$

Thus it is seen that the energy change involved is the same whether the transition is from v_0 to v_1 or v_1 to v_2 etc., The spectrum contains the characteritic fundamental frequency (υ_0). Generally transitions from v = 0 to v = 1 are indicated most in the spectrum since most of the molecules will be at their lowest vibrational level (v = 0) rather than at higher levels (v = 1, 2 etc.,). It should also be noted that even in the ground vibrational state (v = 0), the molecule has vibrational energy.

$$E_v = (0 + 1/2)\, h\, \upsilon_0 = 1/2\, h\, \upsilon_0$$

This energy is called *zero point energy.* The *total* energy absorbed by amolecule in the infrared region is equal to the sum of the rotational and vibrational energies.

$$E_{total} = E_{vib} + E_{rot}$$

$$E = (v + 1/2)\, h\, \upsilon_0 + h^2/8\, \pi^2 I \times J(J+1) \qquad \text{... (22)}$$

A molecule at a vibrational energy level can have any one of the possible rotational energy transitions (Fig. 12.4a). For example a molecule at the energy level v = 0, J = 1 can absorb energy and may be promoted to v = 1, J = 2, or v = 1, J = 0. Thus the spectrum will consist of two series of lines corresponding to the two possible values of J. J in v = 0 can change to (J+1) in v = 1 or (J-1) in v = 1. These two series will have increasing and decreasing energy (wave numbers) respectively (Fig. 12.4b).

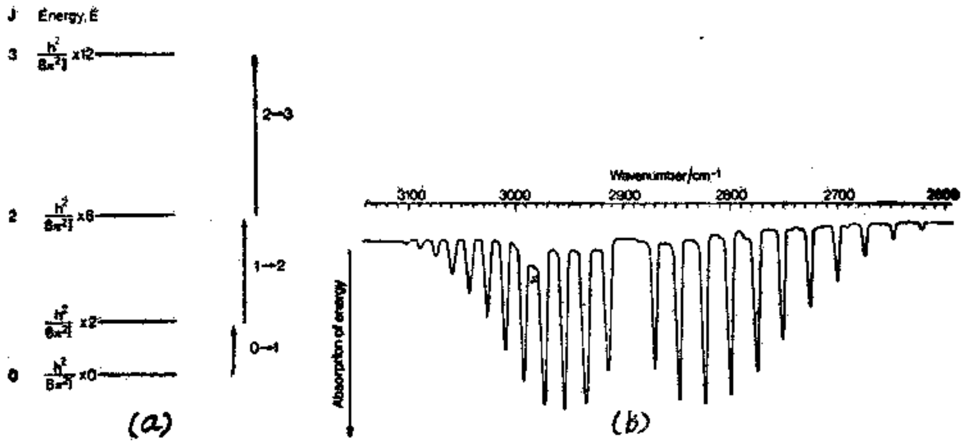
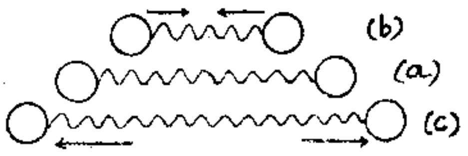


Fig. 12.4 (a) Possible rotational energy transitions.
Fig. 12.4 (b) Increasing and decreasing wave numbers.

12.4.4 Fundamental Vibrations

A polyatomic molecule having 'n' atoms has a total of 3n degrees of freedom. *Three* of these are *translational* degrees of freedom and *three* are *rotational* degrees of freedom (two in the case of linear molecule). There will, therefore, be 3n-6 (or 3n-5 in the case of linear molecule) degrees of freedom for *vibrational* motion. If all these vibrations are infrared active there will be 3n-6 (or 3n-5) *fundamental absorption bands*.. For example, in H_2O vapour (n = 3) there will be three [(3x3) -6 = 3] fundamental absorption bands. In addition to these fundamental bands, the spectra may contain *overtones, combination bands and difference bands.*

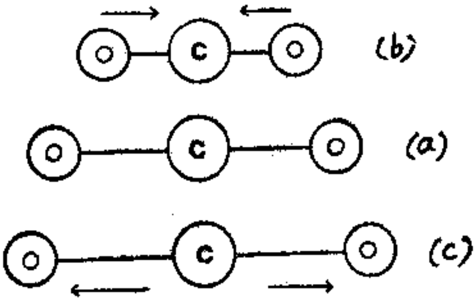
A tetraatomic molecule such as NH_3 shall have 6 vibrational degrees (3x4-6 = 6) of freedom. A penta atomic molecule such as methane CH_4 will have 9 vibrational degrees of freedom (3x5-6 = 9). In order for a vibration to result in the absorption of infrared radiation and to manifest itself as a bank (peak) in the spectrum that vibration must cause as stated earlier a change in the dipole moment of the molecule. Fundamental vibrations are classified as *stretching* and *bending* vibrations. In a stretching vibration of a band, the distance between the two atoms increases or decreases, but atoms remain in the same bond axis.



a)

Fig. 12.5 Stretching vibrations
(a) Equilibrium (b) Compression (c) Expansion

The stretching vibration in polyatomic molecules can be symmetric or asymmetric. For example in (CO_2) molecule there are two carbon-oxygen bonds. In a symmetric stretch, these two bonds increase or decrease simultaneously.

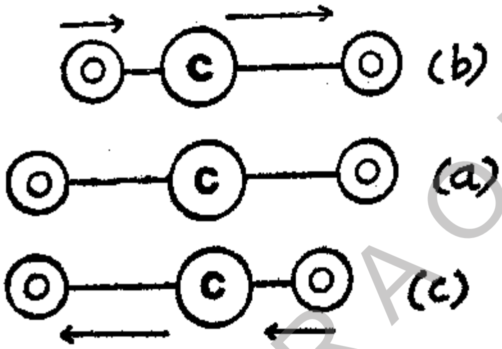


a)
c) Stre

Fig. 12.6 Symmetric stretching

(a) Equilibrium (b) Stretching (bond length decreases) (c) Stretching (bond length decreases)

In an unsymmetric stretching, if one bond length increases, the other bond length decreases or vice-versa.



a) I

Fig. 12.7 Unsymmetric stretching

(a) Equilibrium (b & c) Unsymmetric stretchings

In *bending* (or deformation) vibrations of a bond, the position of the atoms changes relative to the original bond axis. The bending vibrations are therefore, designated as scissoring, twisting, rocking and wagging (based on the type of the motion). These are shown in Fig. 12.8.

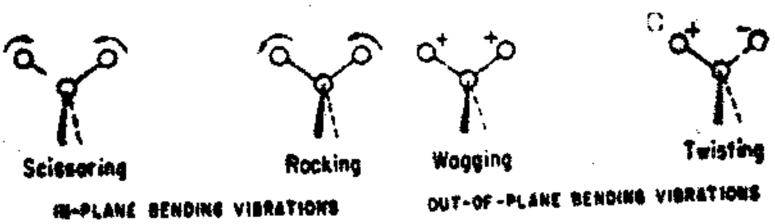


Fig. 12.8 Bending vibrations

12.5 APPLICATIONS

12.5.1 Calculation of force constant

As pointed out earlier $\upsilon_0 = 1/2\pi \sqrt{k/\mu}$ Therefore from the fundamental frequency υ_0, the force constant *k* can be calculated. For example, HCl molecule gives absorption band at wave number (υ_0) 2890 cm^{-1}. From this force constant *k* can be calculated as follows.

$$\upsilon_0 = 1/2\pi \sqrt{k/\mu} \qquad \text{... (23)}$$

$$\bar{\upsilon}_0 = 1/2\pi c \sqrt{k/\mu} \qquad \text{... (24)}$$

$$\bar{\upsilon}^2_0 = 1/4\pi^2 c^2 \sqrt{k/\mu} \qquad \text{... (25)}$$

$$k = \bar{\upsilon}^2_0 \mu \times 4\pi^2 c^2 \qquad \text{... (26)}$$

We have :

$$k = (2890)^2 \times 4 \times (22/7)^2 \times (3 \times 10^{10})^2 \times 1.008 \times 35.36/(1.008 + 35.46) \times 6.0 \times 10^{23})$$

$K = 4.8 \times 10^5$ dynes/cm or 4.8×10^2 N. m^{-1} (where N = Newton)

Force constants determined by spectral methods are presented in table 12.1 along with bond enthalpies.

Table 12.5.2Force Constant and Bond Enthalpies

Molecule	Force constant N.m^{-1}	Bond enthalpy K.J. mol^{-1}
HF	9.7×10^2	562
HCl	4.8×10^2	431
HBr	4.1×10^2	366
HI	3.2×10^2	299

12.5.3 Deduction of the shape of molecule

From the number of fundamental vibrational peaks observed in an infrared spectrum of a molecule, one can make out the shape of the molecule from amongst the possible shapes. The method presented here to arrive at the shape from the study of the spectral characteristics is of course an over simplified one. For example, let us consider NO_2 molecule. It is a three atom molecule. The number of degrees of vibrational freedom is expected to be 3 [(3x3) - 6 = 3] if it is a non-linear molecule and to be 4 [(3x3) - 5] if it is a linear molecule. NO_2 is thus expected to show 3 infrared active absorption peaks if it is a non-linear molecule and four peaks if it is a linear molecule. The molecule has practically exhibited only *three* peaks (at 750, 1323 and 1616 cm^{-}) but not *four* peaks in its infrared spectrum. This suggests that NO_2 is a *bent* molecule (i.e. non-linear molecule). Such arguments can be extended and applied to even larger molecules.

12.5.4 Identification of functional groups in organic molecules

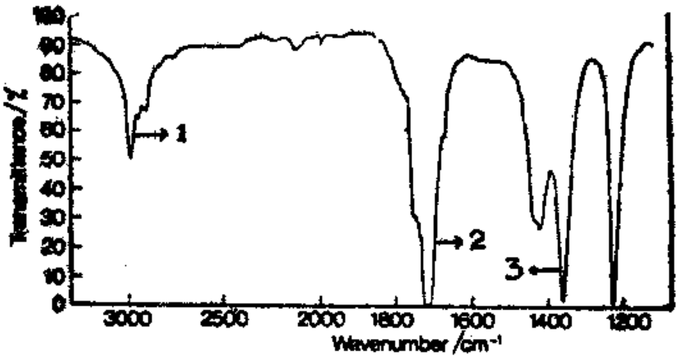
Organic compounds show infrared spectra in which many peaks are spread over a wide frequency range or wave number range (5000 to 650 cm^{-1}) commonly employed in infrared spectral studies. Each peak is associated with a specific vibration (or a combination or vibrations) of a functional group or of a bond in the group. The frequency (wave number) with which a bond or a group vibrates is little affected by the rest of the molecule. Therefore, the absorption at a frequency that is characteristic of a band or particular group can be taken as an indication of the presence of that group (or bond) in the compound.

Thus a particular group of atoms gives rise to a band or bands at characteristic frequencies. These frequencies are the same for all compounds. This fact enables the chemist to identify the functional groups in organic molecules. The characteristic infrared frequencies are given in table 12.2

Table 12.6 The Characteristic infrared frequencies

Groups	Vibration type	Frequency cm^{-1}
Alkyl (CH_3, CH_2, CH)	C - H stretch	2960 - 2850
	C-H bend	1460 - 1370
Alkanal (CHO)	C - H stretch	2900 - 2700
Alkene ($CH = CH_2$)	C - H Stretch	3095 - 3075
	C - H bend	990 - 890
Alkyne ($C \equiv CH$)	C - H stretch	3300 - 3270
Arene	C - H stretch	3040 - 3010
	C - H bend	1300 - 1000
Alkanol (OH)	O - H stretch	3650 - 3590
		1200 - 1050
Aliphatic ketone (CO)	C = O stretch	1740 - 1700
Aliphatic alkanal (CHO)	C = O stretch	1740 - 1720
Aliphatic acid (COOH)	C = O Stretch	1725 - 1700
Aliphatic ester (COOEt)	C = O stretch	1750 - 1730
	C - O stretch	1300 - 1050
Aliphatic ether (R_2O)	C - O stretch	1150 - 1070

The spectra of some of typical molecules are presented in figures 12.9 to 12.11. The assignments for important peaks are given under each spectrum



Infrared spectrum of acetone (CH$_3$ COCH$_3$)
1 C - H stretch (2900 cm^{-1})
2 C = O stretch (1740 cm^{-1})
3 C - H bending (1390 cm^{-1})

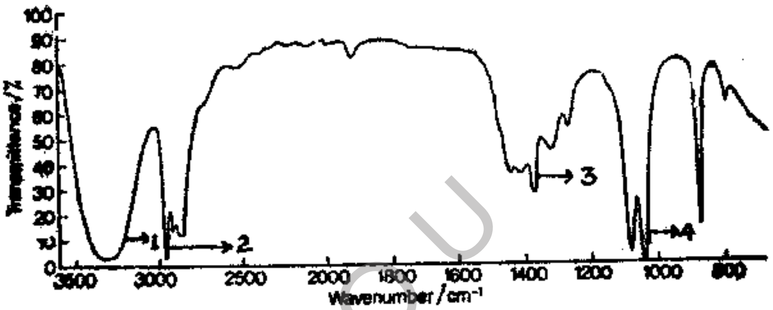


Fig. 12.10 Infrared spectrum of ethylalcohol (CH$_3$CH$_2$OH)
1 O - H stretch (3300 cm^{-1})
2 C - H stretch (2900 cm$_{-1}$)
3 C - H bending (1400 cm^{-1})
4 C - O stretch (1050 cm^{-1})

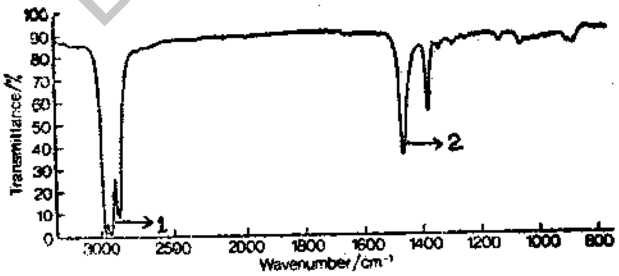


Fig. 12.11 Infrared spectrum of hexane CH$_3$ (CH$_2$)$_4$ CH$_3$
1 C - H stretch (2900 cm^{-1})
2 C - H bending (1460 cm^{-1})

12.7 ELECTRONIC SPECTRA (ULTRAVIOLET-VISIBLE SPECTRA)

Molecules absorbing radiations in the ultraviolet or visible regions of the electromagnetic spectrum undergo electronic transitions. The energy required for electronic transitions is much hgher than the energy required for vibrational and rotational changes. Therefore, all electronic transitions are accompanied by vibrational and rotational transitions also. Consequently the electronic spectra (ultraviolet-visible spectra) are more complex than the infrared spectra or the microwave spectra.

12.7.1 Types of Electronic Transitions

Electrons in molecules occupy molecular orbitals as electrons occupy atomic orbitals in atoms. Molecular orbitals are formed by linear combination of atomic orbitals (LCAO). The molecular orbitals are classified on the basis of their energy into *bonding* molecular orbitals (lower energy) and *antibonding* molecular orbitals (higher energy). The orbitals accommodating non-bonding electrons are called *non-bonding* molecular orbitals. The bonding molecular orbitals are designated as σ (sigma) and π (pi) orbitals depending on their symmetry (shape). The corresponding antibonding orbitals are represented as σ^* and π^*. The non-bonding orbital is denoted by 'n'.

The molecules in the stable state will be in the ground state (E_0). It may have different V and J quantum numbers. The molecule in the ground state (E_0) goes into the higher energy electronic state (E_1) on receiving sufficient energy from an external source. The rotational and vibrational energies are quantised in the higher electronic state also. Thus it is possible for the electrons in the lower energy molecular orbital to jump into higher energy molecular orbitals when a molecule absorbs sufficient energy in the form of ultraviolet-visible radiation. The electronic, vibrational and rotational energy levels are represented schematically in figure 12.12

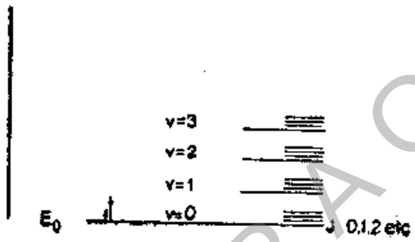


Fig. 12.12 Schematic representation of electronic, vibrational and rotational energy levels.

In general electrons in non-bonding (n) orbitals are least strongly bound in molecule. Electrons in σ, Π orbitals are more strongly bound and electrons in σ^* orbitals are most strongly held. There are six types of electronic transitions theoretically possible as mentioned below:

σ - σ^*, π - σ^*, n - σ^* σ - π^*, n - π^* and π - π^*

A general schematic diagram of possible orbital energies is presented in figure 12.13.

However, quantum theory considerations and energy considerations do not permit some of these transitions to take place. The electronic transitions that are generally involved in the ultraviolet and visible spectra are of the following types:

σ - σ^*, n - σ^*, n - π^*, and π - π^*.

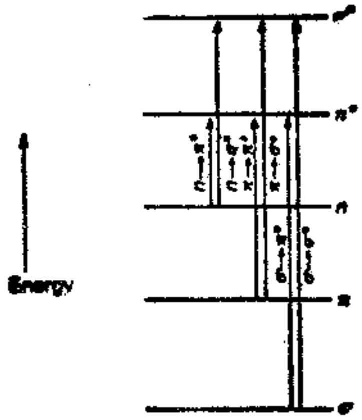


Figure 12.13 A generally schematic diagram of possible energy transitions.

The energy required for σ - σ* tranitions is very high. Therefore, compounds having only single and containing no lone pair electrons do not show absorptions in the ordinary ultraviolet region. Compounds that contain non-bonding electrons (as on oxygen, nitrogen, sulphur or halogen atoms) are capable of showing absorptions owing to n → σ* transitions to antibonding π* orbitals n - π*, π - π* transitions are also possible for aldehydes and ketones.

The relative energies of electrons in different types of molecular orbitals shown schematically in figure 12.13 show that the energy involved in the electronic transitions with the nature of transition. The order of decreasing energy for the absorption is :

$$\sigma - \sigma^* > \sigma - \pi^* \sim \pi - \sigma^* > \pi - \pi^* \sim n - \sigma^* > n - \pi^*$$

Check Your Progress - 2

What are the different allowed electronic transitions in a molecule?

....

....

....

....

12.7.2 Applications

Ultraviolet-visible spectra can be conveniently used to identify the functional groups and nature of organic compounds. Ethane ($CH_3 - CH_3$) shows no absorption in the region since it has no 'n' or Π electrons. Ethanol ($CH_3\ CH_2\ OH$) on the other hand exhibits absorption peak around wavelength of 2000 A°. The absorption occurs due to n - Π* transition of the non-bonded electrons of oxygen atom. The wavelengths corresponding to maximum absorption (λ max) of some organic compounds are shown in table 12.3. Thus structural information of organic compounds can be obtained from the value of λ max of the compounds.

Table 12.7.3 **Wavelengths of maximum ultraviolet-visible absorption (λ max) of some organic compounds**

Compound	Formula	λ max (A)	Transition type
Acetaldehyde	$CH_3\,CHO$	2910	$n - \pi^*$
Acetone	$CH_3\,COCH_3$	2765	$n - \pi^*$
Nitromethane	$CH_3\,NO_2$	2750	$n - \pi^*$
Benzene	$C_6\,H_6$	1840	$\pi - \pi^*$
	2030	$\Pi - \Pi^*$	
	2550		
Butadiene	$CH_2{=}CH{-}CH{=}CH_2$	2170	$\pi - \pi^*$

12.7.4 General conclusions

i) The absence of absorption peaks at wavelengths longer than 2000 A⁰ usually means that there are no conjugated groups, no carbonyl groups and no highly substituted carbon-carbon double bonds.

ii) Intense absorption peaks in the region 2000 - 3000 A⁰ indicate conjugation of at least two groups.

iii) Very weak absorption peaks in the region 2700 - 400 A⁰ signify presence of C = O, C = N, N = N groups.

iv) Medium intensity absorption peaks in the range 2000 - 2800 A⁰ with other peaks at 2500 - 3000 A⁰ show substituted benzene ring.

12.8 SUMMARY

In this unit we have learnt that

i) Spectroscopy in general and absorption spectra in particular as a physical method to determine the molecular structure.

ii) The polar molecules which possess permanent dipole moment interact with the oscillating electric field associated with microwave region and hence undergo rotational changes subject to certain conditions.

iii) A measure of spacing between any two successive lines in the rotation spectrum makes is possible to determine moment of inertia.

iv) Microwave spectroscopy has its limitations.

v) Infrared spectroscopy arises due to vibrational and rotational transitions that take place in a molecule and Infrared spectrum is extremely useful in establishing the presence or absence of many structural features in a molecule.

vi) A polyatomic molecule having n atom has a total of 3n degrees of freedom leading to fundamental absorption bands; overtones, combination bands and difference bands.

vii) Molecular spectra are useful in
   a) Calculating force constants and bond enthalpies
   b) Deduction of the shape of a molecule
   c) Identification of functional groups in organic molecules.

viii) Electronic spectra arise due to electronic transition and are observed in u.v. and visible regions. These are accompained by vibrational and rotational changes.

ix) uv and visible spectra can be used to identify functional groups and nature of organic compounds.

12.9 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines each.

1. Derive the equation relating wave number (υ) of rotational transition and moment of inertia (I) of a diatomic molecule.
2. Explain how the bond length of a diatomic molecule is determined with the help of rotation spectrum.
3. Discuss the origin of vibrational spectra.
4. Illustrate the different types of vibrations in a molecule.
5. How is the shape of a polyatomic molecule inferred through the inspection of infrared spectrum?
6. Give a schematic diagram for the sequence of energies of electronic tranismissions.

II. Answer the following in 30 lines each.

1. Give a critical account of the application of infrared spectroscopy in the elucidation of molecular structure.
2. How are bond lengths and bond energies of molecules determined with the help of rotational spectra?
3. Discuss the application of the ultraviolet-visible spectra in the determination of molecular structure.
4. Give an account of the theoretical principles underlying rotation and vibration-rotation spectra.

12.10 MODEL ANSWERS TO CHECK YOUR PROGRESS

1 Rotational energy $E_j = h^2 \; j (J + 1)/8 \pi^2 I$

In the above equation :

h = Planck's constant, J = rotational quantum number; I = moment of inertia.

2 In the range of 2000 to 8000 A^0 wavelength usually two types of electronic transitions take place. There are $n - \pi^*$ and $\pi - \pi^*$ transitions.

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UNIT - 9 OTHER CHEMICAL BONDS

Contents

9.1 AIMS AND OBJECTIVES

We explain you in this unit the nature of bonds other than ionic and covalent bonds present in some compounds, metals and associated molecules.

- At the end of this unit you should be able to understand that
- The bonds present in electron deficient compounds, metals and associated molecules can not be completely described by the concept of ionic bond or covalent bond.
- Diborane is a typical example of electron deficient compound.
- The chemical bond presnt between the atoms in a solid metal is called *metallic bond.*
- *'Electron Sea'* theory and *'band'* theory are introduced to explain the nature of metallic bond.
- Water, liquid ammonia and liquid hydrogen fluoride show abnormal physical properties. These are attributed to the presence of a special bond called *hydrogen bond* in these substances.
- Hydrogen atom bridges two electronagative elements through hydrogen bond.
- The hydrogen bond formed between two discrete molecules is called *intermolecular* hydrogen bond and the hydrogen bond formed within the same molecule is called *intramolecular* hydrogen bond.
- Hydrogen bond energy lies in the range 3 to 10 K.Cals/mole.
- Presence of hydrogen bond in molecules can be established by infrared spectroscopy.

9.2 INTRODUCTION

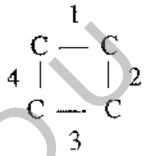
In unit 7 the nature and formation of ionic bond was discussed. In unit 8 the covalent bond was discussed at length. These two types of bonds are the most important types. Besides the above, it is quite possible that certain chemical bonds of special type may exist. In fact such special type of bonds do exist and play a vital role in deciding the properties of substances. In this unit an attempt is made to consider these special types.

9.3. ELECTRON DEFICIENT COMPOUNDS

The ionic and covalent bonds that are discussed in units 7 and 8 respectively are formed between atoms which provide sufficient number of electrons to form such bonds. Most of the molecules we considered till now have had number of electrons equal to or greater than the number of atomic orbitals of low energy present in the molecule. However, the compounds in which the number of low atomic energy orbitals exceeds the number of valence electrons are called *electron deficient* compounds. In a molecule containing 'n' atoms, there must be (n-1) covalent bonds if it is a linear molecule. For example a molecule containing 4 atoms of carbon shall be required to have 3 covalent bonds.

$$C^1 - C^2 - C^3 - C$$

However, if the molecule is a cyclic one, the number of bonds is equal to the number of atoms present in the molecule.



But there are many compounds known where the number of valence electrons available is much less than the number required to form an open chain compound or a cyclic compound. Such compounds are called electron deficient compounds. One typical example of electron deficient compound is diborane (B_2H_6). You will learn about its structure in detail in unit-5 of chemistry course-2. Let us discuss some important aspects of this relevent to our subject of study.

9.4 BONDING IN DIBORANE

Boron with *three* valence electrons can combine with three hydrogen atoms to form BH_3 on considerations of the three possible covalent bonds. But it is unstable and does not exist in appreciable quantities at room temperature. However its dimer i.e., diborane $(BH_3)_2$ or (B_2H_6) is quite stable. In B_2H_6 there are *two* boron atoms and *six* hydrogen atoms. Diborane thus has eight atoms. Those *eight* atoms require 8 bonds (if cyclic) or 7 bonds (if non-cyclic) to form the stable molecule. B_2H_6 molecule provides *12* valence electrons (six [2 x 3]) from the *two* boron atoms and six (6 x 1) from the six hydrogen atoms) and these *12* electrons are sufficient to form only *6* covalent single bonds. But as mentioned earlier, B_2H_6 required at least *7* bonds. Moreover it was observed experimentally that out of *6* hydrogens present in the molecule *4* hydrogens showed similar reactivity while other *2* behaved differently. To account for all these facts many suggestions have been made and different structures were proposed (see unit-5, of course -2)

One of the important suggestions is relevent to the present discussion (electron deficient bond). In one of the structures proposed a pair of electrons is used to bind three atoms. Such a bond involving only *two* electrons instead of *four* electrons usually required to bind chemically 3 atoms (H-B-H) can be called *electron deficient bond.* However in molecular orbital concept the bond is called *three centre bond.* Many similar examples are known for such electron deficient compounds.

Check Your Progress - 1

How do you explain in the bond between two BH_3 units in diborane?

9.5 METALLIC BOND

Metals are characterized by specific properties such as strength, ductility, malleability, lusture, electrical conductivity and thermal conductivity. None of the bonding mechanisms discussed (units 7 and 8) are capable of explaining satisfactorily all the characteristic properties of metals. Further the physico-chemical conditions required to be satisfied for the formation of ionic bond or covalent bond are also not completely met with in metallic structures as mentioned below. In ionic bond formation, one atom (electropositive) of the bond loses an electron to form positive ion and the other atom (electronegative) gains it to form the negative ion. In the case of metals, this is not possible to evoke the mechanism of ions bonding to explain the metallic structure. Similarly the electronegativity of metal atoms is very small. So the tendency to form electronegativity of metal atom is very small. So the tendency to form covalent bond like that present in homoatomic molecules such as H_2, Cl_2, N_2 will also be less. Hence different theories have been proposed which are discussed briefly below.

9.5.1 Free Electron Theory

Drude regarded metals as a *lattice* with electrons moving through it in much the same way as molecules of a gas are free to move. This idea was modified by **Lorentz** later. The metal atoms are present as cations (positive ions) losing one or more electrons as the case may be. These cations form a lattice of rigid spheres and the latter is embedded in a gas (or sea) of free valency electrons, which could move in the interstices. The tendency for the elements to become more metallic as we go down the right hand groups in the periodic table justifies this idea to some extent because the ionization energy becomes smaller in this direction. Since in this type of metallic structure every positive ion (metal ion) is attracted by all the electrons, considerable cohesion occurs within the solid. This cohesion is more than sufficient to over come the repulsion between the positive ions. The existence within the metal of a large number of free electrons accounts very well indeed for its electrical conductivity. It also explains satisfactorily the high thermal conductivity of metals. As mentioned earlier the sea of electrons within the metal can be treated as a gas. Hence the electrons will be moving faster at a point where the metal is hot than at a point where it is cooler. The structure of metals (packing of metal atoms in solid metals) determined experimentally shows that one atom of the metal is surrounded by 6, 8 or 12 other atoms of the metal depending on the pattern of packing. This number of nearest neighbours is known as co-ordination number. In such an event, it is obvious that the number of valence electrons available is much less than the number of bonds expected. For example in sodium metal, each sodium atom is surrounded by *eight* other sodium atoms (body centred cubic packing). If these *eight* atoms are bound to the central sodium atom by *eight* covalent bonds, 16 (8x2) electrons are required. But the central sodium atom and the surrounding eight sodium atoms together provide only 9 electrons since each sodium atom has only one valence electron in its outer orbit. Thus sodium metal can also be taken as an electron deficient system. Hence a bond other than the normal electron pair co-valent bond has to be evoked to explain the bonding in the metal. The type of bond present in metals is named as *metallic bond.* We shall discuss in brief some of the ideas proposed by different scientists to explain the nature of *metallic bond* or *bonding* in metals. Since the electrons are free to move through out the metal, the fast moving electrons drift from hot point towards the cooler part of the metal carrying the heat energy. This explains the thermal conductivity. In a similar way the electrical conductivity under the influence of a potential difference can be explained satisfactorly.

9.5.2 Valence bond approach

Let us consider a simple metal, like sodium. This has a body centred cubic structure with *eight* nearest neighbours. Sodium atom has one electron in its outer shell. This has to be shared with one of its neighbours forming a two-electron covalent bond. The atom could equally will be bonded to any other of its eight neighbours. Thus it is quite clear that the number of electrons available is not sufficient for the central metal atom to bind all the neighbouring 8 atoms of the metal through covalent bonds. To overcome this difficulty a structure involving delocalized bonds is envisaged and the true structure is considered to be a resonance hybrid (a mixture of all the many possible bonding forms). In view of the large number of resonance structures, the resonance energy will be large, hence the cohesive energy. However the theory failed to explain metallic character in the liquid state.

9.5.3 Band theory or Molecular orbital theory

In a metal the large number of atomic orbitals of a given type combine to give rise to a series of molecular orbitals of closely spaced energies called an *energy band.* Due to low degrees of orbital overlap the band width for inner shell electrons is very small. The energy of the electrons in these bands is almost the same as in isolated atoms. For the valence electrons, on the other hand, the energy range in a band is relatively large. The width of different bands may lead to overlap of different bands also. The spacing of these bands and the filling of the bands determine the electrical conductivity of the metal. If the bands are completely empty and the bands are widely separated the substance will be an insulator. A metal with partially filled band will serve as a *conductor.*

The number of molecular orbitals must by definition be equal to the number of constituent atomic orbitals. In the case of sodium, since there is only one valence electron, and since a molecular orbital can hold two electrons, it follows that one half of the molecular orbitals (bonding orbitals) only are filled. A little energy is sufficient to perturb an electron to an un-occupied molecular orbital. These orbitals extend in three dimensions over all the atoms in the crystal. Electrons thus have a high degree of mobility. This explains high electrical and thermal conductivity of metals. The formation of bands, partial filling-up of bands and overlapping of bands are diagramatically shown in figure 9.1

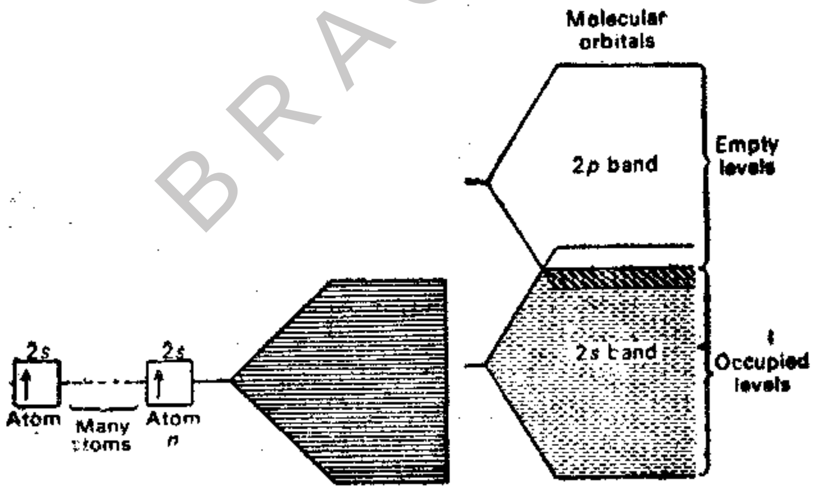


Fig. 9.1 Metallic molecular orbitals (bands)

A more detailed discussion about the metallic bond is presented in course-3 of chemistry.

9.6 THE HYDROGEN BOND

Physical properties such as vapour pressure, surface tension, freezing point and boiling point of some liquids were found to have abnormal values. This abnormality has been attributed to the occurence of associated molecules in these liquids. Water is a typical example of such a liquid with abnormal properties. Oxygen, sulphur, selenium and tellurium are all present in group VI of the periodic table. All of them form hydrides of the type (H_2X) with hydrogen. But water, an hydride of oxygen (H_2O) exhibits abnormally high boiling point compared to the hydrides ((H_2S, H_2Se, H_2Te) of other elements (S, Se, and Te) in group VI of the periodic table. However the discrepancy is not observed in the compounds in which the hydrogens are replaced by methyl groups (CH_3). $(CH_3)_2O$, $(CH_3)_2S$, $(CH_3)_2Se$, $(CH_3)_2Te$. Hence, it suggests that the hydrogens of the hydride molecules are responsible for this abnormality.

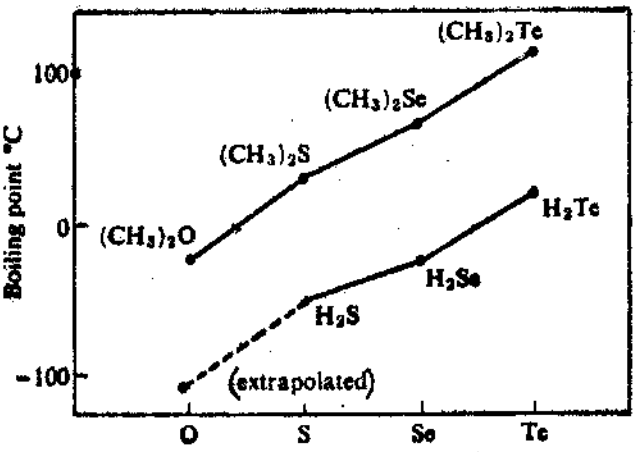


Fig. 9.2 Boiling points of hydrides and methyl substituted hydrides of oxygen, sulphur, selenium and tellurium

In a similar way the hydride of fluorine (HF) and the hydride of nitrogen (NH_3) possessed higher boiling points than those of the hydrides of other elements in the respective (halogen and nitrogen) groups. These abnormal properties are attributed to the existence of a class of associated molecular substances in the liquid state of these hydrides. **Lattimer** and **Rodebush** in 1920 introduced the term *hydrogen bond* to describe the nature of association in the liquid state of water, and hydrogen fluoride.

They pointed out that a slightly acidic hydrogen and a non-bonding electron pair are essential to form hydrogen bond. This requirement is met with in HF, H_2O and NH_3 molecules and consequently they are present as associated molecules in their liquid states. The association in the case of HF and H_2O are shown in Figure 9.3.

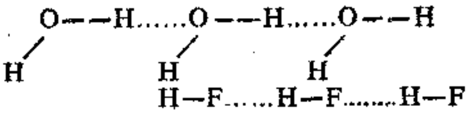


Fig. 9.3 Hydrogen bond in H_2O and HF

The bond represented by *dotted line* is known as *hydrogen bond.* In the examples cited it is evident that the hydrogen bond is present between two neighbouring molecules. Such type of hydrogen bond between two descrete molecules is called *inter molecular hydrogen bond.*

However hydrogen bond can as well form between two electronegative elements present in the same molecule provided the distance between the two atoms is favourable. For example organic molecules with two functional groups in the neighbouring positions (ortho) containing electronegative elements can form hydrogen bonds. Ortho hydroxy benzaldehyde, for example, can form hydrogen bond between the two oxygen atoms as shown in figure 9.4. The hydrogen bond formed in such an instance is known as *intramolecular hydrogen bond.* It is for this reason that intramolecularly hydrogen bonded substances (ortho) are more soluble in organic solvents and have lower melting and boiling points than their intermolecularly hydrogen bonded isomers (meta and para isomers).

Hydrogen bond is larger than the corresponding covalent bond. It is for this reason the hydrogen bond is weaker than the corresponding covelant bond. The energy of hydrogen bond varies from about 3 K.Cals/mole to 10 K.Cals/mole depending on the two electronegative atoms between which the bond is formed. Typical values of bond energy are present in table 9.6.1

Check Your Progress - 2

Distinguish between intramolecular and intermolecular hydrogen bonds.

Table 9.6.1 Energies of some hydrogen bonds formed by neutral molecules.

H.Bond	K.Cals/mole
F-H.....O	10
F-H.....F	6.8
O-H.....O	4.5 - 7.0
O-H.....F	3.0
O-H.....S	4.0
N-H.....N	3.5 - 6.0
N-H.....O	4 - 6.0

9.6.2 Nature of Hydrogen Bond

Hydrogen atom with only one stable orbitals (1s) containing one electron can form only one covalent bond and further according to Pauli's principle, a hydrogen atom cannot be associated with more than two electrons. It is therefore not possible for the hydrogen to form two covalent bonds with the two electronegative atoms. The experimental results also suggest that the two atoms between which hydrogen bond is formed must be strongly electronegative. Thus the hydrogen bond is largely to be electrostatic or ionic in nature. The bond energy of hydrogen bond (3 to 10 K.Cals) is also very small compared to the expected value for covalent bond. The difference between intramolecular hydrogen bonded compounds and intermolecular hydrogen bonded compounds are illustrated by the melting and boiling points of the isomers of hydroxy benzaldehyde presented in table 9.6.3.

9.6.3 Melting and Boiling points of hydrogen bonded substances

Substance	Nature of hydrogen bond	Melting point (^0C)	Boiling point (^0C)
0-hydroxy benzaldehyde	inter	-7	126.5
m-hydroxy benzaldehyde	inter	106.7	240
p-hydroxy benzaldehyde	inter	116	----

The ammonia molecule has a dipole moment of 1.46 D. This suggests that the molecule has no planar structure, since in a symmetrical traingular planar structure the vector sum of the dipole moments of N-H bonds is 'zero'. This confirms that the ammonia molecule has a pyramidal structure (b). Boron trichloride (BCl_3), on the other hand, has a zero dipole moment. It suggests that BCl_3 has a triangular planar structure as shown below:

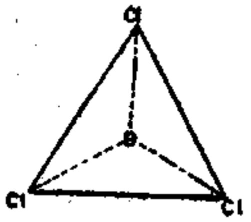


Fig. 10.6 Shape of boron trichloride molecule.

10.5.4 Polyatomic molecules

Methane (CH_4), chloroform ($CHCl_3$) and carbontetrachloride (CCl_4) are some of the polyatomic molecules. The dipole moments of these compounds are $CH_4 \rightarrow O$, $CHCl_3 \rightarrow 1.5$ and $CCl_4 \rightarrow O$. The zero values suggest a symmetrical tetrahedral structure with carbon at the centre and hydrogen and chlorine atoms at the four corners in the case of CH_4 and CCl_4. In the case of methane, each C - H bond has a dipole moment of 0.4 D. If the methane molecule is tetrahedral the bond moment of the four bonds cancel out one another and leave zero dipole moment for methane. Similar arguments apply to CCl_4 molecule also. In fact, all molecules possessing a centre of symmetry are non-polar. If three of the hydrogen atoms are replaced by chlorine atoms ($CHCl_3$) the resulting chloroform molecule loses its symmetry and possesses a net dipole moment 1.15 D.

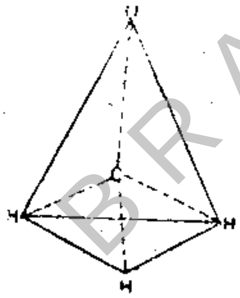


Fig. 10.7 Shape of methane molecule

10.5.5 Disubstituted aromatic compounds

It is convenient to consider the resultant moment of a functional group in benzene compounds rather than those of the individual bonds. The values derived for some important groups by **J.W. Williams** from measurements in solution on the assumption that C - H linkage in benzene has no dipole moment and that benzene ring is planar are given below:

NO_2	CN	OH	Cl	H	CH_3	NH_2
-3.9	-3.8	-1.7	-1.5	0	+0.4	+1.5 D

The sign preceeding the value indicates the direction in which the moment operates (remember that the moment is a vector quantity). Nitro group, strangely is electronegative and is presumably negatively charged with respect to the benzene ring. The group moment is, therefore, given negative sign. For similar reasons, methyl and amine groups have positive signs.

The dipole moment of di-substituted benzene molecule can be evaluated by adding vectorially the moments of the groups present in the substituted benzene. This is done graphically or by means of the equation.

$$\mu^2 = \mu_1^2 + \mu_2^2 + 2\mu_1 \mu_2 \cos\theta$$

μ_1 cos μ_2 represents the group moments and 'θ' the angle between the dipole vectors of the groups. Since the benzene ring is flat, the angle is 60° for *ortho* groups, 120° for *meta* groups and 180° for *para* groups. The position of group (ortho, meta or para) can be established if the dipole moment of the di-substituted benzene and the group moments of the substituents are known with the help of the equation mentioned earlier. But in a number of instances the observed dipole moment differs apparently from the value calculated from the individual group moments. This deviation is generally attributed to the structural changes such as loss in planarity of the molecule.

Dipole moment measurements help to distinguish between *cis* and *trans* isomers. The trans isomer has generally a centre of symmetry and, consequently, is non-polar. The dipole moment is, 'zero' for the trans isomers. *Cis* forms have relatively large moments.

In a similar manner it is possible to distinguish between *syn* and *anti* oximes. The former will have large moments while the latter have negligible moments.

Thus dipole moments help considerably to arrive at useful information regarding the structure of molecules.

10.6 SUMMARY

In this unit we have studied about

i) The equal sharing of bonded electron pair between two atoms leading to non-polar molecules.

ii) The unequal sharing of bonded electron pair leading to polar molecules.

iii) The dipole moment as a measure of the polarity of a molecule and its vectorial nature.

iv) The experimental methods for the determination of dipole moment; the vapour temperature method and the dilute solution method.

v) Applications of dipole moment in the elucidation of molecular structure with specific examples of di, tri, tetra and poly atomic molecules and also disubstituted atomic compounds.

10.7 MODEL EXAMINATION QUESTIONS.

I. Answer the following in 10 lines each.

1 How is the dipole moment of disubstituted benzene calculated from the group moments?

2 How is dipole moment determined by vapour-temperature method.

3 Discuss the application of dipole moment data to distinguish cis and trans isomers.

II. Answer the following in 30 lines each.

1 Describe in detail the dilute solution method to determine dipole moment of a polar solute.

2 Discuss the application of dipole moment values in the elucidation of geometry of polyatomic molecules.

10.8 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. Dipole moment (μ) is expressed by the following equation.

$$\mu = e \times d$$

e = charge and d = distance between the two poles of the molecule.
Dipole moment is expressed in Debye units. (10^{-18} e.s.u. cm. = 1 debye)

2. Since water is an angular molecule the individual OH bond moments do not cancel each other. Therefore its dipole moment is not zero.

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UNIT - 11 MOLECULAR SPECTRA

Contents

11.1 AIMS AND OBJECTIVES

This unit is mainly to describe you the wave length and energies of different regions of the electromagnetic spectrum and explain the different types of molecular spectra.

When you have finished this unit you must be able to understand that

- There are apparently several different regions of electromagnetic spectrum
- The regions are referred to γ-ray, x-ray, ultraviolet, visible, infrared, microwave and radio wave regions.
- The spectra exhibited by molecules are called *'molecular spectra'* and contain *bands and not* lines (as in spectra exhibited by atoms)
- Molecular spectra are broadly classified as *rotation* (microwave), *rotation-vibration* (infrared) and *electronic* (ultraviolet - visible) spectra.
- The energy of molecules is quantized just like the energy of atoms.
- Energy levels are referred to as electronic, vibrational and rotational depending upon the type of transition.
- The magnitude of energy involved in electronic, vibrational and rotational transitions is 5.0, 0.1 and 0.005 electron volts respectively.

UNIT - 13 : APPLICATIONS OF VISIBLE ABSORPTION SPECTRA

Contents

13.1 AIMS & OBJECTIVES

This unit aims to describe the important quantitative relations between the intensity of radiation absorbed and the concentration of the absorbing species and to discuss the applications of these quantitative relations.

- At the end of this unit you will be able to understand that :
- The intensity of absorbed radiation is expressed as *absorbance* or *optical density.*
- Absorbance depends on the concentration of the absorbing species and the path-length of the cell containing the absorbing species.
- The Laws that relate the intensity of transimitted light, the path length and the concentration of the absorbing species are *lambert's Law* and *Beer's Law.*
- The laws are useful in the determination of the concentration of absorbing species in solution.
- A mixture containing two solutes also can be analysed for determining the concentration of the individual solutes with the help of Beer's Law.

13.2 INTRODUCTION

As pointed out in lesson 11, molecules absorb electromagnetic radiation when they are exposed to is radiation. However, the region of the electromagnetic spectrum absorbed by any particular molecule

15.2 INTRODUCTION

You are learnt in lesson-14 that some naturally occuring elements (e.g. uranium, thorium) emit characteristic radiations on their own without any external agency and this behaviour of the elements is called *Radioactivity*. It is further said that these radiations contain three types of rays namely alpha, beta and gamma rays. These rays differ in their properties in respect of their electrical nature, penetrating power and ionizing power. But with little variations in the actual values, every radioactive element produced the same three types of rays. This suggests that the process involved in the radioactivity of any element is basically the same. the process has been shown to be the spontaneous disintegration of the *nucleus* of the atoms of these elments. This phenomenon of disintegration of radioactive elements is ascribed to the instability of the nucleus of the atoms of radioactive elements. In an elementary fashion, the instability has been traced to the unfavourable ratio of protons to neutrons in the nuclei of the atoms.

15.3 RADIOACTIVE DISINTEGRATION

The early workers in radioactivity observed very interesting facts about the behaviour of compounds of radioactive elements in solution. These facts were useful to understand the complex phenomenon of radioactivity. H. Becquerel observed that a precipitate is formed when ammonium hydroxide is added to a solution containing a uranium compound and a ferric salt. But still the solution contained some amount of uranium salt. It was noticed by him that the precipitate showed most of the original activity of uranium salt solution and that the liquid (containing still uranium) is *inactive*. This observation shows that the most activity of uranium compound is not due to the element uranium but to another species as uranium-X. On standing for some months, uranium in solution gradually regained its activity and the precipitate lost its activity. These two reactions were found to occur with same rate. The total activity of the system remains constant. These facts lead him to conclude that uranium continuously producing the active product uranium-X and that this gradually decays and loses its activity.

15.3.1 Radioactive Disintegration - Theory

E. Rutherford and **F. Soddy** in 1903 proposed a theory to explain the phenomenon of radioactivity as well as the observations described in section 15.2. This theory is known as theory of *radioactive disintegration.*

The atoms of radioactive elements unlike others undergo spontaneous disintegration with the emission of alpha or beta particles. this disintegration results in the formation of a new element which is quite different physically and some times chemically from the parent element. This new element may in turn also be unstable and emit a particle (α or β) with the production of still another new element. there may be a succession of this type of disintegrations or transformations. The nature of the element (atomic mass and chemical properties) produced during the disintegration depends on the nature of the particle emitted. For example every emission of α particle means that the new element has an atomic mass 4 units less than that of its parent. the emission of β particle, on the other hand, involved no appreciable change in atomic mass because of the negligible mass of a β particle. In spite of there being no apparent change in atomic mass the chemical and physical properties of the new element are quite different from those of its parent. *Three* radioactive disintegration series, viz., the *thorium* series, the *actinium* series and the *uranium* series, have been identified. These will be cnsidered in detail in lesson - 16.

15.3.2 Radioactive Disintegration - Rate

The measurement of radioactivity from time to time of the new element formed in a disintegration process has revealed that the rate of decay follows an exponential law.

If 'I_t' is the activity at any time 't' and I_o the initial activity at zero time, the decay can be represented as

$$I_t = I_o e^{-\lambda t} \qquad ..... (1)$$

Where λ is a constant called *radioactive constant.* The activity may be taken to be proportional to the number of atoms which have not yet disintegrated (or decayed). It, therefore, follows that

$$N = N_o e^{-\lambda t} \qquad ..... (2)$$

N_o and N are the number of atoms initially and after time 't' in respect of the particular radio-element the decay of which is being studied. λ, the radioactive constant is characteristic of the element responsible for the activity. It does not depend on the physical condition or the state in which a particular combination of th atoms is found.

Check Your Progress - 1

How is the rate of radio active desintegration at any instant mathematically related to initial activity?

15.3.3. Average Life of a Radioactive element

The life of any radioactive atom (the length of time during which it can exist before disintegrating) can have all possible values from zero to infinity. However, the *average life period* for an aggregate of a large number of atoms is of practical use.

The activity 'I_t' is proportional tothe number of atoms 'N' which have not disinegrated. Hence, the rate of disintegration of atoms ('dN/dt) is proportional to the number of atoms at that instant. This can be written mathematically as,

$$-\frac{dN}{dt} \; \alpha \; N$$

or

$$-\frac{dN}{dt} = \lambda N \qquad .... (3)$$

inserting value of 'N' from equation (2) into equation (3) we get

$$-\frac{dN}{dt} = \lambda No \, e^{-\lambda t} \qquad ..... (4)$$

$$-dN = \lambda No \, e^{-\lambda t} dt \qquad ..... (5)$$

Approximately dN can be taken as the number disintegrating at time 't' reckoned from any instant, 't' is the expected life peirod. This can have any value from zero to infinity. The period of average life (τ - tau) is, therefore, obtained by multiplying every possible life period (t = o to t= α) by the number of atoms (dN) having that expectation of life and dividing the sum of products by the total number of atoms (No) present at the beginning of the period. This can be mathematically represented as

$$\tau = \int_o^\alpha \frac{dtN}{N_o} \qquad ... (6)$$

Table 16.3.3 Actinium Series

Radioelement	*Corresponding Element*	*Symbol*	*Radiation*	*Half-life*
Actinouranium ↓	Uranium	^{235}U	α	7.13×10^3 yr
Uranium Y ↓	Thorium	^{231}Th	β	25.6 hr
Protoactinium ↓	Protactinium	231Pa	α	3.43 x 104 yr
Actinium 98.8% 1.2%	Actinium	227Ac	β and α	21.8 yr
↓ Radioactinium	Thorium	227Th	β	18.4 days
Actinium K	Francium	223Fr	β	21 min.
↓ Actinium X	Radium	223Ra	α	11.7days
Ac Emanation ↓	Radon	219Rn	α	3.92 sec
Actinium A ~100% ~5 x 10⁻⁷	Polonium	215Po	α and β	1.83×10^{-3} sec
↓ Actinium B	Lead	211Pb	β	36.1 min
Astatine - 215	Astatine	215At	α	$\sim 10^{-4}$ sec
↓ Actinium C 99.7% 0.3%	Bismuth	211Bi	α and β	2.16 min
Actinium C'	Polonium	211Po	α	0.52 sec
↓ Actinium C"	Thallium	207Tl	β	4.8 min
↓ Actinium D (End Product)	Lead	207Pb	stable	--

Check Your Progress - 1

How many radioactive disintegration series are identified and what are they?

16.4 GROUP DISPLACEMENT LAW

You have learnt that a radioactive element disintigrates spontaneously emitting an α -particle or β -particle or both. Emission of an α -particle leads to loss of four units in the atomic mass while emission of β - particle will not result in any change in the atomic mass of the daughter element. Since α - and β- Particles are respectively positive and negative charged particles, the daughter element produced due to the ejection of these particles from the parent element, shall occupy a different place in the periodic table. The generalizatons regarding the displacement of the product of an element in the periodic table are known as *group displacement law*. **Fajans, Russel** and **Soddy** independently proposed such generalisations, which go by the name group displacement law. This law accounts for the fact that the large number of radioactive elements can be fitted into the limited number of spaces in the prriodic table.

The law states that *when an α - particle is emitted in a radioactive disintegration, the product is displaced by two places to the left in the periodic table, that is, the atomic number is two less than that of its parent, but the emission of β-particle results in a displacment of one place to the right, the atomic number of the product being one greater than that of its parent.*

These generalisations are observed in tables 16.3.1 to 16.3.3.

16.5 ISOTOPES

One consequence of the group displacement law is that a daughter element produced due to the emission of one α - particle and two β -particles successively, shall have the same position as that of the parent element in the periodic table. But the atomic masses of the parent and daughter elements will not be the same.

For example, Uranium (238) loses one α - particle and two β - particles successively and gives the daughter element with atomic mass 234. The parent element and the daughter element are named as Uranium-I and Uranium-II. They occupy the same place (92) in the periodic table since there is no change in the charge of the nucleus or the atomic numbers of the elements but possess different atomic masses. Elements with same atomic number have identical chemical properties. **Soddy** proposed the name *isotopes* (Greek : same place) for such elements because they occupy the same place in the periodic table.

The decrease in atomic number and atomic mass by two and four units respectively when an α - particle is expelled can be ascribed to the loss of *two protons* and *two neutrons* from the nucleus of the parent element. But the increase in atomic number by a loss of β - particle cannot be explained in a similar way. It is therefore assumed that in the expulsion of β - particle, a neutron is converted into a proton and an electron, perhaps together with a *neutrino* and subsequently the electron is expelled. The positive charge of the nucleus therefore increases by one unit when this electron is expelled. The atomic number of the product consequently increase by *one unit.*

Check Your Progress - 2

What is a radioactive isotope?

16.6. SUMMARY

In this unit we have studied that:

i) a radioactive element emits α, β or γ rays so as to achieve stability. This can be done in a series of steps called radioactive disintegration series.

ii) in detail uranium series
Thorium series
Actinium series

iii) group displacement law

iv) the formation of isotopes.

16.7 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines each.

1. What information do you derive from half life of a radioactive element?
2. Discuss briefly group displacement law.
3. How is the occurrence of isotopes explained by the radioactive disintegration process?

II. Answer the following in 30 lines each.

1. Give a detailed account of radioactive disintegration series.
2. discuss the significance and utility of group displacement law.

16.8 MODEL ANSWERS TO CHECK YOUR PROGRESS

1 Four radioactive disintegration series are identified.

They are
a) 4N series or Thorium series
b) 4N +1 series or Neptunium series
c) 4N +2 series or Uranium series
d) 4N +3 series or Actinium series

2 There are a number of non-radioactive or stable elements.
eg.:- Carbon, nitrogen. If an isotope of such elements is radioactive then it is called radioactive isotope. eg: C^{14}_{6}

16.9 GLOSSARY

Electroscope (gold leaf)	:	A simple device to detect ionizing radiation.
Penetrating power	:	The ability to travel through.
Range	:	The distance traversed in air by the particle of a radioactive ray from its source before the particle ceases to have any appreciable power of producing ionisation.
Spontaneous disintegration.	:	A disintegration or a decay process taking place without any external agency.

Author: Prof. S. BRAHMAJI RAO

Block - 5

BEHAVIOUR OF GASES

The behaviour of all forms of matter is explained on the basis of the atomic and molecular hypothesis. The matter exists in nature in the form of aggregates of molecules. We do not deal with individual molecules as such, but with aggregates. Matter can be broadly categorised into solids, liquids and gases. These three are know as the **States of matter.**

UNIT - 17 : GAS LAWS

Contents

17.1 AIMS AND OBJECTIVES

The purpose of this unit is to give you an account of the experimental laws describing the behaviour of gases.

At the end of this unit you will be able to understand that:

- The gas laws are facts aimed at as a result of experimental observation. The four parameters necessary to explain gas behaviour are amount of gas, pressure, volume and temperature.
- Boyle's law describes the relation between the pressure and volume of a gas (at constant number of moles and temperature)
- Charles' Law describes the volume-temperature relationship of a gas (at constant number of moles and pressure).
- Dalton's law gives the relationship between the total pressure of a mixture of gases in terms of the individual pressure of each constituent.
- Graham's law describes the diffusion of gases and the relationship between the rate of diffusion and the molecular weight of a gas.

17.2 INTRODUCTION

The gaseous state is characterised by the fact that it has neither a definite shape nor size. A gas simply occupies all the space made available to it. A gas, unlike a liquid, has no surface at all. When we speak of the volume of a gas, what we mean is the volume of the container in which the gas permeates.

pressure of a dry gas when it is collected over water. The pressure of a dry gas is obtained by substracting, from the atmospheric pressure at which the gas is collected, pressure of water vapour, at the temperature at which the gas is collected.

17.8 DIFFUSION OF GASES

Diffusion is a property by which a substance tends to spread throughout the space made available to it. Diffusion is exhibited by solids, liquids and gases, but is most rapid in the case of gases. if two jars, each containing a different gas, are kept mouth-to-mouth with one another, it is found soon that the gases would have spread throughout the two jars. This would happen even if the jar containing the lighter gas is placed at the bottom, indicating that diffusion occurs inspite of gravity.

Thomas Graham (1827) proposed a law relating the rate of diffusion of a gas to its density. The law, known as Graham's law of diffusion is stated as: *"The rate of diffusion of gas is inversely proportional to the square root of its density"*. If r is the rate of diffusion of a gas and d its density, then,

$$r \propto (1/\sqrt{d})$$

$$r = \text{Constant}/\sqrt{d} \qquad \text{.... (19)}$$

If r_1 and r_2 are the rates of diffusion of two gases under certain specific conditions, and d_1 and d_2 are their densities respectively, then

$$r_1/r_2 = \sqrt{d_2}/\sqrt{d_1} \qquad \text{.... (20)}$$

The density of a gas is directly proportional to its molecular weight. Hence equation 20 can be written as

$$r_1/r_2 = \sqrt{M_2}/\sqrt{M_1} \qquad \text{.... (21)}$$

Where M_1 and M_2 are the molecular weights of the gases.

From equations, 20 and 21 it is evident that a lighter gas (or one with less molecular weight) would diffuse more rapidly than a heavier one (or one with great molecular weight). Conversely, the time of diffusion of a given quantity of a lighter gas is proportionately lesser than that for the same quantity of a heavier gas under similar conditions. Thus if t_1 and t_2 are the times of diffusions, under identical conditions, of two gases of densities d_1 and d_2, are molecular weights M_1 and M_2 respectively, it follows that

$$t_2/t_1 = \sqrt{d_2}/\sqrt{d_1} = \sqrt{M_2}/\sqrt{M_1} \qquad \text{.... (22)}$$

Diffusion studies, therefore provide a method of determination of molecular weights of gases.

17.9 SUMMARY

In this unit we have studied that:

i) The Boyle's law: pressure-volume relation of a gas when its mass and temperature are constant.

ii) Charles law: Volume-Temperature relation of a gas when its mass and pressure are constant.

iii) The equation of state obtained by combining Boyle's law, Charles law and Avogadro's law. This gives relationship between pressure, volume, temperature and number of moles of gas.

iv) The universal gas constant, R and its valume in various units.

v) Dalton's law of partial pressures and its applications

vi) Phenomenon of diffusion and Graham's law governingit.

17.10 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines each.

1. State and explain Avagadro's law.
2. State and explain Dalton's law of partial pressures.
3. How is rate of diffusion of a gas related to the density of gas? Give reasons for your answer.

II. Answer the following in 30 lines each.

1. Give a concise account of the different experimental laws of gases.
2. Derive ideal gas equation.

17.11 MODEL ANSWERS TO CHECK YOUR PROGRESS

1 Absolute zero is the temperature at which the volume of an ideal gas becomes zero. Theoretical and experimental evidence indicates that it is the lowest temperature possible. -273°C = 0K.

2 For one mole of an ideal gas PV/T is constant and it is called universal constant. This is indicated by R called molar gas conwstant or first gas constant. R = 0.0821 lit-atm deg^{-1} - $mole^{-1}$.

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UNIT - 18: KINETIC MOLECULAR THEORY

Contents :

18.1 AIMS AND OBJECTIVES

This unit aims to present you a theoretical model for an ideal gas and hence to derive an equation of state explaining the gas behaviour.

By the end of this unit you should be able to understand that:

- The Kinetic Theory of gases is a model, the postulates of which help in co-ordinating the various laws of gas behaviour.
- The mathematical expression derived from the postulates of the Kinetic theory, is known as 'Kinetic equation for gases'.
- Mean free path is the distance that a molecule moves between two successive collisions.
- The molecules of a gas do not all move with the same velocities; instead there is a definite distribution of velocities from very low to very high values.
- The most probable velocity is the velocity possessed by majority of molecules in a gas than in any other velocity. The average (or mean) velocity is the average of the velocities of all the molecules in a gas.
- The collision number is the number of collisions in unit volume per second. The collision diameter is the closet distance of approach between the centres of two molecules taking part in a collision.

18.2 INTRODUCTION

The gas laws that have been described in unit 17 have been laid down as a result of experimental investigation. Though arrived at as a result of observations of the behaviour of real gases, it is to be noted that the laws, in their strictest sense, are postulated to be obeyed only by ideal gases. It is evident that gases, as they exist, obey the laws only under very limited conditions, and deviate markedly from ideal behaviour under other conditions. There is an obvious need, therefore, to postulate a theory which provides a basis for the experimental laws.

18.3 THE KINETIC THEORY OF GASES

This theory makes certain assumptions regarding the characteristics of an ideal gas and enables the derivation of a mathematical expression, with the help of which the gas laws can be correlated. The Kinetic theory of gases was the result of the work of many, chief among whom were **D. Bernouilli** (1738), **J.J. Waterston** (1845), **K.A. Kronig** (1856), **R. Clasius** (1857) and others. It was presented in a mathematical form by **J. Clerk Maxwell** (1860) and **L. Boltzmann** (1868). It had been developed long before the "molecule" was accepted into chemical terminology and the electrical nature of matter was clearly understood. The fundamental postulates of this theory are

1. A gas consists of a large number of extremely small, perfectly elastic particles, which may be identified with chemical molecules, moving in all directions.
2. Because of the continual movement the molecules of the gas they collide with each other and also with the walls of the container.
3. These impacts of the gas molecules with the walls of the container are elastic and responsible for the pressure exerted by the gas. When the same gas is kept in a vessel of smaller volume than the original volume the molecules collide with the walls of the container more frequently. This results in increased pressure of the gas.
4. When the temperature is increased keeping the volume constant, the molecules move more vigorously. and the pressure increases.
5. In an ideal gas the molecules exert no attraction upon one another.
6. The molecules are assumed to be so small that their actual volume is negligible in comparison with the volume of the gas (when we talk of the volume of a gas, we mean the volume of the container in which the gas is kept).

With the help of these pbstulates, we shall derive a simple expression for the pressure of an ideal gas.

Consider a cube of size 1 cm, containing a total of **n** molecules of a gas, each molecule having a mass **m** grams. In the gas the molecules are all in random motion, moving in all directions and with a wide range of velocities. Let a given molecule have a velocity **c** cm per sec. This velocity may be resolved into three components **x**, **y** and **z**, in three directions, mutually at right angles and parallel to the edges of the cube. (Fig. 18.1).

Check Your Progress - 1

What do you know about kinetic molecular theory?

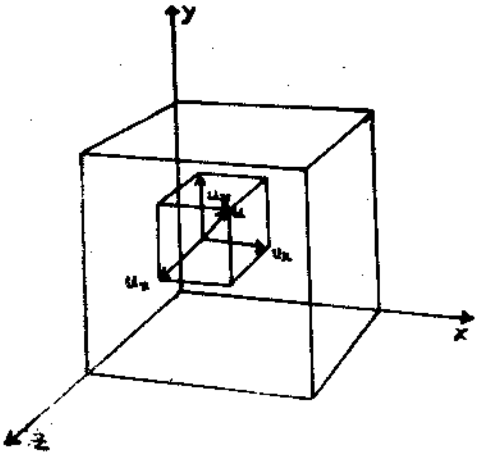

Fig. 18.1 The resolution of molecular velocity.

In reality **c** is not the velocity of any particular molecule, not is it the arithmetic mean of the velocities of the molecules, since such a quantity can be zero, owing to the fact that velocity is a vector. Instead **c** is a quantity such that its square is the mean of the squares of the velocities of all the molecules (the squares are always positive). In consequence **c** is called the **root-mean-square velocity**, or simply, the r.m.s., velocity. Thus,

$$C^2 = C^2_1 + C^2_2 + C^2_3 + \ldots\ldots + C^2_n \ldots \ldots \ldots /n$$

The theory assumes that the impacts of the molecules on the walls of the container are all elastic. This means that the velocities are the impact and rebound remain unchanged in magnitude. The sign is, however, changed because of the change of direction.

Consider, for instance, the movement of a molecule in the x-direction, with its component velocity x. Let the velocity component be x before the impact and -x after impact. Consequently the momentum before impacts is 'mx' and that after impact is '-mx'. The change in momentum in the x-direction is thus [mx -(-mx)] = 2mx for each impact of a molecule with the wall of the container.

The size of cube is 1 cm. Hence, the number of impacts on the two walls prependicular to the x-direction will be x/l per sec. Thus, the change of momentum per sec (in other words, the rate of change of momentum) due to the impacts in the direction will be.

$$2\,mx \times x/l, \text{ i.e., } 2\,mx^2/l.$$

Like wise the rate of change of momentum due to impacts in the other two directions, y and z, will be

$$2\,my^2/l \quad \text{and} \quad 2\,mz^2/l \quad \text{respectively.}$$

The total rate of change of momentum due to the impacts of a single molecule on all the six walls of the cube will therefore be

$$2\,mx^2/l + 2\,my^2/l + 2\,mz^2/l = 2m\,(x^2 + y^2 + z^2)/l.$$

$$= 2mc^2/l \quad \because \quad c^2 = x^2 + y^2 + z^2$$

As there are 'n' molecules in the cube, the total rate of change of momentum of the impacts of all the 'n' molecules will be

$$2\,mn\,c^2/l$$

From Newton's laws of motion, it follows that the rate of change of momentum is equal to the force acting, thus,

$$\text{Total force} = 2\,mn\,c^2/l$$

$$\text{But Pressure} = \text{Force/area}$$

The total surface area of the cube is $6 \times l^2$

$$\text{Hence, Pressure, } P = 2\,mn\,c^2/l \times 6 \times l^2$$

$$P = 1/3.\,mn\,c^2/l^3 = 1/3.\,mn\,c^2/V, \qquad (\text{since } l^3 = V)$$

$$\text{Thus} \quad PV = 1\,mn\;c^2/3 = 1/3\,mnc^2 \qquad \text{.... (1)}$$

This equation, derived from the assumptions of the kinetic theory of gases is known as **kinetic equation of state** for an ideal gas. Although the derivation is somewhat approximate, it has the advantage of its simplicity. Besides, with the help of this theoretical equation it is possible to deduce the gas laws, which, as mentioned already, are experimental laws. Thus a coordination between theory and experiment is provided.

Check Your Progress - 2

Explain the concept r.m.s. . velocity ?

18.4 DEDUCTION OF THE GAS LAWS FROM THE KINETIC EQUATION

18.4.1 Boyle's Law

The velocity of the molecules of a gas will increase with rise of temporature. In fact, it has been possible to show, on the basis of the kinetic theory that the temperature is proportional to the mean kinetic energy of the molecules in a gas. We have already derived the expression,

$$PV = RT$$

for one mole of an ideal gas.

And, according to equation (1)

$$PV = 1\,mnc^2/3 = 1/3\,mnc^2$$

If we now assume that 'n' represents Avogadro number (N) of molecules, then this equation could be rewritten as:

$$PV = 1\,m\,Nc^2/3 = RT$$

The Kinetic energy, E_k, of the molecules will be

$$E_k = 1/2\,m\,Nc^2$$

$$= 3/2 \times 1m\,Nc^2/3$$

$$\text{But} \quad 1\,m\,Nc^2/3 = RT$$

$$\therefore E_k = 3/2\,RT \text{ per mole} \qquad \text{.... (2)}$$

Thus the kinetic energy of 1 mole of any ideal gas will be directly proportional to its **absolute temperature.** This is an important and useful conclusion from the kinetic theory. This is also in agreement with the theoretical conclusion drawn by **J.C. Maxwell** (1860) that the mean kinetic energies of the molecules of all gases are the same at the same temperature.

At constant temperature, therefore, the kinetic energy $1/2\ mc^2$ will be a constant for every gas. From equation (1) we find that for a definite quantity of any gas at constant temperature, the quantity $1/3\ mn\,c^2$ will be constant. That is,

$$PV = 1/3\ mnc^2 = \text{Constant,}$$

at constant, temperature.. This is in agreement with **Boyle's Law.**

18.4.3 Charles' Law

Consider once again the Kinetic equation

$$PV = 1/3\ mnc^2$$

$$= 2/3 \text{ X } 1/2\ mn\,c^2$$

The Kinetic energy, $1/2\ mnc^2$ is proportional to the absolute temperature T of the gas, Thus

$$PV = \text{Constant X } T$$

$$\text{Or} \quad V = \text{Constant}/P \text{ X } T.$$

If now pressure is kept constant, it follows that the volume of the gas is directly proportional to the absolute temperature. This is **Charles' Law.**

18.4.3 Avagadro's Law

For two gases 1 and 2 the Kinetic equation (2) can be written as,

$$P_1 V_1 = 1/3\ m_1 n_1 c_1^2$$

$$\text{and} \quad P_2 V_2 = 1/3\ m_2 n_2 c_2^2$$

If both gases have the same pressure and occupy the same volume, then $P_1 = P_2$ and $V_1 = V_2$. Therefore,

$$1/3\ m_1 n_1 c_1^2 = 1/3\ m_2 n_2 c_2^2 \quad \text{.... (3)}$$

Also, if the two gases are kept at the same temperature, the average kinetic energies of their moleucles will also be the same, i.e.,

$$1/2\ m_1 c_1^2 = 1/2\ m_2 c_2^2 \quad \text{.... (4)}$$

Upon dividing equation (3) by equation (4), it immediately follows that,

$$n_1 = n_2 \quad \text{.... (5)}$$

i.e., equal volumes of different gases at the same pressure and temperature contain equal number of moleucles. This is **Avogadro's law.**

18.4.4 Dalton's Law of Partial Pressures

Suppose n_1 moleucles of a gas 1, each of mass m_1 and r.m.s. velocity c_1 occupy a volume V. The pressure, P_1, of the gas is given by

$$p_1 = m_1n_1c_1^2/3V \quad \text{.... (6)}$$

If n_2 moleucles of gas 2, each of mass m and r.m.s. velocity c_2 occupy the same volume V, the pressure p_2, is given by

$$p_2 = m_2n_2c_2^2/3V \quad \text{.... (7)]}$$

By similar reasoning, we could write expressions for the pressures of different gases occupying the same volume V.

Now, if all the gases occupy the same volume V simultaneously, then the total pressure P will be given by,

$$P = m_1n_1c_1^2/3V + m_2n_2c_2^2/3V + m_3n_3c_3^2/3V + \quad \text{.... (8)}$$

$$\text{Or} \quad P = p_1 + p_2 + p_3 + \quad \text{.... (9)}$$

This equation represents **Dalton's Law of partial pressures,** and p_1, p_2, p_3, etc., will now represent the partial pressures of the constituent gases in the mixture. The assumption, of course, is made, here that the gases do not interact with each other and that they behave ideally.

Thus, we find that from the simple postulates of the Kinetic theory, it is possible to derive an expression - the kinetic equation from which in turn, the gas laws could be deduced. This represents an elegant correlation between theory and experiment.

18.5 The Mean Free Path.

It is the average distance that a molecule moves between two successive collisions. It is evaluated with the help of another property called **collision diameter** (which will be discussed later). *The collision diameter may be considered as the closet distance between the centres of two molecules which take part in a collision.* The mean free path, 'l' of a molecule is given by the expression (10).

$$l = 1/2\,\pi\,n \quad \sigma^2 \,x\, c \quad \text{.... (10)}$$

Where n is the number of molecules in unit volume of a gas

One mole of a gas occupies a volume of 22400 cc at S.T.P. (i.e., 1 atmosphere pressure and 0^0 C). The number of molecules in one mole of a gas is approximately 6.0×10^{23}. Thus, n, the number of molecules in unit volume (1 c.c) of the gas would be 2.7×10^{19}. The diameters of gaseous molecules are approximately of the order of 2.0×10^{-8} cm. Using these values, we can calculate the value of the mean free path of a gas by means of equation 10.

$$l = 1/2 \times 3.1416 \times 2.7 \times 10^{19} \times (2.0 \times 10^{-8})^2$$

$$= 2.1 \times 10^{-5} \text{ cm.}$$

Thus we find that between two successive collisions, the distance that molecules of a gas travel is indeed very short. The mean free path is more or less the same for all gases under similar conditions.

Better values of mean free path are obtained from viscosity measurements. The expression, derived from the kinetic theory, is

$$\eta = 1/3.\, cd/l \quad \text{.... (11)}$$

Where 'η' (neta) is the coefficient of viscosity of the gas, 'c' its mean velocity, 'd' its density and 'l' its mean free path.

Decrease of pressure increases the mean free path of a gas molecule. The product of the pressure and the mean free path is a constant.

18.6 DISTRIBUTION OF MOLECULAR VELOCITIES.

In a gas all the molecules do not have the same velocity, owing to incessant collisions, there is a continual interchange of momentum between the molecules. Therefore, the velocities vary. This would be so, even if all the molecules, to begin with, start moving along parallel lines with the same velocity. Because of gravitational and other forces, collision would take place and eventually the (hypothetical) orderly movement will be replaced by the chaotic or random motion that is characteristic of the gaseous state.

J.C. Maxwell first calculated the manner in which the velocities of the molecules in a gas are distributed over all possible values, right from zero to very high velocities. This he derived from probability consideration. He expressed the results in the form of a mathematical expression. One form of the law of distribution of molecular velocities is.

$$1/n \;.\; dn/dc \;=\; 4\pi\,(M/2\pi\,RT)^{3/2}\; e^{-M.c2/2RT}\; X\; c^2$$

Where 'M' is the moleculer weight of the gas, 'R' the gas constant and 'T', the absolute temperature and 'e' is the base of natural logarithms. The left hand side of the equation gives the fraction of the total number of molecules (n) possessing a particular velocity 'c'. At this stage, however, it is sufficient to know that the molecules of a gas have all possible velocities, from very low to very high values and that it is possible to calculate what fraction of the molecule would have, that velocity (the **law of distribution of molecular velocities**). Using this law it is possible to calculate the fraction of the total number of molecules possessing a particular velocity, from known parameters such as the molecular weight of the gas under consideration, the gas constant R and the absolute temperature T.

A graphical representation of the results of Maxwell's law is shown below in figure 18.2

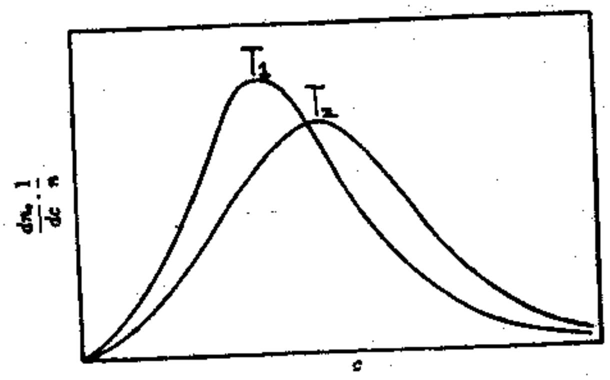

Fig. 18.2 Distribution of molecular velocities
T_1 = lower temperature T_2 = higher temperature

The general form of the curve is more or less the same for all gases, but the actual curve is determined by the molecular weight of the gas and the absolute temperature. In this curve the abscissa (X-axis) represents the molecular velocities (c), while the ordinate (Y-axis) gives the fraction of the molecules possessing the velocities indicated on the abscissa. The maximum of the curve gives the **most probable velocity** (μ). This is the velocity possessed by large number of molecules, it has been shown that the most probable velocity, μ, is given by the expression,

$$\mu = \sqrt{2}\,RT/M \qquad .... (12)$$

Where 'M' is the molecular weight of the gas and 'T' its absolute temperature.

Another quantity, known as the mean (or average) velocity, c, is given by,

$$c = c_1 + c_2 + c_3 + \ldots\ldots c_n/n \qquad .... (13)$$

The mean velocity is given by the equation,

$$c = \sqrt{8}\,RT/\sqrt{\pi}M \qquad .... (14)$$

The root-mean-square velocity, described earlier is given by the equation,

$$c = \sqrt{3}\,RT/\sqrt{M} \qquad .... (15)$$

Increase of temperature leads to an increase in molecular velocities and also to a wider distribution of velocities. But the important point to note is that the number of molecules with velocities higher than the mean velocity is considerably increased.

18.7 COLLISION DIAMETER AND COLLISION NUMBERS:

Mention has already been made, in Sec. 18.3, about collision diameter. During their random movement in a gas, the molecules collide with one another. When two molecules approach each other, a point is reached, at which, the repulsion between the two molecules becomes large enough to make them reverse their direction of motion. *The closest distance of approach between the centres of the two colliding molecules is known as* **collision diameter** (σ) (Fig. 18.3).

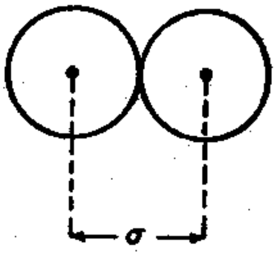

Fig. 18.3 Collision diameter.

In the case of molecules which are infinitesimally small, as in ideal gases, there would be an effective collision diameter, owing to their mutual repulsion.

The **collision number,** Z, *may be defined as the number of collisions in unit volume per second.* This is given by the equation.

$$Z = 2n^2 \sigma^2 \sqrt{\Pi}\, RT/\sqrt{M} \qquad \text{.... (16)}$$

Where 'n' is the number of molecules of the gas in unit volume ' σ ', the diameter collision and the rest of the quantities have their usual significance.

Calculations show that the number of collisions between molecules under ordinary conditions is of order of 10^{28} per sec. per cc of gas. This quantity does not change greatly with temperature but increase of pressure markedly increases the number of collisions.

18.8 SUMMARY

In this unit we have studied

i) Kinetic molecular theory as an acceptable model to explain the behaviour of gases.

ii) Postulates of kinetic theory and derivation of kinetic equation of state $PV = 1/3\ mnc^2$.

iii) Deduction of various gas laws from kinetic equation.
Boyle's law, Charle's law, Avogadro's law

iv) Maxwell's law of distribution of molecular velocities and most probable velocity

v) Collision diameter and collision number.

18.9 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines each.

1 State the postulates of kinetic molecular theory.
2 Derive any two gas laws from kinetic gas equation.

3 Give a concise account of law of distribution of molecular velocities.

II. Answer the following in 30 lines each.

1 State the postulates of kinetic molecular theory of gases and derive kinetic gas equation.

2 State kinetic gas equation and deduce the gas laws from the same.

18.10 MODEL ANSWERS TO CHECK YOUR PROGRESS

1 Gas law indicate the regularity in the behaviour of gases, but as to how this behaviour is achieved by them is not indicated. Therefore certain assumptions are proposed for molecules of the gases in the form of a theory called kinetic theory of gases. It explains as to how the regularity is achieved by gases.

2 It is the root of the average of the squares of the velocities of different molecules of gases. This velocity is proposed in order to overcome the complexity in the derivation of equation of kinetic theory of gases.

Author: M.D. SIDDHANTI

UNIT - 19 : DEVIATIONS OF GAS LAWS

Contents

19.1 AIMS AND OBJECTIVES

The main purpose of this unit is to discuss the deviations of real gases from ideal behaviour to arrive at an expression which takes into account the causes of deviation and to show how the expression explains behaviour of real gases.

When you have worked through the unit you should be able to understand that:

- The Kinetic theory is a model postulated essentially for ideal gases. But gases, are far from being ideal, and show considerable deviations from ideal behaviour.
- In real gases the molecules, unlike those in the hypothetical ideal gases, have considerable intermolecular forces. Also, the actual volume of the molecules is a considerable fraction of the volume of gas. These two aspects are more pronounced at high pressures and low temperatures.
- Vander Waal's equation of state is, among the various equations developed to explain the behaviour of real gases, by far the simplest question. It modifies the equation of state for ideal gases by introducing correction terms for the attractions between molecules and also for the actual volume of the molecules in real gases. However, even this equation is only of limited applicability.

19.2 INTRODUCTION

The gas laws like Boyle's law are empirical laws. Kinetic molecular theory was developed as an acceptable model to explain the behaviour of gases. The gas laws as deduced from kinetic equation of state are not strictly obeyed by any gas. A gas under study deviates from ideal behaviour. For instance the product (P x V) will not be a constant for a fixed mass of gas at constant temperature at all pressures and shows slight variations. We have to investigate the reasons for these deviations.

19.3 DEVIATIONS OF REAL GASES FROM IDEAL BEHAVIOR

The gas laws, strictly, are obeyed in their entirety only by what have been termed ideal gases. These ideal gases as we have emphasised already, are only hypothetical or imaginary. Gases, as they actually exist, are far form being ideal. As such, these "real gases" show considerable deviation from ideal behaviour. For instance the equation PV = RT, as derived for one mole of a gas, is obeyed to a fair degree of approximation at low pressures and moderately high temperatures.

But once the pressure is increased or the temperature lowered, a marked deviatin from ideal behaviour becomes noticeable. This can be seen from a consideration of the plot of product PV for a gas at various pressures and constant temperature. If Boyle's law were to be obeyed, as it should be by an idealgas, the product PV should be constant at various pressures. Consequently the plot of PV vs P should be a straight line parallel to the pressure axis as shown in the broken line in figure 19.1

But the experimental data collected for various gases show that such is not the case with almost every gas. Fig. 19.1 also indicates the PV-P plots for hydrogen and nitrogen at 0°c and for carbondioxide at 40°c (The plots are all relative to the assumption that product PV is unity at 1 atmosphere), The figure clearly indicate that real gases deviated considerably from ideal behaviour, this is no more so at higher pressures.

From the figure it is evident that hydrogen behaves in a manner different from other gases. The PV values for hydrogen increase continuously with pressure, where as for the other gases there is decrease to begin with, but later on there is an increase. helium and neon behave in a manner similar to hydrogen at ordinary temperatures. As the temperature is lowered, the behaviour eventually corresponds to that of nitrogen and carbondioxide. At sufficiently high temperature the pressure-volume curves become similar to those for hydrogen and helium at ordinary temperatures.

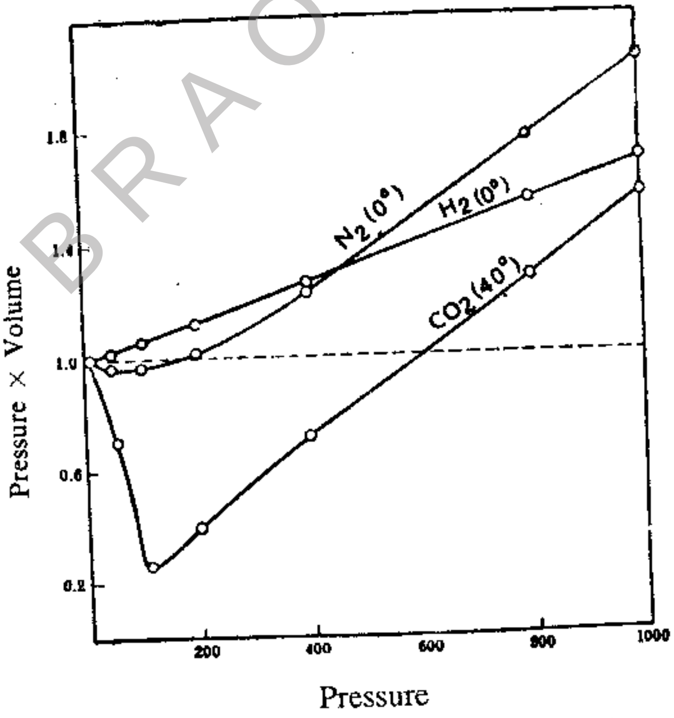

Fig. 19.1 Variation of PV with pressure (P).

Thus temperature is an important factor in deciding the deviations of a gas from ideal behaviour.

Considerable deviations occur in the case of real gases, from Charles's law as well as Avogadro's law. A general observation is that the more easily liquifiable a gas is, the greater is the deviation from ideal behaviour.

At a pressure of about one atmosphere or less, and at a temperature not too close to the point of liquifaction, the deviation from ideal behaviour occurs only to a small extent. Under these conditions, the equation PV = RT can be expected to hold, atleast to a fair degree of approximation. But at higher pressures and lowest temperatures, modifications to the equation are necessary.

Check Your Progress - 1

How and why real gases differ from ideal gases?

19.4 CAUSE OF DEVIATION FROM IDEAL BEHAVIOUR - VAN DER WALLS EQUATION

The gas laws, derived from the kinetic theory, and applicable to ideal gases, are based on two important assumptions. These are, that the actual volume of the molecules is negligible in comparision with the volume of the gas as a whole, that the molecules do not exert any attraction on one another. There can be no doubt that these two assumptions are invalid so far as real gases are concerned. There is considerable evidence that the molecules do possess a volume which, under certain conditions, constitues a not inconsiderable part of the total volume of the gas.

The fact that gases can be liquified is a clear indication that the molecules in a gas do attract one another. The cohesive forces in a liquid have their origin in these attractions between the molecules. These attractions are evidently present in gases too. These two aspects concerning real gases, which are contrary to the assumptions of the kinetic theory, are thus reasponsible for the deviation of real gases from ideal behaviour. It is therefore necessary to take these two factors into consideration in order to make any modifications to the ideal gas equation PV = RT, so that it may be in closer conformity to the behaviour of real gases.

19.4.1 Correction for internal pressure

Of the many attempts made in this direction, a simple and elegant one was one proposed by **J.D. van der Walls** (1873). His treatment of the problem was somewhat along the following lines. Consider a molecule A in the interior of a gas (Fig. 19.2).

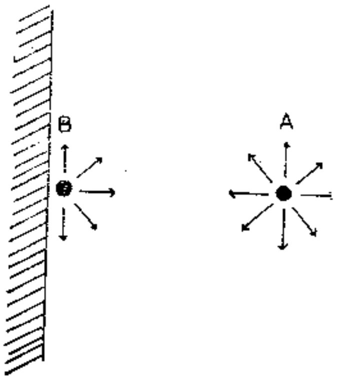

Fig. 19.2. Molecules in a gas contained in a vessel.
A. Molecule in the middle of the container
B. Molecule approaching the wall.

In this condition it is surrounded by other molecules uniformly on all sides. Hence whatever are the attractive influences to which this molecule is subjected, they mutually cancel out. Therefore there will be no resultant force acting on the molecule. But as the molecule approaches the wall of the container, there is a drastic change in the situation. The molecule (now represented by B) is no more surrounded by other molecules uniformly. The surrounding molecules are present on only three sides of the molecule under consideration. Consequently the molecule experiences a force tending to pull it inwards into the bulk of the gas. In other words, as this particular molecule is about to strike the container wall and make its contribution to the total pressure of the gas, it is pulled inwards by the surrounding molecules. As a result the actual pressure P, will be some what less than the ideal pressure (That is, the pressure which it might have exerted, had it not been subject to the attractions of the molecules behind it). It therefore becomes necessary to introduce a correction term taking into account these attractive forces.

The attractive force on a molecule that is about to hit the container wall will be proportional to the number of moelcules per unit volume in the interior of the gas. And the number of molecules striking the walls will also be proportional to this number. If we assume this number to be 'n', then total attractive force on the molecules about to strike the container wall, will be proportional to n^2. Assuming that the volume of the mole of the gas is V, then 'n' will be inversely proportional to V. The attractive force will then be proportional to $1/V^2$.

Thus the corrected pressure (or the ideal pressure) will be equal to $P + a/V^2$, where 'a' is a constant and P is the real (observed) pressure of the gas.

19.4.2. Correction for actual volume of gas

One more correction is necessary, and that is the volume correction to account for the actual volume of the molecules of the gas. This correction term 'b' is known as the **covolume.** But, 'b' is not equal to the exact volume of the molecules as such. It has been shown to be four times the actual volume of the molecules.

Thus, the corrected (ideal) volume is equal to (V-b). Hence, the product of the ideal pressure and ideal volume for 1 mole of gas will be equal to RT.

$$(P + a/V^2)(V-b) = RT \quad \text{.... (1)}$$

This equation, known as the van der Waals equation is by far the simplest and best known equations of state for **real gases.**

19.4.3. van der Waals' constant

The constant 'a' and 'b' in equation 1 are usually referred to as van der Waals constants. The constant 'a' is a measure of the molecular attractions, and the constant 'b' is, as mentioned already, a measure of the

Table 19.4.3 van der Waals constants

Gas	a (Litre², atm. mole⁻²)	b (litre. mole⁻¹)
Hydrogen	0.245	0.0266
Helium	0.034	0.0237
Nitrogen	1.39	0.0391
Oxygen	1.32	0.0318
Carbondioxide	3.60	0.0428
Sulphurdioxide	6.7	0.056
Chlorine	5.5	0.049
Ammonia	4.0	0.037

dissolved in some suitable non-absorbing solvent. The most common solvents used for determination in the ultraviolet region are *alcohol, water* and *hexane*, λ_{max} may shift with the nature of solvent. However, λ_{max} for non-polar compounds is generally the same in alcohol and hexane. But λ_{max} for polar compounds is usually shifted.

For measurement of absorbance (A), the solution is placed in some suitable container which is transparent to light (electromagnetic radiation) in the required region (visible or ultraviolet). The container is called 'optical cell' or 'cuvette'. Cells made of glass are useful for studies with visible light but not suitable for studies with ultraviolet light, since glass absorbs ultraviolet light. Hence, quartz cells are used for studies with ultraviolet light. The most commonly used cells have 1.0 cm path length. The source of light in the ultraviolet region (1800 - 4000 A^0) is the hydrogen discharge lamp. Tungsten filament lamp is generally employed for the visible light (4000 - 8000 A^0). The device or the instrument used to measure absorbance at different wavelengths of light is called *spectrophotometer*. Most recording spectrophotometers record automatically absorbance and wavelength. The graph showing the absorbance at different wavelengths is called the 'absorption curve' or 'absorption spectrum'. A typical absorption curve is shown in figure 13.1.

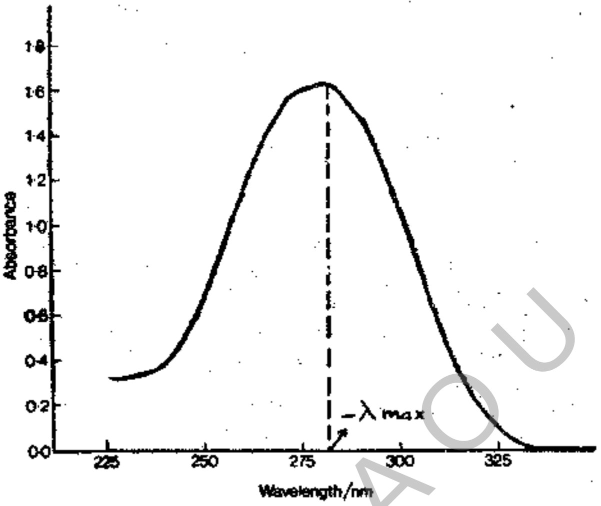

Fig. 13.1 Typical absorption curve

Check Your Progress - 2

What do you understand by λ max ?

13.6 DETERMINATION OF CONCENTRATION

13.6.1 Simple Solution Analysis

The solution of different concentrations of the compound are prepared and their absorbances (A) are measured at the wavelength of maximum absorbance (λ_{max}). The absorbance is plotted against concentration. A linear curve passing through the origin is obtained if Beer's Law is obeyed. This linear curve is generally referred to as *calibration curve*. The absorbance of the solution of unknown concentration is measured in a similar way and its concentration corresponding to this value is read from the calibration curve (Fig. 13.2).

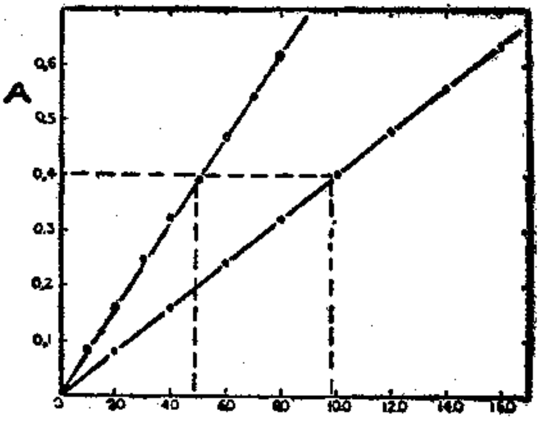

Fig. 13.2 Beer's law obedience or calibration curves

13.6.2 Mixture Analysis

The absorbance (A_1 and A_2) of the two solutes (S_1 and S_2) present in the solution are additive, if there is no chemical reaction between the solutes. The wave lengths. (λ_1 and λ_2) of maximum absorbance of the two solutes are determined in two separate experiments. The absorbance (A_1 and A_2) of the mixture at each of these two wavelengths (λ_1 and λ_2) is measured using a cell of path length 1cm and the results are used to determine the concentrations (C_1 and C_2) of the solutes in the mixture. The following simultaneous equations can be written for the absorbance measured at wavelength (λ_1 and λ_2).

$$A_1 = \underset{\lambda_1}{\varepsilon^1} c_1 + \underset{\lambda_2}{\varepsilon^1} c_2$$

$$A_2 = \underset{\lambda_2}{\varepsilon^2} C_1 + \underset{\lambda_2}{\varepsilon^2} C_2 \qquad \ldots \qquad (7)$$

[since l = 1 cm]

$\underset{\lambda_1}{\varepsilon^1}$ $\underset{\lambda_2}{\varepsilon^1}$ and $\underset{\lambda_1}{\varepsilon^2}$ $\underset{\lambda_2}{\varepsilon^2}$ are the molar extinction coefficients of the solutes 1 and 2 at the wavelengths λ_1 and λ_2.

Equations 6 and 7 are solved and concentrations C_1 and C_2 obtained.

13.7 SUMMARY

In this unit we have studied

i) The quantitative relations between intensity of radiation absorbed and the concentration of the absorbing substance and their important applications.

ii) Grothuss-Draper Law: Light radiation absorbed by the reacting system alone is capable of producing chemical change.

iii) Fluorescence and phosphorescence

iv) Lambert-Beer Law : The absorbance at a given wave length by an absorbing species in the dissolved state in a non absorbing solvent depends on the concentration of the species and the optical path length of the cell.

v) Applications of Beer's Law namely simple solution analysis and mixture analysis.

13.8 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines each.

1. Derive the mathematical equation for Beer's Law.
2. How are absorbance (A), intensity of light transmitted (I_t) and intensity of light incident (i_0) related?
3. Calculate the value of 'ε ' for a substance whose absorbance (A) is 0.6 in its 10^{-6}m solution. The path length of the cell is 1 cm.

II. Answer the following in 30 lines each.

1. Discuss the application of visible spectrophotometry in chemical analysis.
2. Explain how a binary mixture containing copper and chromium can be analysed for determining the concentration of the metals.
3. What are the basic requirements for the analysis of a dilute metal solution by spectrphotometric method?

13.9 MODEL ANSWERS TO CHECK YOUR PROGRESS

1 Log I_0/I_t is called absorbance or transmittance. In the equation I_0 = intensity of incident radiation and I_t = intensity of transmitted radiation.

2 In the electronic transition of molecules by the absorption of radiation, the wave length where maximum amount of radiation is absorbed is called λ max.

13.10 GLOSSARY

Induced dipoles	:	Symmetrical molecule such as chlorine, hydrogen which suffer deformation under the influence of electric field and exhibit temporary polarity.
Rotation quantum number	:	Rotation energy is quantized in the molecule. The number signifying this quantization.
Vibration quantum number	:	Vibration energy is quantized in the molecule. The number signifying this quantization.
Spectral assignments	:	The attributing of absorption spectral peaks to the rotational or vibrational or electronic transitions in the molecule.

Block - 4

RADIOACTIVITY

You are all familiar with the name X-rays. These are widely and frequently used in hospitals for detecting bone fractures, lung diseases, and other diagnostic purpose. These rays were discovered by **Rontgen** in 1896. Soon after Rontgen's announcement of his discovery of X-rays, the French Physicist **Henry Antonie Becquerel** became interested in the subject. This interested **Becqerel** who was also a physicist. He made a particular Edmond study of a luminiscent phenomenon known as *fluorescence* exhibited by some chemical substances on exposure to sun light. **Edmond Becquerel** had used a pure sample of a chemical called potassium uranyl sulphate in his fluorescence studies. Henry Becquerel was in possession of this chemical and used the same in an attempt to discover the relation, if any, between X-rays and the luminiscence exhibited by the uranium salt. For this purpose, Henry Becquerel placed a thin crystal of the salt on a photographic plate wrapped in a black paper and exposed the whole thing to sunlight. To his pleasant surprise and amazement, Becquerel on developing the photographic plate, found that it was darkened. This fact was interpreted by Becquerel as being due to the emission of some type of radiations by the uranium salt, which could penetrate the black paper and darken the photographic plate. In the subsequent experiments, he could show that these radiations (rays) could pass through even thin sheets of aluminium and copper and darken the photographic plate. H. Becquerel was also of the opinion that uranium salt had emitted the rays as a result of exposure to sun light.

But owing to the force of circumstances (sun not shining continuously on certain days) Becquerel was forced to wind up the experiment and put the photographic plates alongwith the uranium salt back in the drawer o f his table. There was no sun light for many days that followed. This disappointment at the non-availability of sun light continued for a few days. In sheer frustration he took the photographic plates out and developed them thinking that there would be no darkening or at best nly a faint darkening of the plates. But to his great surprise Becquerel found that there was darkening of the plate of great intensity. So he came to the conclusion that uranium salt emitted some sort of rays even without being exposed to sunlight. He further discovered that these rays persisted for a long time. All these observations took place 1896, when Henry Becquerel was inspired by the discovery of X-rays by Rontgen. This remarkable phenomenon discovered in 1896 by Henry Becquerel was named **Marie Curie** in 1898 as *radioactivity*.

UNIT - 14 DISCOVERY OF RADIOACTIVITY

Contents

14.1 AIMS AND OBJECTIVES

In this unit we give you a brief historical amount of the discovery of radioactivity and to explain the phenomenon of radioactivity.

After completing this unit you should be able to understand the following:

- The spontaneous emission of a certain kind of rays by compounds such as Uranium salts.
- Many other elements such as Polonium, Radium, Thorium also exhibit radioactivity.
- **Rutherfod** (1899) concluded that radioactive emanations consist of two types of rays called *alpha* rays and *beta* rays.
- Shortly afterwards **Curie** (1900) discovered third type of rays called *gamma* rays.
- The properties of alpha (α) ,beta (β) and gamma (γ) rays were established mainly by subjecting the radiations to magnetic field.
- α-rays are positively charged, β-rays are negatively charged and γ-rays are neutral.
- α-rays consist of particles of charge (+2) and mass (4 units). They move with a velocity of the order of 1.4 to 2.0×10^9 cm. per sec. The iônizing power is great.
- β-rays consist of rapidly moving negatively charged particles (electrons). They move with a velocity of 2×10^{10} cm. per sec. Their ionizing power is less than that of α-ray.
- γ-rays consist of electro-magnetic radiations analogous to X-rays.

14.2 INTRODUCTION

Henry Becquerel had discovered that uranium salt emits radiations (even in the absence of sun light) which are similar to X-rays in that they could penetrate materials opaque to ordinary light (black paper, aluminium sheet or copper sheet) and affect a photographic plate. In his curiosity to find out whether these rays would be able to produce ionization in air like x-rays, he conducted experiments with a *gold-leaf electroscope*. The electroscope is a device to detect ionized, it becomes an electrical conductor and permits the discharging of the charged gold sheet. This makes the like charged gold sheet move apart (bcause of the electrical repulsion between them) or opposite charged gold sheets to come together. Becquerel observed that uranium salt brought close to the charged gold leaf electroscope would cause the latter to discharge which made him conclude that the rays from uranium salt could ionize the air in their vicinity. Later experiments conducted by Becquerel revealed that this is not the exclusive property of potassium uranyl sulphate, but common to all uranium salts and even the metallic uranium. Soon after Becquerel's discovery, many chemical elements such as thorium, polonium, and radium were shown to exhibit radioactivity.

Systematically following these early discoveries, investigators have shown that more than forty elements in nature exhibit radioactivity in the elemental state or in the compound state. A large number of elements not found in nature but generated by special methods are also now known to show radioactivity.

14.3 NATURE OF RADIOACTIVITY (PROPERTIES OF A, B AND P RAYS)

E. Rutherford in 1899 during his studies on the penetrating power of the radiations found that they are made up of two types of rays. These rays were named by him as α-rays (alpha rays) and β -rays (beta rays). The former produce stronger ionization than the latter. Shortly afterwards in 1900 **p. Curie** found that a part of the radiation was not deflected by a magnetic field. The rays in this part of the radiations were shown to have exceptional penetrating power. Thus the rays differed in their properties from the earlier rays. These rays were therefore called the γ -rays (gamma rays). These γ -rays are about 10 to 100 times more penetrating than β -rays. These β -rays have a penetrating power about 100 times greater than that of α-rays, Thus it was found that the radiations compose of three types of rays α, β and γ rays.

The radiations emanated by radioactive elements are subjected to magnetic field to establish the nature of the rays (α, β and γ)

The experiment (as shown in figure 14.1) reveleaed that α rays were bent in the direction and β rays in the opposite direction, while γ rays were not bent at all.

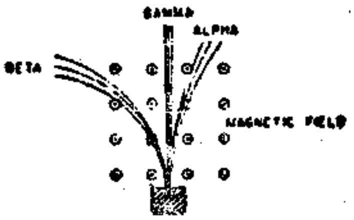

Fig 14.1 Radioactivity - alpha, beta and gamma rays.

From the direction of bending it is concluded that α– rays are positively charged and β-rays negatively charged while γ -rays are uncharged. The charge and mass of the particles constituting these rays are determined experimentally. The penetrating ability and the ionizing power of the rays are determined, by different experiments. The data obtained in respect of charge, mass, penetrating ability and ionizing power of the rays are given for each type of rays in section 14.2a to 14.2c.

Check Your Progress - 1

What kind of rays, the radioactive radiations consist of?

14.3.1 Alpha Rays

The direction of deflection of these rays in a magnetic field shows that they are positively charged. The charge to mass ratio (e/m) is determined by studying the deviation in their path as a result of the superimposition of electric and magnetic fields. This ratio is found to be 4.813×10^3 e.m. units per gram. The magnitude of the charge determined through a separate experiment is found to be 9.3×10^{-10} e.s. units which is twice the charge of an electron. These results indicate that α partides carry a *positive* charge of *two units* and a mass of *four units*. From this it is concluded that α- particle is a helium nucleus consisting of *two* neutrons and *two* protons firmly bound together. The initial velocity of the α-particle determined from the deflection of α- rays in electric and magnetic fields is of the order of 1.4 to 2.0×10^9 cm per sec. that is, one-fifteenth to one-twentieth of the velocity of light. The initial velocity is releated to the range of the α- particle in air. The range is the distance from its source traversed by the particle in the air before it ceases to have any appreciable power of producing ionization. The initial velocity and the range of α- particle vary from element to element (Table 14.1) emitting the particle.

Table 14.1 Initial velocity and range of α-particle

Radio elements	Velocity (cm/sec)	Range (cm)
Uranium	1.39×10^9	2.63
Radon	1.61×10^9	4.12
Thorium	1.38×10^9	2.58

Since α-particles have an appreciable mass and move with high velocity, they have considerable kinetic energy. They, therefore, produce considerable ionization. The majority of the α-particles travel in straight line through a thin sheet of metal.

14.3.2 Beta Rays

The direction of deflection of β-rays in a magnetic field shows that they carry a negative charge. measurements in electric and magnetic fields indicate that the ratio of charge to mass is 1.77×10^7 e.m. units per gram. This is almost identical with that obtained for electrons. This fact shows that β-rays consists of fast moving electrons. The velocity of β-rays also vary from element to element. The velocity approaches that of light, the average value being 2.0×10^{10} cm. per sec. The β-rays have considerable penetrating power because of their high speeds. Because of negligible mass they do not move in a straight line. It is, therefore, not possible to measure the range of β-particles. The mass makes the β-particles have less ionizing power than β-particles.

14.3.3 Gamma Rays

The great penetrating power of γ-rays and the failure of electric and magnetic fields to deflect γ-rays indicate that γ-rays are similar to electromagnetic radiaions such as x-rays. The wave length of γ-rays range between 10^{-8} and 10^{-11} cm. It was thought at one time that the emission of γ-rays occured simultaneously with that of α or γ-particle. Now it is known that it takes place subsequent to the emission.

Thus it may be seen that radioactive elements emit radiations consisting of α, β and γ -rays and α, β rays are found to be consisting of positively and negatively charged particles respectively while γ -rays are electromagnetic radiations. The velocities, penetrating abilities, and ionizing power vary from one kind of rays to another.

◆

Check Your Progress - 2

How the properties of α, β and γ -rays are determined?

14.4 SUMMARY

In this unit we have studied:

i) The discovery of natural radioactivity by Henry Becquerel and later by Marie Curie.

ii) The types of radioactive emanations α, β and γ -rays.

iii) The properties of α, β and γ -rays.

14.5 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines each.

1. Describe briefly the discovery of Radioactivity.
2. Give a brief account of the nature of the radioactive radiations.
3. Describe the properties of α-rays.

II. Answer the following in 30 lines each.

1. Give a critical account of the discovery and nature of radioactivity.
2. Describe in detail the properties of α, β and γ -rays. Discuss how these properties are established.

14.6 MODEL ANSWERS TO CHECK YOUR PROGRESS

I. 1. By applying electric field their change is being determined.

2. By allowing them to pass through metals their penetration capacity is measured.

3. By allowing them to fall on ZnS Plate their tendency to develop luminosity is measured.

II. Radioactive radiations possess three types of rays. They are α, β and γ -rays. α–rays consist of helium muclei, β-rays contain electrons and γ -rays are only electromagnetic waves.

Author: Prof. S. BRAHMAJI RAO

UNIT - 15 : RADIOACTIVE DISINTEGRATION RATE

Contents

15.1 AIMS AND OBJECTIVES

The aim of this unit is to explain you the process of radioactive disintegration, the radioactive equilibrium and to define the terms average life and half-life period of radio elements.

When you have finished this unit you must be able to know that :

- Atoms of radio-active elements undergo spontaneous disintegration, with the emisson of α and β-particles.
- The atomic mass and properties of new species produced in the distintegration depend on the nature of particle emitted.
- Every emission of α-particle means that the new element (daughter element) has an atomic mass 4 units less than the parent element.
- The emission of β-ray involves no appreciable change in atomic mass because of the negligible mass of β-particle.
- The rate of decay of radio-element follows an exponential law.
- The activity at any instance (I_t) and the ativity at zero time (I_o) are related by the equation $I_t=I_o e^{-\lambda t}$.
- λ is called radioactive constant or *decay constant* and is characteristic of element responsible for the activity.
- The reciprocal of λ is referred to as the average life τ (tau) of a radioactive element.
- The *half-life peirod* (T) is the time that elapses for the radioactivity at any instant to decrease to half its value.
- The half-life period (T) and radioactive constant (λ) are related by the equation $T=0.693/\lambda$.

15.2 INTRODUCTION

You are learnt in lesson-14 that some naturally occuring elements (e.g. uranium, thorium) emit characteristic radiations on their own without any external agency and this behaviour of the elements is called *Radioactivity*. It is further said that these radiations contain three types of rays namely alpha, beta and gamma rays. These rays differ in their properties in respect of their electrical nature, penetrating power and ionizing power. But with little variations in the actual values, every radioactive element produced the same three types of rays. This suggests that the process involved in the radioactivity of any element is basically the same. the process has been shown to be the spontaneous disintegration of the *nucleus* of the atoms of these elments. This phenomenon of disintegration of radioactive elements is ascribed to the instability of the nucleus of the atoms of radioactive elements. In an elementary fashion, the instability has been traced to the unfavourable ratio of protons to neutrons in the nuclei of the atoms.

15.3 RADIOACTIVE DISINTEGRATION

The early workers in radioactivity observed very interesting facts about the behaviour of compounds of radioactive elements in solution. These facts were useful to understand the complex phenomenon of radioactivity. H. Becquerel observed that a precipitate is formed when ammonium hydroxide is added to a solution containing a uranium compound and a ferric salt. But still the solution contained some amount of uranium salt. It was noticed by him that the precipitate showed most of the original activity of uranium salt solution and that the liquid (containing still uranium) is *inactive*. This observation shows that the most activity of uranium compound is not due to the element uranium but to another species as uranium-X. On standing for some months, uranium in solution gradually regained its activity and the precipitate lost its activity. These two reactions were found to occur with same rate. The total activity of the system remains constant. These facts lead him to conclude that uranium continuously producing the active product uranium-X and that this gradually decays and loses its activity.

15.3.1 Radioactive Disintegration - Theory

E. Rutherford and **F. Soddy** in 1903 proposed a theory to explain the phenomenon of radioactivity as well as the observations described in section 15.2. This theory is known as theory of *radioactive disintegration.*

The atoms of radioactive elements unlike others undergo spontaneous disintegration with the emission of alpha or beta particles. this disintegration results in the formation of a new element which is quite different physically and some times chemically from the parent element. This new element may in turn also be unstable and emit a particle (α or β) with the production of still another new element. there may be a succession of this type of disintegrations or transformations. The nature of the element (atomic mass and chemical properties) produced during the disintegration depends on the nature of the particle emitted. For example every emission of α particle means that the new element has an atomic mass 4 units less than that of its parent. the emission of β particle, on the other hand, involved no appreciable change in atomic mass because of the negligible mass of a β particle. In spite of there being no apparent change in atomic mass the chemical and physical properties of the new element are quite different from those of its parent. *Three* radioactive disintegration series, viz., the *thorium* series, the *actinium* series and the *uranium* series, have been identified. These will be cnsidered in detail in lesson - 16.

15.3.2 Radioactive Disintegration - Rate

The measurement of radioactivity from time to time of the new element formed in a disintegration process has revealed that the rate of decay follows an exponential law.

If 'I_t ' is the activity at any time 't' and I_0 the initial activity at zero time, the decay can be represented as

17.4 TEMPERATURE - VOLUME RELATIONSHIP OF A GAS

Charles' Law

This law is sometimes referred to as Gay-Lussac's law also. In its original form, the law states that *"at constant temperature the volume of a given mass of a gas increases by the same fraction of its volume at* 0^0C., for every one degree rise of temperature".

If V_0 is the volume of a given mass of a gas, then according to Gay - Lussac's or Charles's law, the volume, V_t, at t^0c is given by $V_t = V_0 (1 + \alpha t)$, where α is a constant, which is the same for all gases (at least at low pressures and high temperatures). The value of α has been found to be 0.00366 (or 1/273). This value is the accepted one for an 'ideal gas'.

Thus, equation can be written as

$$V_t = V_0 (1 + t/273) \qquad .... \; (4)$$

From this equation it can be seen that the volume of an ideal gas should become zero at - 273^0 C. This temperature is known as the **"absolute zero"**. Theoretical and experimental evidence indicates that this is the lowest possible temperature.

Addition of 273^0 to the Celsius temperature gives the absolute temperature known as the **Absolute** or **Kelvin** scale of temperature, in honour of **Lord Kelvin** (William Thomson).

According to moden notation, when temperature is mentioned in the absolute or Kelvin Scale, the word "degree" is omitted. Thus, we should say 273 K and not 273^0 K. again 25^0 C is 298^0 K (or 298 degrees Kelvin). This point may be noted,

$- 273^0$c = 0K
0^0c = 273 K
t^0c = (273 + t) K

It is the common practice to indicate the absolute temperature in capital letter T.

Equation 4 can be rearranged as

$$V_t = V_0 \text{ X } (273 + t)/273$$

$$V_t = V_0 \text{ X } T/273 \qquad \text{Where } T = (273 + t)$$

This can be generalised as

$$V_1/V_2 \quad = \quad T_1/T_2 \qquad .... \; (5)$$

Where V_1 and V_2 are the volumes of a given mass of gas at the absolute temperatures T_1 and T_2 respectively (at constant pressure).

Thus,

$$V/T \quad = \quad \text{Constant} \qquad .... \; (6)$$

Equation 6 provides an alternate statement of Charles's Law : *"The volume of a given mass of gas at constant pressure is directly proportional to the absolute temperature of the gas"*.

It should be noted that though theoretical deduction indicates that the volume of a gas should be zero at the absolute zero (-273°C), all gases either turn to liquid or solid before this temperature is reached. Besides, it has also been shown that the law does not really hold good at extremely low temperatures.

Graphical relation between the volume and the absolute temperature of a gas indicates that straight lines are obtained when V is plotted against T (at constant P). This is shown in figure 17.2. These straight lines are known as 'isobars', cut the abscissa at a point where the temperature is zero absolute.

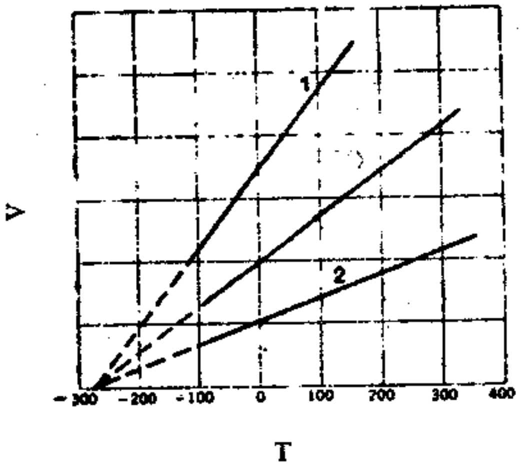

Fig. 17.2 Volume-temperature relationship of an ideal gas.
1. at low pressure 2. at high pressure 0. normal pressure

Check Your Progress - 1

How do you define absolute zero?

17.5 THE EQUATION OF STATE

The equations representing Boyle's Law and Charles' Law can be combined to give a relationship between pressure, volume and temperature of a gas.

Suppose a **given mass of gas** has a volume V_1 at a pressure P_1 and temperature T_1. Keeping the temperature constant, let the pressure be changed from P_1 to P_2. Then according to Boyle's Law,

$P_1 V_1 = P_2 V_2$, where V_2 is the volume at the pressure P_2.

Therefore, $V_2 = P_1 V_1 / P_2$

Let now, temperature be changed from T_1 to T_2 keeping the pressure constant at P_2. Then according to Charles's Law.

$$V_1/T_2 = V_2/T_2$$

$$\text{Or} \quad P_1V_1/T_1 = P_2V_2/T_2 \qquad \text{.... (8)}$$

This generalised relationship will hold good under other conditions too, Thus,

$$P_1V_1/T_1 = P_2V_2/T_2 = P_3V_3/T_3 \qquad \text{.... (9)}$$

Or $PV/T = \text{Constant}$ .... (10)

This equation is called the **"equation of state"** for an ideal gas, and is arrived at by combining Boyle's Law and Charles's Law.

Strictly, the constant in equation 10 is a quantity which depends on the mass and nature of the gas. But with the help of Avogadro's law, a commonality can be obtained. According to the law, *equal volumes of different gases under the same conditions of temperature and pressure, contain the same number of molecules"*. To put it in another way, this means that equal number of moles of different gases, at the same temperature and pressure, will occupy the same volume. Thus, if we take one mole of every gas at the same temperature and pressure (i.e., one **Avogadro number** of molecules, 6.02×10^{23}, of every gas), they will all have the same volume. Hence, the constant in equation 10 will be same for every gas and will be independent of the nature of the gas. *For one mole of any gas PV/T will be a universal constant. This constant indicated by the symbol R, is known as the molar gas constant or simply, the "gas constant".* Therefore, the general equation of state for any gas can be written as

$PV/T = R$ Or $PV = RT$ .... (11)

It may be noted that V in equation 11 is the volume of one mole of a gas. For 'n' moles of gas at the same temperature and pressure, the volume will be n times V: thus.

$V = nV$; where V is the volume of n moles of gas, then,

$PV = nRT$ .... (12)

The discussion thus far has been based on the assumption that gases obey Boyle's Law and Charles's Law. But gases, as they exist, obey these laws to a certain degree of approximation only, at relatively low pressures, high temperatures. Real gases, as those existing in nature are called, cannot, therefore, be regarded as obeying the gas laws implicitly under all conditions. We therefore postulate that *such gases as do strictly obey the gas laws are called "ideal gases"*. These ideal gases are, of necessity, hypothetical or imaginery. Thus equations 11 and 12 may be called **ideal gas equations.** This is just as well, because a knowledge of the extent of deviation of real gases from ideal behaviour, under a given set of conditions, will throw light on the imperfections that are characteristic of natural systems.

17.6 THE GAS CONSTANT, R.

It is necessary now to consider the units in which gas constant, R, is expressed. This is of considerable importance in dealing with many problems that arise in physical chemistry.

starting with equation 12, we see that

$R = PV/nT$ .... (13)

Thus the gas constant has the dimentions,

R = Pressure x Volume/degrees x moles

= Force/area x Volume/degrees x moles

= Force x $(\text{length})^{-2}$ x $(\text{length})^{3}$/degrees x moles

= Force x length/degrees x moles

= Energy/degrees x moles

Which clearly shows that R has the dimension of energy. Degree^{-1}. mole^{-1}. Let us evaluate R in the various units that are commonly in use. The product of pressure and volume, PV, has also the dimensions of energy. The student may usefully work this out. Let us evaluate R in the various units that are commonly in use.

Check Your Progress - 2

What is gas constant R?

17.6.1 R in absolute units.

Consider one mole of an ideal gas, under standard conditions P = 1 atmosphere, V = 22.4 litres and T = 273 K. Converting to absolute Units

$P = 1 \times 13.6 \times 980.1$ dynes/sq.cm.

$V = 22.4 \times 1000$ cc.

$T = 273$ K

Therefore

$$R = 13.6 \times 980.1 \times 22400/273 \text{ ergs degrees}^{-1} \text{ mole}^{-1}$$
$$= 8.314 \times 10^7 \text{ ergs, degree}^{-1} \text{ mole}^{-1}$$

17.6.2 R in joules

$R = 8.314$ Joules, degree^{-1} mole^{-1} (since 1 Joule = 10^7 ergs).

17.6.3 R in calories

One calory is equivalent to 4.184 Joules. Therefore 8.314 joules would be equivalent to 1.987 calories. Thus,

$R = 1.987$ Calories, degrees^{-1} mole^{-1}

17.6.4 R in litre - atmospheres

$$R = PV/nT = 1 \times 22.4/1 \times 273$$
$$= 0.0821 \text{ lit-atm. degree}^{-1} \text{ mole}^{-1}.$$

These several units of R should be used under different conditions, depending on the actual units in which P and V are expressed. The student should get familiar with these various units of R and the actual unit to be used under a specific set of conditions.

17.7 MIXTURE OF GASES : THE LAW OF PARTIAL PRESSURES

The relationship between the total pressure of a mixture of (nonreacting) gases and the pressures of the individual constituents was given by **John Dalton** (1801). This relationship is known as the law of partial pressures. The partial pressure of each gas in a mixture of gases is the pressure which the gas would exert if it had occupied the entire volume of the mixture at the same temperature.

According to Dalton's law of partial pressures, *the total pressure of a mixture of gases is equal to the sum of the partial pressures of the individual gases present in the mixture.* Suppose a gaseous mixture consists n_1 moles of constituent 1, n_2 moles of constituent 2, n_3 moles of constituent 3 and so on. Let the mixture be placed in a vessel of volume V at a given temperature. If constituent 1 alone had occupied the container, the pressure P_1 which it would exert is the partial pressure of constituent 1. Likewise, P_2, P_3 are the partial pressures of constituents 2,3, respectively.

If P is th total pressure exerted by the mixture of all the gases, then according to Dalton's law of partial pressures.

$$P = P_1 + P_2 + P_3 + \dots\dots \qquad \dots. \ (14)$$

As with Boyle's law and Charles's Law, Dalton's law of partial pressures is not strictly obeyed by real gases. It could be said that it is strictly applicable only to ideal gases.

Assuming, for the present, that the gases behave ideally to a fair degree of approximation, if each of the gases separately occupied the vessel, we could write.

$$P_1V = n_1 RT$$

$$P_2V = n_2 RT$$

$$P_3 V = n_3 RT, \text{ and so on.}$$

$$(p_1 + p_2 + p_3 +) \ x \ V = (n_1 + n_2 + n_3 +). \ RT$$

According to the law of partial pressures,

$$P = p_1 + p_2 + p_3 +, \qquad \text{and}$$

n, the total number of moles in the mixture is given by

$$n = n_1 + n_2 + n_3 +$$

$$\text{Hence, } PV = n\,RT \qquad \dots. \ (15)$$

From this it follows that

$$P_1V/pV = n_1RT/nRT \quad , \text{Or}$$

$$p_1 = P\,(n_1/n) \qquad \dots. \ (16)$$

Similarly $$p_2 = p\,(n_2/n) \qquad \dots. \ (17)$$

$$P_3 = p\,(n_3/n) \qquad \dots. \ (18)$$

The ratios n_1/n, n_2/n, n_3/n etc., are known as the mole fractions of each of the constitutent gases. The mole-fraction of a given constituent of a mixture is defined as the ratio of the number of moles of that constituent to the total number of moles of all the constituents in the mixture. From equation 16, 17 and 18 we can calculate the partial pressure of any constituent of a mixture of gases from a knowledge of the total pressure (at the same temperature) and the mole-fraction of the constituent.

An important application, among others, of the law of partial pressures is in calculating the pressure of a dry gas when it is collected over water. The pressure of a dry gas is obtained by substracting, from the atmospheric pressure at which the gas is collected, pressure of water vapour, at the temperature at which the gas is collected.

17.8 DIFFUSION OF GASES

Diffusion is a property by which a substance tends to spread throughout the space made available to it. Diffusion is exhibited by solids, liquids and gases, but is most rapid in the case of gases. if two jars, each containing a different gas, are kept mouth-to-mouth with one another, it is found soon that the gases would have spread throughout the two jars. This would happen even if the jar containing the lighter gas is placed at the bottom, indicating that diffusion occurs inspite of gravity.

Thomas Graham (1827) proposed a law relating the rate of diffusion of a gas to its density. The law, known as Graham's law of diffusion is stated as: *"The rate of diffusion of gas is inversely proportional to the square root of its density"*. If r is the rate of diffusion of a gas and d its density, then,

$$r \ \alpha \ (1/\sqrt{d})$$

$$r = \text{Constant}/\sqrt{d} \qquad \text{.... (19)}$$

If r_1 and r_2 are the rates of diffusion of two gases under certain specific conditions, and d_1 and d_2 are their densities respectively, then

$$r_1/r_2 = \sqrt{d_2}/\sqrt{d_1} \qquad \text{.... (20)}$$

The density of a gas is directly proportional to its molecular weight. Hence equation 20 can be written as

$$r_1/r_2 = \sqrt{M_2}/\sqrt{M_1} \qquad \text{.... (21)}$$

Where M_1 and M_2 are the molecular weights of the gases.

From equations, 20 and 21 it is evident that a lighter gas (or one with less molecular weight) would diffuse more rapidly than a heavier one (or one with great molecular weight). Conversely, the time of diffusion of a given quantity of a lighter gas is proportionately lesser than that for the same quantity of a heavier gas under similar conditions. Thus if t_1 and t_2 are the times of diffusions, under identical conditions, of two gases of densities d_1 and d_2, are molecular weights M_1 and M_2 respectively, it follows that

$$t_2/t_1 = \sqrt{d_2}/\sqrt{d_1} = \sqrt{M_2}/\sqrt{M_1} \qquad \text{.... (22)}$$

Diffusion studies, therefore provide a method of determination of molecular weights of gases.

17.9 SUMMARY

In this unit we have studied that:

i) The Boyle's law: pressure-volume relation of a gas when its mass and temperature are constant.

ii) Charles law: Volume-Temperature relation of a gas when its mass and pressure are constant.

iii) The equation of state obtained by combining Boyle's law, Charles law and Avogadro's law. This gives relationship between pressure, volume, temperature and number of moles of gas.

Check Your Progress - 2

Explain the terms average life and half life of a radio active element?

15.5. RADIOACTIVE EQUILIBRUIM

A radioactive element disintegrates into another element (radioactive or non-radioactive). The former element is called the *'parent'* element and the element produced (the latter element) in the disinteration process is called *'daughter'* element. In nature the radioactive *parent* element sometimes has a long average life and its decay product or *daughter element* is not separated from the parent. In such instances a state of equilibrium called *'secular equilibrium'* is attained after a time. The daughter element disintegrates as fast as it is being formed from its parent. The rate of disintegration of parent element (1) is equal to λ_1N_1. This quantity generally represents the rate of formation of the daughter element (2) also. In a similar way, the rate of distintegration of the daughter element can be expressed at λ_2N_2. In the equilibrium the rate of formation of daughter from the parent is equal to the rate of disintegration of daughter itself.

Hence $\lambda_1N_1 - \lambda_2N_2$ ..... (12)

If the daughter element is disintegrating, itself becomes the parent of a another daughter element (3). Hence an equilibrium $\lambda_2N_2 = \lambda_3N_3$ exixts when the secular equilibrium is attained. Thus if there are a number of such successive disintegrations, the general condition for *radioactive equalibrium* is given by

$$\lambda_1N_1 = \lambda_2N_2 = \lambda_3N_3 = \lambda_4N_4 \qquad ..... (13)$$

Where 1,2,3,4, etc. represent the radioactive species (elements). For any two elements 1 and 2, in the equilibrium the equation can be written as N_1/N_2 = constant, since λ_1 and λ_2 are constants.

This shows that the ratio of amounts of any two members in a disintigration series will be a constant in a *radioactive secular equilibrium.*

15.6 SUMMARY

In this unit we have studied that:

i. The radioactive disintegration follows an exponential law.
ii. The rate of disintegration of atoms is proportional to the number of atoms present at that instant.
iii. The average life of a radioactive element is equal to reciprocal of decay constant.
iv. Half life period is obtained by multiplying average life with 0.693.
v. Radioactive equilibrium.

15.7 MODEL EXAMINATION QUESTIONS

I Answer the following in 10 lines each.

1. Explain the phenomenon of radioactive secular equilibrium with illustrations.

2. Derive the equation that relates average life and decay constant of a radioactive element.

II Answer the following in 30 lines each.

1. Give a critical account of radioactive disintegration theory.

2. Explain the term 'secular equilibrium' and derive an equation relating average life and decay constant.

15.8 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. Radioactive disintegration is a first order process. Rate of radioactive desintegration at any instant is related to initial activity (a) by the following equation.

$$\frac{dx}{dt} \quad \alpha \, (a - x)$$

$$\frac{dx}{dt} = K \, (a-x)$$

2. Average life:- It (τ) is the reciprocal of disintegration constant (K).

$$\tau = 1/\kappa$$

Half life: It ($t^{1}/_{2}$) is the time required for a radioactive element to get reduced to half of the initial quantity.

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UNIT - 16 RADIOACTIVE DISINTEGRATION SERIES

Contents

16.1 AIMS AND OBJECTIVES

This unit is to describe you the important radioactive disintegration series and to present the numerical values of half life of the different elements in the series.

By the end of this unit you should be able to understand that:

- There are about 42 radioactive elements in the high atomic mass region.
- These elements of high atomic mass at the end of periodic system fall mainy into *three* distinct series.
- These series are known as *thorium series*, the*uranium series* and the *actinium series.*
- Thorium and uranium series are named after the longest lived elements of the series namely *thorium and uranium.*
- The half lives are 1.4×10^{10} and 4.5×10^{9} years respectively.
- The parent of actinium series is not actinium but much longer lived element called *Actinouranium* (uranium - 235)
- The half life of *uranium - 235* is 7.1×10^{8} years.
- The last stable element of the series is *lead.*
- **Fajans, Soddy and Russel** proposed group displacement law.
- Group displacement law leads to the concept of isotopes.

16.2 INTRODUCTION

In unit - 14, you learnt that radioactive elements undergo spontaneous disintegration and the process is generally referred to as radioactivity. In the process of radio active disintegration, the element gives α (alpha), β(beta) and γ (gamma) - rays. Alpha rays consist of positive particles and alpha particle is identified with helium nucleus (He +). It has a mass of 4 on the atomic mass scale and charge of +2. β- rays consist of fast moving beta particles. A beta particle is identified with an electron. the mass of electron on the atomic mass scale is negligible. Hence in a radioactive disintegration process if an atom of element (parent) loses α -particle, the product (daughter element) will have an atomic mass which is less by four units than that of the parent element. On the other hand, in thedisintegration accompanied by the emission of beta particle, the parent and daughter will virtually have the same atomic masses.

16.3 DISINTEGRATION SERIES

It has been observed that elements, uranium, thorium and actinium undergo spontaneous radioactive disintegration giving rise to respective daughter elements. These daughter elements in turn are found to exhibit similar phenomenon of producing the other radioactive elements. This process is found to continue till a non-radioactive element is formed. In the three series mentioned, the last element is identified to be *lead*. Generally the elements disintegrate in one way only. But few elements are found to be exceptions and disintegrating in two ways. One mode is accompanied by α - particle. Hence, branched series will form in such cases. The three series are presented in tables 16.3.1, 16.3.2 and 16.3.3.

Table 16.3.1 Uranium Series

Radioelement	Corresponding Element	Symbol	Radiation	Half-life
Thorium ↓	Thorium	^{223}Th	α	1.39 x 10^{10}yr
Mesothorium I ↓	Radium	^{228}Ra	β	6.7 yr
Mesothorium II ↓	Actinium	^{222}Ac	β	6.13 hr
Radiothorium ↓	Thorium	^{223}Th	α	1.91 yr
Thorium X ↓	Radium	^{234}Ra	α	3.64 days
Th Emanation ↓	Radon	^{230}Rn	α	52 sec
Thorium A ↓	Polonium	^{213}Po	α	0.16 sec
Thorium B ↓	Lead	^{212}Pb	β	10.6 hr
Thorium C 66.3% 33.7% ↓	Bismuth	^{212}Bi	β and α	60.5 min
Thorium C' ↓	Polonium	^{212}Po	β	3 x 10^{-7} sec
Thorium C" ↓	Thallium	^{208}Tl	β	3.1 min
Thorium D (End Product)	Lead	^{208}Pb	stable	----

Table 16.3.2 Thorium Series

Radioelement	Corresponding Element	Symbol	Radiation	Half-life
Uranium I	Uranium	^{238}U	α	4.51×10^9 yr
Uranium X_1	Thorium	^{234}Th	β	24.1 days
Uranium X_2 *	Protoactinium	^{234}Pa	β	1.18 min.
Uranium II	Uranium	^{234}U	α	2.48×10^5 yr
Ionium	Thorium	^{230}Th	α	8.0×10^4 yr
Radium	Radium	^{226}Ra	α	1.62×10^2 yr
Ra Emanation	Radon	^{222}Rn	α	3.82 day
Radium A 99.98% 0.02%	Polonium	^{218}Po	α and β	3.05 min.
Radium B	Lead	^{214}Pb	β	26.8 min
Astatine - 218	Astatine	^{218}At	α	2 sec
Radium C 99.96% 0.04%	Bismuth	^{214}Bi	β and α	19.7 min.
Radium C'	Polonium	^{214}Po	α	1.6 x 10-4 sec
Radium C"	Thallium	^{210}Tl	β	1.32 min.
Radium D	Lead	^{210}Pb	β	19.4 yr
Radium E ~100% 2×10^{-4}%	Bismuth	^{210}Bi	β and α	5.0 days
Radium F	Polonium	^{210}Po	β	138.4 days
Thallium - 206	Thallium	^{204}Tl	β	4.20 min.
Radium G (End Product)	Lead	^{204}Pb	stable	---

Table 16.3.3 Actinium Series

Radioelement	*Corresponding Element*	*Symbol*	*Radiation*	*Half-life*
Actinouranium ↓	Uranium	^{235}U	α	7.13×10^3 yr
Uranium Y ↓	Thorium	^{231}Th	β	25.6 hr
Protoactinium ↓	Protactinium	231Pa	α	3.43 x 104 yr
Actinium 98.8% 1.2%	Actinium	227Ac	β and α	21.8 yr
↓ Radioactinium	Thorium	227Th	β	18.4 days
↓ Actinium K	Francium	223Fr	β	21 min.
↓ Actinium X	Radium	223Ra	α	11.7days
Ac Emanation ↓	Radon	219Rn	α	3.92 sec
Actinium A ~100% ~5 x 10⁻⁷	Polonium	215Po	α and β	1.83×10^{-3} sec
↓ Actinium B	Lead	211Pb	β	36.1 min
↓ Astatine - 215	Astatine	215At	α	$\sim 10^{-4}$ sec
↓ Actinium C 99.7% 0.3%	Bismuth	211Bi	α and β	2.16 min
↓ Actinium C'	Polonium	211Po	α	0.52 sec
↓ Actinium C"	Thallium	207Tl	β	4.8 min
↓ Actinium D (End Product)	Lead	207Pb	stable	--

Check Your Progress - 1

How many radioactive disintegration series are identified and what are they?

----

volume of the molecules. These quantities have been obtained in many ways. If the pressure is measured in atmospheres and the volume in litres, then the units of 'a' and 'b' are litre^2 atom mole^{-2} and litres. mole^{-1} respectively. Strictly speaking 'a' and 'b' are not exactly constants, they do vary slightly with temperature. This fact makes the van der Waals equation one of limited applicability. But to a fair degree of approximation, 'a' and 'b' may be taken to be constants and to that extent they serve as a means for correcting departures from ideal behaviour. The values of 'a' and 'b' for some gases are given below.

Check Your Progress - 2

State the units of constants used in van der Waals equation.

19.5 APPLICABILITY OF THE VAN DER WAALS EQUATION

Though not exact, the van der Waals equation is, nevertheless, a major advance in the attempts to explain the behaviour of real gases. We shall now consider the applicability of equation 1 under different conditions.

19.5.1 At low pressures

The 'b' term in equation 1 may be ignored in comparison with V. Thus, the equation 1 is reduced to

$$(P + a/V^2)V = RT \quad \text{.... (2)}$$

Or $$PV + a/V = RT$$

$$PV = RT - a/V \quad \text{.... (3)}$$

PV is therefore less than RT at low pressures and decreases as the pressure increases (as V decreases and so a/V becomes larger). This accounts for the dip in the curve for nitrogen and carbondioxide in figure 19.1. Thus at low pressures, the a/V^2 term, or the attraction term is relatively predominant.

19.5.2 At high pressures

At high pressures either the term a/V^2 or the term 'b' should not be neglected. The equation 1 can be rearranged as follows.

$$(P + a/V^2)(V-b) = RT$$

Or $$P(V-b) + a/V^2(V-b) = RT \quad \text{.... (4)}$$

$$P(V-b) + a(1/V - b/V^2) = RT \quad \text{.... (5)}$$

At higher pressures the terms 1/V and b/V^2 being approximately of equal magnitude but of opposite sign, may be neglected.

The above equation becomes

$$PV - Pb = RT$$

$$PV = RT + Pb \quad \text{.... (6)}$$

PV is now greater than RT and increases with pressure. The rise in the PV curve in figure 19.1, after going through a minimum, can therefore be attributed to the 'b' term i.e., the term involving the volume of the molecules.

19.5.3 At extremely low pressures

'V' will be relatively very large, so that both the 'b' term as well as the a/V^2 may be ignored. Under these conditions equation 1 becomes PV = RT, which is the ideal gas equation. Thus, at extremely low pressures, gases obey the ideal gas law. This is quite understandable; at extremely low pressures the volume is relatively so large that the actual volume of molecules will be only a negligible part of the total value of the gas. Also, the molecules are so for apart that they practically do not attract one another.

19.5.4 The exceptional behaviour of hydrogen and helium

This is attributed to the extremely small value of 'a', i.e., the molecular attraction term, in comparison with the 'b' term, i.e., the volume of the molecules. The result, is that even at low pressures; the 'b' term is comparatively predominant so that the PV plot for hydrogen and helium shows no minimum but shows a continual increase as the pressure is increased.

The van der Waals equation provides a very satisfactory explanation for the behaviour of real gases, but at a quantitative level, it is rather inadequate. One reason for this is that the terms 'a' and 'b' are not exactly constant; infact they do vary with temperature. Several attempts have been made to improve the van der Waals equation. Actually, as many as about a hundred equations of state have been proposed, but none of them has the simplicity of the van der Waals equation. Infact, some of the equations are very complex, involving a large number of empirical constants. Inspite of all its inadequacies, the van der Waals equation may be considered as a satisfactory means of accounting for the behaviour of real gases, and is eminently suitable for a qualitative treatment of real gas behaviour.

19.6 SUMMARY

In this unit we have studied

i) The deviations of real gases from ideal behaviour

ii0 The causes of deviations from ideal behaviour, leading to vander Waals equation.

iii) Van der Waals equation as a modfication of ideal gas equation, incorporting the correction terms for pressure and volume.

iv) Applicability of vander Waals equation.

v) The exceptional behaviour of hydrogen and helium.

19.7 MODEL EXAMINATION QUESTIONS

I Answer the following in 10 lines each.

1. Explain the deviation exerted by of nitrogen, hydrogen and carbondioxide gases from Boyle's law with the help of a graph.
2. Explain the exceptional behaviour of hydrogen and helium gases.
3. How corrections were carried out regarding molecular attractions and molecular volume in ideal gas equation?

II. Answer the following in 30 lines each.

1. Discuss the causes of deviation of real gases from ideal behaviour in detail.
2. Explain applicability of van der Waals equation at high, low and extremely low pressures.

19.8 MODEL ANSWERS TO CHECK YOUR PROGRESS

1 Ideal gases obey the gas laws under all conditions of temperature and pressure but real gases do not obey. Real gases do not obey the gas under all conditions in view of the existence of intermolecular attractions and volume occupied by them.

2 a,b and R are the constants used in van der Waal's equation. Their units are

a litre^2 - atm - mole^{-2}

b litre - mole^{-1}

R litre - atom - deg^{-1} - mole^{-1}.

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UNIT - 20 : CRITICAL PHENOMENA

Contents

20.1 AIMS AND OBJECTIVES

This unit aims to discuss about the phenomenon of transition from the gaseous state to the liquid state and to study such phenomenon concerning gases and liquids.

By the end of this unit you should be able to understand that:

- Andrew's experiments on carbondioxide helped in removing the erroneous distinction between the "liquefiable" gases and the so-called "permanent gases", which it was once believed, could not be liquefied at all.
- As the critical temperature approaches, the densities of the gas and liquid come closer and closer.
- At (or very near to) the critical temperature, the separation between the gas phase and liquid phase disappears. This establishes the concept of a continual transition from the gas to the liquid state (or vice versa).
- A combination of the van der Waals constants and he P-V diagram leads to a completely general equation known as the **"reduced equation of state"**, which will be applicable to all substances. This equation, in turn, establishes the **Law of corresponding states.**
- Expansion of a gas, under certain conditions, from a region of high to a region of low pressures, leads to a lowering of temperature. This is the basis of the **Joule-Thomson effect**, which has a major application in the liquefaction of gases. The Joule-Thomson effect also provides conclusive evidence of the existence of intermolecular forces in gases.

20.2 INTRODUCTION

A liquid when heated attains the gaseous state. Hence it is obvious that a gas on cooling and compression should be converted into a liquid. However the liquefication of gases needs a careful study because this can't be done under all conditions of temperature and pressure. An attempt is made hereunder in finding those conditions.

20.3 THE CRITICAL PHENOMENA

It has long been known that some gases could be liquefied as a result of cooling. **J.B. Von Helmont** was one of the earliest investigators to realise this in the early part of the seventeenth century.

But serious attempts on liquefaction began only in the beginning of nineteenth century, mainly by **Michael Faraday** and others. By about the 1820's, number of gases like sulphur dioxide, ammonia, chlorine, hydrogen chloride, hydrogen sulphide, carbon dioxide, nitrous oxide, etc., were successfully liquefied by application of pressure. In Faraday's experiments very low temperatures were obtained from mixtures of ice and salt. **M. Thoiler** (1835), by using a mixture of solid carbondioxide and other, was able to attain temperatures as low as −110°c. This enabled Faraday to liquefy gases such as ethylene, phosphine, boron trifluoride, silicon tetrafluoride, etc. In fact he even succeeded in solidifying a few gases.

In view of these results it was concluded that certain gases could not be liquified at all. (under any conditions of temperature and pressure). Such gases were termed as 'permanent gases'. But later experiments of Andrews showed that even so called permanent gases are liquiefiable.

Check Your Progress - 1

Explain the term permanent gases.

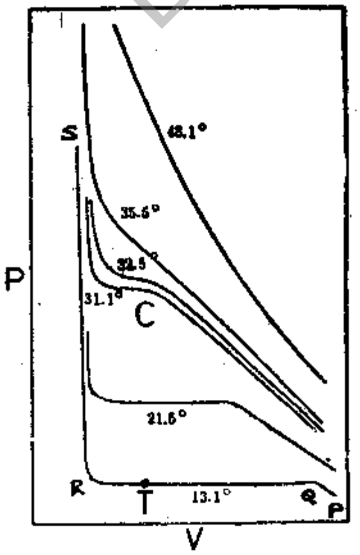

Fig. 20.1 P-V isotherms of carbon dioxide.

The primary conditions required for the liquefaction of a gas, "**permanent**" or otherwise, were discovered by **T. Andrews** (1869) as a result of his famous experiments on the P-V-T relationship of carbondioxide. He took a definite amount of carbon dioxide in a glass tube kept at a constant temperature and the volumes were measured at different pressures. P-V. plots at a number of temperatures were obtained. These curves are shown in figure 20.1.

To begin with, at the lowest temperature used (13.1°c), the carbon dioxide is all gas, as at P. Increase of pressure results in a corresponding decrease in volume as is indicated by the portion PQ of the isotherm. This, of course, is in accordance with Boyle's law. But at the pressure corresponding to Q, the gas begins to liquefy and the volume decreases rapidly as more and more of the gas is changed to liquid with considerably higher density.

At the point R liquefaction is complete and steep nature ot the curve RS indictes that the liquid is more or less incompressible. There is, as a result, hardly any change in the volume as the pressure is increased. The point to note is that the isotherm consists of three distinct parts. The part PQ of the curve represents gas only and the portion RS, liquid only. But along QR liquid and gas are present together. Since QR is parallel to the abscissa (or the volume axis), it means that the pressure remains constant when gas and liquid coexist at equilibrium with each other. This pressure is the vapour pressure of the liquid at the particular temperature. As the parameters of the system change from Q to R, the amount of liquid increases, while that of the gas decreases. At any point T on the plot, the ratio of liquid to gas will be given by RT to QT.

The isotherm at 21.5°c is similar to the one at 13.1$_0$c, with the difference that the horizontal portion along which liquefaction takes place is shorter. As the temperature is raised this part of the isotherm becomes shorter and shorter, till ultimately, at 31.1°c, there is no horizontal portion at all, indicating that there is no evidence of liquefaction. In fact, the isotherms are in conformity with Boyle's law. Andrews found that at only temperature above 31.1°c, carbondioxide could not be liquefied at all, irrespective of the pressure applied. On the other hand, at or below 31.1°c, a pressure of 75 atmospheres was found to be sufficient to cause liquefaction.

Subsequently it has been found that every gas behaves in the same way as does carbon dioxide, ie., every gas has a characteristic temperature, above which it is impossible to liquefy the gas, whatever is the pressure applied. This temperature depends on the nature of the gas. It now becomes clear as to why the so called **permanent** gases could not be liquefied earlier. They were not cooled sufficiently before applying pressure to bring about liquefaction.

20.4 CRITICAL CONSTANTS

The maximum temperature at which a gas can be liquefied, and above which its liquid form cannot exist is known as **the critical temperature** (T_c). The pressure that is just necessary to liquefy the gas at its critical temperature, is called the **criticall pressure P_c**. And the volume occupied by one mole of the substance at its critical temperature and pressure is known as the **critical volume** (V_c). These three together are known as the **critical constants.** The isotherm that corresponds to the critical temperature is known as the **critical isotherm.** In figure 20.1 the isotherm at 31.3°c is the critical isotherm of carbondioxide, as this temperature is its critical temperature. At the point C on the isotherm at the temperature, the gas is said to be in its **critical state**: the pressure and the volume corresponding to its critical values. A gaseous substance which is below its critical temperature is called **Vapour.** A vapour can be condensed to a liquid by applying pressure alone.

20.5 DETERMINATION OF CRITICAL CONSTANTS.

By plotting P-V isotherms for any gas at a number of temperatures, as Andrews did for carbon dioxide, it is possible to determine the critical constants. But this has not always been proved convenient.

Hence other methods have been used. A simple but elegant method is the one due to **de la Tour** (1822). This was based on an observation made by him that when a liquid is heated in a closed container, the surface of separation between the liquid and vapour disappears at a particular temperature. On cooling, the two layers reappear. Much later (1863) Andrews established that this occurs at the critical temperature of the substances. In other words, this means that at critical temperature, the distinction between the liquid and gaseous phases of substance disappears.

Instead the entire space is filled by a homogeneous fluid which is neither a liquid nor a gas as is normally understood. Once the temperature is lowered, however, the surface of separation between the two appears once again. Present evidence, both theoretical and experimental, suggests that for some liquids, the liquid-vapour surface disappears over a certain range, rather than at a definite temperature.

L. Cailletet and E. Mathias (1866) established a rule, according to which, **the mean values of the densities of liquid and its saturated vapour at the same temperature is a linear function of the temperature.** This is known as **the law of the rectilinear diameter,** According to this law.

$$\rho_t \quad = \quad A + Bt$$

Where ρ_t is the mean density of the liquid (ρ_l) and that of the saturated vapour (ρ_v) in equilibrium with it at the temperature t and A and B are constants. ρ_l and ρ_v are called **orthobaric densities.**

Figure 20.2 shows the orthoboric densities of n-pentane plotted against the temperature.

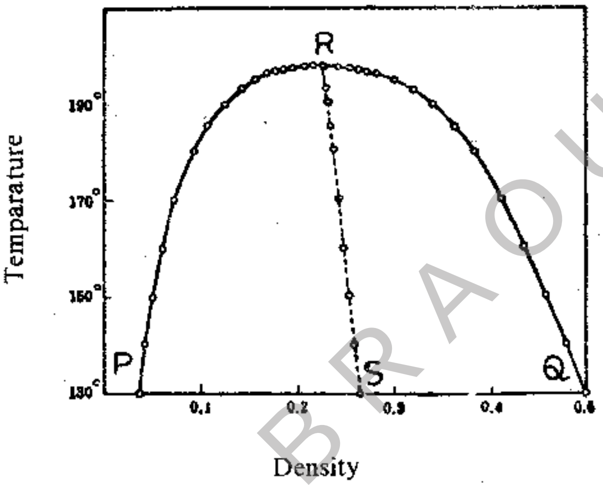

Fig. 20.2 Orthobaric densities of n-pentane.

PR is the plot of the densities of the saturated vapour and temperature while QR represents the plot of the densities of the liquid and temperature. RS represent the mean density plotted against the temperature. In accordance with equation1; RS is a straight line. The temperature corresponding to the point R is the critical temperature, the density (S) at this temperature will be the **critical density.** The reciprocal of this value gives the critical volume per gram of the substance.

The orthobaric densities are determined as follows. A definite mass of a given liquid is taken in a graduated tube, which is then sealed off. The tube is heated to particular temperature and the volume of the liquid and vapour are read off from the graduations. If 'm' is the mass of the liquid, V_l and V_v the volumes of the liquid and vapour respectrively at any definite temperature, and ρ_l and ρ_v the corresponding densities of liquid and vapour respectively then

$$m \quad = \quad V_l \cdot \rho_l + V_v \cdot \rho_v \qquad \text{.... (2)}$$

The measurements are carried out at the same temperature, but with a different masses of liquid. We thus get two sets of equations containing ρ_l and ρ_v these are then calculated.

$$m_1 = v^1{}_l \rho_r + v^1{}_v \rho_v$$

$$m_2 = v^2{}_l \rho_l + V^2{}_v \rho_v$$

The critical constants for some substances are given in table 20.5.1

Table 20.5.1 Critical constants

Substance	Critical temperature (T_c) (in Kelvin scale)	Critical pressure (P_c) (in atmosphere)	Critical valume (V_c) (ml per mole of substance)
Hydrogen	33.2	12.8	68
Nitrogen	126.0	33.5	90
Oxygen	154.3	49.7	74
Carbon dioxide	304.2	73.0	95
Hydrogen chloride	324.5	81.5	89
Ammonia	405.5	112.3	72
Chlorine	417.1	76.1	124
Sulphur dioxide	430.3	77.6	125
Water	647.3	217.7	57

A consideration of the data makes one point clear, namely, it is easily explained as to why the so called 'permanent gases', like hydrogen, nitrogen, oxygen, could not be liquefied at about room temperature by mere application of pressure. Their critical temperatures are all far below room temperature (300 T)

We are used to think of water as a liquid only. But above 647.3 K (i.e., above 374.3°c) water cannot exist as a liquid, irrespective of the pressure applied. The knowledge of the critical phenomena makes this point clear.

20.6 CONTINUITY OF STATE

Generally, the change from the liquid state to vapour (or vice-versa) takes place rather suddenly, with the two states being clearly distinguishable from one another. This is evident, for example, from the isotherm at 13.1°C in figure 20.1. But as the temperature is increased and reaches the critical value the densities of the liquid and saturated vapour come closer and closer, and become identical as the critical point. In other words, there is no difference between liquid and gas at the critical point. This fact is in agreement with the obserbvation that at the critical point, the boundary between the liquid and gas phases disappears. It would appear, therefore, that there is a gradual transition from liquid to vapour, because just below or above the critical temperature, there would be practically no difference between liquid and vapour. This gradual transition from liquid to vapour is known as **Continuity of State.**

A consideration of the P-V isotherms is helpful in bringing out the idea of continuity of states. For instance, consider the isotherm PQRS in figure 20.3. If the gas at P is compressed (the temperature being below the critical temperature), there will be continuous transitions from gas to liquid along QR where both phases will exist together.

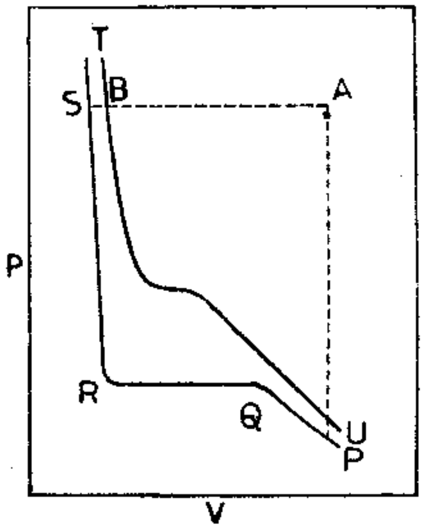

Fig. 20.3 Continuity of state

But if the volume is kept constant and the temperature is increased from P to A then the pressure will increase. Now the pressure is, in turn, kept constant and the temperature is lowered till the volume is reduced to S. We thus find that the substance which was totally gaseous at P is now a liquid at S. And P and S are both on the same isotherm. Thus the transition from gas to liquid has been brought about without a discontinuity. The transition from gas to liquid takes place between A and S during which compression occurs. The substance is in the form of gas to the right of the critical isotherm TU, while it is liquid to the left. Actually, the change from gas to liquid occurs at the point B. When the system moves from A to S, the temperature falls; hence the density of the gas increases. At the point B liquefaction occurs. But the change from gas to liquid can be considered to be occurring in a gradual manner, i.e., the transition emphasises the continuity of states.

20.7 Relation between van der Waals constants and the critical constants.

The van der Waals equation,

$$(P + a/V^2)(V-b) = RT$$

may be rearranged to read as

$$P V^3 - (RT + Pb) V^2 + aV - ab = 0 \quad \text{.... (3 a)}$$

on dividing the equation by P

$$V^3 - \frac{(RT + Pb)}{P} V^2 + aV/P - ab/P = 0 \quad \text{.... (3 b)}$$

This is a cubic equation in V, and so for a given value of a and b, would have three roots. The three roots may all be real, or, one may be real and the other two imaginary. From a theoretical consideration of equation (3) a plot of V against P, at any given constant temperature T, will give a curve as shown in figure 20.4.

In lower curve there are three values of V for a given value of P, as at the points B,D and F. As the temperature is increased, another curve similar to first is obtained except that the three values of V are closer together. At a particular temperature, a P-V, curve represented by upper curve is obtained, in which the three roots of V are identical. At still higher temperatures, a curve is obtained, in which there is only real value of V, the other two are imaginary.

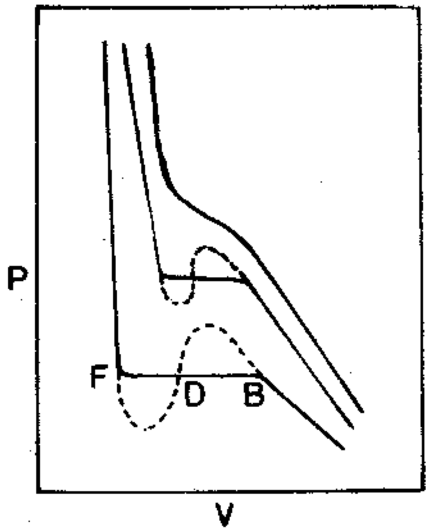

Fig. 20.4 Theoretical isotherms (calculated) from van der Waals equation

If we compare the theoretical isotherms in figure 20.4 with the experimental ones obtained by Andrews for carbondioxide as in figure 20.1, we find a close similarity between the two. The only difference is that the horizontal portions of the experimental curves are replaced by the " ~" shaped theoretical curves. The upper curve in figure 20.4 corresponds to the critical isotherm in figure 20.1.

These facts can be utilised to derive expressions for critical constants in terms of van der Waals constants. At the critical point in figure 20.4, the values of V will be equal to the critical volume, V_c, thus,

$$(V - V_c) = 0 \qquad \text{....(4)}$$

Or $$V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3 = 0 \qquad \text{.... (5)}$$

By substituting P_c and T_c for P and T in equation 3(b) and rearranging, we obtain,

$$V^3 - V^2(RT_c + P_c b)/P_c + aV/P_c - ab/P_c = 0 \qquad \text{.... (6)}$$

This equation is identical with (5). Comparing the appropriate coefficients, we have,

$$3V_c = RT_c + P_c b/P_c \qquad \text{.... (7)}$$

$$3V_c^2 = a/P_c \qquad \text{.... (8)}$$

$$V_c^3 = ab/P_c \qquad \text{.... (9)}$$

If equation (9) is divided by (8), it turns out that

$$V_c = 3b \qquad \text{.... (10)}$$

From (8) and (10) it follows that

$$P_c = a/27b^2 \qquad \text{.... (11)}$$

Substituting (10) and (11) in equation (7) we get

$$T_c = 8a/27\,Rb \qquad \text{.... (12)}$$

Equations (10), (11) and (12) thus express the critical constants of a substance in terms of its van der Waals constants and the gas constant R. These relations provide a method for testing the applicability of the van der Waals equation by determing the critical constant of a gas from 'a' and 'b', or vice-versa. However, these calculations do not yield entirely satisfactory results, for one thing 'a' and 'b' are strictly not constants; they vary some what with temperature. It is found that when the van der Waals constants desired temperatures not too far from the critical points, are used, then fairly reliable results are obtained.

20.8 THE LAW OF CORRESPONDING STATES

The van der Waals equation can be modified by expressing the actual pressure, volume and temperature of a gas in terms of the respective critical constants, as follows.

$$P = \Pi P_c, \quad V = \phi V_c, \quad T = \theta T_c \qquad \dots (13)$$

Then the van der Waals equation becomes

$$(\pi P_c + a/\phi^2 V_c^2)\ (\phi V_c - b) = R\theta T_c \qquad \dots (14)$$

By substituting the values of the critical constants given by equation 10, 11 and 12, we obtain

$$(\pi a / 27 b_2 + a/9^2 \phi^2 b^2)\ (3\phi b - b) = 8a\ \theta/27b \qquad \dots (15)$$

$$(\pi + 3/\phi^2)\ (3\phi - 1) = 8\theta \qquad \dots (16)$$

The terms π, ϕ and θ are known as the **reduced pressure, Volume and temperature,** respectively. Equation (16) is known as the van der Waals **reduced equation of state.**

This equation does not contain either R or the van der Waals constants 'a' and 'b' for any particular gas. As such it is perfectly general and is applicable to all substances.

Suppose two or more substances are at the same reduced pressure and reduced temperature, then it follows from equation (16) that they all should have the same reduced volume. Substances which have the same reduced pressure, reduced volume and reduced temperature are said to be in **corresponding states,** and equation (16) may be regarded as an expression for **the law of corresponding states,** which may be stated as follows.

"If two or more substances are at the same reduced pressure, and at the same reduced temperature, then they have the same reduced volume".

20.9 JOULE - THOMSON EFFECT

According to the kinetic theory of gases, an ideal gas is one in which the molecules do not have intermolecular attractions. But there is now considerable evidence to indicate that this postulate is invalid for real gases. For one thing, if the molecules in a gas do not attract one another, it is if gases could ever be liquified at all. Liquids possess the characteristic property of cohesion, which is attributable to the attractions between the molecules. Evidently these attractions are present in gases too, though their magnitude may be obviously of a lesser order. More convincing evidence for the existence of attraction between the molecules in gases was provided by the investigations of **J.P. Joule** and **W. Thomson** (Lord Kelvin) carried out between 1852, and 1862. A tube, made of boxwood, was fitted with a porous plug made of absorbent cotton or silk. The tube was thermally insulated from its surroundings, and a stream of gas at constant pressure was forced ("throttled") through the porous plug.

It was found that there was a considerable drop in the temperature of the gas emerging, from the plug, that is, the gas, after passing through the plug, was cooler than it was before. This change of temperature is known as the **Joule-Thomson Effect**. This cooling effect is explained as being due to the work done in overcoming the attractions between the molecules. The energy required to overcome these attractions is mobilised from the internal energy of the gas itself, thus leading to a fall in temperature.

Check Your Progress - 2

State Joule-Thomson effect.

It may be mentioned, that in addition to attractions, molecules also exert forces of repulsion among themelves. The fact that molecules have a definite collision diameter is an indication of the existence of these repulsions,. The collision diameter may be regarded the distance at which the repulsive forces between two molecules become so large that their direction of motion is reversed. These repulsive forces fall off much more rapidly with distance than do the forces of attraction. Consequently, a net attraction exists between molecules when they are considerably apart from one another, and a repulsion when they are in very close proximity.

20.10 LIQUEFACTION OF GASES

The experimental work of Andrews on carbon dioxide established the fact every gas must be cooled to a characteristic **critical temperature** before it can be liquefied. Many attempts were made to liquefy gases after this discovery.

20.10.1 Pictet's method

R.P. Pictet (1877) succeeded in liquefying oxygen, working on the following principle. When a readily liquefiable gas is allowed to evaporate, the heat of evaporation must be supplied to the liquid in order that it may evaporate. When this heat is not supplied from outside, it is obtained from the liquid itself. This leads to fall in temperature. This method of cooling by evaporation is employed to produce solid carbon dioxide or "dryice" and also in refrigeration, both domestic and commercial.

Pictet used this principle to liquefy oxygen. For example a temperature of 65°C was reached by rapid evaporation of **liquid sulphur dioxide**. At this temperature carbon dioxide could be easily liquefied, and by evaporating the liquid under reduced pressure a temperature as a low as - 130°C was reached. This is sufficient to liquefy compressed oxygen.

20.10.2 Linde and Hampson method

The principle that is widely employed to bring about a large scale liquefaction of gases is the Joule-Thompson effect. A gas initially at a high pressure (usually of the order of 200-300 atmospheres) is passed through porous partition (throttle). This leads to a fall in pressure to 40 atm (Linder) or 1 atm (Hampson) and the gas is thus cooled. The cooled gas is used to further cool the incoming gas. By repeated passage of the cooled gas through the throttle, the gas is cooled sufficiently to be liquefied.

20.10.3 Debye method

This method works on the principle of adiabatic demagnetisation. A paramagnetic substance such as rare earth salt was cooled and magnetised keeping it in a thermally insulated container. The applied magnetic field is hence removed under adiabatic conditions. This leads to a fall of temperature. This fact is employed in the liquefaction of gases.

20.11 SUMMARY

In this unit we have studied

i) Andrew's experiments on carbon dioxide leading to isotherms.

ii) The critical phenomena and critical constants T_c, P_c and V_c.

iii) Determination of critical constants.

iv) Continuity of state.

v) Relation between vander Waals constants and critical constants.

vi) The law of corresponding states.

vii) Joule-Thomson effect

viii) Liquefaction of gases and various methods employed for the purpose.

20.12 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines each.

1. Explain with a neat diagram the effect of temperature of the pressure-volume curves of carbondioxide.
2. Discuss the principle underlying the determination of critical constants.
3. Deduce the equation for the law of corresponding states.
4. Derive relation between van der Waals constant 'a' and the Critical constants.
5. State and explain law of Corresponding States.

II. Answer the following in 30 lines each.

1. Give a critical account of the meaning and determination of critical constants.
2. Explain the meaning of permanent gases with the help of critical phenomena.
3. Derive reduced equation of states and discuss its significance.
4. Derive the relationship between van der Waals constants and critical constants.
5. Give a critical account of liquefaction gases.

20.13 MODEL ANSWERS TO CHECK YOUR PROGRESS

1 In the initial investigation of gases it was found that H_2, N_2, O_2 & CO could not be liquidfied at - 110°C and high pressure. Therefore it was proposed that these gases cannot be liquiefied and they are permanent gases. But later on this assumption was found to be wrong.

2 The decrease of temperature of a gas when it is passed from a region of higher pressure to a region of lower pressure through a porous pot is called Joule-Thomson effect. This effect proves the existence of inter-moleuclar attractive forces in real gases.

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Block - 6

SOLUTIONS

What is a Solution

Take some water in a glass. It is clear and transparent. Add a little of solid potassium permanganate and stir with a glass rod. Soon you observe that clear, transparent water in the glass turns pink. This pink liquid is a solution of potassium permanganate in water. Everyone is familiar with bottled soda (aerated water). This is a solution of carbondioxide in water. Similarly when you add a little dark red coloured bromine liquid into clear colourless water. Thus a solution results when a solid, gas or a liquid is added to water. Of course it needed not necessarily be the water to dissolve these substances in the solid, gas or liquid state. It can be any other liquid or even a solid or as a matter of fact a gas even. Thus in general a solution may be defined as a homogeneous mixture containing a single phase of two or more components. A solution is called **binary** if it contains two components only. In this block we shall discuss some important properties of such binary solutions. A mixture is said to be homogeneous generally if any part or portion of the mixture exhibits the same physical and chemical properties as the rest of the mixture. In a homogeneous mixture, no surface of separation between the constituent components is noticed. There is no fundamental difference between the roles of the two components in a solution. But for practical purposes, it is convenient to call the components present in excess. The **solvent** and the other component the **solute.** The substance present in small amounts is referred to as **dissolved substance** (solute). A homogeneous binary mixture (binary solution) results by thoroughly mixing two components in the gaseous, liquid or solid state. For example carbondioxide (gas) dissolves in water giving a solution of **gas in Liquid** (water). Alcohol (liquid) disolves in water giving a solution of **liquid in liquid** (water). In a similar way binary solutions are expected if a solute in the gaseous, liquid or solid state is dissolved in a solvent in the gaseous, liquid or solid state. Different types of solutions are thus possible depending on the physical states of the solute and the solvent.

Types of binary solutions

A binary solution results by mixing thoroughly and homogeneously two components. The possible types of solutions are presented below:

Solute	Solvent	Solution
Gas	Gas	Air Any gas mixture
Gas	Liquid	Carbondioxide in water, ammonia in water
Gas	Solid	Gydrogen in pallaadium metal
Liquid	Gas	No true solution (mist)
Liquid	Liquid	Alcohol-water mixture
Liquid	Solid	Mercury in gold
Solid	Gas	No true solution (Smoke)
Solid	Liquid	Salt Solution Sugar solution
Solid	Solid	Alloys Copper in gold Copper in silver.

Of the different types of solutions mentioned earlier the solutions of gases in liquids and liquids in liquids are discussed in units 21 and 22 respectively.

UNIT - 21 GASES IN LIQUIDS

Contents

21.1 AIMS AND OBJECTIVES

The main purpose of this unit is to describe you the phenomenon of solubility of a gas in a liquid and to discuss the influence of temperature and pressure on the solubility.

After completing this unit you should be able to understand that :

- Gases dissolve in water and in other liquids also. The solubility depends on the nature of gas as well as on the liquid (solvent).
- Easily liquefiable gases dissolve to a great extent in water.
- Solubility can be determined by simple methods involving the measurement of weights of solvent and of solution.
- Solubility of gas in liquid is expressed by 'Absorption coefficient' or 'Solubility coefficient'.
- Increase of temperature decreases the solubility of a gas in a liquid.
- The mass of a gas dissolved by a given volume of solvent is proportional to the pressure of gas. This is called Henry's Law.
- Solutes which form hydrates or undergo ionization or form complexes show deviations from Henry's Law.
- The solubility of a gas in salt solution is les than in pure solvent (water). This is known as salting-out phenomenon.
- The influence of salt is independent of the nature of gas.

- The saltingout of an ion is larger, the smaller is its size and greater is its charge.
- The decrease in solubility of a gas in aqueous salt solutions is attributed to the preferential orientation of water molecules around the dissolved substance.

21.2 INTODUCTION

Gases dissolve in liquids such as water to give solutions of gases in liquids. For example carbondioxide dissolves in water to give a dilute solution of carbondioxide in water (carbonic acid). In fact it is rather difficult, to obtain water devoid of dissolved carbondioxide. The solubility of a gas in a liquid has a limit and definite nature. The solubility depends not only on the nature of gas and liquid but also on the temperature and pressure. For water as solvent, ammonia is the most soluble gas. At 0°C and 1 atm. pressure about 1300 ml. of ammonia gas dissolves in 1 ml. of water. On the otherhand helium dissolves to the extent of 0.01 ml. in 1 ml. of water at the same temperature and pressure. Gases that chemically react with water are generally more soluble than those which do not react with water. Gases that are easily liquefied dissolve to considerable extent in water. Ammonia and carbondioxide are easily liquefied compared to oxygen and hydrogen. It is for this reason that ammonia or carbondioxide is more soluble in water than oxygen or hydrogen. The binary system of 'gas in liquid' follows the general rule that **"like dissolves like"**. For example gaseous hydrocarbons dissolve to a great extent in organic liquid hydrocarbons like benzene, than in water. But this can not be considered as a general rule since many exceptions are known.

21.3 DETERMINATION OF SOLUBILITY

Various forms of apparatus have been used to measure the solubility of a gas in liquid. The principle underlying these measurements is generally the same. A known volume of the gas at required temperature and pressure is allowed to pass into the liquid (solvent) and the whole system is agitated in a suitable manner until the liquid is saturated with the gas. The initial volume of the gas and the volume of the residual gas (after saturation process is completed) are measured at the required temperature with the help of a gas burette. The difference between the original volume and the final volume (residual volume) after making a correction for the vapour pressure of the solvent gives the volume of gas dissolved in the volume of the liquid employed.

For highly soluble gases such as ammonia and hydrogenchloride in water, this method is not quite suitable. Hence, an alternative procedure based on chemical analysis is used. A thin walled glass bulb of capacity about 30 ml. with a bent in-let at the bottom and an out-let at the top is weighed (W_1). The bulb is filled to half its capacity with the liquid (solvent). Later the gas whose solubility is to be determined is bubbled through the liquid till the later is saturated. The ends of the in-let and out-let tubes are then sealed off by a flame. The bulb with the contents is finally weighed (W_2). The difference in the final and initial weights ($W_2 - W_1$) will be equal to the weight of the solution. The amount of the dissolved gas in the solution is determined by a suitable analytical method. From the weight of solution and the weight of the gas, its solubility is calculated.

21.4 HOW THE SOLUBILITY OF A GAS IS EXPRESSED?

21.4.1 Absorption and solubility coefficients

The solubility of a gas in liquid is expressed by **Absorption coefficient** (α) proposed by **R. Bunsen** (1857) or **Solubility coefficient** (β) suggested by **W. Ostwald** (1888).

The Absorption coefficient (α) is defined as the volume of gas reduced to 0°C and 1 atm. dissolved by unit volume of solvent at the temperature of the experiment under a partial pressure of gas at 1 atm. If 'v' is the volume of dissolved gas reduced to S.T.P., 'V' is the volume of solvent, 'p' is the partial pressure of gas in atmosphere, the absorption coefficient (α) is given by equation (1).

$$\alpha = v/V.p \qquad \text{.... (1)}$$

The solubility coefficient is defined as the volume of gas measured under the temperature and pressure which the gas dissolves, taken up by unit volume of the liquid. If the volume of gas dissolving in a volume 'V' of the liquid at the experimental temperature 'T', and at the partial pressure 'p' atm. of the gas is 'v' ml, the solubility coeffieicnt (β) is given by equation (2)

$$\beta = v/V \qquad \text{.... (2)}$$

α and β are related by the equation (3)

$$\beta = \alpha T/273 \qquad \text{.... (3)}$$

The Absorption coefficients of few gases at 20° C in water and in some organic liquids are given in Table 21.4.2.

Table 21.4.2 Absorption Coefficient (α) of gases at 20° C

Liquid Solvent	H_2	N_2	O_2	CO_2	NH_3	HCL
Water	0.017	0.015	0.028	0.88	710	442
Alcohol	0.080	0.130	0.143	3.00	----	----
Benzene	0.066	0.104	0.163	----	----	----

The solubility of a gas in a liquid is influenced to a measurable extent by the temperature and the pressure of the gas. These are discussed in sections 21.5 and 21.6

Check Your Progress - 1

What is absorption coefficient?

21.5 INFLUENCE OF TEMPERATURE ON THE SOLUBILITY OF GAS IN LIQUID

Increase of temperature will result generally in the decrease of solubility of a gas in water. This fact makes it possible to readily expel a gas from its aqeuous solution by heating. The effect of temperature on the concentration of the gas solution can be expressed by equation (4).

$$\text{Log } C_2/C_1 = - \Delta H/2.303\,R \quad (1/T_2 - 1/T_1) \qquad \text{.... (4)}$$

Where C_1 and C_2 are the concentrations of solution at T_1 and T_2. ΔH is the differential heat of solution of one mole of the gas in a saturated solution at T^0 K.

Equation (4) can be rewritten as equation (5) in terms of Bunsen absorption coefficient (α).

$$\text{Log } \alpha_2/\alpha_1 = -\Delta H/2.303\,R \quad (1/T_2 - 1/T_1) \qquad \text{.... (5)}$$

Some volumes for the absorption coefficients of nitrogen, oxygen and carbondioxide at 0^0C and 30^0 C in water are presented in Table 21.5.1.

Table 21.5.1 Influence of temperature on absorption coefficient (α) of gases in water

Gas	0^0 C	30^0 C
Nitrogen	0.0235	0.0134
Oxygen	0.0489	0.0261
Carbondioxide	1.713	0.6650

As mentioned earlier the increase of temperature is generally accompanied by a decrease of solubility of a gas. But some sparingly soluble gases such as hydrogen and helium behave differently especially in non-aqueous solvents. In water the solubility first decreases, passes through a minimum and then increases with increase of temperature.

21.6 INFLUENCE OF PRESSURE ON THE SOLUBILITY OF A GAS IN LIQUID - HENRY'S LAW

The quantitative relation between solubility of a gas in a liquid and the pressure was proposed by **W. Henry** (1803). This relation is hence known as **Henry's law.** *The law states that the mass of gas dissolved by a given volume of solvent, at constant temperature is proportional to the pressure of the gas with which it is in equilibrum.*

If 'm' is the mass of gas dissolved by unit volume of solvent at the equilibrium pressure 'p' then,

$$m \propto p \qquad \text{.... (6)}$$

$$m = Kp$$

$$\text{Or} \quad m/p = k \qquad \text{.... (7)}$$

Where, K = Constant.

The mass 'm' of gas dissolved per unit volume of solvent is the concentration of the gas in grams per ml. This is also proportional to the concentration expressed in moles per litre of solvent or per litre of solution since there will not be considerable volume change. Further the pressure 'p' of the gas is proportional to the concentration of the gas in moles per litre in gas phase. Hence equation (7) can be written as :

Concentration of gas in liquid phase/Concentration of gas in gas phase = Constant .... (8)

The results obtained in the study of the solubility of gases in liquids showed that Henry's law is obeyed satisfactorily for gases of low solubility. Moreover the pressures should not be too high and temperatures should not be too low for the obedience of Henry's law. It is for these reasons, deviations are noticed at low temperatures and high pressures especially with easily liquefiable gases.

21.7 DEVIATIONS FROM HENRY'S LAW

Deviations are generally encountered if there is departure from ideal behaviour of the gas. Gases, especially easily liquefiable gases generally show non-ideal behaviour at low temperature and high pressure. In addition to the non-ideal behaviour of the gas, the other causes for the deviations are (a) the molecular species in the gas and liquid phases are not the same. (b) solute forms a compound with the solvent and (c) solute undergoes ionization. Few instances, where deviations from Henry's law were observed are briefly described below.

Ammonia shows deviations at low temperatures as well as at 100° C. The deviation at higher temperatures is attributed to the occurrence of the folloing reaction.

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$$

Carbondioxide exhibits deviations at low temperatures and high pressures. This is ascribed mainly to the compound formation between carbondioxide and water.

$$CO_2 + H_2O \longrightarrow H_2CO_3$$

Hydrogen chloride shows considerable deviations from Henry's law and this is attributed to the strong ionization of hydrogen chloride at low concentrations.

$$HCl \longrightarrow H^+ + Cl^-$$

21.8 SOLUBILITY OF GASES IN AQUEOUS SALT SOLUTIONS

Gases are less soluble in aqueous solution of electrolytes than pure water. This is generally referred to **salting - out effect.** The influence of a salt is independent of the nature of the gas. From study of the influence of a number of salts, it is concluded that salting-out effect is larger if the size of an ion is smaller and greater the charge it carries. The solubility of a gas in pure water and in an aqueous solution of a salt is expressed by equation (9).

$$\text{Log } S/So = KC \qquad (9)$$

Where C = Concentration of salt solution.
K = Constant for the given salt.
S = Solubility in salt solution.
S_o = Solubility in pure water.

non-electrolytes such as sugar are also found to reduce the solubility of a gas in aqueous solution.

The decrease in solubility of a gas in aqueous solutions of electrolytes of non-electrolytes is generally attributed to the preferential orientation of water molecules around those of the added substance (salt or non-electrolyte). This phenomenon can be broadly referred to as **hydration** of the added ions or non-electrolyte. It is for this reason the gas solubility measurements are used to calculate the extent of hydration (hydration number).

Check Your Progress - 2

What do you know about salting out phenomenon ?

21.9 SUMMARY

In this unit we have studied

i) The determination of solubility of a gas in a liquid.

ii) Absorption coefficient and solubility coefficient as measures of solubility of gas.

iii) Influence of temperature on the solubility of a gas in a liquid.

iv) Henry's law : the influence of pressure on the solubility of a gas.

v) Deviations from Henry's law.

vi) Solubility of gases in aqueous salt solutions.

21.10 MODEL EXAMINATION QUESTIONS

I. Answer each of the following in 10 lines.

1 Discuss the influence of pressure on the solubility of a gas in liquid.

2 How is solubility of a gas determined experimentally?

3 Explain with examples the reasons for departure from Henry's Law.

II. Answer the following in 30 lines.

1 Give a critical account of Henry's law.

2 Discuss the influence of temperature on the solubility of a gas in a liquid.

3 Give a detailed account of the methods used to measure the solubility of a gas in a liquid.

21.11 MODEL ANSWERS TO CHECK YOUR PROGRESS

1 Solubility of a gas in a liquid is expressed by absorption coefficient (α). It is the volume of a gas reduced to 0^0 C and 1 atm. Which dissolves in unit volume of the liquid partial pressure of the gas at 1 atm.

2 Gases are less soluble in the aqueous solutions of electrolytes than in pure water. This generalisation is called salting out phenomenon.

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UNIT - 22 : LIQUIDS IN LIQUIDS

Contents

22.1 AIMS & OBJECTIVES

This unit describes the different types of binary liquid mixtures and to explain some important properties of such liquid mixtures.

At the end of this unit you must be able to understand that:

- A system of two liquids is called **binary liquid mixture.**

- These are classified as (a) completely miscible, (b) partially miscible and (c) completely immiscible liquid mixtures.
- The total vapour pressure composition curve of an ideal system of completely miscible system is a horizontal line parallel to composition axis.
- A system in which the components exhibit a large difference in internal pressure, in polarity and hydrocarbon chain length show deviations from ideal behaviour.
- Separation of the components of a liquid mixture by vapourisation at the boiling point of the mixture into its pure components is called fractional distillation.
- It is not always possible to separate a liquid mixture into its pure components by fractional distillation.
- The liquid mixture which distills out a mixture of constant composition at constant temperature at any given pressure is called **azeotrope.**

22.2 INTRODUCTION

It was mentioned at the beginning of this unit that liquids too dissolve in liquids giving binary solutions. A system consisting of two liquids is called **binary system of liquids.** These systems are also called **binary liquid mixtures.** These are broadly classified into three types.

1 Completely miscible liquids.
2 Partially miscible liquids.
3 Completely immiscible liquids.

22.2.1 Completely miscible liquids

Binary mixtures consisting of two liquids which are miscible with one another or soluble in another at all proportions of the components are called **completely miscible liquids.** For example alcohol dissolves in water at all concentrations and like-wise water dissolves in alcohol at all concentrations. Alcohol-water mixture thus illustrates **completely miscible** pair of liquids. In such a mixture is not possible to distinguish between solute and solvent, since the two liquids are mutually soluble in all proportions.

22.2.2 Partially miscible liquids

Binary liquid mixtures consisting of liquids that exhibit complete miscibility in a **limited range of proportions** of the components are referred to as **partially miscible liquid mixtures.** If a little phenol, (an organic liquid) is added to water at ordinary temperatures, the former will dissolve completely in water. But if the addition is continued, a point is reached when no further dissolution of phenol takes place in water. This consequently leads to the formation of two liquid layers. These layers correspond to a **saturated solution of phenol in water** and a **saturated solution of water in phenol** respectively. These two systems (layers) will be in equilibrium with each other and are called **conjugate solutions.** Other examples of organic liquids which form partially miscible mixtures with water are ether and aniline. It is not always necessary for one of the liquids to be water. For example aniline and hexane, carbondisulphide and methyl alcohol at ordinary temperatures form partially miscible liquid pairs. At higher temperatures, liquid sulphur and liquid phosphorus also form partially miscible mixtures with organic liquids.

22.2.3 Completely immiscible liquids

Many examples of binary liquid mixtures are known where the two liquids exhibit no miscibility or no mutual solubility in the entire range of composition of the mixture. For example carbondisulphide is not miscible with water at any composition of the mixture. Such binary liquid mixtures are called **completely immiscible liquid pairs.**

22.3 VAPOUR PRESSURE OF LIQUID

The molecules of a liquid like those of a gas will be in continual motion. Since liquid has an open surface, some of the molecules will penetrate the surface and enter the space above the liquid. In a closed system the molecules will steadily accumulate in the space above the liquid. As the number of molecules in this increases, the molecules show a tendency to return to the liquid phase. (Fig. 22.1)

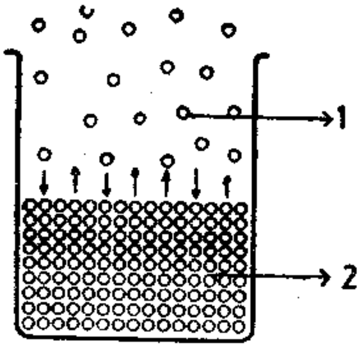


Fig. 22.1 Liquid - vapour equilibrium.
1. vapour 2. liquid.

At each temperature, a condition of equilibrium will be attained, when the number of molecules leaving the liquid, to enter the space above it is equal to the number returning in a given time. The space over the liquid is then said to be **saturated** with vapour of the liquid. The pressure exerted by the vapour of the liquid is called **vapour pressure** of the liquid at that given temperature. This equilibrium pressure or vapour pressure **depends only** on the temperature but not on the area of the liquid surface. The number of molecules in unit volume of the liquid is greater than in the saturated vapour at equilibrium. This is because only molecules possessing sufficient energy are able to vapourize. If n_v and n_l represent the number of molecules or moles per unit volume of vapour and liquid respectively, it follows that.

$$n_v/n_l = e^{-L/RT} \quad .... (1)$$

Where 'L' is the mean potential energy difference per mole, n_l does not vary very much with temperature, but n_v/n_l increases. Therefore n_v increases with increase of temperature. This means that vapour pressure increases with temperature. The above discussion indicates that at any temperature the liquid is in equilibrium with its vapour.

22.4 PARTIAL VAPOUR PRESSURES OF LIQUIDS IN A BINARY MIXTURE OF LIQUIDS

A mixture of two liquids A, B as mentioned earlier is referred to as a binary liquid mixture. The vapour pressure exerted by a liquid in a liquid mixture is known as **partial vapour pressure** (p) of that liquid. The total vapour pressure 'P' of a liquid mixture is equal to the sum of the partial pressures (p_A, p_B) of the component liquids.

$$P = p_A + p_B \qquad \text{.... (2)}$$

The partial vapour pressure of a liquid is proportional to its mole fraction in the liquid mixture.

$$P_A \quad \alpha \quad X_A \qquad \text{.......... (3)}$$

$$\text{Or} \quad P_A = p^0{}_A X_A \qquad \text{.......... (4)}$$

$$p_B \quad \alpha \quad X_B \qquad \text{.......... (5)}$$

$$\text{Or} \quad p_B = p^0{}_B X_B \qquad \text{.......... (6)}$$

Where p_A & P_B are partial vapour pressure, $p_A{}^0$, $p_B{}^0$ are vapour pressures of pure liquids and X_A and X_B are mole fractions of the liquids in the mixture. The generalization is known as **Raoult's Law.** *A liquid mixture which obeys satisfactorily Raoult's Law in respect of each liquid of the mixture at all compositions of the liquid mixture is called an ideal system.*

22.5 APPLICATION OF RAOULT'S LAW

22.5.1 Completely miscible liquids (Ideal systems)

If a mixture of two liquids A and B behaves ideally (i.e., obey Raoult's law) each of the liquid is expected to obey Raoult's law. This means that the partial pressures p_A and p_B of the constituents shall obey the equations 7, 8.

$$p_A = p_A{}^0 X_A \qquad \text{.... (7)}$$

$$p_B = p_B{}^0 X_B \qquad \text{.... (8)}$$

Where X_A, X_B are the mole fractions of the liquids A and B.

The total vapour pressure P, the sum of the two partial pressures p_A, p_B is given by equation.

$$P = p_A{}^0 \,.\, X_A + p^0{}_B \,.\, X_B \qquad \text{.... (9)}$$

The equations 7, 8 suggests that a plot between mole fraction and vapour pressure yields a straight line of Raoult's Law is obeyed.

The plot between vapour pressure and mole fraction for an ideal system is presented in Fig. 22.2.

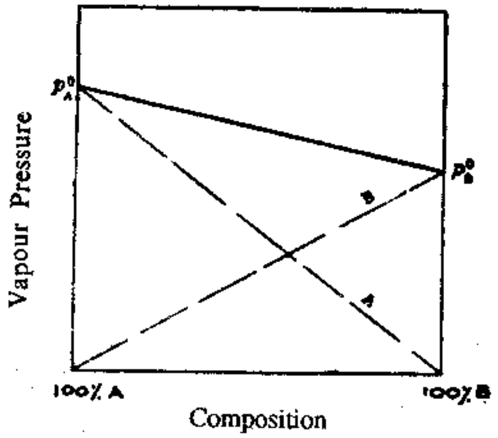
A limited number of systems are known, which obey Raoult's law over the whole range of concentrations and give straight line plots of vapour pressure against the composition expressed in mole fractions. Few important examples are :

i) Ethylene dibromide and propylene dibromide at 85° C

ii) Benzene and ethylene dichloride at 50°C

iii) N-Hexane and n-heptane at 30°C

iv) Ethyl bromide and ethyl iodide at 30°C.



(-) Total vapour pressure curve, (- - - -) Partial vapour pressure curves.

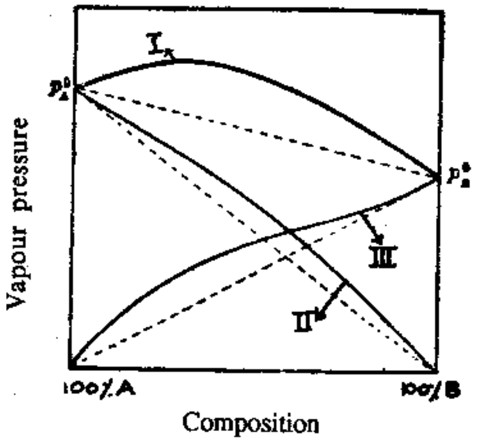
Fig. 22.2 Vapour pressure vs composition : System obeying Raoult's law

A close inspection of the nature of the liquids in the mixtures mentioned above indicates that the liquids are physically and chemically similar. The inter-molecular forces in such liquid mixtures are identical.

Further there will be very little difference in the environment in the pure liquid and the mixture. These facts therefore suggest that a binary liquid system in which the constituent liquids show similar intermolecular forces and environment, generally exhibits ideal behaviour.

22.5.2 Systems with positive deviations

Many liquid mixtures are known where measured vapour pressures are greater than those to be expected from equations 7 and 8. However in some cases the deviations are small and in other cases they are large. Some of the liquid pairs which exhibited positive deviations are carbon tetrachloride and heptane at 50°C, ethylether and acetone at 30°C and heptane and ethyl alcohol at 50°C. The vapour pressure composition (ideal and experimental) curve for mixtures of the kind under consideration are shown in Fig. 22.3. The dotted curves indicate ideal behaviour. The solid curves indicate experimental curves and these approach the ideal ones the system approaches pure components. A, (solvent) tends to obey Raoult's law when the concentration of B (solute) becomes very small. Similarly B, obey Raoult's law as the concentration of A becomes small.



I. Total vapour pressure curve; II and III. Partial vapour pressure curves

Fig. 22.3 Positive deviations from Raoult's law.

The total vapour pressure curve for an ideal system should be a horizontal line. But the total vapour curve shows a maximum if the positive deviations are large. This indicates total vapour pressure of the mixture is maximum for one particular composition of mixture.

A system shows deviations from ideal behaviour if the components of the mixture exhibit the following

i) Large difference in internal pressure

ii) Large difference in polarity

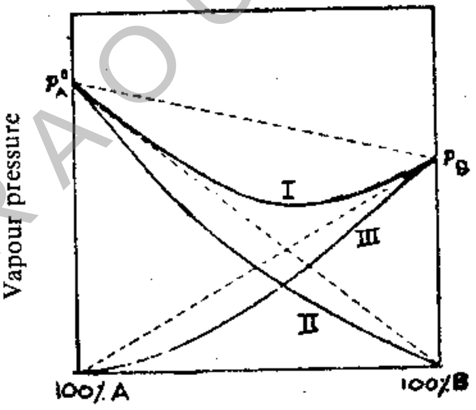
iii) Large difference in hydrocarbon chain length and

iv) Association.

A pair of liquids which exhibits large positive deviations i.e., the magnitude of the above mentioned causes is great, there is a possibility that the component liquids may become incompletely miscible as the temperature is lowered. For example in the case of n-heptane and ethylalcohol, the components separate into two layers as the temperature is diminished. Mixtures of water and isobutyl alcohol illustrate large positive deviations unlike mixtures of water and methyl alcohol. This can be traced to the long hydrocarbon chain in butyl alcohol ($CH_3 - CH_2 - CH_2 - CH_2 OH$) unlike in methyl alcohol ($CH_3 OH$).

22.5.3 Systems with negative deviations.

In contrast to the examples mentioned in 22.5.2 liquid mixtures, pyridine-acetic acid, and chloroform - acetone exhibit vapour pressure lower than expected from Raoult's equations. They thus show negative deviations from Raoult's law (Fig. 22.4)



1. Total Vapour pressure curve; II and III Partial Vapour pressure curves
Fig. 22.4 Negative deviation from Raoult's law.

These deviations are attributed to partial compound formation between the liquids, the two molecules being bound by hydrogen bond. The experimental partial vapour pressure curve approaches the ideal curves as the composition approaches pure component. This observation is similar to that observed in the systems with positive deviation.

22.6 EFFECT OF TEMPERATURE

A system of binary liquid mixture generally approaches ideal behaviour on increase of temperature. Lowering of temperature however leads to the increase of deviations. Changes in the form of the vapour pressure curves are therefore expected with the change of temperature. The mole fraction of a constituent in the vapour of a liquid mixture at any temperature is proportional to the partial vapour pressure of that component. The composition of the vapour in equilbrium with any particular liquid mixture can therefore be found at any temperature.

D.P. Konowaloff (1881) proposed that the vapour is relatively richer in the component, if its addition to the liquid mixture results in an increase of total vapour pressure. He made measurements of the total vapour pressure of homogenous liquid mixtures could be divided into three types. This classification is based on the fact whether the vapour pressures either increased regularly with the composition or showed a maximum or a minimum.

22.7 DISTILLATION OF HOMOGENEOUS BINARY LIQUID MIXTURES

The separation of the volatile components from a homogeneous liquid mixture by raising the temperature of the mixture to its boiling point is called **distillation.**

For example it is possible to separate a mixture of acetone and benzene successively into acetone (B.P. 56°C) and benzene (B.P. 80°C) by raising the temperature of the mixture. As the temperature of the mixture reaches the boiling point of acetone it begins to separate out as its vapour, leaving behind the liquid mixture richer in benzene. The process continues till all acetone is separated. The benzene, remaining behind experiences arise in temperatures and is converted into its vapour as soon as the temperature reaches the boiling point of benzene. This process of separation by rise of temperature is called **fractional distillation.** The separation into pure components is possible only when the system satisfies the following conditions. The boiling point of the mixture shall show a regular increase with increase in the percentage of more volatile (lower boiling point) component in the mixture. **The boiling point of a mixture, distilling freely, is the temperature at which the total vapour pressure is equal to that the atmosphere.** For ideal systems the boiling point of the mixture varies regularly with the composition of the mixture. The process of separation of the components by raise of temperature at constant pressure (at atmospheric pressure) is of generally greater interest than the separation carried out at constant temperature. The latter is called **isothermal distillation.**

The experimental results concerning the boiling point and composition of the liquid-liquid mixtures are best represented graphically. The boiling points are taken as ordinates and the compositions as abscissae. In this method of representation two curves are obtained. One curve gives the composition of the liquid and the other curve represents the composition of the vapour which is in equilbrium with the liquid at the boiling point. The upper curve is called **Vapour Curve** and represents the vapour and the lower curve is called **Liquid Curve** and represents the liquid. The vapour phase is relatively richer in the more volaatile component (i.e., lower boiling point component of the liquid mixture). The liquid phase will be richer in the less volatile component (the component with high boiling point). Three different types of curves were observed when experimental results were plotted. These are, type-1 where the boiling point rises steadily, type-2, where there is a minimum in boiling point, type-3 where there is a maximum in boiling point, with change of composition from more volatiles to less volatile constituents.

22.7 .1 Type-1: The boiling point increase regularly

The boiling point - composition curves are shown in Fig. 22.5

The upper curve represent the composition of the vapour phase and the lower curve represents the composition of the liquid phase. The vapour contains more A, the component with lower boiling point. The mixtures belonging to this type are exemplified by carbondisulphide and benzene, benzene and toluene, acetone and water, acetone and ether, chloroform and carbon tetrachloride, chloro benzene and bromo benzene.

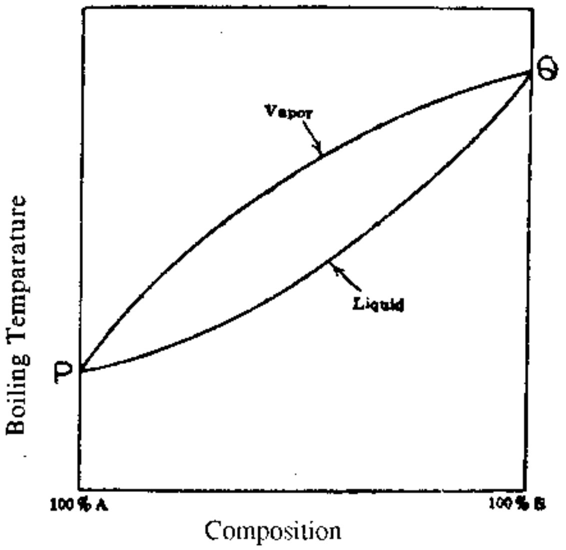


Fig. 22.5 Liquid mixture with regularly increasing boiling point.

22.9.2 Type - 2: The boiling point exhibits minimum

The boiling point - composition curves typical of this type are shown in fig 22.6.

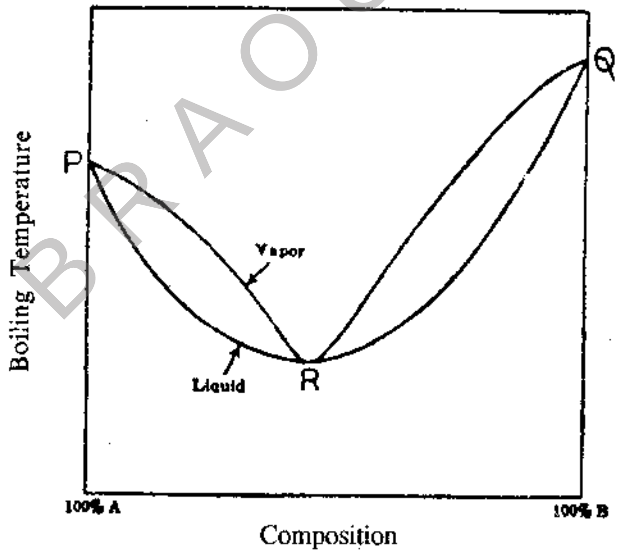


Fig. 22.6 Liquid mixture with boiling point (minimum)

The upper curve represents the vapour curve and the lower curve represents the liquid curve. The two curves meet at a point R which represents the composition of the liquid mixture with minimum boiling point. The liquid and the vapour in equilibrium will have the same composition at this temperature. The liquid represented by this point R boils at constant temperature i.e., distills over completely without change in composition. **Such systems which distill unchanged in composition have been called azeotropic mixtures or azeotropes** (Greek : *to boil unchanged)* by **J. Wade** and **R.W. Merriman** (1911). However the composition and boiling point of such constant boiling mixtures may vary with pressure (see table 22.6.2.1)

Table 22.6.2.1 **Composition and boiling point of constant boiling mixture at different pressures.**

Ethyal Alcohol - Water

Pressure (mm)	Boiling Point (0^0 C)	Composition (% Water)
200	37.6	5.79
300	46.8	6.56
500	59.4	7.54
760	70.4	8.43
900	75.1	8.80

In the case of liquid mixtures having a minimum boiling point, it is therefore only possible to obtain in pure form by fractional distillation, the liquid present in excess over the quantity corresponding to the azeotropic mixture. The distillate tends towards the mixture of minimum boiling point. The azeotropic mixture thus behaves as if it were a simple liquid in distillation. Some typical liquid mixtures which show a minimum in their boiling points are ethyl alcohol-benzene; methyl alcohol-chloroform and acetone-carbontetrachloride.

Check Your Progress - 1

Explain the meaning of azeotrope.

22.7.3 The boiling point exhibits maximum

In this type also vapour composition curve is above that of the liquid composition curve. The two curves meet at the maximum point R. The liquid mixture corresponding to R is called here also the azeotropic mixture.

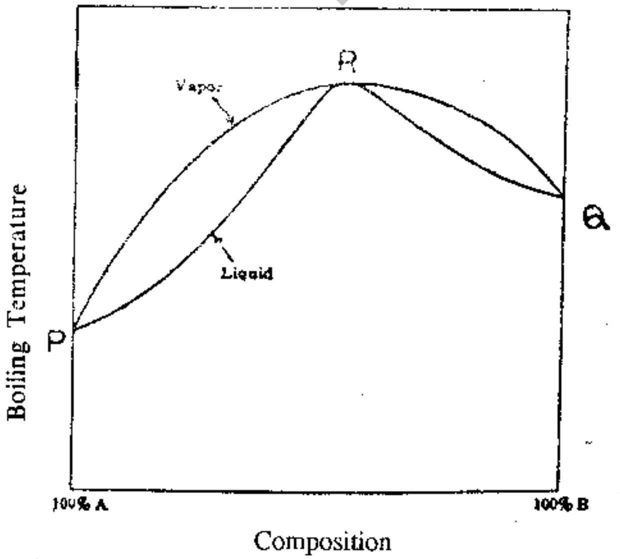


Fig. 22.7 Liquid mixture with boiling point maximum.

The boiling point of the azeotropic mixture varies with pressure. Typical values of boiling point in respect of hydrochloric acid - water mixture are shown in Table 22.7.3.1.

Table 22.7.3.1 : Composition and boiling point of azeotrope of different pressures.

$HCl - H_2O$ mixture

Pressure (mm)	Boiling Point (°C)	Composition (% HCl)
400	92.08	21.24
500	97.58	20.92
600	102.21	20.64
700	106.42	20.36
800	110.01	20.16

As in the earlier case, it is not possible to separate the liquid mixture by distillation into the two pure liquid components. It is only possible to obtain as a pure liquid, the constituent that is present in excess of that required by the composition of the azeotropic mixture. Some typical azeotropic mixtures and the compositions corresponding to the constant boiling point (maximum or minimum) are presented in Table 22.7.3.2.

Table 22.7.3.2 : Some typical azeotropic mixtures.

Component A	Boiling Point °C	Component B	Boiling Point °C	Constant Boiling °C	%, B
H_2O	100	HCl	80	108.6	20.24
H_2O	100	HNO_3	86	120.5	68.0
H_2O	100	$HCOOH$	100.7	107.1	77.5
H_2O	100	C_2H_5OH	78.3	78.1	95.6
H_2O	100	$CH_3CH_2CH_2OH$	97.1	88.1	71.8

22.8 SEPERATION OF A LIQUID MIXTURE INTO ITS PURE LIQUID COMPONENTS.

By raising the temperature of the mixture to its boiling point the separation can be effected if certain conditions are satisfied.

As mentioned earlier, the conversion of the liquid into its vapour at its boiling point by raising the temperature of the liquid is called distillation. It is thus possible to separate liquid mixture into its pure components by a process of volatilization or vapourisation of the liquid mixture at the boiling point of the mixture. This process of separation of a binary liquid mixture into its components is called **fractional distillation.**

In fractional distillation, special types of long tubes containing good number of condensation surfaces, are used and these are called fractionating columns (Fig. 22.8).

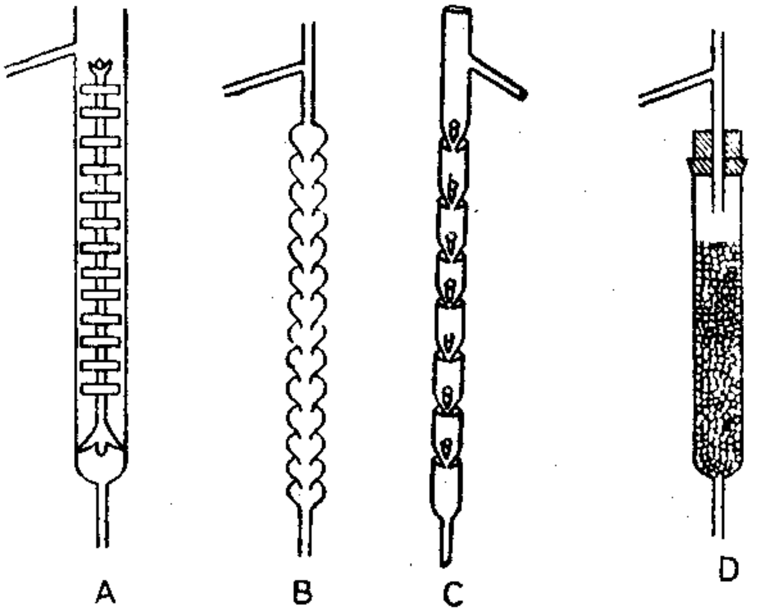


Fig. 22.8 Fractionating columns.

The liquid mixture is taken in a round bottomed flask fitted with a fractionating column and carefully heated. As the temperature reaches the boiling point of the mixture, the liquid is converted rapidly into vapour. The vapour will be rich in that component which has a lower boiling point. The vapour partially get condensed into the liquid on the condensing surfaces as it reaches the surface. The condensate then recedes into the flask. The vapour escaping uncondensed will be richer in the more volatile component, while the vapour condensing into the liquid and receding into the flask will be richer in the less volatile component.

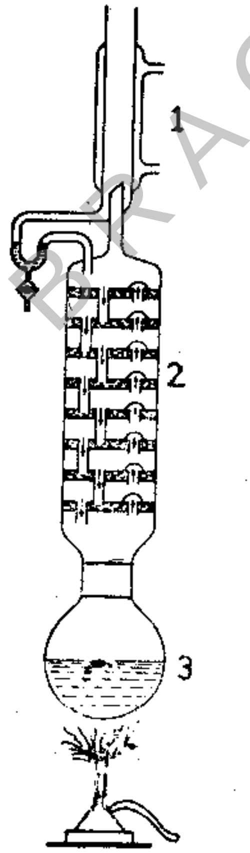


Fig. 22.9 Fractional distillation
1. Reflux condenser 2. Fractionaing column 3. Flask

The principle underlying the separation is explained with the help of boiling point - Composition curve.

22.8.1 The Principle underlying fractional distillation.

The boiling point-composition curves for a system consisting of liquids A and B, where the boiling point of the mixture changes regularly with the composition of the mixture are presented in figure 22.10.

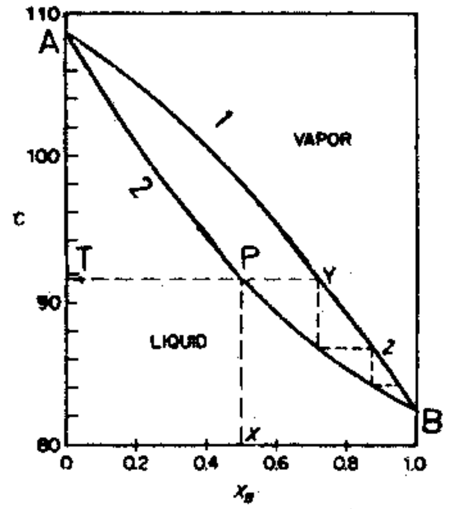


Fig. 22.10 Distillation of binary liquid mixture : boiling point-composition curves
1. Condensation curve 2. Boiling-point curve.

The upper curve represents the composition of the vapour phase in equilibrium with the liquid phase. The lower curve represents the composition of the liquid phase. It is obvious from the curves that the vapour contains more B which has the lower boiling point. It is seen from the figure that a liquid mixture of composition represented by 'X' boiled at temperature 'T'. The composition of the first vapour formed at this temperature is known by extra-polating the dotted horizontal line to cut the vapour curve at Y. This extra-polated line joining the two points P and Y giving the percentage of the liquid and vapour in equilibrium is called a **tie line.** The composition of the first vapour formed is thus given 'Y'. This will be richer in **B,** the more volatile component. If this is condensed and reboiled, vapour of composition **Z** is obtained. This vapour contains still higher percentage of the more volatile component B. The process of condensation and reboiling is repeated until the vapour formed (distillate) is composed of pure component B. In practice, the successive fractions will each cover a range of compositions. The vertical lines in figure 22.10 represent only average compositions within these ranges. As mentioned earlier, the automatic successive condensations and vapourisations required are achieved through the use of fractionation column. The efficiency of the column depends on the number of equilbrium stages. Each stage is called a **theoretical plate.**

22.9 PARTIALLY MISCIBLE LIQUIDS

22.9.1 Introduction

Water and alcohol are completely miscible with each other. The two liquids are mutually soluble in each other in all proportions. For example, alcohol is soluble in water in all proportions and water is soluble in alcohol in all proportions. But water and mercury are completely immiscible with each other. Water does not dissolve in mercury and similarly mercury does not dissolve in water. Besides these two classes of liquid mixtures namely completely miscible with each other. For example, as mentioned earlier if a little phenol (an organic liquid) is added to water at room temperature, it will dissolve completely. That is, phenol and water form at this low percentage of phenol, a miscible system. But if the addition of phenol is continued, it will be observed, that dissolution of phenol ceases beyond a point. This is indicated by the formation of two visible liquid layers. One of these layers is a saturated solution of **phenol in water** and the other is a saturated solution of **water in phenol.** These two solutions in equilibrium with each other are called **conjugate solutions.** The other pairs of liquids which exhibit the phenomenon of partial miscibility are ether-water, and aniline-water. But it is not necessary for one of the substances to be water. Partially miscible or incompletely miscible systems are frequently obtained even with two organic liquids. For example, aniline and hexane, and carbondisulphide and methy alcohol are examples of partially miscible pairs of organic liquids. An organic liquid and a molten liquid of inorganic substance can also form a partially miscible pair of liquids. Liquid sulphur or liquid phosphorus forms partially miscible liquid pairs with some organic liquids.

22.9.2 Effect of temperature

The two layers in a partially miscible binary liquid system attain the same composition with raise of temperature. This means that the mutual solubilities of the two components increase with increasing temperature. The typical composition - temperature curve for aniline - hexane system is shown in Fig. 22.11.

The two layers become identical in composition at temperature 't_c'. The two layers become actually only **one layer** and the composition of which is represented by C. The temperature (t_c) at which the two layers (conjugate solutions) merge into a single layer of one composition is called the **critical solution temperature.** (D. O. Masson 1891) or the **consolute temperature (W.D. Bancroft.** 1894) of the system. Above this temperature the two partially miscible liquids became miscible in all proportions. The compositions lying outside this curve consist of one liquid layer only.

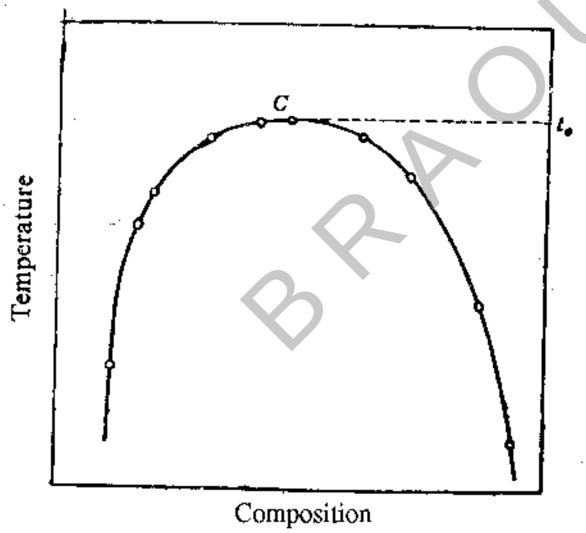


Fig. 22.11 The aniline - hexane system.

In the example given above it is seen that, two partially miscible liquids become completely miscible at a temperature above the room temperature. Such systems are referred to as **systems with upper critical solution temperature or upper consolute temperature**. Many systems were later discovered where the mutual solubilities of the two components decreased instead of increasing with increasing temperature. For example in ethyl ether and water system the mutual solubilities decreased with rise of temperature. But it was later discovered that the mutual solubilities increased on lowering the temperature. It was observed that below a definite temperature the two liquids became miscible in all proportions. The solubility curve of such system is similar to that given in Fig. 22.11 but is inverted. The temperature below which the two liquids are completely miscible at all proportions is called **lower critical solution temperature or lower consolute temperature.**

In the case of some systems with **lower consolute temperature** it is found that the mutual solubility does not decrease indefinitely with rise of temperature. But the mutual solubility is found to increase again beyond a point with rise of temperature and in the process a temperature is reached above which the two liquids are again completely miscible. The system will thus have a **lower consolute temperature** and also **upper consolute temperature.**

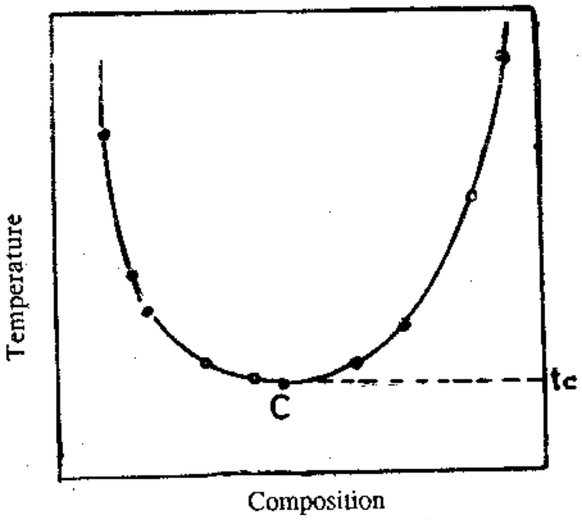


Fig. 22.12 Ethyl ether-water system

The solubility curve illustrating such a system is a closed curve as shown in Fig. 22.13.

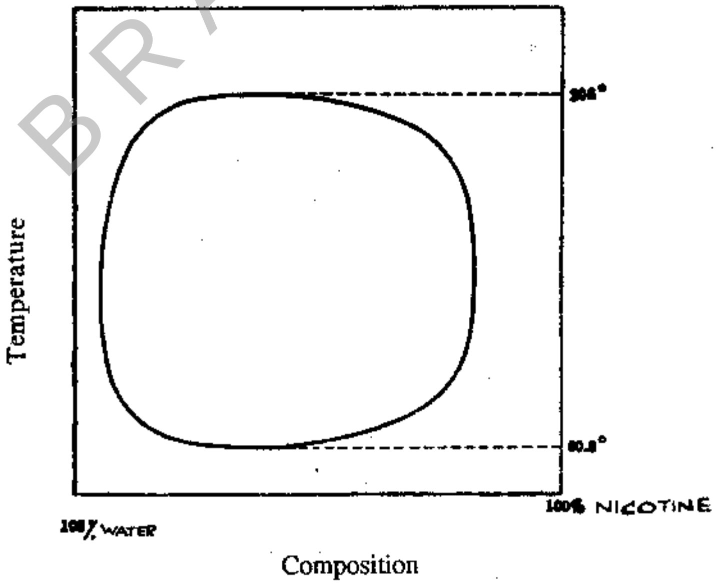


Fig. 22.13 Nicotine - water system

But all systems which exhibit lower consolute temperature may not exhibit upper consolute temperature too. Few tyical systems whch possessed both lower upper consolute temperatures are given in table 22.9.3

Table 22.9.3 systems wiht lower and upper consolute temperatures.

System	Consolute temperature (°C)	
	Lower	Upper
Nicotine - Water	60.8	208
Methyl ethyl ketone - Water	-6	133
β–Picoline - Water	49	153
Glycerol - mToluidine	6-7	120

Check Your Progress - 2

What is critical solution temperature?

22.10 EFFECT OF ADDED SUBSTANCES ON CONSOLUTE TEMPERATURES

The mutual solubilities of the liquids are influenced by the added substance and depend on the nature and quantity of the added material.

If the added substance is soluble in only one of the two liquids, the mutual solubilities of the two liquids are decreased and the added substance raises the consolute temperature. For example addition of potassium chloride to phenol - water system raises the consolute temperature considerably. This is because potassium chloride is soluble in water but not in phenol. Similarly addition of napthalene (an organic substance) to the system raises the consolute temperature much more considerably. The rise occurs in the value of consolute temperature because naphthalene is soluble in phenol but not in water. In a system of alcohol-hydrocarbon, addition of trace of water produces a marked increase in the consolute temperature because water is soluble in alcool but not in hydrocarbon. Determination of critical solution temperature is therefore sometimes used as a method of testing the purity of hydrocarbon.

In contrast to the observations mentioned above, an added substance whch is soluble in both the liquids lowers the consolute temperature. For example, succinic acid (an organic acid) lowered the consolute temperature of phenol-water system since succinic acid is soluble both in phenol and water.

Salts are usually insoluble in organic liquids. so the consolute temperature of sytem consisting of organic liquid and water is raised by the addition of salt to such system. This can be generally referred to as **salting out effect.**

22.11 COMPLETELY MISCIBLE LIQUIDS

There are many pairs of liquids which do not show any mutual solubility at all, at room temperature or at temperatures higher or lower than room temperatures. Such pairs of liquids are called **completely immiscible liquid pairs.** For example, carbondisulphide and water are immiscible at all proportions of the components.

The total vapour pressure of such a system is the sum of the independent vapour pressures of the two pure components of the system. The total pressure is independent of the relative amounts of the two liquids. Each liquid exerts its own vapour pressure. Moreover, the number of each constituent in the vapour is proportional to the vapour pressure of the molecules of pure liquid at that temperature. If p^oA, and p^oB are the vapour pressure of pure liquid components A and B, the total vapour pressure P is given by euqation (10).

$$P = p^oA + P^oB \qquad \text{.......... (10)}$$

The number of molecules n_A and n_B of A and B in the vapour are proportional to vapour pressures (equation 11).

$$\frac{n_A}{n_B} = \frac{p^o{}_A}{p^o{}_B} \qquad \text{.......... (11)}$$

The weights W_A and W_B of A and B in the vapour are obtained by multiplying n_A and n_B by the respective molecular weights M_A and M_B, therefore

$$\frac{W_A}{W_B} = \frac{M_A \quad n_A}{M_B \quad n_B} = \frac{M_A.p^oA}{M_B.p^oB} \qquad \text{........ (12)}$$

The mixture will boil when the total vapour pressure, P is equal to the atmospheric pressure. since the vapour pressure of each constituent is les than the total pressure, the boiling point of the mixture is less than the boiling jpoint of either constituent. Theboiling point also remains constant as long as the two liquids are present in the mixture.

This fact is utilised in **steam distillation,** a distillation process used to separate high boiling organic components from a natural source by passing steam through it.

For example, chlorobenzene (an organic liquid) has a boiling point of 132°C. But when steam is passed through a source containing it, the mixture of water and chlorobenzene distills over at about 90°C. the disstillate contains nearly 70 percent of the organic liquid.

22.12 NERNST DISTRIBUTION LAW

The distribution of a solute soluble in either of the liquids of a binary immiscible liquid-liquid mixture follows certain definite conditions. The manner in which this distribution occurs is known as **distribution law.**

If C_1 and C_2 are the concentrations of a solute at a given temperature in the liquid layers 1 and 2 of the binary system of immiscible liquids.

$$\frac{C_1}{C_2} = \text{Constant (K)} \qquad \text{...... (13)}$$

The constant (K) is independent of the total amount distributing. The law can be stated as : *at constant temperature a solute distributes itself between the two layers of a binary system of immiscible liquids such that the ratio of its concentrations in the two layers is constant and independent of the total concentraton of the solute.* This statement is known as *distribution of law* or *partition law.* The 'K' is called the **distribution coefficient** or **partition coefficient.** The law showed deviations in cases where the solute exhibited association or dissociation in one or both the liquid layers.

22.13 APPLICATIONS OF DISTRIBUTION LAW

22.13.1 Study of chemical equilibrium

The law finds application in the study of chemical equilibium in solution. For example, the equilibrium reaction (complex formation) between iodine (I_2) and Iodide (I^-) canbe investigated by the method of distribution.

$I_2 + KI = KI_3$ OR $I_2 + I^- = I_3$

The equilibrium constant $K = \frac{[KI_3]}{[I_2]\,[KI]}$

The equilibrium constant can be evaluated by determining the distribution coefficient of iodine between water and carbon tetrachloride and also distribution of Iodine between potassium iodide solution (KI solution) and carbontetrachloride. The procedure involves the determination of concentration of I_2 in aqueous and organic layers when it is distributed between (a) water and carbon tetrachloride and (b) between potassium iodide solution and carbontetrachloride. The calculations are described below.

Calculations

Total concentration of I_2 n water = C_x

Total concentration of KI in water = C_y

Concentration of I_2 in carbontetrachloide = C_1

Distribution coefficient of I_2 = K

$$[KI_3] = (C_x - \frac{C_1}{K})$$

$$\text{Free } [I_2] = C_1/K$$

$$\text{Free } [KI] = C_Y - (C_x - \frac{C1}{K})$$

$$\text{Equilibrium Constant} = \frac{[KI_3]}{[I_2]\,[KI]}$$

$$= \frac{(Cx - \frac{C_1}{K})}{(\frac{C_1}{K}) \times C_y - (C_x - \frac{C_1}{K})}$$

$$= \frac{(C_x - \frac{C_1}{K})}{(\frac{C_1}{K}) \times (C_y - C_x + \frac{C_1}{K})} \qquad \text{..... (14)}$$

2? 13.2. Extraction of dissolved substances from aqueous solutions.

The separation of organic substance present in the dissolved state from their aqueous solutions is generally referred to as 'extraction'. This is achieved by shaking the aqueous solution with an organic liquid immiscible with water. The dissolved organic substance distributes itself between the solvents in the process. Since organic substances are generally more soluble in organic liquids than in water, the concentration of the dissolved substance in organic liquid is greater than in water. This therefore helps to extract the dissolved substance from the aqueous solutions into the organic liquid. the process of extraction can further be improved if salts are added to the aqueous solution. In the presence of salts, the solubility of the organic compound in water is furtehr depressed due to salting-out phenomenon. The efficiency of the extraction process increases if the extraction is carried out large number of times using each time a small volume of the organic liquid.

Let 'V' ml of aqueous solution containing 'm' gms of a dissolved substance be shaken repeatedly with small portions ('x' ml) of an organic liquid which is immiscible with water. Let 'm_1' be the weight of dissolved substance remaining in aqueous solution after first extraction (after shaking with first portion). The concentration of the dissolved substance in aqueous solution is m_1/V gms per ml. The concentration of the substance in organic liquid (extractant) is '$(m=m_1)/x$' gms per ml. The distribution coefficient K will be given by.

$$\frac{m_1/V}{(m-m_1)/x} = K \quad \text{.... (15)}$$

$$m_1 = m_1 \frac{KV}{KV+x} \quad \text{.... (16)}$$

Let 'm_2' gms remain in aqueous solution after second extraction (after shaking with second 'x' ml portion). The distribution coefficient is given by

$$\frac{m_2/V}{(m_1-m_2)/x} = K \quad \text{.... (17)}$$

$$m_2 = m_1 \frac{KV}{KV+x} \quad \text{.... (18)}$$

Or $$m_2 = m.\frac{KV}{KV+x} \ X \ \frac{KV}{KV+x} \quad \text{.... (19)}$$

Since $m_1 = m\frac{KV}{KV+x}$

$$m_2 = m\,(KV/KV+x)^2 \quad \text{.... (20)}$$

The arguments can be extended further and the equation 20 after the nth extraction can be written as

$$m_n = m\,(KV/KV+x)^n \quad \text{.... (21)}$$

An extraction is said to be efficient if m_n is as small as possible for a given volume (V) of extracting liquid.

Equation (21) indicates that m_n will be small if n is large and x small. It is thus clear that it is always advantageous to increase the number (n) of extractions and decrease the volume (x), of the extraction liquid used in each batch of extraction.

22.14 SUMMARY

In this unit we have studied

i) Different types of binary liquid mixtures and their characteristics with examples.

ii) Vapour pressure of a liquid as a characteristic property of the liquid.

iii) Partial vapour pressures of liquids in a binary liquid mixture and Raoult's law.

iv) Ideal solution is one which obey's Raoult's law. Discussion on vapour pressure curves.

v) Non-ideal systems with positive deviations and the reasons for such a behaviour.

vi) Non-ideal systems with negative deviations and the reasons for such a behaviour.

vii) Effect of temperature on such systems.

viii) Distillation of homogeneous binary liquid mixtures wherein

(a) Boiling point increases regularly

(b) Boiling point exhibits minimum

(c) Boiling point exhibits maximum

ix) Azeotropic mixtures

x) Principle underlying fractional distillation

xi) partially miscible liquids with examples of systems having lower CST and upper CST and beta.

xii) Distribution law and partition coefficient.

xiii) Extraction of dissolved substances from aqueous solutions.

22.15 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines each.

1. Give a short account of the effect of temperature on the behaviour of partially miscible liquids.

2. Explain the principle underlying fractional distillation.

3. What is meant by constant boiling mixture? While systems exhibit this phenomenon?

4. Discuss the application of distribution law in the study of chemical equilbrium involving complex formation.

5. Describe the process of steam distillation explaining the underlying principle.

6. The efficiency of solvent extraction increases with increase in the number of extractions Substantiate this statement.

II. Answer the following in 30 lines each.

1. Give a detailed account of the different types and behaviour of binary liquid mixtures.
2. Explain clearly the process of distillation of binary liquid mixtures.
3. Give a critical account of consolute temperatures.
4. State and explain distribution law. Discuss its application in solvent extraction.

22.16 MODEL ANSWERS TO CHECK YOUR PROGRESS

1 At a particular temperature a liquid mixture may have the same composition as its vapour in equilibrium with it. It cannot be separated into individual components by fractional distillation. Such a liquid mixture is called azeotrope or azeotropic mixture. Ex:- 95% ethanol.

2 In partially miscible liquid mixtures, one liquid mixes in the other at a particular temperature or higher temperatures, in some cases at a particular temperature or lower temperatures in all proportions. Such temperature is called the critical solution temperatures of that liquid mixture.

Author : Prof. S. BRAHMAJI RAO

Block - 7

COLLIGATIVE PROPERTIES

A solution is a homogeneous mixture constituting a single phase of two or more components. There is no fundamental difference between the roles of these components. The component present in small amounts is generally called **solute** and the one present in higher amounts is referred to as **solvent.** The solution is referred to as aqueous solution, if the solvent is water. The properties of solutions depend to a significant extent on the concentration of chemical nature of the solute and solvent. The properties of a system can be broadly classified as **intensive** and **extensive.** The properties that depend on the nature of the substance but not on the quantity of the substance are called **intensive properties.** For example density, refractive index, melting and boiling points are **intensive properties.** Those properties that depend on quantity or concentration are called **extensive properties.** Volume and mass are such properties. The properties depending on particles only deserve special mention in the case of dilute solutions. These are **Lowering of vapour pressure, Elevation of boiling point, Depression of freezing point** and the **Osmotic pressure.** These properties are a function of number of particles (molecules or ions) of solute in the solution rather than the chemical nature of the particles. **Such properties which depend on the number of solute particles are called colligative properties.** In the discussion of these properties, for convenience the solute is assumed to be non-volatile. Substance that can be rapidly converted into its vapour at room temperature can be called **volatile substance.**

UNIT - 23 LOWERING OF VAPOUR PRESSURE

Contents

23.1 AIMS AND OBJECTIVES.

The main aim of this unit is to explain the meaning of lowering of vapour pressure of a liquid caused by the substance dissolved in the liquid and to discuss its application in the determination of the molecular weight of the dissolved substance.

When you have finished this Unit you should be able to understand that:

- The pressure exerted by molecules of a liquid in the vapour phase, when a liquid and its vapour are in equilibrium is called vapour pressure of the liquid.
- The vapour pressure (p) of a solution of a non-volatile solute dissolved in a solvent is less than the vapour pressure (p^0) of the solvent.
- The difference (p^0 - p) between the vapour pressure of solvent and solution is called *lowering of vapour pressure.*
- The ratio between lowering of vapour pressure and the vapour pressure of solvent is called *relative lowering of vapour pressure* ($p^0 - p/p^0$)
- The relative lowering of vapour pressure of a dilute solution of non-volatile solute is equal to the molefraction of the solute in the solution. This statement is called **'Raoult's Law'.**
- The solutions which obey Raoult's Law are called ideal solutions.
- Raoult's Law is useful to determine the molecular weight of a dissolved substance.

23.2 INTRODUCTION

The vapour pressure is a characteristic property of a given liquid and remains constant as long as temperature is constant. A dynamic equilibrium exists between the liquid and vapour phases. However when a non-volatile solute is dissolved in a pure solvent, a solution is obtained. The vapour pressure of the solution is less than the vapour pressure of the pure solvent. This is because a part of the surface area of the liquid phase is occupied by solute molecules which are non-volatile. This property can be made use of for determination of the molecular weight of the solute.

23.3 VAPOUR PRESSURE OF A LIQUID

Liquids too like gases consist of molecules moving in a random fashion with a range of velocities. Consequently, molecules with sufficient kinetic energy leave the liquid surface (liquid phase) and enter the space above the liquid surface (vapour phase). Moleucles in the vapour phase soon tend to return to the liquid and become a part of the liquid. At first there are large number of molecules leaving the liquid surface each second than those returning to the liquid from the vapour phase. The increase in the number of molecules in the vapour phase thus increases the pressure due to the molecules accumulated in the vapour phase. As a result the chance of a molecule in the vapour phase returning into the liquid phase increases. Soon the two processes balance each other. At this stage the pressure due to molecules in the vapour phase stays constant at any particular temperature. **This pressure is called the vapour pressure of the liquid.** The vapour pressure of a liquid at a given temperature is constant and independent of the quantity or the volume of the liquid. The vapour pressures of some typical liquids are given in table 23.1

Table 23.1 Vapour pressures of some liquids at 30° C

Liquid	Vapour Pressure (mm of Hg).
Water	31.82
Ethyl alcohol	78.80
Acetic acid	20.60
Acetone	282.70
Ethyl acetate	118.70
Carbon tetrachloride	143.00
Chloroform	246.00
Chlorobenzene	15.45

Check Your Progress - 1

How do you explain colligative properties?

23.4 LOWERING OF VAPOUR PRESSURE BY DISSOLVED SUBSTANCE

L. Von Babo (1847) measured the vapour pressure of solutions of different substances in water at a number of temperatures. These results indicated that the vapour pressure of a liquid containing a dissolved substance in it is less than the vapour pressure of the pure liquid. For example the vapour pressure of water containing sugar in the dissolved state in it is less than the vapour pressure of pure water. It was also concluded from the results that for any given solution the decrease of vapour pressure over that of the pure solvent, is a constant fraction of the latter at any temperature.

For example if 'p^0' is the vapour pressure of the pure solvent and 'p', that of the solution, p^0-p is called lowering of vapour pressure. The ratio (p^0-p/p^0) between the lowering of vapour pressure (p^0-p) and the vapour pressure of the pure solvent (p^0) is known as **relative lowering of vapour pressure.** According to **Babo**, this ratio is constant for a solution of given concentration and is independent of the temperature at which it is measured. Inspite of extensive studies **Babo** could not discover any relationship between the lowering of vapour pressure and the amount of dissolved substance in a liquid. But **A. Willner** (1856) also working with solutions of salts in water concluded that the lowering of vapour pressure was proportional to the concentration of the solution.

23.5 RAOULT'S LAW

The studies undertaken by **F.M. Raoult** (1887-88) on the measurement of vapour pressure of aqueous solutions of different concentrations not only confirmed the results of **Babo** and **Willner** but revealed significant trends. The results of these studies helped to putforth a generalization of fundamental importance. **Raoult** carried out his studies mostly on solutions of organic solutes in organic solvents. Some of the solutions investigated were nitrobenzene in ether, aniline in ether and benzaldehyde in ether. *These results equal to the molefraction of the solute.* The above statement is known as Raoult's law.

$$\frac{p^0-p}{p^0} = \frac{n_2}{n_1 + n_2} = x_2 \qquad .... (1)$$

(Where n_1 and n_2 are molecules of solvent and solute. x_2 is mole fraction of solute).

By substracting unity from each side of equation (1) and rearranging the equation, we get

$$\frac{p}{p^0} = \frac{n_1}{n_1 + n_2} = x_1 \qquad .... (2)$$

Draw conclusion from this and give it in the form of a statement.

$$p = p^0 . x_1$$

At a given temperature the vapour pressure of pure solvent p^0 is a constant.

$$\therefore p \propto x_1$$

Thus we can conclude

The vapour pressure of solvent in solution is directly proportional to the mole fraction of solvent.

This is another form of stating Raoult's law.

Check Your Progress - 2

What do you mean by relative lowering of vapour pressure ?

23.6 DETERMINATION OF MOLECULAR WEIGHT OF DISSOLVED SUBSTANCE

The measurement on lowering of vapour pressure of dilute solutions can be used to determine the molecular weight of the dissolved substance (solute). For this purpose Raoult's law is expressed mathematically (equation 3) in terms of the molecular weights of solute and solvent instead of the mole fractions.

$$\frac{p^0-p}{p^0} = \frac{(W_2/M_2)}{(W_1/M_1)+(W_2/M_2)} \quad \text{.... (3)}$$

Where W_1, W_2 are weights of solvent and solute and M_1, M_2 are molecular weights of solvent and solute.

For a dilute solution n_2 may be neglected in comparison to n_1 in the denominator of equation (1) The equation (1) can therefore be rewritten as equation (4).

$$\frac{p^0-p}{p^0} = \frac{n_2}{n_1} \quad \text{.... (4)}$$

$$\text{Or} \quad \frac{p^0-p}{p^0} = \frac{W_2/M_2}{W_1/M_1} = \frac{W_2 \times M_1}{W_1 \times M_2} \quad \text{.... (5)}$$

From equation 3 or 5, it is evident that the molecular weight of the solute (M_2) can be determined provided, the vapour pressure of the solvent (p^0), the solution (p), the molecular weight of the solvent (M_1) are known for a series of solutions of known weights of the solvent (W_1) and the solute (W_2).

23.7 MEASUREMENT OF VAPOUR PRESSURE LOWERING

In view of the small value of the relative lowering of vapour pressure and the consequent difficulties encountered in the determination, special methods are generally utilised for the purpose. These are (1) Differential method (2) Air transpiration method and (3) Isopiestic method.

23.7.1 Differential method

The method involves the use of an accurate differential manometer. In the apparatus used by **C. Dieterici** (1893), the saturated vapours of solution and solvent were exposed to the two sides of a thin glass disc of 70 mm diameter and 0.08 mm thickness. The difference in pressure causes the disc to move. The movement is magnified by a beam of light reflected from a mirror. The instrument was calibrated with a manometer of lower sensitivity. The apparatus devised by **J.C.W. Frazer** and **B.F. Lovelace** was found to give better results than Dieterici apparatus. The apparatus is shown in Figure 23.1.

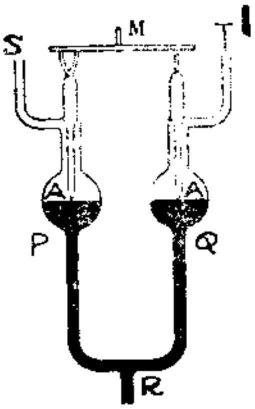


Fig. 23.1 Frazer and Lovelace apparatus.

Two bulbs P and Q connected by a movable mercury reservoir were attached to R. The glass points A, A associated with mirror M were sealed into these bulbs P and Q. The pressure in the bulbs can be equalised with the help of side tubes S and T. The mercury reservoir is adjusted with a fine screw such that points A, A correspond exactly to their images in the mercury surfaces. This position corresponds to zero reading of the manometer. The two bulbs are respectively connected through the side tubes to the solution and solvent respectively. Because of the difference in vapour pressure values, mercury levels show a difference. The apparatus is tilted and with the help of reservoir, the points A, A are made to coincide with their images. The extent of tilt measured by a beam of light reflected from M is a measure of the pressure difference in the two bulbs.

23.7.2 Air transpiration method

In this method dry air was passed in succession through a set of bulbs containing the solution and then through the bulbs containing the pure solvent (water). The air is finally allowed to pass into the absorption tubes filled with calcium chloride. The dry air becomes saturated with water vapour (solvent vapour) to a pressure 'p' (vapour pressure of solution) as it passed through the first set of bulbs containing the solution. The pressure of the vapour carried by the air (already saturated with water vapour) will be raised to p^0 (vapour pressure of pure solvent) as the air coming out from first set of bulbs passed containing the solvent (water). As a result of air carrying with it the vapour, the solution bulbs as well as the solvent bulbs suffer a loss in weight of the contents of these bulbs. The loss in weight (W_1) of the contents in the first set of bulbs is proportional to 'p' while the loss (W_2) in the contents of second set of bulbs is proportional to p^0-p. However, the contents in the absorption tubes experience a gain in weight (W_3) since the vapour carried by the air is absorbed by the contents of the tubes. These results can be written as.

$$W_1 \quad \alpha \quad p$$

$$W_2 \quad \alpha \quad p^0-p$$

$$W_3 \quad \alpha \quad p^0$$

$$\frac{W_2}{W_3} = \frac{p^0-p}{p^0} \qquad \text{.... (6)}$$

Thus the ratio (W_2/W_3) of the loss in weight experienced by the contents of the second set of bulbs to the gain in weight experienced by the contents of absorption tubes is equal to the relative lowering of vapour pressure (p_0-p)/p^0.

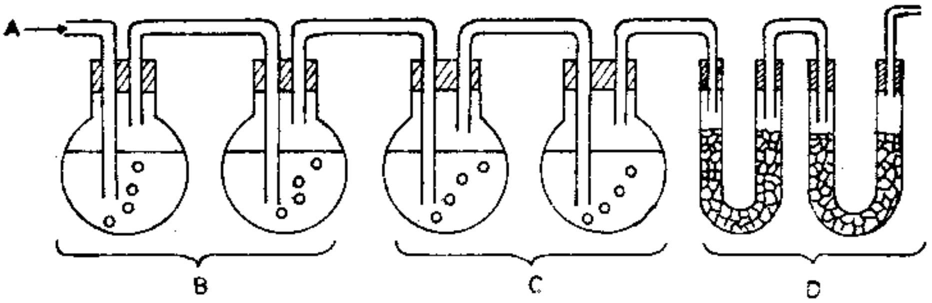


Fig. 23.2 Air transpiration method

A = Dry air, B = Bulbs containing solution, C = Bulbs containing solvent and D = Absorption tubes having calcium chloride.

The chief sources of error in the method are:

(i) The volume of air drawn through the two sets of bulbs may not be the same.

(ii) The process of saturation by bubbling may introduce some errors.

23.7.3 Isopiestic method

The solutions exerting the same vapour pressure are said to be isopiestic (these are also referred to as **isotonic** solutions). Vapour will distil from the solution of high vapour pressure into solution of low vapour pressure till equilibrium is attained when these two solutions are kept side by side in a closed space. The concentrations of the two solutions after equilbrium can be known by carrying out analysis of the solutions in separate experiments. Therefore, if the vapour pressure of one of the solutions is known at different concentrations, the vapour pressure of the other solutions can be calculated. Solution of potassium chloride or mannitol is used for the calibration because the vapour pressures of these solutions are known accurately at different concentrations of the solutions. One of the drawbacks of the method is the slowness with which the equilibrium is attained. It is for this reason that the concentration of potassium chloride is fixed at a value where its vapour pressure is close to the vapour pressure of the experimental solution.

23.8 SUMMARY

In this unit we have studied about

i) Lowering of vapour pressure and relative lowering of vapour pressure as a colligative property.

ii) Raoult's law : Relative lowering of vapour pressure of a solution is equal to mole fraction of solute.

iii) Determination of molecular weight of the solute by applying Raoult's law.

iv) Experimental method for determination of lowering of vapour pressure (special mention may be made about air transpiration method.

23.9 EXAMINATION QUESTIONS

I. Answer the fllowing in 10 lines each.

1. Derive the relationship between relative lowering of vapour pressure and the molecular weight of solute for a dilute solution.

2. State and explain Raoult's law.

II. Answer the following in 30 lines each.

1. Discuss in detail explaining the underlying theoretical principle, the method of determining molecular weight of solute by measuring the relative lowering of vapour pressure.
2. Describe with a neat sketch, the differential method of determining the lowering of vapour pressure of a solution.
3. Give a detailed account of air transpiration method of determining the molecular weight of a dissolved substance.

23.10 MODEL ANSWERS TO CHECK YOUR PROGRESS

1 Those properties of solutions which are related by established equations and which depend only on the number of the solute particles are colligative properties.

Ex: Elevation of boiling point depression of freezing point

2 The vapour pressure of a liquid decreases when a nonvolatile solute is dissolved in it. The ratio of the decrease of this vapour pressure and the vapour pressur of the pure solvent is called relative lowering of vapour pressure.

i.e., Relative lowering of vapour pressure = p/p^0.

Author: Prof. S. BRAHMAJI RAO

UNIT - 24 : ELEVATION OF BOILING POINT AND DEPRESSION OF FREEZING POINT

Contents

24.1 AIMS AND OBJECTIVES

This unit mainly aims to discuss the effect of non-volatile solute on the boiling point or freezing point of a liquid (solvent) and to describe the relation between this effect and the molecular weight of the solute.

By the end of this unit you will be able to understand that:

- The boiling point of a liquid is the temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure.
- The boiling point of a liquid is elevated if a non-volatile solute is dissolved in the liquid.
- The elevation in boiling point of a solution over the boiling point of the solvent is called the **elevation of boiling point (T_e).**
- The elevation of boiling point is independent of chemical nature of solute but is proportional to the molal concentration of the solution for any given solvent

- The relationship between elevation of boiling point (ΔT_e), molal elevation constant (K_e) and molality of the solution, is useful to determine the molecular weight of the dissolved substance (solute).

- Some methods in use for such determination are (1) The Beckmann method, (2) The Landsberger method and (3) The Cottrell method.

- The freezing point of a liquid is lowered when a solute is dissolved in it.

- The depression of freezing point, similar to elevation of boiling point, is independent of the nature of solute but is dependent on the concentration of the solution for any given solvent.

- The molecular weight of a dissolved substance can be determined if the depression of freezing point T_f, the molal depression constant (K_f) of the solvent and the molal concentration of the solution are known.

- Some methods in use for such determination are 1) The Beckmann method and 2) the Rast method.

24.2 INTRODUCTION

In the previous unit we studied lowering of vapour pressure as a colligative property. A logical consequence of the lowering of vapour pressure will be the elvation of boiling point or depression of freezing point of the solution. We will study in this unit, the elevation of boiling point or depression of freezing point as a means to determine the molecular weight of a nonvolatile solute.

24.3 BOILING POINT OF A SOLUTION

The boiling point of a liquid is defined as the temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure. This applies equally well to a liquid solvent or a dilute solution of solute in the solvent. You have learnt in unit - 23, that the vapour pressure of solution is less than that of the pure solvent. The temperature at which the vapour pressure of a solution is equal to the atmospheric pressure of a solution must therefore be higher than that for a solvent. This means that the boiling point of a solution is higher than the boiling point of the solvent. It is therefore evident that the boiling point of a liquid rises when a solute is dissolved in it. Studies of the elevation of boiling point produced by dissolved substances were made by **M. Faraday** (1830) and others.

24.4 RELATION BETWEEN RELATIVE LOWERING OF VAPOUR PRESSURE AND ELEVATION OF BOILING POINT

The vapour pressure-temperature curves for the solvent and solution are presented in figure 24.1.

From the figure 24.1 it is seen that the boiling point of solution and solvent are T and T_0 respectively (the temperatures at which the vapour pressures are respectively equal to the atmospheric pressure). The rise in boiling point ($T-T_0$) is given by the distance AB. The vapour pressure (p^0) of solvent (vapour pressure at T_0) is given by AT_0 and the vapour pressure (p) of solution at T is given by CT_0. The lowering of vapour pressure (p^0-p) is therefore equal to distance AC in the figure. AC can be taken proportional to $(p^0-p)/p^0$ since the vapour pressure of solvent is assumed to be 1 atmosphere. The vapour pressure curves for a series of dilute solutions can be regarded parallel in the region of boiling point. In such an event, the ratio AB/AC can be constant for different solutions. This indicates that the elevation of boiling point for a dilute solution is proportional to the relative lowering of vapour pressure (p^0-p).

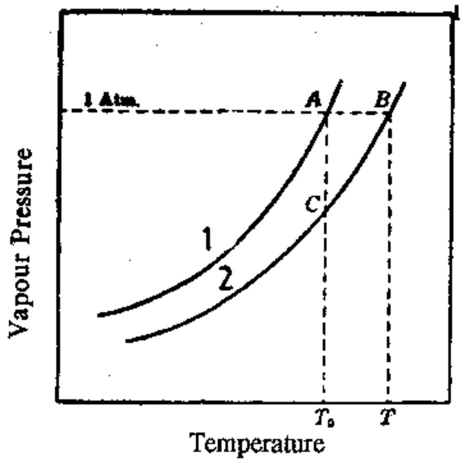


Fig. 24.1 Vapour pressure-temperature curves for a solvent and a solution
1. solvent 2. solution.

From Raoult's Law it is known that the relative lowering of vapour pressure is equal to the molefraction of solute (see 23.3). This shows that for a dilute solution

$$\Delta T_e \ \alpha \ x_2$$

$$\Delta T_e = K_e \, x_2 \qquad \text{.... (1)}$$

For a dilute solution $\frac{p^0 - p}{p^0}$ is $\frac{W_2 M_1}{W_1 M_2}$ (See equation 5 in 23.4)

$$\therefore T_e = K_e \frac{W_2 M_1}{W_1 M_2} \qquad \text{.... (2)}$$

W_2/M_2 is the number of moles of solute dissolved in W_1 gms of solvent (molal concentration), K_e and M_1 being constant, it points out that ΔT_e is proportional to the molal concentration. It also suggests that the elevation of boiling point is independent of the nature of solute but proportional to the molal concentration of the solution.

24.5 ELECATION OF BOILING POINT AND CLAPEYRON-CLAUSIUS EQUATION

The mathematical relation between the vapour pressure (p) - the temperature (T) and latent heat of evaporation (Le) of a liquid is known as **Clapeyron - Clausius** equation.

$$\frac{d \ln p}{dT} = \frac{Le}{R T^2} \qquad \text{.... (3)}$$

Where p = vapour pressure of liquid
L = molar heat of evaporation of liquid
T = temperature
and R = gas constant

Equation (3) can be written in the integral form (equation 4) for the temperatures T and T_0, the boiling points of solution and solvent respectively assuming Le to be constant.

$$\ln \quad (p/p^0) = Le/R\ (1/t_0 - 1/T)$$

$$= Le/R\ (T - T_0/T\ T_0)$$

$$= Le/R.\ \Delta T_e/T\ T_0 \qquad \ldots\ (4)$$

For dilute solutions, the boiling point of solvent (T_0) and the boiling point of solution (T) are not very much different. Therefore $T\ T_0$ can be conveniently replaced by T_0^2. Equation (4) can therefore be re-written as.

$$\ln (p/p^0) = Le/R.\ \Delta T_e/T_0^2 \qquad \ldots\ (5)$$

(p/p_0) Can be replaced by x_1 (mole fraction of solvent) from Raoult's Law.

Therefore equation (5) is rewritten as

$$\ln x_1 = Le/R\ \ \Delta T_e/T_0^2 \qquad \ldots\ (6)$$

But $x_1 = 1-x_2$ where x_2 - mole fraction of solute.

$$\therefore \ln (1-x_2) = Le/R\ \ \Delta T_e/T_0^2 \qquad \ldots\ (7)$$

For a dilute solution x_2 is small, and therefore $1-x_2$ will be equal to ($-x_2$). Therefore equation (7) can be written as

$$-x_2 = -Le/R\ \ \Delta T_e/T_0^2 \qquad \ldots\ (8)$$

$$\text{Or} \quad x_2 = -Le/R\ \ \Delta T_e/T_0^2$$

$$\text{Or} \quad \Delta Tc = -\frac{x_2 . R. T_0^2}{Le} \qquad \ldots\ (9)$$

x_2 can be written equal to $\dfrac{W_2 .\ M_1}{W_1 .\ M_2}$

$$\therefore \Delta T_e = -\frac{T_0^2 . R}{Le} \cdot \frac{W_2 . M_1}{W_1 . M_2}$$

$$= -\ RT_0^2 \cdot \frac{M_1}{Le} \cdot \frac{W_2}{W_1 M_2}$$

$$= -\frac{RT_0^2}{\,} \cdot \frac{1}{l} \cdot \frac{W_2}{W_1 M_2} \qquad \ldots\ (10)$$

Where $1/lc = M_1/Le/1$, is the reciprocal of the latent heat of vaporization per gram of solvent. Right hand side of the equation (10) is multiplied by 1000 and devided by 1000 and equation (10) is rewritten as equation (11).

$$\Delta T_e = \frac{RT_0^2}{1000\ le} \qquad \frac{1000\ W_2}{W_1 M_2} \qquad \ldots\ (11)$$

$$\Delta T_e = Ke\ .\ m$$

$$\text{Where } Ke = \frac{RT_0^2}{1000\ le} \quad \text{and } m = \frac{1000 . W_2}{W_1 M_2}$$

'K_e' is a constant for a solvent and 'm' is the molality of the solution. The constant K_e is called **molal elevation constant or the ebullioscopic constant.**

It is evident from equation (11) that for a dilute solution obeying Raoult's Law, **the elevation of boiling point is proportional to the molality of the solution.**

The equations mentioned earlier thus suggests that

(1) The elevation in boiling point of a dilute solution is proportional to the molality of solution.

(2) The proportionality constant Ke is independent of the nature of the solute and is dependent only on the nature of solvent. The molal elevation constants for some typical solvents are presented in table 24.1.

Table 24.5.1 Molal elevation constants Ke for typical solvents

Solvent	K_e
Water	0.52
Methyl alcohol	0.80
Ethyl alcohol	1.20
Acetone	1.70
Benzene	270
Choloform	3.70
Carbon tetrachloride	5.00

Check Your Progress - 1

What is molal elevation constant?

24.6 DETERMINATION OF MOLECULAR WEIGHT

The molecular weight of non-volatile solute can be determined from the experimentally determined value of ΔT_e (the elevation of boiling point) for a dilute solution of known concentration of the solute. The method is generally known as **ebullioscopic method.**

24.6.1 The Principle of the method

A known weight (W_2) of the solute whose molecular weight is to be determined, is dissolved in a known weight (W_1) of the solvent and a dilute solution is prepared. Later the boiling point of the solution or directly the elevation (ΔT_e) of boiling point of the solution is determined experimentally. By substituting the values of ΔT_e, W_1, W_2 and K_e in equation (12).

$$M_2 = K_e \cdot \frac{1000\, W_2}{W_1\, \Delta T_e} \qquad \text{.... (12)}$$

M_2, the molecular weight of solute is calculated

In the case of liquids, for which K_e is not known, it is determined in a separate experiment by following a procedure similar to the one described above and using a solute of known molecular weight. The experimental value ΔT_e obtained in this experiment is substituted along with W_1, W_2 and M_2 in equation (12) and K_e is calculated.

Check Your Progress - 2

How is the molecular weight of a non-volatile solute be determined by elevation of boiling point?

Experimental Procedures.

Three methods are in use for the purpose. These are (i) the Beckmann Method, (ii) the Landsberger method and (iii) the Cottrell method.

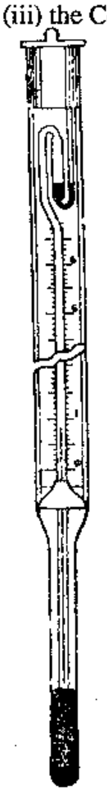


Fig. 24.2 Beckmann thermometer

24.6.1 The Beckmann method.

E. Beckmann (1888) developed a special thermometer which goes by his name to determine accurately and directly the elevation of the boiling point.

The thermometer contains a reservoir at the top end and the bulb at other end unlike thermometers usually employed. With the help of this reservoir, it is possible to vary the amount of mercury in the thermometer bulb. This provision for the adjustment of amount of mercury in the bulb, make it possible to use the thermometer over a wide range of temperature from - 39° to+250°C with sufficient accuracy (0.001°). The thermometer is shown in figure 24.2.

Beckmann apparatus consists of a boiling tube A with a thick platinum wire fused to the bottom, and a side tube attached at the top as shown in figure 24.3 The experimental liquid is taken in the boiling tube A and heated from the bottom. The platinum wire fused at the bottom, helps to conduct the heat through it into the liquid in the bulb. This facilitates the bubble formation and avoids super heating. Addition of glass beads in the solution permits steady boiling. The boiling tube A is surrounded by a jacket B made out of glass or porcelain with mica windows. Some times an indirect method of heating is adopted as an additional precaution against superheating. An asbestos box with asbestos rings are used for the purpose. Reflux condensers are attached to both A and B to minimise loss of liquid.

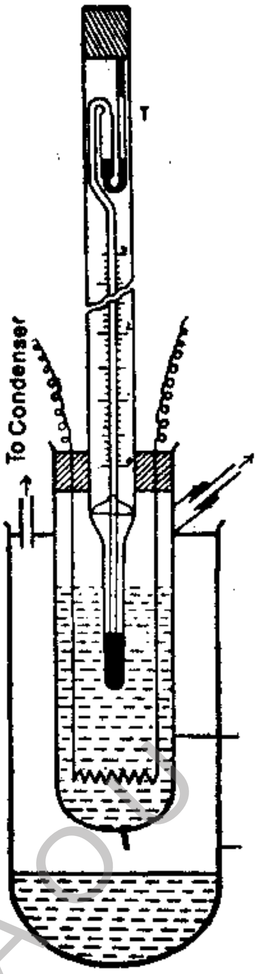


Fig. 24.3 Beckmann boiling point apparatus.
A - boiling tube, B - Jacket,
T - Beckmann thermometer

24.6.2 The Landsberger method

In this method, the superheating is minimised or eliminated by adopting the heating procedure developed by **J. Sakurai** (1892). The solution is heated in this method by passing hot vapours of the solvent generated separately from the boiling solvent. The apparatus introduced by **W. Landsberger** and improved by **J. Walker** and **J.S. Lumsden** is shown in figure 24.4.

Known amount of solvent is placed in Q which is placed inside a Jacket tube R and its temperature raised by sending in the hot vapour of the solvent from P. The temperature of the solvent Q is read when it is constant. Any excess of vapour passes out through a small hole on the right side of Q near the top and then on the condenser S. A weighed amount of the solute is added to Q and the temperature of the solution is raised to its boiling point by passing the hot vapour from P as is done earlier. The temperature is read when it is constant and steady. From the measured boiling points of solvent and solution ΔT_e, W_1, W_2 in equation (12) molecular weight is calculated.

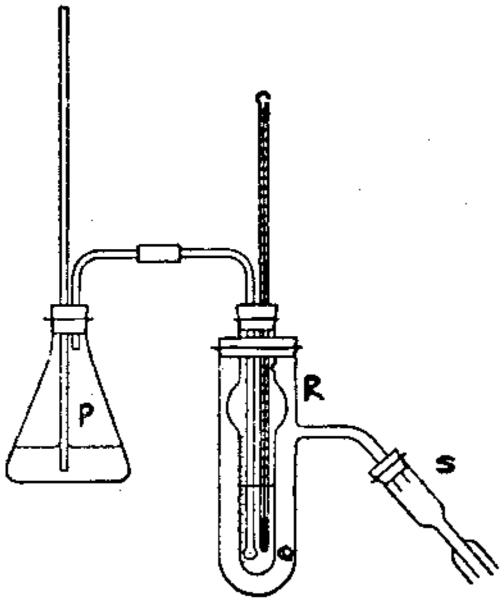


Fig. 24.4 Landsberger's apparatus (modified).

24.6.2.3.2 The Cottrell method

F.G. Cottrell (1919) pointed out that the boiling points measured by placing the thermometer directly in the liquid with the bulb at depth of 3 to 4 cm are approximately higher by 0.1°C than the bulb is at the surface. To avoid this difficulty Cottrell improvised boiling point apparatus in which an arrangement (pump) is provided to pump the boiling solution continuously over to the bulb of the thermometer placed in the **vapour** phase above the surface of the liquid. The pump originally employed by Cottrell consisted of a piece of glass tubing opened out at the lower end into a funnel shape. The tube was partly in the boiling liquid and partly out of it. A stream of bubbles with entrapped liquid is boiling. Thus, the liquid and its vapour will be in equilibrium with each other at the surface of the bulb. This helps the thermometer bulb to register a steady temperature. A simple form of the apparatus is shown in figure 24.5.

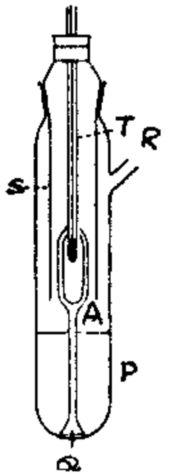


Fig. 24.5 Cottrell's apparatus.

Tube P containing the boiling liquid (solvent or solution). The platinum wire Q sealed into the bottom of the tube helps to attain uniform boiling. The side tube R leads to a condenser, T is thermometer. The mantle S prevents the cold liquid (condensate) reaching the thermometer. The pump A helps to push the boiling liquid over to the surface of the thermometer bulb.

The procedure adopted for the determination is the same as the employed in the earlier determinations.

24.7 DEPRESSION OF THE FREEZING POINT

F.M. Raoult observed that equimolar solutions of different substances of similar type lowered the freezing point of a given solvent to the same extent. The study of the freezing point of solution is called **Cryoscopy.**

24.8 FREEZING POINT AND VAPOUR PRESSURE

The relationship between vapour pressure and the freezing point of a pure solvent or solution is represented in figure 24.6.

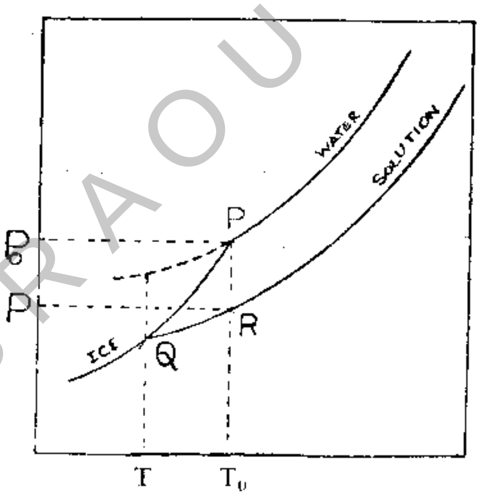


Fig. 24.6 Temperature, freezing point and vapour pressure.

The vapour pressure curves for water and ice meet at P. Therefore temperature T_0 can be taken as freezing point of water (solvent), since water and ice are in equilibrium at this point. Similarly the solution and ice curves meet at Q, Therefore T gives as freezing point of solution. QR (T_0-T) is therefore equal to the lowering (ΔT_f) of the freezing point. The distance PR is equal to the lowering of vapour pressure (p^0-p) at the freezing point of water (solvent). The vapour pressure curves for a number of dilute solutions are parallel near the freezing point. Consequently QR/PR will be constant for dilute solutions. It therefore follows for a dilute solution.

$$\Delta T_f = K_f . x_1$$

$$\Delta T_f = K . \frac{W_2 . M_1}{M_2 . W_1} \qquad (1)$$

24.9 DEPRESSION OF FREEZING POINT AND CLASIUS - CLAPEYRON EQUATION

The vapour pressures of solid (p_s) and solvent (P_l) are respectively related to molar heat of sublimation (L_s) and molar heat of evaporation of the liquid (L_e) by the equations (14, 15). These relations are valid only if the vapour obeys ideal gas laws and its volume is large in comparison with that of solid or liquid.

$$\frac{d \ln p_s}{dT} = \frac{Ls}{RT^2} \quad \text{.... (14)}$$

$$\frac{d \ln p_L}{dT} = \frac{Le}{RT^2} \quad \text{.... (15)}$$

If equation (14) is valid for a super cooled liquid, then equations, 14, 15 are applicable at the same temperature (T).

$$\frac{d \ln(p_s/p_l)}{dT} = \frac{L_s - L_e}{RT^2} = \frac{L_f}{RT^2} \quad \text{.... (16)}$$

L_f = molar heat of fusion.

At the freezing point of the solution, the vapour pressure of the solid (ice) is equal to that of the solution (p_l) with which it is in equilibrium.

Hence at freezing point of the solution

$$\frac{d \ln (p_l/p_l)}{dT} = \frac{L_f}{RT^2} \quad \text{.... (17)}$$

Where p_l is vapour pressure of solution. p_l/p_L is equal to x_1, if Raoult's Law is applicable.

$$\frac{d \ln x_1}{dT} = \frac{L_f}{RT^2} \quad \text{.... (18)}$$

Integration of equation 18, between temperatures T and T_0 gives equation 19.

$$\ln x_1 = - L_f/R \quad [1/T - 1/T_0]$$

$$= - \frac{L_f}{R} \frac{\Delta T_f}{T_0^2} \quad \text{.... (19)}$$

When T T_0 is put equal to T_0^2 for a dilute solution, x_1 can be replaced by $1\text{-}x_2$ and for a dilute solution i.e., when x_2 is very small in $1\text{-}x_2$ is approximately equal to $-x_2$.

Therefore equation (19) can be written as :

$$\Delta T_f = RT_0^2/L_f \text{ X } x_2$$

By multiplying by 1000 and dividing by 1000

$$\Delta T_f = \frac{RT_0^2}{1000\,L_f} \quad \frac{1000\,W_2}{M_2.W_1}$$

$$= K_{fm} \qquad \text{.... (20)}$$

Where K_f is called **molal depression constant** of freezing point, or **Cryoscopic constant.**

The molal freezing point depression constants for some typical liquids are given in Table 24.9.1

Table 24.9.1 Molal freezing point depression constants (K_f) of typical solvents

Solvents	K_f
Water	1.86
Benzene	5.10
Napthalene	7.0
Cyclohexane	20.2
Camphor	40.0

24.10 DETERMINATION OF MOLECULAR WEIGHT

The freezing point depression method is frequently employed for the determination of molecular weights of dissolved non-volatile solutes. The equation employed for the purpose is.

$$M_2 = K_f \frac{1000\,W_2}{\Delta T_f.\,W_1} \qquad \text{.... (21)}$$

Where K_f = Molal freezing point depression constant

W_1 = Weight of solvent

W_2 = Weight of non-volatile solute

ΔT_f = Depression in freezing point

and M_2 = Molecular weight of solute

The two important and popular methods are (i) Beckmann method and (ii) Rast's Micro method.

24.10.1 The Beckmann method.

The form of apparatus used by Beckmann is shown in figure 24.7

The apparatus consists of a freezing tube P. A known weight (W_1) of the pure solvent is taken in this tube and a pre-set Beckmann thermometer T is placed in it. The freezing tube P with the thermometer is placed inside a jacket tube Q through a rubber cone C. The whole set up is finally put in a vessel R containing the freezing mixture. The temperature of the freezing mixture is maintained at a value which

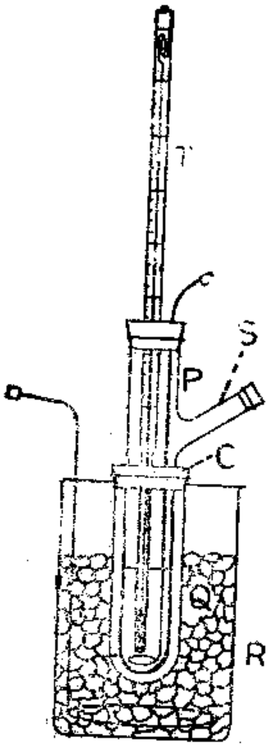


Fig. 24.7 Beckmann freezing point apparatus.

is not more than 5⁰C below the freezing point of solution. The liquid in P is first allowed to freeze and the reading on the pre-set Beckmann thermometer T is noted. Tube P is next removed, warmed slightly to melt the solid solvent and a weighed amount of solute is added as quickly as possible through the side tube S provided. The contents of the tube are well shaken to dissolve the solute completely in the solvent. The tube P with the solution is replaced into Q and the experiment is repeated. The reading on the thermometer T is read again when thermometer registers constant reading corresponding to the freezing of the solution. The difference in the two readings of thermometer gives ΔT_f. From this value of ΔT_f and W_1, W_2, K_f, M_2 is calculated. If K_f is not known for the solvent under study, it is determined in a separate experiment by adopting a similar procedure as described above with a solution of known solute.

24.10.2 Rast's Micro method.

This method is generally used for solutions of solids in solid solvents like camphor or naphalene. A few milligrams of the solute are mixed with a known weight (10 times the weight of solute) of the solid solvent and the whole mass is melted. The molten mass is allowed to solidify. After solidification the mixture is finely ground in a clean mortor and transferred to a capillary tube (similar to that used in the melting point determination of organic substances).

24.11 SUMMARY

In this unit we have studied about

i) The relation between the lowering of vapour pressure and elevation of boiling point of a solution.

ii) Elevation of boiling point and clapeyron - clausius equation.

iii) For a dilute solution the elevation of boiling point is proportional to the molality of solution.

iv) Determination of molecular weight by measuring the elevation of boiling point.

v) Experimental methods for measuring ΔT_b.

vi) Depression of freezing point as a means to determine molecular weight of solute on similar lines as above

vii) Experimental methods for determining ΔT_f.

24.12 EXAMINATION QUESTIONS

I. Answer the following in 10 lines each.

1. Derive the relation between elevation of boiling point and the molecular weight of the dissolved substance.

2. Describe Beckmann method for the determination of molecular weight of a dissolved substance.

3. How is depression of freezing point useful in the determination of molecular weight of a dissolved substance?

II. Answer the following in 30 lines each.

1. What are colligative properties? Discuss critically how depression of freezing point is useful to determine the molecular weight of dissolved substance.

2. Compare and contrast the different methods available for the deterrniantion of molecular weight of dissolved substance by elevation of boiling point method.

24.13 MODEL ANSWERS TO CHECK YOUR PROGRESS

1 It is the elevation in boiling point that is expected when one mole of a solute is dissolved in 100 g of a solvent. It is usually indicated by K_e.

2 Non-volatile solute is dissolved in a suitable solvent and the elevation in the boiling point is experimentally determined. The values are substituted into the following equation and the molecular weight of the solute is calculated.

$$M_2 = K \cdot \frac{1000\, W_2}{\Delta T_e\, W_1}$$

Author : Prof. S. BRAHMAJI RAO

UNIT - 25 : OSMOSIS

Contents

25.1 AIMS AND OBJECTIVES

This unit is to explain you the phenomenon of osmosis and osmotic pressure and to describe how the osmotic pressure of a dilute solutions is used to determine the molecular weight of a dissolved substance.

After completing this unit you must be able to understand that:

- The inflow of solvent from a dilute solution into a concentrated solution when the former is separated from the latter by a semi permeable membrane is called **Osmosis.**

- A membrane that allows through it the passage of solvent but not solute when the solutions of two different concentrations are separated by it is called a **semipermeable membrane.**

- Animal bladders, plant cells, animal cells and some synthetic chemical compounds such as copper ferrocyanide act as semipermeable membranes.

- Osmotic pressure π is equal to the excess hydrostatic pressure developed at equilibrium on the solution side when the solution is separated from a solvent or a dilute solution by semipermeable membrane.

- Osmotic pressure is experimentally determined by (a) Pfeffer's (b) Mores and Frazer (c) Berkeley and Hartely (d) Plasmolytic and (e) Haemolytic methods.
- Osmotic pressure and the concentration of the solution are related by the equation $\pi = CRT$.

25.2 INTRODUCTION

Abbe Nollet (1748) observed that when a large flask filled with alcohol and its mouth tied with an animal bladder is immersed in water, the bladder gradually becomes swollen and some times even bursts. This was due to the inflow of water through the bladder into alcohol. At the same time alcohol is not passing through the bladder into water. The increased pressure in the flask caused by passage of water into it is responsible for the swelling and subsequent bursting of the bladder.

25.3 OSMOSIS

The inflow of water into alcohol through the bladder was later named by **R. Dutrochet** (1832) as **'end-Osmosis'**. The bladder was named **semipermeable** membrane since it allowed only water to pass through it but not the alcohol. In the later years, the prefix 'end' in 'end-osmosis' was dropped and the phenomenon was named as **'Osmosis'** (Greek: *push* or *impulse*). The term was actually used to describe the spontaneous flow of water from a **dilute** solution to **concentrated** solution when the two are separated by a semipermeable membrane.

25.4 SEMIPERMEABLE MEMBRANE

Let us consider an arrangement in which a thistle funnel A tied with pig's bladder B partly filled with a concentrated solution of sugar and placed in a beaker D containing a dilute solution of sugar C or pure water.

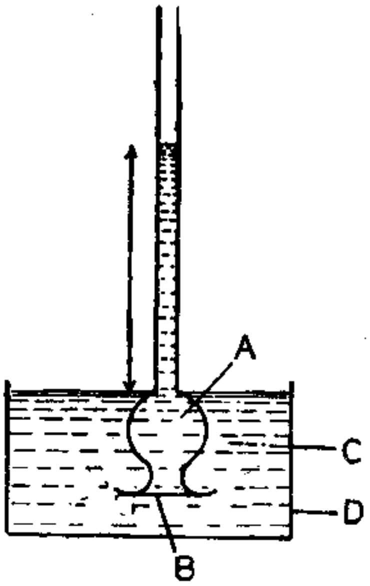


Fig. 25.1 Osmosis through animal membrane

The water in beaker flowed into the funnel through the bladder membrane. The process continued till the excess hydrostatic pressure, the water caused, on the solution in the funnel pushed back the water into the beaker. The backward flow of water was found to take place at the same rate as the inward flow of water from the beaker into the funnel through the membrane. The inward flow is caused by osmosis and the outward flow (backward flow) is caused by the excess hydrostatic pressure developed on the solution in the funnel. This state is referred to as equilibrium state. The membrane (pig's bladder) which allowed the flow of water only through it but not the sugar is called semipermeable memberane. **The membrane which permits solvent only, of the two components (solute & solvent) but not both to pass through it is called semipermeable membrane.** Such membranes are of component of a binary solution (solvent) to pass through it and prevent the membranes and plant cell membranes illustrate such semipermeable membranes. Copper-ferrocyanide, a chemical compound is an example for chemical semipermeable membrane. It allows free passage of water of an aqueous solution but not the substance dissolved in it. Prussian blue and calcium phosphate were other chemical compounds which served as semipermeable membranes.

M. Traube thought that semipermeable membrane functions as a sieve retaining the large molecules but allowing the passage of the smaller ones. But soon it was found that membranes with pores many times larger in diameter than even the large molecules of the solute are able to prevent the passage of the solute. **M.L. Hermite** and others soon conducted osmotic experiments using different types of membranes and proposed that the semipermeability is due to the solubility of solvent and insolubility of the solute in the membrane. The solubility here is meant **surface solubility** or **adsorption.**

Check Your Progress - 1

What do you know about semipermeable membrane?

25.5 OSMOTIC PRESSURE (π)

Let us imagine that a dilute solution of a non-volatile solute or a pure solvent is separated from a concentrated solution of the solute by a semipermeable membrane (see figure 25.1).

Since the membrane is permeable to solvent (water) only, it flows from dilute solution into concentrated solution through the membrane due to osmosis. The inflow of solvent from dilute solution into concentrated solution continues till the hydrostatic pressure developed on solution B as a result of flow of water (solvent) opposes further inward flow and equilibrium is attained. The hydrostatic pressure that has developed at the equilibrium stage when a dilute solution is separated from a concentrated solution by a semipermeable membrane is numerically equal to the osmotic pressure. It is therefore evident that osmotic pressure is responsible for the inflow of solvent (water) into the concentrated solution, while the hydrostatic pressure developed on the solution side prevents this inward flow. As a result, when the hydrostatic pressure is numerically equal to the osmotic pressure, the inflow of solvent ceases. In view of this the osmotic pressure is defined as *the excess hydrostatic pressure which must be applied to a concentrated solution to prevent the passage into it the solvent from the dilute solution when these two solutions are separated by a semipermeable membrane.*

25.6 MEASUREMENT OF OSMOTIC PRESSURE

Different methods were proposed for determining the osmotic pressure. These methods are briefly outlined below.

25.6.1 Pfeffer's method

Pfeffer used a porcelain porous osmotic cell which contained in its pores the semipermeable membrane deposited. The apparatus is shown in figure 25.2.

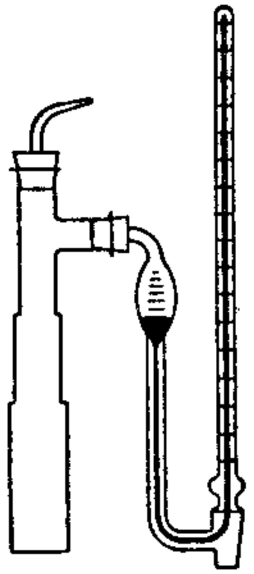


Fig. 25.2 Pfeffer's apparatus

The membrane cells are prepared from porous pots made of grained unglazed porcelain. The cells are cleaned with distilled water and air is completely removed from the pores by evacuation, keeping the pot immersed in water. The cells are later filled with three percent copper sulphate solution and placed for several hours in another vessel containing the same solution. The cell is finally taken out from this vessel, quickly rinsed with distilled water, dried, first with filter paper and finally by allowing it to stand in the air. The dried cell is then filled with 3 percent potassium ferrocyanide solution and placed in the vessel containing copper sulphate solution. In this process the two salts diffused from opposite directions into the pores and reacted to precipitate copper ferrocyanide in the form of a membrane. The cell is kept in the copper sulphate solution for two days and finally is closed to enable excess pressure to develop in the interior. This is made possible due to the difference in osmotic pressure of the solutions. This treatment increases the strength of the membrane. The membrane is further strengthened by filling the cell with potassium nitrate and closing it for a day or two. Now the cell is ready for experimental solution and a manometer is attached to it as shown in figure 25.2. The cell is finally closed with a rubber stopper and a glass tube passing through it is sealed off. This prevents the entry of air into the cell. The entire set up is placed in a bath of constant temperature and the osmotic pressure is read from the manometer.

25.6..2 Mores and Frazer method

This method is an improvement over Pfeffer's method. The improvement is in the method of preparation of the membrane (copper ferrocyanide). In this method, the membrane is prepared electrolytically unlike by diffusion method in Pfeffer's method. As in Pfeffer's experiment, the cell is prepared from a porous pot made from a finely grained uniform clay without adding any binder. The pot is washed thoroughly with water and filled with dilute solution of copper sulphate. This is then placed in an outer vessel containing a solution of potassium ferrocyanide. A copper electrode is placed in the pot containing copper sulphate solution, and a platinum electrode is placed in the outer vessel containing potassium ferrocyanide.

The electrodes are connected to a battery to drive the copper and ferrocyanide ions from inside and outside respectively. into the pores of the pot. Copper ferrocyanide is thus precipitated electrolytically in the pores. The contents of the cell are later emptied, the cell is washed with water and allowed to stand in distilled water for several days. The cell is later filled with dilute solution of copper sulphate, placed in the outer vessel containing ferrocyanide and the process of electrysis is repeated. The cell contents are finally emptied, the cell is washed and kept in distilled water for several days. These processes of electrolysis and washing are repeated number of times to produce a membrane capable of withstanding high pressures. The cell prepared in this way is used in the determination of osmotic pressure by a procedure similar to the described Pfeffer's experiment.

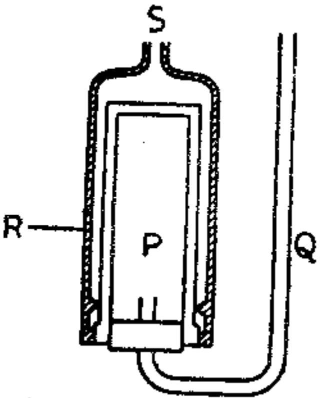


Fig. 25.3 Frazer's apparatus
P - osmotic cell, Q - side tube, R - bronze cylinder, S - manometer.

25.6.3 Berkeley and Hartely method

The method employs a procedure some what different from that employed in the methods described in (1) and (2). In the earlier methods, the pressure developed on the solution due to inflow of solvent is measured through a manometer attached to the osmotic cell. However in the method of **Berkeley** and **Hartely**, a gradually increasing external pressure is applied to the solution and its value at which the entry of solvent into the solution is just prevented is determined. The osmotic cell is an open ended porous tube (P). The membrane is deposited as near the outside as possible. The tube is soaked in copper sulphate solution and dried superficially. The ends of the tube are plugged and the tube is rotated in a solution of potassium ferrocyanide. The memebrane of copper ferrocyanide formed by this treatment is further strengthened by electrolytic treatment. The tube is filled with the pure solvent and plugged with liquid-tight joints. The tube is then fixed in a metal vessel Q containing the solution being studied. A hydrostatic pressure is applied to the solution through the tube R. The direction of movement of the solvent is observed with the help of the capillary 'S' attached to osmotic cell.

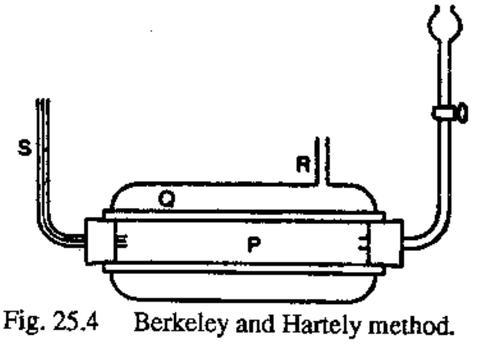


Fig. 25.4 Berkeley and Hartely method.

As a result of osmosis, solvent moves from P into Q. Hence, the liquid level in S recedes. The pressure applied through R is gradually increased till the movement of the solvent in S is reversed. The pressure at which the movement is reversed is taken as the osmotic pressure of the solution.

25.6.4 Plasmolytic and Haemolytic methods

H. de Vries (1884) a botanist described an approximate method for comparing osmotic pressures of different solutions. The method is known as **plasmolytic method.** A plant cell has two membranes called plasma membrane and a vacuolar membrane. Both these membranes are selectively permeable. These will allow the free passage of water molecules but not solutes of high molecular weight. The cell wall made up of cellulose is however permeable to both water and solutes. In a healthy cell the water enters the cell through the cell wall and the plasma membrane and sets up pressure in the interior of the cell. As a result of this pressure the cytoplasm in the cell is forced against the cell wall. This is known as **turgor.** Such a cell is called **turgid cell** (Figure 25.5).

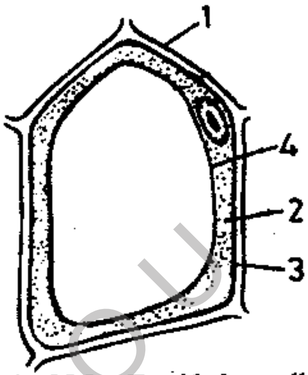


Fig. 25.5 Turgid plant cell

1. cell wall 2. cytoplasm 3. plasma membrane 4. vacuolar memrbane

A turgid cell when placed in a solution of osmotic pressure higher than that of the cell sap (cytoplasm) allows water from the interior of the cell to pass outward. This results in the loss of **turgid** condition. The cytoplasm will then shrink and detaches itself from the wall. This is called **plasmolysis.**

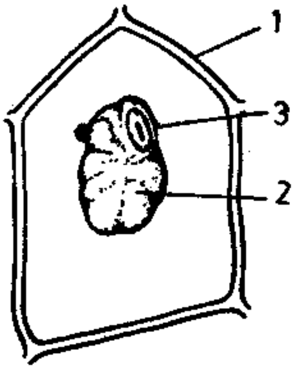


Fig. 25.6 Plasmolysed plant cell

1. cell wall 2. cytoplasm 3. plasma memrane

It is therefore possible to carry out the plasmolysis experiment with solutions whose osmotic pressures are higher than that of the cell sap. A series of solutions of a given substance at different concentrations is therefore prepared and the plant cell is immersed in each of them. Plasmolysis is observed with each of the solutions if the osmotic pressure of the solution is greater than the osmotic pressure of the cell sap. The solution which just fails to bring out plasmolysis is said to have the same osmotic tension as the cell sap. The solution is said to be **isotonic** (Greek : *same tension)* with the cell sap. If the cell membranes are completely semipermeable, these isotonic solutions would have the same osmotic pressure. In such an event **isotonic solutions** are also called **isoosmotic solutions.**

A similar biological method was proposed later by **H.J. Hamburger** (1886) for the comparison of osmotic pressures. This method involves the use of **red blood corpuscles** instead of plant cells. These also have semipermaeable membrane but not possess a supporting cell wall. Hence these are relatively fragile and easily reputured. If a small quantity of blood is added to a solution, osmosis occurs. Water passes through the outer membrane into the corpuscles. This makes the cells distended and eventually burst. As a result of this bursting, the red colouring matter (hamoglobin) escapes from the interior of the cells and gives a red colour to the solution in which the blood is suspended. The cells in such cases are said to be **hemolysed** or said to have undergone **hemolysis.** On the other hand, if blood is suspended in a solution of high concentration, water flows outwards from the interior of the corpuscles. These corpuscles therefore will shrink and become **crenated.** The crenated particles collect at the bottom leaving a colourless supernatant liquid. The red corpuscles method thus helps to compare the osmotic pressures of different solutions.

Check your progress - 2

How do you explain isotonic solutions?

25.7 OSMOTIC PRESSURE AND VAPOUR PRESSURE

Let a solvent and a solution be separated at constant temperature by a semipermeable membrane. Let the pressures exerted on the two liquids the solvent and solution to maintain the equilibrium be P_0 and P respectively. The osmotic pressure (π) of the solution is given by ($P\text{-}P_0$), since osmotic pressure is defined as the excess pressure required to be applied on the solution to just prevent the inflow of solvent into it.

Let the partial vapour pressures p^0 of pure solvent and solution be p° and p respectively. Since the liquids and vapours are in equilibrium with each other, the following relation can be written for vapour pressure (p^0 and p) and the pressures (p° and p) on the solvent and solution.

$$RT \ln.\ p^0/P \quad = \quad \bar{V}\ (P\text{-}P^{\circ}) \qquad \text{.... (1)}$$

Where $\bar{V}$ is the partial molar volume of the solvent in the solution.

But by definition ($P\text{-}P^{\circ}$) is equal to the osmotic pressure (π). Therefore equation (1) can be written as

$$RT \ln.\ p^0/p \quad = \quad \bar{V}\ \pi \qquad \text{.... (2)}$$

The above equation holds good only if the solvent vapour behaves ideally.

25.8 OSMOTIC PRESSURE AND CONCENTRATION

The relationship between vapour pressures of solvent in solution and of pure solvent in equilibrium with it, and the osmotic pressure is shown in 25.5.

$$R \ln.\ p^0/p \quad = \quad \pi\ \bar{V} \qquad \text{.... (3)}$$

Where p^o and p are vapour pressures of pure solvent and solvent in solution respectively, π is osmotic pressure of the solution and $\bar{V}$ is the molar volume of the solvent in the solution. If Raoult's law is applicable to the system under consideration, equation (3) can be written as

$$\pi \ \bar{V} = RT \ln . p^0/p = RT \ln x_1 \qquad \text{.... (4)}$$

Where x_1 = mole fraction of solvent.

Equation (4) is written in terms of mole fraction of solute $(1\text{-}x_2)$ as

$$\pi \ \bar{V} = -RT \ln (1-x_2) \qquad \text{.... (5)}$$

If the solution is dilute x_2 is small, hence $\ln (1-x_2)$ can be put equal to $-x_2$, equation (5) reduces to

$$\pi \ \bar{V} = RT\, x_2 \qquad \text{.... (6)}$$

At the same time x_2 can be expressed as n_2/n_1, where n_1 and n_2 are moles of solvent and solute respectively. Equation (6) reduces to

$$\pi \ \bar{V} = RT.\, n_2/n_1 \qquad \text{.... (7)}$$

$$\pi \ \bar{V} n_1 = n_2 RT \qquad \text{.... (8)}$$

For every dilute solution $n_1 \ \bar{V}$ can be replaced by V, the volume of solvent associated with n_2 moles of solute in the solution or the volume of the solution. Equation (8) is therefore rewritten as

$$\pi V = n_2 RT \qquad \text{.... (9)}$$

$$\pi = n_2/V.\, RT$$

$$\pi = C.\, RT \qquad \text{.... (10)}$$

Where C is the concentration of solution in moles per litre.

Problem

Calculate the osmotic pressure at 27°C of 100 ml solution containing 1.8 gms of glucose dissolved in it.

The concentration of glucose solution in moles per litre is calculated as follows:

100 ml solution contained 1.8 gm of glucose

1000 ml solution contained $\dfrac{1.8 \times 1000}{100} = 18$

Molecular weight of glucose is 180

Concentration of glucose Solution (moles/litre) $= \dfrac{18}{180} = \dfrac{1}{10}$ 0.1 m

Osmotic pressure is calculated from the equation, $\pi = CRT$

$$\therefore \quad \pi = 0.1 \times 0.0831 \times (273 + 27)$$

$$\pi = 0.1 \times 0.0831 \times 300$$

$$\pi = 2.493 \text{ atmospheres}$$

25.9. DILUTE SOLUTIONS AND GAS LAWS

Pfeffer's measurements of osmotic pressure of sucrose solutions revealed very interesting results in respect of the relation between osmotic pressure and concentration of solution or the temperature of the solution. The results relating to the effect of concentration on the osmotic pressure of sucrose solution are presented in table 25.9.1.

Table 25.9.1 : Osmotic pressure of sucrose solution.

Concentration (C) (Grams / 100 gm. water)	Osmotic Pressure (π) (mm of Hg)	π/C
1	535	535
2	1016	508
4	2082	521
6	3075	513

It is observed from the results presented in the last column, that π/C is almost constant.

The results obtained in the experiemtns conducted on the effect of temperature on osmotic pressure of one percent sucrose solution are presented in table 25.9.2.

Table 25.9.2 Influence of temperature on osmotic pressure

Temperature (T) K	Osmotic Pressure (π) (mm of Hg)	π/T
280.0	505	1.80
286.9	525	1.83
295.2	548	1.85
309.2	567	1.83

The results in the last column in table 25.9.2 show that π/T is constant.
These results thus indicate that

$$\pi \propto C$$
$$\pi \propto T$$

or

$$\pi \propto CT$$
$$\pi = KCT$$

Where K is a constant. From the experimental results, constant K is found equal in magnitude to **R**, the gas constant.

The attention of **J.H.van't Hoff** who was studying the problem of equilibrium in gases was drawn to the resutls of Pfeffer's expriments. From these results vant' Hoff concluded that the laws of osmotic pressure were similar to Boyle's and Charles' laws. This implies that the osmotic pressure of a dilute solution is similar to gas pressure and can be treated equal to the pressure which would be exerted by the same number of molecules of solute, if they existed as a gas occupying a volume equal to that of the solution. The similarity between the behaviour of gases and dilute solutions led van't Hoff to suggest that gas pressure and osmotic pressure have the same fundamental origin.

The impacts of gaseous molecules on the walls of the container are responsible for the gas pressure. In a similar way the impacts of molecules of dissolved substance on the semipermeable membrane may be responsible for the osmotic pressure.

25.10 DETERMINATION OF MOLECULAR WEIGHT OF DISSOLVED SUBSTANCE

Measurement of osmotic pressure of a dilite solution makes possible the determination of molecular weight of the dissolved substance, since van't Hoff's equation holds good for dilute solutions. The concentration (C) of a solution can be expressed in terms of the weight of solute and its molecular weight as follows. Let the molecular weight of solute be M_2 and the weight of solute in a volume of V litres of solution be W_2. the concentration 'C' is thus given by W_2/M_2V. Hence Van't Hoff's equation $\pi = CRT$ can be rearranged and written as

$$\pi = \frac{W_2}{M_2 V} RT \qquad \text{........ (11)}$$

Hence $$M_2 = \frac{W_2}{\pi V} RT \qquad \text{......... (12)}$$

Equation (12) indicates that M_2 can be calculated from the weight of solute (W_2) present in the dissolved state in a solution of volume (V) and osmotic pressure of the solution (π).

25. 10.1 Problem

Calculate the molecular weight of glucose, if the osmotic pressure at 270C of 100 ml of its solution containing 0.9 grams of glucose is 1.245 atmospheres.

Molecular weight is calculated by substituting the value of weight of glucose, volume of solution in litres, gas constant R in litre atmospheres and temperature in the absolute scale in the equation,

$$M_2 = \frac{W_2}{\pi V} RT$$

$$M_2 = \left(\frac{0.9 \times 0.831 \times 300}{1.245 \times 0.1} \right) = 180 \text{ gms.}$$

25.11. ISOTONIC SOLUTIONS

Two solutions exhibiting the same osmotic pressure are called **iso osmotic solutions.** If the two solutions have the same solute dissolved in the same solvent, they maintain the same osmostic pressure or tension as well as the numerical values of the osmotic pressure will be the same. However a solution which just fails to bring about the plasmolysis is said to have the smae tension as the cell sap. Similarly another solution which also just fails to bring about plasmolysis is said to possess the same tension as the cell sap. Therefore the two solutions are referred to as isotonic solutions. But their absolute osmotic pressures may not be the same, since cell membrane may not be equally impermeable to the solutes of the two solutions. For example blood is known to be isotonic with saline (solution of sodiumchloride). But the absolute osmotic pressure of blood may not be equal to the absolute osmotic pressure of saline. The isotonc nature of blood and saline is however attributed to the fact that either of them just fails to bring out haemolysis with red corpuscle.

25.12. SUMMARY

In this unit we have studied about

i) Osmosis is the spontaneous flow of water from a dilute solution to a more concentrated solution when the two are separated by a semipermeable membrane.

ii) Nature of a semipermeable membrane and its function

iii) Osmotic pressure is the excess hydrostatic pressure which must be applied on a concentrated solution to present osmosis.

iv) Experimental methods for the measurement of osmotic pressure and their comparitive merits.

v) The laws of osmotic pressure and osmotic equation.

vi) Relation between osmotic pressure and vapour pressure

vii) Vant Hoff's theory of dilute solutions

viii) Measurement of osmotic pressure as a means to find the molecular weight of solute.

ix) Isotonic solutions.

25.13 MODEL EXAMINATION QUESTIONS

I Answer the following in 10 lines each.

1. Explain with a neat sketch the phenomenon of osmosis.
2. Give the practical definition of the term osmotic pressure with the help of a schematic diagram.
3. Derive the relation between osmotic pressure and the vapour pressure of a solution.
4. How is the osmotic cell prepared in Morse and Frazer method?
5. Calculate the osmotic pressure of a solution containing 0.6 gms. of urea dissolved in 100 ml. of the solution.
6. Explain the terms haemolysis and plasmolysis.

II Answer the following in 30 lines each.

1. Explain the terms osmosis, osmotic pressure and derive the relation between osmotic pressure and the concentration of the solution.
2. Describe in detail one method for the determination of osmotic presure of a solution.
3. How is measurement of osmotic pressure useful in the determination of molecular weight of a dissolved substance?
4. "The osmotic pressure of a dilute solution is similar to the gas pressure". Substantiate the statement.

25.14 MODEL ANSWERS TO CHECK YOUR PROGRESS

1 A membrane is said to be semipermeable if it allows to pass through it only the solvent molecules, when it separates a solution from a solvent or two solutions of different concentration.
eg :- Animal membrane or copper ferrocyanide layer.

1 Solutions whose osmotic pressures are equal are called isotonic solutions. Therefore they are also called isoosmotic solutions. Their concentrations may be same or different.

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UNIT - 26 : ABNORMAL BEHAVIOUR OF SOLUTIONS

Contents

26.1 AIMS AND OBJECTIVES

This unit is mainly to explain you the reasons for the abnormal behaviour of certain solutions in respect of colligative properties.

At the end of this unit you should be able to understand that:

- A solution is said to be an ideal solution, if it obeys Raoult's Law in the entire range of concetrations.
- Solutions which show deviations in behaviour from Raoult's Law are said to be non-ideal solutions.
- The behaviour in respect of colligative properties shown by non-ideal solutions is called abnormal behaviour.
- The abnormal behaviour is attributed to the association or dissociation of solute molecules, the compound formation between the solute molecule and the solvent molecule and intermolecular forces between different molecules in the solution.
- To correct the calculated osmotic pressure of solutions showing abnormal behaviour, van't Hoff introduced an orbitrary factor 'i' and revised the equation to $\pi = i.CRT$
- The van't Hoff's factor 'i' is related to the experimentally determined colligative property and the theoretically calculated property by the equation

$$i = \frac{\text{Experimental Value}}{\text{Theoretical Value}}$$

- Factor 'i' can also be expressed in terms of molecular weight of solute as

$$i = \frac{\text{Theoretical molecular weight}}{\text{Experimental molecular weight}}$$

- Since the abnormality is due to association or dissociation of the solute 'i' can be written in terms of α , the degree of dissociation or association.

$$i = \frac{1 + \alpha\ (n-1)}{1} \text{ for dissociation and } i = \frac{1 - \alpha\,(1 - \frac{1}{n})}{1} \text{ for association}$$

26.2 INTRODUCTION

In the preceeding three units we have seen how colligative properties help us to determine the molecular weights of non-volatile solutes. All the while a tacit assumption is made that the solute exists as normal species in solution. However this may not be true always. The dissolved solute may dissociate into ions as in the case of sodium chloride forming Na^+ and Cl^- ion. May be the solute molecules associate to form dimer to trimer. The experimental data for these abnormal behavour of solutes may be used to estimate the extent of dissociation or association.

26.3 IDEAL SOLUTIONS

The results described in Units 23 to 25 indicate that colligative properties of solutions namely **lowering of vapour pressure, depression of freezing point, elevation of boiling point and osmotic pressure,** can be conveniently used to determine molecular weight of the dissolved substance. But the experimental results in this respect revealed that unsatisfactory results were obtained in specific instances. such unsatisfactory behaviour is termed as **abnormal behaviour.** Solutions which exhibit such unsatisfactory results are generally called **non-ideal solutions** or **abnormal solutions.** It was made clear in unit 23, that solutions which obey Raoult's law are called **ideal solutions.**

The solutions which mainly satisfy the following conditions are known to exhibit ideal behaviour.

1. The solution must be dilute.
2. The solute shall be non-volatile.
3. There shall not be interactions between one molecule of solute and the another molecule of the solute (i.e. absence of intermolecular attraction between solute molecules) and similarly there shall be no interaction between the molecules of the solvent (absence of intermolecular attraction between solvent molecules).
4. There shall be no interaction between molecules of solute and the molecules of solvent.

In general it can be stated that such solutions which obey Raoult's law or the other equations obtained from it and the equations that relate the colligative properties and the molar composition of the solution are called ideal solutions.

But it is customary to define an ideal solution in terms of Raoult's law rather than in terms of other equations of colligative properties.

Check Your Progress - 1

What do you mean by abnormal behaviour of solutions?

26.4 NON-IDEAL SOLUTIONS

It was observed, as mentioned in the earlier section, that the molecular weights of solutes determined by methods based on the measurement of lowering of vapour pressure or other colligative properties differed greatly from the values expected from the molecular formulae of the solutes. This suggests that there is an uncertainty about the nature of solute molecules to which the experimental results refer.

For example, the results obtained by **Raoult** and **Re-coura** for the lowering of vapour pressure of solutes in acetic acid solution near the boiling point were found to be very abnormal. In a similar way, the molecular weights of electrolytic solutes determined by osmotic pressure method were different from those expected from the formula weights of the solutes.

For example, it is expected that the osmotic pressure of 0.1 m glucose solution should be equal to the osmotic pressure of 0.1 m sucrose solution or 0.1 m sodium chloride solutin. The reason for the above expectation is that the osmotic pressure, being a colligative property shall depend only on the number of molecules (or particles) of solute rather than on the nature of the solute. The number of solute particles in a 0.1 m solution of glucose, or sucrose or sodium chloride is expected to be the same, since the molarity is the same. But the experimental values of osmotic pressure indicate that the measured osmotic pressure of 0.1 glucose solution and 0.1 m sucrose solution as expected, are same, but the osmotic pressure of 0.1 m sodium chloride is approximately twice that of 0.1 m glucose solution or 0.1 m sucrose solution. In a similar way, it was realised that the elevation observed in the boiling of benezene when benzene is dissolved in it approximately half the value expected from the colligative equations.

These experimental observations clearly suggest that in real situations the solutions exhibit measurable deviations from the ideal behaviour.

26.5 REASONS FOR NON-IDEAL BEHAVIOUR

Two main reasons were attributed for the departure from ideal behaviour these are

1. The two constituents (solute and solvent) of the solution do not behave ideally at the given concentration. They are incapable of forming an ideal system. The molecules of one component, effect the intermolecular forces of the other. This eventually brings a change in the escaping tendency of a molecule. The escaping tendency of a molecule may be taken roughly as a measure of its vapour pressure. Thus the solution shows deviations from Raoult's law.

2. The molecular species of the solute present in the solution may be different from the one expected on the basis of the molecular formula. The solute molecule in the solution condition may undergo dissociation or association. There can also be compound formation between the solute molecule and the solvent molecule.

26.6 VAN'T HOFF'S EQUATION

It was observed that the osmotic pressure of salt solutions determined experimentally is much greater than what is calculated from the equation $\pi = CRT$.

To make correction for such a deviation and to make the experimental value agree with calculated value, the osomotic pressure equation is modified as $\pi = i\,CRT$. The letter 'i' is generally referred as van't Hoff's factor. The factor 'i' is the ratio between the observed (experimental) osmotic pressure and calculated osmotic pressure.

$$i = \frac{\text{Osmotic pressure observed}}{\text{Osmotic pressure calculated}} = \frac{\pi \text{ observed}}{\pi \text{ calculated}}$$

Osmotic pressure and the other properties namely relative lowering of vapour pressure, elevation of boiling point and depresson of freezing point, being colligative properties depend on the number of solute particles instead on the chemical nature of the solute. As such van't Hoff's factor 'i' can be expressed as

$$i = \frac{\text{Colligative property observed (expermental)}}{\text{Molecular weight observed (theoretical)}}$$

The above equation can be conveniently written in terms of moleculare weights of solute instead of the colligative property of the solution.

$$i = \frac{\text{Molecular weight anticipated (theoretical)}}{\text{Molecular weight observed (experimental)}}$$

Check Your Progress - 2

Why do the solutions of electrolytes show higher colligative properties?

26.7 VALUE OF 'i'

The value of 'i' depends as mentioned earlier on the ratio of number of solute particles actually present in the soluton to the number of particles anticipated from the molecular formula. The number of particles actually present may be greater or lesser than the number anticipated from the formula, since the solute may undergo dissociation or association. For example electrolytes such as NaCl, KNO_3, $MgSO_4$, $CaCl_2$ and K_2SO_4 undergo ionization in (see unit - 30) aqueous solutions to give the corresponding cations and anions. In dilute solutions if the electrolytes are assumed to be completely ionized NaCl, KNO_3, and $MgSO_4$ are expected to yield two ions (particles) each,

NaCl	gives	1 Na^+	1 Cl^-	(total 2 ions)
KNO_3	gives	1 K^+	1 NO_3^-	(total 2 ions)
$MgSO_4$	gives	1 Mg^{++}	1 SO_4^{-}	(total 2 ions)

While K_2SO_4 and $CaCl_2$ give three ions each.

K_2SO_4	gives	2 K^+	1 SO_4^-	(total 3 ions)
$CaCl_2$	gives	Ca^{++}	2 Cl^-	(total 3 ions)

'i' value for these two categories is therefore 2 and 3 respectively,

$$\text{i.e.} \quad i = \frac{\text{No. of particles actually present}}{\text{No. of particles theoretically anticipated (if no ionization)}}$$

$$i = \frac{2}{1} \text{ for NaCl, } KNO_3, MgSO_4$$

$$i = \frac{3}{1} \text{ for } CaCl_2, K_2SO_4$$

For an electrolyte giving after complete ionization 'n' particles, 'i' value is equal to $\frac{n}{1}$ or n.

In case of solutions of higher concentration where the ionizaion is not complete and the value of degree of ionization 'α' (see unit - 30) is very much les than one, the situation is quite different. Let us consider a binary electrolyte such as NaCl. Let the degree of ionization be 'α', then we have

$$NaCl \xrightarrow[\text{ionization}]{\text{incomplete}} Na^+ + Cl^-$$

The number of particles at equilibrium in such a situation is given as

$$\begin{array}{ccccc} NaCl & \Leftrightarrow & Na^+ & + & Cl^- \\ 1-\alpha & & \alpha & & \alpha \end{array}$$

The total number of particles is $1 - \alpha + \alpha + \alpha = 1 + \alpha$ ∴

$$\therefore \; i = \frac{1+\alpha}{1}$$

In general for an electrolyte which gives 'n' particles on complete ionization and whose degree of ionization is 'α', the number of particles at equilibrium is given as

$$\begin{array}{cc} \text{undissociated electrolyte} & \text{(cation + anion)} \\ (1-\alpha) & n\alpha \end{array}$$

The total number of particles is therefore equal to $1 - \alpha + n\alpha = (1 + (n-1)\alpha)$

$$i = (1 + (n-1)\alpha)/i$$

In a similar way 'i' value can be evaluated for solutions where the solute exhibits association instead of dissociation. In such situations the total number of particles will be less than what is anticipated from the formula of the solute if there is no association.

For example if a molecule A undergoes association completely into a dimer, A_2, the number of molecules will be half instead of one.

$$A \longrightarrow 1/2\, A_2$$

Hence 'i' value will be 1/2/1 i.e., half (1/2)

The magnitude of the measured osmotic pressure or any other colligative property will be half the value expected from the corresponding theoretical equations.

As in the case of dissociation, the phenomenon of association may not be complete at a given concentration and for a given solute. In such a situation the extent of association is represented by 'α' the degree of association. In such instances of partial dimerization 'i' can be calculated as shown below

$$A \xrightarrow[\text{association}]{\text{in complete}} 1/2\ A_2$$

At equilibrium the number of simple molecules is $(1-\alpha)$

And the number of dimers is $(\alpha/2)$.

$$\therefore \text{ Total number of molecules} = 1-\alpha + \alpha/2$$

$$= 1-\alpha/2$$

$$\therefore\ i = \frac{1-\alpha/2}{1} = 1-\alpha/2$$

In similar way, for a solute A exhibiting the phenomenon of association (partially), yielding a polymer (A_n), the equilibrium can be written as

$$n\ A \qquad A_n$$

$$\text{Or} \quad A = \frac{1}{n} A_n$$

If the degree of association is 'α' the number of particles present at equilibrium is given by,

Number of unassociated molecules $= 1-\alpha$

Number of associated molecules $= \alpha/n$

Total number of molecules $= 1-\alpha + \alpha/n$

$= 1-\alpha(1-1/n)$

$$i = \frac{1-\alpha(1-1/n)}{1}$$

$$i = 1-\alpha(1-1/n)$$

It was already mentioned that "i" factor is related to the experimentally determined value of colligative property and theoretically calculated value of the property by the equation,

$$i = \frac{\text{Experimental value}}{\text{Theoretical value}}$$

Similarly 'i' factor is related to experimentally determined value of the molecular weight of the solute to the theoretically anticipated value from the molecular formula by the equation,

$$i = \frac{\text{Theoretical molecular weight}}{\text{Experimetnal molecular weight}}$$

These equations in turn are related to equations derived for 'i' in terms of α the degree of dissociation or the degree of association.

UNIT - 27 : REVERSIBLE REACTIONS

Contents

27.1 AIMS AND OBJECTIVES

This unit aims to illustrate reversible nature of chemical reactions and express mathematically the relation between the concentrations of resultants and reactants when the reaction attaining equilibrium state.

By the end of this unit you will be able to understand that:

- The reactions capable of taking place to measurable extent in the forward as well as backward directions are called **reversible reactions.**
- A reversible reaction is said to have attained equilibrium state if the composition of the system remains constant with time at any given temperature.
- The rate of change in concentrations of the reacting substances in a chemical reaction is known as **rate of a reaction.**
- The rate of a reaction is proportional to the product of the concentrations (active masses) of the reacting substances. This generalization is known as **law of mass action.**
- A reversible reaction is said to have attained equilibrium if the rate of forward reaction is equal to the rate of backward (reverse) reaction.
- The ratio of the rate constants of the forward (k_f) and reverse reactions (k_b) is called equilibrium constant (K).
- The liquilibrium constant can be written as the ratio of the product of concentrations of resultants, to the product of concentrations of the reactants at equilibrium.
- The equilibrium constant of a reaction is designated as K_p or K_c depending on whether the concentrations are expressed as partial pressures (for gaseous reactions), or as molarities for reactions in solution).

27. 2 INTRODUCTION

Nitrogen combines with hydrogen and gives ammonia.

$$N_2 + 3H_2 \rightarrow 2NH_3 \quad \text{......... (1)}$$

It is observed that if this reaction is carried out in a closed vessel, ammonia formed decomposes back into nitrogen and hydrogen to a measurable extent.

$$2NH_3 \rightarrow N_2 + 3H_2 \quad \text{......... (2)}$$

The above observation suggests that the reaction between nitrogen and hydrogen under suitable conditions takes palce in either direction. Such a reaction capable of taking place in the forward as well as in the backward directions is referred to as **reversible reaction** and is represented as

$$3H_2 + N_2 \rightleftharpoons 2NH_3 \quad \text{....... (3)}$$

In equation (3), the two arrows pointing out in the opposite directions indicate the reversible nature of the reaction. Reversible reactions can as well occur in solution conditions.

For example, the reaction between an alcohol and an organic acid to form an ester is an example for reversible reaction in solution

$$\underset{\text{alcohol}}{C_2H_5OH} + \underset{\text{acid}}{CH_3\,COOH} \rightleftharpoons \underset{\text{ester}}{CH_3COOC_2H_5} + \underset{\text{water}}{H_2O} \quad \text{.... (4)}$$

Consider, for example the reaction between sodium carbonate and calcium chloride to give rise to a precipitate of calcium carbonate and a solution of sodium chloride.

$$Na_2CO_3 + CaCl_2 \rightarrow CaCO_3 \downarrow + 2NaCl \quad \text{..... (5)}$$

The reverse reaction namely the reaction between sodium chloride and calcium carbonate to give back sodium carbonate and calcium chloride

$$2NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2 \quad \text{..... (6)}$$

does not take place to any detectable extent under normal conditions. such reactions which take place in one direction (forward direction) only are called **non-reversible reactions.**

It was however observed that reacton (6) takes place to meausrable extent if the concentration of at least one of the reacting substance (NaCl or $CaCO_3$) is taken in very high concentrations.

Cheque your Pogress - 2

What do you mean by a reversible reaction?

27.4 LAW OF MASS ACTION

Guldberg and **Waage** postulated that for a homogenous system (homogenous system is one where the reactants and resultants are in the same physical state) **the driving force of a chemical reaction is**

proportional to the active masses of the reacting substances. If it is assumed that the driving force is equal to the rate of reaction and that the active mass is equivalent to the concentration, the earlier mentioned fact can be re-stated as law. The law is known as **the law of mass action** which can be stated in the following form.

"The rate of a chemical reaction is proportional to the product of the active masses of the reacting substances".

Let us consider a reversible reaction in which the reactants A and B and the resultants C and D are at equilibrium concentrations. The reaction is represented as,

$$A + B \rightleftharpoons C + D \qquad \ldots (7)$$

Then according to law of mass action, the rate of the forward reaciton (v_f) is proportional to the product of molar concentrations of A and B. If the proportionality constant is taken as k_f, then the rate of the forward reaction (v_f) is given by equation (8).

$$v_f \quad = \quad k_f.\, C_A.C_B \qquad \ldots\ldots (8)$$

Where C_A and C_B are the equilibrium molar concentrations of A and B respectively. similarly the rate of the backward reaction (v_b) is proportional to C_C and C_D where C_C and C_D are the equilibrium molar concentrations of C and D. If the proportionality constant of the backward reacton is k_b, the rate of the backward reaction (v_b) is given by equation (9).

$$V_b \quad = \quad k_b.C_C.C_D \qquad \ldots\ldots. (9)$$

Since the two rates are equal at equilibrium, it follows

$$k_f C_A.C_B \quad = \quad k_b.C_C.C_D \qquad \ldots.. (10)$$

The concentration terms are usually represented by square brackets [ ]. The equation 11 can therefore be written in the form

$$\frac{C_C.\,C_D}{C_A.\,C_B} = \frac{[C]\ [D]}{[A]\ [B]} = \frac{k_f}{k_b} = K \qquad \ldots\ldots (11)$$

k_f and k_b are called rate constants or specific rates and the constant K is called the **equilibrium constant.** The reciprocal of the above constant is of course, also a constanstant but the convention universally adopted in expressing the equilibrium constant is to put the concentration terms of the resultants (the right hand side components of the chemical equation) in the numerator and the concentration terms of the reactants (left handside components in the denominator). The equation (11), derived on the basis of the law of mass action, gives the condition of equilibrium for a reversible chemical reaction. The equation gives the relationship between the concentrations of the reactants and the resultants at equilibrium irrespective of the initial concentrations of A and B or C and D.

The reaction $A + B \Leftrightarrow C + D$ considered above, involved a single mole of each of the reactants and the resultants. A general reaction involving more number of moles of reactants and resultants can be represented as

$$aA \quad + \quad bB \quad + \quad \ldots\ldots \quad \rightarrow l\,L + mM \;+ \quad \ldots\ldots \qquad \ldots. (12)$$

The equilibrium constant K for such a reaction is given by equation (13)

$$K \quad = \quad \frac{[L]^l \ \times \ [M]^m \ \times \ \ldots .}{[A]^a \ \times \ [B]^b \ \times \ \ldots} \qquad \ldots. (13)$$

In equation 13, the concentration of each species is raised to the power by a number which represents the number of moles of that substances taking part in the reaction at equilibrium.

27.5 FORMS OF EQUILIBRIUM CONSTANT - GASEOUS REACTIONS

If the reactants A, B - - - and the resultants L, M - - - of the general reaction mentioned earlier are gases showing ideal behaviour or approximately close behaviour to ideal gases, the equilibrium constant 'K' can be expressed in terms of the partial pressures, or in terms of the molar concentrations of the reactants and resultants. The two alternate forms K_p and K_c are given by equations 14 and 15 respectively.

$$K_p = \frac{p_L^{\,l} \times p_M^{\,m} \times \quad \cdots}{p_A a \times p_B^{\,b} \times \quad \cdots} \qquad \text{.... (14)}$$

$$K_c = \frac{C_L^{\,l} \times C_M^{\,m} \times \quad \cdots}{C_A^{\,a} \times C_B^{\,b} \times \quad \cdots} \qquad \text{.... (15)}$$

Where p and C terms represent the equilibrium partial pressures and equilibrium molar concentrations respectively.

It must be remembered that the equation 14 is valid for gases which show ideal behaviour. At moderate pressures and relatively high temperatures, the gases generally show deviations from ideal behaviour.

27.6 RELATIONSHIP BETWEEN K_p AND K_c

A simple relationship between K_p and K_c in the case of gases exhibiting ideal behaviour can be derived as shown below.

The partial pressure p_i, of any gas in a mixture of ideal gases occupying a total volume V litres at the temperature T is related to the number of moles n_i, of the given gas by the equation 16 or 17.

$$p_i V = n_i RT \qquad \text{.... (16)}$$

Or $$p_i = (n_i/V)\, RT \qquad \text{.... (17)}$$

Where R is the gas constant and V is the total volume in litres. The quantity n_i/V is equal to the number of moles in unit volume in litres and this is the same as the molar concentration C_i. Equation 17 can therefore be written as,

$$p_i = C_i RT \qquad \text{.... (18)}$$

Where $C_i = n_i/V$

If the equilibrium partial pressures in equation 14 are replaced by the corresponding C_iRT terms, it is seen that

$$K_p = \frac{(C_L RT)^l \;.\; (C_M RT)^m \;\cdots}{(C_A RT)^a \;.\; (C_B RT)^b \;\cdots} \qquad \text{.... (19)}$$

$$K_p = \frac{C_L^{\,l} \;.\; C_M^{\,m} \;\cdots}{C_A^{\,a} \;.\; C_B^{\,b}} \times \frac{(RT)^{l+m+\cdots}}{(RT)^{a+b+\cdots}} \qquad \text{.... (20)}$$

$$K_p = \frac{C_L^{\,l} \,.\, C_M^{\,m}}{C_A a \cdot C_B^{\,b}} \,.\, (RT)^{(l+m+\ldots) - (a+b+\ldots)} \qquad \ldots\ldots (21)$$

$$K_p = K_c\, RT^{\Delta n} \qquad \ldots\ldots (22)$$

Where Δn is $[\,(l+m+\ldots) - (a+b+\ldots)\,]$

If the reaction is one in which the number of molecules of the reactants is equal to the number of molecules of the resultants, Δn is equal to zero. For such a reaction K_p and K_c are equal. For example, for the reaction,

$$H_2 + I_2 \rightleftharpoons 2\,HI$$

Where $\Delta n = 0$, $K_p = K_c .\, RT^0$

$$K_p = K_c \qquad \ldots\ldots (23)$$

However for the reaction between nitrogen and hydrogen giving ammonia,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Δn is not equal to zero.

Therefore, $K_p = K_c .\, RT^{(2-4)}$

$$K_p = K_c \,.\, RT^{-2}$$

Or $$K_c = K_p \,.\, RT^2 \qquad \ldots\ldots (24)$$

The equilibrium constant K_p and K_c for the reaction

$$N_2O_4 \rightleftharpoons 2NO_2$$

Are similarly related by equation (25)

$$K_p = K_c \,.\, RT^{(2-1)} = K_c \,.\, RT \qquad \ldots\ldots (25)$$

27.7 SUMMARY

In this unit we have studied

i) Reversible reactions are those which can take place to a measurable extent in both forward and backward direction.

ii) A reversible reaction attains the state of equilibrium after a certain time interval and thereafter the composition of the system remains unaltered.

iii) The dynamic nature of the equilibrium state and its significance.

iv) Application of law of mass action to a system at its equilibrium state

v) Equilibrium constant and its evaluation in various forms K_p and K_c.

vi) Relation between K_p and K_c.

$$K_p = \frac{p^2\ HI}{PH_2 \cdot PI_2}$$

- K_p and K_c are not equal for the reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ and $K_p = \alpha^2 p/(1-\alpha^2)$, where α is degree of dissociation of PCl_5.

- The formation of ester from acid and alcohol illustrates the homogeneous reaction in liquid phase.

- The reactions $CaCO_3 \rightleftharpoons CaO + CO_2$ and $NH_4HS \rightleftharpoons NH_3 + H_2S$ exemplify the heterogeneous reactions.

28.2 INTRODUCTION

Law of mass action can be applied to chemical reactions at equilibrium and obtain useful information about the extent to which the reaction takes place under given experimental conditions and to study the influence of parameters such as pressure or concentration of the reactants or resultants and the temperature on the course of the reaction. Similar information could be obtained qualitatively by the application of a principle of mobile equilibrium called **Lechatelier Principle.** These qualitative and aspects of reversible reactions under different experimental conditions are discussed in this unit.

28.3 APPLICATIONS OF LAW OF MASS ACTION

Homogeneous gaseous reversible reactions can be considered under the two main headings, first the reactions in which the number of molecules of reactants is the same as the number of molecules of the resultants and second, the reactions in which these numbers are not equal.

The formation of hydrogen iodide from the elements hydrogen and iodine belongs to the first category of homogeneous reactions. The typical examples for the second category are the dissociation of phosphorus penta chloride into phosphorus trichloride and chlorine and the combination of nitrogen and hydrogen to give ammonia.

28.3.1 Formation of Hydrogen iodide from hydrogen and iodine

Let us first consider the combination of hydrogen and iodine to give hyerogen iodide.

$$H_2 + I_2 \rightleftharpoons 2HI \qquad \text{.... (1)}$$

Since the number (two) of molecules of reactants is equal to the number (two) of molecules of resultants, K_p and K_c will be identical. The equilibrium constant can be expressed in terms of partial pressure or molar concentrations of the reactants and resultants.

Let us consider that a mixture of 'a' moles of hydrogen and 'b' moles of iodine are taken in a closed vessel of volume 'V' litres and kept at 450°C until equilibrium is attained. Let it be assumed that 'x' moles of hydrogen and 'x' moles of iodine had combined at equilibrium to form '2x' moles of hydrogen iodide. The number of moles of unreacted hydrogen and iodine at equilibrium will be equal to (a-x) and (b-x) respectively. There will however not be any change in the total number of moles and it will be equal to a+b. Number of moles at equilibrium

$$H_{2(a-x)} + I_{2(b-x)} \rightleftharpoons 2HI_{(2x)} \qquad \text{.... (2)}$$

The partial pressures of the reactants hydrogen and iodine, and the resultant hydrogeniodide can therefore be expressed as

$$PH_2 = \frac{(a - x)}{(a + b)} \times P \quad \text{.... (3)}$$

$$PI_2 = \frac{(b - x)}{(a + b)} \times P \quad \text{.... (4)}$$

$$PHI = \frac{2x}{(a + b)} \times P \quad \text{.... (5)}$$

Where PH_2, PI_2, PHI are partial pressures of H_2, I_2 and HI and P pressure respectively.

Applying law of mass action to the equilibrium, we have

$$K_p = \frac{(PHI)^2}{PH_2 \times PI_2} \quad \text{.... (6)}$$

Or $$Kp = \frac{[2x/(a+b) \times P]^2}{\frac{(a-x)}{(a+b)} \times P \times \frac{(b-x)}{(a+b)} \times P} \quad \text{.... (7)}$$

$$K_p = \frac{4x^2}{(a-x)\ (b-x)} \quad \text{.... (8)}$$

Since the total pressure does not appear in the final equation (8) it is evident that the equilibrium constant is dependant of total pressure. The above equation is useful to calculate the amount of hydrogen iodide formed at any given temperature K_p and the initial concentrations are known.

If nH_2, and nHI represent the number of moles of hydrogen, iodine and hydrogen iodide respectively present at equilibrium and V (litres) is the volume of the system, the respective molar concentrations are written as

C_{H_2} = nH_2/V

CI_2 = nI_2/V

C_{HI} = n_{HI}/V

Substituting these values in equation (9) for equilibrium constant K_c, we have

$$K_c = \frac{C^2_{\ HI}}{C_{H2} \times C_{I2}} \quad \text{.... (9)}$$

$$K_c = \frac{\frac{n_2\,HI}{V^2}}{\frac{nH_2}{V} \times \frac{nI_2}{V}} \quad \text{.... (10)}$$

$$K_c = \frac{n^2\,HI}{nH_2 \times nI_2} \quad \text{.... (11)}$$

It is seen from equation 11, that V does not find a place in the final equation for the equilibrium constant. The equilibrium constant K_p (equation 6) can be written in terms of number of molecules or moles as shown below:

The partial pressure of hydrogen $P_{H_2} = nH_2/N \times P$

The partial pressure of iodine $P_{I_2} = nI_2/N \times P$

The partial pressure of hydrogen iodide $P_{HI} = NHI/N \times P$

Where N = total number of moles of the resultants and reactants and P is the total pressure at equilibrium.

$$\text{Therefore,}\quad K_p = \frac{p^2_{HI}}{P_{H_2} \times P_{I_2}} = \frac{\dfrac{n^2HI \times P_2}{N^2}}{\dfrac{nH_2}{N} \times P \quad \dfrac{nI_2}{N} \times P} \qquad \text{.... (12)}$$

$$= \frac{n^2\,HI}{nH_2 \times nI_2} \qquad \text{.... (13)}$$

From equations 11 and 13, it is evident that K_c and K_p are equal. Similar conclusion is drawn from the equation $K_p = K_c \,.\, RT^{\Delta n}$.

Since $\Delta n = 0$ for the reaction.

28.3.2 Discussion of Phosphorus Penta Chloride

This reaction illustrates an equilibrium process in which there is a change in the number of molecules from reactants to resultants. The reaction is written as

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \qquad \text{.... (14)}$$

The equilibrium constant K_p in terms of partial pressures is expressed as

$$K_p = \frac{pPCl_3 \times pCl_2}{pPCl_5} \qquad \text{.... (15)}$$

Where $pPCl_3$, pCl_2 and $pPCl_5$ are partial pressures of phosphorus trichloride, chlorine and phosphorus penta chloride respectively.

Let us assume that when one mole of PCl_5 is kept at dissociation temperature, a fraction 'α' of it dissociates at equilibrium state, giving 'α' moles of PCl_3 and 'α' moles of Cl_2.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \qquad \text{.... (16)}$$

Number of moles
at equilibrium $(1 - \alpha)$ $\quad \alpha \quad \alpha$

The total number of moles = $1 - \alpha + \alpha + \alpha = 1 + \alpha$. The partial pressures are therefore represented as

$pPCl_5 = 1 - \alpha/1+\alpha \times P$

$pPCl_3 = \alpha/1+\alpha \times P$

$pCl_2 = \alpha/1+\alpha \times P$

Where 'P' is total pressure.

The equilibrium constant K_p can therefore be written as

$$K_p = \frac{pPCl_3 \ x \ PCl_2}{pPCl_5} = \frac{[\alpha/1+\alpha] \ x \ [\alpha/1+\alpha] \ x \ P_2}{[1-\alpha]/[1+\alpha] \ x \ P} \quad .... (17)$$

$$K_p = \alpha^2P/(1-\alpha^2) \quad .... (18)$$

It is seen from equation (18) that the expression for K_p contains in it, the pressure term 'P'. This suggests that the dissociation of PCl_5 is dependent on total pressure.

28.4.4 Dissociation of nitrogen tetroxide

Nitrogen tetroxide (N_2O_4) on heating dissociates into nitrogen dioxide (NO_2). The reaction can be writen as

$$N_2O_4 \rightleftharpoons 2NO_2 \quad .... (19)$$

at equilibrium.

If the number of moles of N_2O_4 and NO_2 are nN_2O_4 and nNO_2 respectively and the total pressure is P, the partial pressure pN_2O_4 and pNO_2 are written as

$$pN_2O_4 = nN_2O_4/N \ x \ P$$

$$PNO_2 = nNO_2/N \ x \ P$$

The equilibrium constant, K_p is, therefore expressed as

$$K_p = \frac{p_2NO_2}{pN_2O_4} \quad .... (20)$$

$$K_p = \frac{[nNO_2/N \ x \ P]^2}{[nN_2O_4/N \ x \ P]} \quad .... (21)$$

$$K_p = \frac{nNO_2/N \ x \ P}{nN_2O_4/N \ x \ N} \quad .... (22)$$

Since equation (22) contains in it the pressure term 'P', it indicates that the dissociation of N_2O_4 depends on the total pressure P.

The equilibrium constant K_p can be written in different form too, in terms of the degree of dissociation of N_2O_4 at equilibrium as shown below:

Let 'α' be the fraction of one mole of N_2O_4 dissociating at equilibrium, and '2α' be the NO_2 formed.

$$\text{at equilibrium} \quad \underset{(1-\alpha)}{N_2O_4} \rightleftharpoons \underset{2\alpha}{2NO_2}$$

The total number of moles at equilibrium is given by 1-α + 2α i.e., 1+α. The partial pressuers pN_2O_4 and pNO_2 are therefore written as:

$$pN_2O_4 = (1-\alpha)/(1+\alpha) \quad x \quad P$$

$$pNO_2 = 2\alpha/(1+\alpha) \quad x \quad P$$

Where 'P' is total pressure. Therefore K_p is expressed as

$$K_p = \frac{p^2NO_2}{pN_2O_4}$$

$$= \frac{[2\alpha/1+\alpha \text{ x } P]^2}{[1-\alpha/1+\alpha \text{ x } P]} \quad .... (23)$$

$$= \frac{4\alpha^2}{(1+\alpha)\ (1-\alpha)} \text{ x } P \quad .... (24)$$

$$= \frac{4\alpha^2}{(1-\alpha^2)} \text{ x } P \quad .... (25)$$

28.3.4 Synthesis of ammonia

Ammonia is synthesised from its elements nitrogen and hydrogen. The reaction was first investigated by **Haber** and later by **Larson** and **Doldge.** But the process is generally referred to as Haber's synthesis of ammonia.

A mixture of **one** mole of nitrogen and **three** moles of hydrogen when subjected to optimum temperature and pressure gives **two** moles of ammonia.

$$N_2 + 3H_2 \rightleftharpoons 2\,NH_3$$

The equilibrium constant K_p in terms of partial pressure is written as

$$K_p = \frac{p_2\,NH_3}{pN_2 \text{ X } p^3H_2} \quad .... (26)$$

Let the reaction mixture initially contain one mole of nitrogen and three moles of hydrogen at a total pressure of P. Let x moles of nitrogen combine with 3 x moles of hydrogen at equilibrium to give 2 x moles of ammonia. There will be (1-x), 3(1-x) and 2x moles of nitrogen, hydrogen and ammonia respectively at equilibrium.

	N_2 +	$3\,H_2$	$\rightleftharpoons$	$2NH_3$
at equilibrium	(1-x)	3(1-x)		2x

The total number of moles of the reactants and resultants at equilibrium therefore is equal to (1-x) + 3(1-x) + 2x i.e., 4-2x.

The partial pressures pN_2, pH_2 and pNH_3 are therefore written as,

$$pN_2 = (1-x)/(4-2x) \text{ x } P$$

$$pH_2 = (3-3x)/(4-2x) \text{ x } P$$

$$pNH_3 = (2x)/(4-2x) \text{ x } P$$

The equilibrium constant K_p is therefore written as

$$K_p = \frac{p^2\,NH_3}{pN_2 \text{ x } p^3H_2} \quad .... (27)$$

$$= \frac{(2x/4-2x \,.\, p)^2}{(1-x/4-2x \,.\, P) \times (3-3x/4-2x \,.\, P)^3} \qquad \text{.... (28)}$$

$$= \frac{4x^2\,(4-2x)^2}{(1-x)\,(3-x)^3 \,.\, P^2} \qquad \text{.... (29)}$$

$$= \frac{16x^2 \,.\, (2-x)^2}{27\,(1-x)^4 \,.\, P^2} \qquad \text{.... (30)}$$

If x is assumed small, in comparison to unity; equation 30 can be simplified and written as :

$$K_p = \frac{16\,x^2 \,.\, 2^2}{27\,P^2} = \frac{64\,x^2}{27\,P^2} \qquad \text{.... (31)}$$

$$\text{Or} \quad x^2 = \frac{Kp \,.\, 27 \,.\, P^2}{64} \qquad \text{.... (32)}$$

Equation (32) shows that ammonia formed (3x) at a given temperature is directly proportional to P^2. The efficiency of the synthesis thus depends on total presure.

28.4 HOMOGENEOUS EQUILIBRIA IN LIQUID SYSTEMS

One of the most familiar instances of a reversible reaction in homogeneous liquid system is that between ethyl alcohol and acetic acid to give ethylacetate, an ester. **Berthelot** and **Gilles** studied this reaction and found that the reaction did not go to completion. But the proportion of acid converted into ester increased as the amount of alcohol was increased. Only 66 percent of the acid was converted into ester, when equimolar concentrations of alcohol and acid were taken initially. But the percentage of acid converted into ester rose up to 88, when the concentrations of alcohol was increased four fold. The reaction can be written as

$$\underset{\text{acid}}{CH_3\,COOH} + \underset{\text{alcohol}}{C_2H_5OH} \rightarrow \underset{\text{ester}}{CH_3\,COO\,C_2\,H_5} + \underset{\text{water}}{H_2O}$$

Let 'a' and 'b' be the initial number of moles of acid and alcohol respectively. And if 'y' is the number of moles of ester formed at equilibrium, then an equivalent amount of water is also produced, (a-y) and (b-y) moles of acid and alcohol respectively therefore remain unreacted at equilibrium. It follows therefore

$$CH_3\,COOH + C_2H_5OH \rightleftharpoons CH_3\,COO\,C_2\,H_5 + H_2O$$

At equilibrium (a-y) (b-y) y y moles

If the total volume of the system is V litres, the equilibrium concentrations are given by

$$C_{CH_3COOH} = \frac{(a-y)}{V}$$

$$C_{C_2H_5OH} = \frac{(b-y)}{V}$$

$$C_{CH_3COOC_2H_5} = \frac{y}{V}$$

$$C_{H_2O} = \frac{y}{V}$$

The equilibrium constant Kc is written as

$$Kc = \frac{C_{ester} \times C_{H_2O}}{C_{acid} \times C_{alcohol}}$$

$$= \frac{y/V \times y/V}{\frac{(a-y)}{V} \times \frac{(b-y)}{V}}$$

$$Kc = \frac{y^2}{(a-y)\ (b-y)} \qquad \text{... (33)}$$

Check your progress - 1

How do you explain homogeneous equilibrium ?

28.5 HETEROGENEOUS EQUILIBRIA

A system is designated as heterogeneous if all the constituents of the system are not in the same physical state. For example in the thermal dissociation of **calcium carbonate** into **calcium oxide** and **carbon dioxide,** two components (calcium carbonate and calcium oxide) are solids and the third component (carbondioxide) is gas. Hence, the thermal dissociation of $CaCO_3$ into CaO and CO_2 can be cited as an example of heterogeneous equilibrium system.

28.5.1 The thermal dissociation of calcium carbonate.

The system can de represented as

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$$

The letters 's' and 'g' the brackets indicate the phases (s=solid and g = gas) of the components of the system. The active masses (concentrations or partial pressures) of solid components are regared as constant. The equilibrium constant K_p for the system can be written as

$$K_p = \frac{PCaO \times PCO_2}{PCaCO_3}$$

PCaO and $PCaOCO_3$ are taken as constants and equal to each other since $CaCO_3$ and CaO are solids.

$$\text{Tehrefore } Kp = PCO_2 \qquad \text{....... (34)}$$

Since Kp is a constant at a given temperature, the system exhibits a definite constant pressure of CO_2. This is called the **equilibrium dissociation pressure.** This conclusion is in agreement with the experimental observation.

28.5.2 The thermal dissociation of ammonium hydrosulphide

The thermal dissociation of ammonium hydrosulphide (NH_4HS) into ammonia (NH_3) and hydrogen sulphide (H_2S) can be represented as

$$NH_4HS\,(s) \rightleftharpoons NH_3\,(g) + H_2S\,(g)$$

This reaction too illustrates a heterogeneous system involving one solid (NH_4HS) and two gases (NH_3 and H_2S). The equilibrium constant Kp is written as

$$K_p = \frac{PNH_3 \times PH_2S}{PNH_4HS}$$

$$= P_{NH_3} \times P_{H_2S} \qquad \text{.....} \; (35)$$

PNH_4HS is taken as unity, since NH_4HS is a solid.

Since equivalent amounts of ammonia and hydrogen sulphide are produced P_{NH_3} will be equal to P_{H_2S} provided the reaction vessel does not contain initially an excess of either gas. The total pressure P is therefore equal to the sum of these partial pressures.

$$P = P_{NH_3} + P_{H_2S}$$

Therefore each partial pressure is equal to p/2, hence

$$K_P = P_{NH_3} \times P_{H_2S}$$

$$= p/2 \times p/2 = p^2/4 \qquad \text{..........} \; (36)$$

In the reversible reaction (1) the forward reaction $PCl_5 \rightarrow PCl_3 + Cl_2$ involves an increase in the number of molecules and the backward reaction

$PCl_5 \rightarrow Cl_2 + PCl_3$ involves a decrease in the number of molecules.

According to Le Chatelier principle, increase of external pressure shall favour the reaction in the direction in which there is decrease in the numbe of molecules. Therefore increase of pressure is expected to favour the backward reaction i.e. formation of PCl_5. In a similar way the decrease of external pressure shall favour the reaction in the direction in which there is increase in number of molecules. That is, the forward reaction namely the decomposition PCl_5 occurs. Same conclusions will be drawn from the equation of the equilibrium constant (K_p) of the reaction.

$$K_p = \frac{\alpha^2 P}{1 - \alpha^2} \qquad \text{(see equation 18)}$$

From the above equation it is evident, that increase of P (pressure) shall result in the decrease of 'α', i.e. the decrease of dissociation of PCl_5 to keep (K_p) constant. In a similar way decrease of P (pressure) shall result in the increase of α, to keep Kp constant. Thus decrease of pressure favours dissociation of (α) of PCl_5.

(ii) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

In this reaction, the forward reaction

$N_2 + 3H_2 \rightarrow 2NH_3$

involves a decrease in the number of molecules, while the

$2NH_3 \rightarrow N_2 + 3H_2$ involves an increase in the number of molecules.

Tehrefore according to Le Chatelier principle increase of pressure shall favour the forward reaction since there is decrease in the number of molecules in this direction. In a similar way decrease of pressure favours backward reaction since it involves an increase in the number of molecules. Similar conclusions are arrived at from the equation representing the euqilibrium constant K_P.

$$K_p = \frac{64\,x^2}{27\,P^2} \qquad \text{(see equation 31)}$$

Check Your Progress - 2

What is the effect of the increase of pressure on the gaseous dissociation of PCl_5?

28.6 LECHATELIER - BRAWN PRINCIPLE

A principle known as **principle of mobile equilibrium** is proposed by **LeChatelier** and **Brawn** to explain and as well as to predict the effect of temperature or pressure on a system at equilibrium. This is popularly known as Le Chatelier principle. this principle can be stated as

If a change occurs in one of the factors, such as temperature or pressure, under which a system is in euqilibrium, the system tends or will tend to adjust itself in such a way as to annul the effect of the change.

28.6.1 Effect of pressure on equilibrium processes

For example, if the pressure of a gaseous reaction at equilibrium is increased the reaction tends to shift in the direction in which, there is decrease of pressure (decrease in the number of molecules). Similarly decrease of external pressure will favour the reaction in the direction in which there is increase of pressure (i.e. the increase in the numbe of molecules).

28.6.2 Effect of temperature on equilibrium process

If the temperature of the reaction at equilibrium is increased, the reaction tends to occur in the direction in which heat is absorbed. On the other hand if the temperature is lowered the reaction tends to shift in the direction in which there is liberation of heat.

28.7 APPLICATION OF LE CHATELIER PRINCIPLE

In this section, the application of LeChatelier principle to gaseous homogeneous equilibrium reactions will be considered.

There will be no effect of presure on the reactions, where the number of molecules of reactants is equal to the number of molecules of resultants. However in cases where this is not the situation, the effect of pressure on the reaction can be predicted by the application of Le Chatelier principle.

Let the following reactions be considered for the purpose.

i) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

ii) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

28. 7. 1 Effect of temperature

Le Chatelier princile helps to predict the effect of external temperature too, on the reactions involving heat changes.

Let us consider the reaction

$$H_2 + I_2 \rightleftharpoons 2HI : \quad \Delta H = -3000 \text{ Cals.}$$

The forward reaction $H_2 + I_2 \rightarrow 2HI$ + heat, is an exothermic reaction, (evolution of heat), while the backward reaction $2HI \rightarrow H_2 + I_2$ - heat is endothermic reaction (absorption of heat). According to Le Chatelier principle, rise of external temperature shall favour such reaction where there is absorption of heat (which helps to nullify the external effect of increase of temperature). Hence raise of temperature favours the backward reaction namely the dissociation of HI into H_2 and I_2. In a similar way, decrease of temperature shall favour the reaction involving evolution of heat. Lowering of temperature thus shall favour the formation of HI from H_2 and I_2.

Similar conclusions can be drawn in the case of reaction involved in the synthesis of ammonia i.e. $N_2 + H_2 \rightarrow 2NH_3$ + heat. The forward reaction is exothermic reaction and hence rise of external temperature favours the backward reaction i.e. de-composition of ammonia. Lowering of external temperature shall in a similar fashion favours the forward reaction $N_2 + H_2 \rightarrow 2NH_3$ involving evolution of heat.

28.8 NUMERICAL PROBLEMS

28.8.1 Problem - 1

At 50° C under a total pressure of 260 mm of mercury, N_2O_4 is 65 percent dissociated into NO_2. Calculate its degree of dissociation at the same temperature but under a pressure of 91.2 m.m. of mercury.

$$\begin{array}{ccc} N_2O_4 & \rightleftharpoons & 2NO_2 \\ 1 - x & & 2x \end{array}$$

Where x is the degree of dissociation.

The total number of moles = 1 - x + 2x.

$$K_p = \frac{P^2NO_2}{PN_2O_4}$$

$$pNO2 = \frac{2x}{1+x} P, \quad pN_2O_4 = \frac{1-x}{1+x} P$$

where P is the total pressure,

$$\therefore Kp = \frac{\left(\frac{2x}{1 + x} P\right)^2}{\left(\frac{1 - x}{1 + x} P\right)} = \frac{4x^2}{(1 - x)\ (1 - x)} P \qquad \text{(equation 37)}$$

As per the data in the problem the degree of dissociation at 50° C

$$\text{is} \quad \frac{65}{100} = 0.65 \ \text{mol. (x)}$$

$$\text{total pressure } P = 260 \text{ m.m.} = \frac{260}{760} \text{ atm.}$$

$$\therefore Kp = \frac{4\ (0.65)2}{(0.35)\ (1.65)} \times \frac{260}{760} = 1.0002 \qquad \text{(equation 37)}$$

When the pressure is equal to 91.2 m.m. i.e., $\frac{91.2}{760} = 0.12$ atm.

the degree of dissociation x_1 is given by

$$Kp = \frac{(1.0002)}{(1.000)} = \frac{4x_1^2}{(1-x_1)\ (1+x_1)} \times 0.12$$

$$1 - x_1^2 = 0.48x_1^2$$

$$1.48x_1^2 = 1; \quad x_1^2 = \frac{1}{1.48}; \ x_1 = \frac{1}{1.216}$$

$$\% \text{ dissociation} = \frac{1}{1.216} \times 100 = 82.21$$

28.8.2 Problem - 2

In a mixture of 1 part of N_2 and 3 parts of H_2 the mole percent of NH_3 was found to be 1.20 at 500°C and a pressure of 10 atmospheres. Calculate the value of K_p and the pressure at which the equilibrium mixture at this temperature contains 10.4 mole percent of NH_3.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Let x be the mole fraction of NH_3 at equilibrium. And that 100x is the mole percent. the sum of the mole fractions of N_2 and H_2 remaining at equilibrium is (1 - x), and since these gases are in the ratio of 1 to 3, it follows that,

$$X_{N_2} = \frac{1}{4} (1 - x), \qquad X_H = \frac{3}{4} (1 - x),$$

If P is the total pressure, the partial pressures are given as

$$p_{NH_3} = \frac{x}{1} P, \quad p_{N_2} = \frac{1}{4} (1-x) P, \quad p_{H_2} = \frac{3}{4} (1 - x) P$$

$$\therefore \ K_p = \frac{p2NH_3}{pN_2 \times p3H_2} = \frac{(x\ P)2}{\frac{1}{4} (1 - x) P \times \left(\frac{3}{4} (1-x) P\right)^3}$$

P is 10 atm. and mole percent of ammonia is 1.20, so that $x = 0.012$ and $1-x = 0.988$

$$\therefore \quad K_p = \frac{(0.0120 \times 10)^2}{(\frac{1}{4} \times 0.988 \times 10)\,(\frac{3}{4} \times 0.988 \times 10)^3}$$

$$= 1.43 \times 10^{-5}$$

It is now required to calculate P corresponding to a mole percent of 10.4 for ammonia, $x = 0.104$ and $1 - x = 0.896$

$$K_p = 1.43 \times 10^{-5} = \frac{(0.104 \times P)^2}{(\frac{1}{4} \times 0.896 \times P)\,(\frac{3}{4} \times 0.896 \times P)^3}$$

On simplification $P = 105$ atm.

28.8.3 Problem - 3

At high temperature and under atmospheric pressure, carbon dioxide is 1.80 percent dissociated, the reaction being

$$CO_2 \rightleftharpoons CO + {}^1/_2 O_2$$

or

$$2CO_2 \Leftrightarrow 2CO + O_2$$

Calculate the equilibrium constant of the reaction using partial pressures (in atmospheres).

If the concentration of CO_2 is 1 mole and the degree of dissociation is x then the number of moles of CO_2, CO and O_2 at equilibrium are (1 - x), x, x/2 respectively.

$$\text{Total number of moles} = 1 - x + x + \frac{x}{2} = 1 + \frac{x}{2} \text{ moles}$$

If P, is the total pressure, then

$$pCO_2 = \frac{1-x}{1+\frac{x}{2}} P; \quad pCO = \frac{x}{1+\frac{x}{2}} P$$

$$pO_2 = \frac{\frac{x}{2}}{1+\frac{x}{2}} P$$

$$Kp = \frac{[pCO]^2 \, [pO_2]}{(pCO_2)2}$$

$$= \frac{\left[\frac{x}{1+\frac{x}{2}} P\right]\left[\frac{\frac{x}{2}}{1+\frac{x}{2}} P\right]}{\left(\frac{1-x}{1+\frac{x}{2}} P\right)^2}$$

$$= \frac{\frac{x^2}{(2+x)^2} 4P^2 \frac{x}{(2+x)} P}{\left(\frac{1-x}{2+x}\right)^2 4P^2}$$

$$= \frac{x^3 P}{(2+x)\ (1-x)^2}$$

The given values of x and P are 0.018 and 1 atm.

$$K_p = \frac{(0.018)^3}{2.018 \times 0.982 \times 0.982} = 2.997 \text{ X } 10\text{-}6$$

28.9 SUMMARY

In this unit we have studied

i) Application of law of mass action to homogeneous gaseous equilibria with
   a) no change in the number of molecules
   b) increase in the number of molecules
   c) decrease in the number of molecules.

ii) Evaluation of Kp and Kc in each of the above case with specific examples being taken for consideration.

iii) Homogeneous equilibria in liquid systems

iv) Heterogeneous equilibria

v) Lechatlier principle and its application to various systems at equilibrium with detailed study of synthesis of ammonia.

28.10 MODEL EXAMINATION QUESTIONS

I Answer the following in 10 lines each.

1. **State Le Chatelier principle and explain its significance in the study of reversible reactions at equilibrium.**

2. **Discuss the application of Le Chatelier principle to the synthetic reaction of ammonia.**

3. **What is the effect of temperature on the reaction.**
   $2SO_2 + O_2 = 2SO_3$ + Heat

4. **Discuss the application of law of mass action to the formation of ester from acid and alcohol.**

II Answer the following in 30 lines each.

1. State and explain law of mass action. Discuss its application to homogeneous gaseous reactions,

2. State and explain Le Chatelier principle. Discuss its application to homogeneous gaseous reactions.

28.11 MODEL ANSWERS TO CHECK YOUR PROGRESS

1 An equilibrium process in which the reactants and products remain in one phase is known as homogeneous equilibrium.

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

$PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$

2 According to Leachatlier's principle increase of pressure of an equilibrium process shifts the position in the direction of decrease of volume. Therefore incrase of pressure decreases the dissociation of PCl_5.

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Block - 9

ACIDS AND BASES

You come across the words 'acid' and 'base' a number of times in day-to-day life as well as in chemistry. Acids and bases are among the most comon and most important chemicals we find in a chemical laboratory. Further, you come acorss acids and bases very often in your homes. Lemon juice owes its sour taste to citric acid. Similarly baking soda contains sodium hydrogen carbonate.

The word **'acid'** comes from the latin word *'acidus'* meaning sour, since sour taste was one of the early recognised characteristic properties of this class of substances. Other distinctive properties described by Boyle are the high solvent power, ability to change the colour of some vegetable dyes and the capacity of precipitating sulphur from its solutions in alkalies. The first distinctive term introduced for substances which possessed properties opposing those of acids was base or alkali. This word **'alkali'** is derived from the Arabic words *al, quili* meaning 'ashes of plants'. The chief characteristic property first established for an alkali (base) was its ability to destroy the action of an acid. Later the term 'base was introduced in place of alkali and was used to describe certain substances such as heavy metal oxides, which reacted with acids but did not possess typical properties of akalies.

$$= \frac{\text{Theoretical molecular weight}}{\text{Experimental molecular weight}} = \frac{94}{137.5}$$

$$= \frac{1-\alpha(1-1/2)}{1}$$

$$= 1-\alpha(1-1/2) \quad \text{for dimerization } (n=2)$$

$$i = 1-1/2\alpha = 2-\alpha/2$$

$$\therefore \quad 2-\alpha/2 = 94/137.5$$

$$(2-\alpha)\ 137.5 = 2 \times 94$$

$$275 - 137.5\ \alpha = 188$$

$$137.5\ \alpha = 275 - 188 = 87$$

$$\alpha = 87/137.5 = 0.633$$

The percentage association is 63.3%

26.9 SUMMARY

In this unit we have studied

i) That ideal solutions are those which obey Raoult's law

ii) That non-ideal solutions do not obey Raoult's law; to ascertain the reasons for non-ideal behaviour.

iii) Van't Hoff's factor "i" and Vant Hoff's equation

iv) Application of Vant Hoff's factor to find out the extent of dissociation or association with specific examples.

26.10 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines each.

1. Explain the term "abnormal behaviour" of a solution with special reference to colligative properties. Assign reasons for such a behaviour.

2. Derive the equation that relates the Van't Hoff's factor 'i' and the measured and calculated values of colligative properties.

3. A solution of Zn SO_4 prepared by dissolving 0.5811 gms of $ZnSO_4$ in 1800 ml of water has frozen at - 0.053°C. Calculate the percentage ionization of $ZnSO_4$ assuming that molal depression constant of water is 1.86.

II. Answer the following in 30 lines each.

1. Give a critical account of the abnormal behaviour of electrolytes in respect of colligative properties.

2. Describe how measurement of colligative properties is useful to establish the associative or the dissociative nature of the solute. Illustrate your answer with specific examples.

3. Discuss how colligative properties are useful in establishing the degree of association or dissociation of a solute in its solutions.

26.11 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. Solutions of some solutes either lower or higher colligative properties than expected. This was found to be due to either molecular dissociation or association of solutes. This behaviour of solutions is called abnormal behaviour.

2. Colligative properties depend on the number of solute particles. Electrolytes undergo dissociation in solutions giving more number of solute particles. Therefore solutions of electrolytes show higher colligative properties.

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Block - 8

CHEMICAL EQUILIBRIUM

In the reaction between nitrogen and hydrogen to give ammonia, it was observed that considerable amounts of nitrogen and hydrogen were noticed even after a long interval of time. This suggests that this reaction is not going to completion and that the forward reaction, namely combination of nitrogen and hydrogen, as well as the reverse reaction, namely decomposition of ammonia are taking place.

In a reversible gaseous reaction taking place in a closed vessel, the resultants accumulated regenerate evidently reactants. For example in the reaction between nitrogen and hydrogen, the accumulated resultant, ammonia, regenerates the resultants nitrogen and hydrogen. This implies that the forward reaction does not go to completion. In a similar way, a mixture of hydrogen and iodine vapour when heated to a temperature of 450°C in a closed vessel does not give completely hydrogen iodide. At this temperature, the hydrogen gas and iodine vapour react to yield hydrogen iodide in the forward reaction but the latter decomposes back, to an appreciable extent into hydrogen and iodine.

$$H_2 + I_2 \rightleftharpoons 2\,HI$$

A reference can be made to a reversible reaction taking place in a liquid phase at ordinary temperatures. It is the reaction between ethanol and acetic acid to form ethyl acetate and water. If equi-molecular amounts of the reactants are taken, the reaction apparently ceases when only two thirds of the initial amounts of alcohol and acetic acid have been used up.

$$\underset{\text{acid}}{CH_3\,COOH} + \underset{\text{alcohol}}{C_2H_5OH} \rightleftharpoons \underset{\text{ester}}{CH_3COOC_2H_5} + \underset{\text{water}}{H_2O}$$

If sufficient time is allowed, all revsible reactions reach a state of chemical euilibrium. It is a state in which no further change in composition of the system with time can be detected, provided the temperature is not altered. Under similar set of conditions, it can be shown that the same state of equilibrium may be attained from either direction for a given reversible reaction. For example, at a temperature of 450° C, the equilibrium mixture consists of 12 molecular percent of hydrogen, 12 molecular percent of iodine vapour and 76 percent of hydrogen iodide, irrespective of whether the starting point is hydrogen idoide or an equivalent mixture of hydrogen and iodine vapour.

It should not be considered that the state of chemical eqilibrium is a state where the reaction ceases or comes to a stop. The more reasonable explanation may be that the forward and reverse reactions are taking place simultaneously at the same rate: when the system is at equilibrium. then it may be stated that the system is in a state of **dynamic equilibrium.**

Check Your Progress - 1

How do you state dynamic equilibrium.

UNIT - 28 : APPLICATIONS OF LAW OF MASS ACTION

Contents

28.1 AIMS AND OBJECTIVES

The aim of this unit is to apply law of mass action to different chemical reactions at equilibrium and to state the qualitative principle called Lechatlier principle and to discuss its application to different chemical systems at equilibrium.

After completing this unit you should be able to understand that:

- The reactions for convenience are classified as homogeneous and heterogeneous for the application of law of mass action.

- A reaction in which all the components (reactants and resultants) of it are in the same physical state is generally referred to as homogeneous systems. The systems with the components in different physical states are called heterogeneous.

- The quantitative effect of concentration or pressure on the extent and direction of the reaction can be examined with the application of law of mass action on the reaction.

- For the reversible reaction $H_2 + I_2 \rightleftharpoons 2HI$ K_p and K_c are equal in magnitude.

$$K_p = \frac{p^2\ HI}{PH_2 \cdot PI_2}$$

- K_p and K_c are not equal for the reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ and $K_p = \alpha^2 p/(1-\alpha^2)$, where α is degree of dissociation of PCl_5.
- The formation of ester from acid and alcohol illustrates the homogeneous reaction in liquid phase.
- The reactions $CaCO_3 \rightleftharpoons CaO + CO_2$ and $NH_4HS \rightleftharpoons NH_3 + H_2S$ exemplify the heterogeneous reactions.

28.2 INTRODUCTION

Law of mass action can be applied to chemical reactions at equilibrium and obtain useful information about the extent to which the reaction takes place under given experimental conditions and to study the influence of parameters such as pressure or concentration of the reactants or resultants and the temperature on the course of the reaction. Similar information could be obtained qualitatively by the application of a principle of mobile equilibrium called **Lechatelier Principle.** These qualitative and aspects of reversible reactions under different experimental conditions are discussed in this unit.

28.3 APPLICATIONS OF LAW OF MASS ACTION

Homogeneous gaseous reversible reactions can be considered under the two main headings, first the reactions in which the number of molecules of reactants is the same as the number of molecules of the resultants and second, the reactions in which these numbers are not equal.

The formation of hydrogen iodide from the elements hydrogen and iodine belongs to the first category of homogeneous reactions. The typical examples for the second category are the dissociation of phosphorus penta chloride into phosphorus trichloride and chlorine and the combination of nitrogen and hydrogen to give ammonia.

28.3.1 Formation of Hydrogen iodide from hydrogen and iodine

Let us first consider the combination of hydrogen and iodine to give hyerogen iodide.

$$H_2 + I_2 \rightleftharpoons 2HI \qquad .... (1)$$

Since the number **(two)** of molecules of reactants is equal to the number **(two)** of molecules of resultants, K_p and K_c will be identical. The equilibrium constant can be expressed in terms of partial pressure or molar concentrations of the reactants and resultants.

Let us consider that a mixture of 'a' moles of hydrogen and 'b' moles of iodine are taken in a closed vessel of volume 'V' litres and kept at 450°C until equilibrium is attained. Let it be assumed that 'x' moles of hydrogen and 'x' moles of iodine had combined at equilibrium to form '2x' moles of hydrogen iodide. The number of moles of unreacted hydrogen and iodine at equilibrium will be equal to (a-x) and (b-x) respectively. There will however not be any change in the total number of moles and it will be equal to a+b. Number of moles at equilibrium

$$H_{2(a-x)} + I_{2(b-x)} \rightleftharpoons 2HI_{(2x)} \qquad .... (2)$$

The partial pressures of the reactants hydrogen and iodine, and the resultant hydrogeniodide can therefore be expressed as

UNIT - 29 : CONCEPTS OF ACIDS AND BASES

Contents

29.1. AIMS AND OBJECTIVES

This unit is to describe the concepts classical and modern proposed to explain the behaviour of acids and bases.

When you have finished this unit you should be able to understand that;

- An acid according to earlier views is a substance which is sour to taste, changes the colour of the dye, litmus, from blue to red.
- A base or an alkali is a compound that tastes bitter, feels slippery and changes the colour of litmus from red to blue.
- By Arrhenius an acid was defined as a substance that when dissolved in water furnishes hydrogen ion H^+. Similarly a base is substance that could furnish the hydroxide ion, OH^- in water.
- **J.N. Bronsted** and **T.M. Lowry** independently defines an acid is a substance that can donate a proton. A base is a substance that can accept a proton.
- The concept of conjugate pairs of acids and bases and the co-existence of acid-base reactions came into existence as a consequence of Bronsted-Lowry concept of acids and bases.
- Lewis proposed the modern definition that is an acid is a substance which is capable of accepting a pair of electrons. A base is similarly a substance capable of donating a pair of electrons.

29.2 INTRODUCTION

A definition used to classify or define something in terms of "what happens" is called operational definition. Suppose we come across a new compound and we want to classify it into an acid or base, we carry out some simple experiments. From the experimentally observed properties, it is possible for us to classify the substances. For example an acid is a compound that dissolves in water to give a solution that reacts with metals such as Zinc or Magnesium liberating H_2, changes the colour of the dye, litmus, from blue to red, tastes sour.

Similarly, a base is a compound that dissolves in water to give a solution that reacts with an acid to destroy or neutralises its properties, changes the colour of the dye, litmus from red to blue, tastes bitter and feels slipping.

29.3 EARLIER CONCEPTUAL DEFINITIONS OF ACIDS AND BASES

It was **Lavoisuer** in 1787 who proposed the first important definition of acids. According to him acids are those binary compounds containing oxygen. This definition of acids remained valid for nearly a generation, when it was recognised that acids need to contain oxygen. In 1787 **Berthollet** showed that certain acids did not contain oxygen. In 1810 **Davy** produced the convincing proof that hydrochloric acid contained no oxygen. He showed that no particular elementary substance is responsible for the acidity of a substance. He further said that a peculiar arrangement of different elementary substances is responsible for this acidity. It was proved later that this statement is also wrong.

But it was shown soon that acids to contain a particular substance namely hydrogen responsible for the acidity. This early **hydrogen theory** may be stated as follows. **All acids to contain hydrogen, but all hydrogen substances are not acids.** It was stated that acids are those substances which contain hydrogen that is replaced by metals. This concept of acids was in use for nearly 50 years.

29.4 ARRHENIUS CONCEPT OF ACIDS AND BASES

Arrhenius proposed conceptual definitions of acids and bases as a part of his theory of ionic dissociation. He is the man who offered the first or the earliest modern approach to the acid-base concept, eventhough it is modified substantially in recent years.

According to Arrhenius, *an acid is defined as a substance that when dissolved in water furnishes hydrogen ion,* H^+. *Similarly, a base is a substance that when dissolved in water furnishes hydroxide ion,* OH^-.

Arrhenius concept of acids and bases could overcome a number of objections of the earlier definitions of acids and bases. The following are the important postulates of Arrhenius theory.

1. Acids and bases are required to be defined in terms of the aqueous solutions but not in terms of substances in the undissolved state. Accordingly hydrochloric acid can not be treated as an acid. Its solution in water alone can be considered as an acid.
2. An acid shall contain hydrogen that can separate out as hydrogen ions in solution.

This theory could not explain the acidic properties of NH_4NO_3 dissolved in liquid ammonia. It could not explain the basic character of an aqueous solution of ammonia. Similarly the theory had no satisfactory explanation for the acidity exhibited by certain salts dissolved in water. Another strong objection to the Arrhenius concept of acids is the improbability of existence of a **bare proton** (unhydrated) in aqueous solutions.

29.5 BRONSTED - LOWRY CONCEPT OF ACIDS AND BASES

In 1923, the Danish chemist **J.N. Bronsted** and the English chemist **T.M. Lowry,** independently proposed new conceptual definitions for acids and bases. According to these definitions *an acid is a substance showing tendency to lose one or more protons. That is an acid is a substance that can donate a proton.*

In a similar way *a base is a compound showing a tendency to add proton to it.* In other words *a base is a substance that can accept a proton.*

Thus Bronsted - Lowry theory envisages in a reaction between an acid and a base the formation of another base and an acid.

These fundamental ideas are indicated by the following equations:

$$\text{Acid 1} \rightleftharpoons H^+ \text{ (Proton)} + \text{Base 1}$$

$$\text{Base 2} \rightleftharpoons H^+ \text{ (Proton)} + \text{Acid 2}$$

The above two equations can be combined and together written as

$$\text{Acid 1} + \text{Base 2} \rightleftharpoons \text{Acid 2} + \text{Base 1}$$

The acid-base reaction is thus expected to involve two acids and two bases and these acids and bases are called **conjugate pairs.**

In the preceeding equations Base 1 is the conjugate base of Acid 1 and similarly Acid 2 is the conjugate acid of Base 2. Consequently Acid 1 and Base 1 form a conjugate pair of Base 2 and Acid 2 likewise form the other conjugate pair. Bronsted - Lowry proton donar concept of an acid therefore is illustrated by the following equation,

$$HCl + H_2O \rightleftharpoons H_3O^- + Cl^-$$

In the above reaction the acid HCl loses a proton to the solvent water, H_2O to form chloride ion, the conjugate base. Similarly the base water, H_2O accepts a proton from the acid to form the conjugate acid H_3O^+.

Even ions can be classified as acids in this concept if they can donate a proton. For example, ammonium ion NH_4^- functions as acid in aqueous solution containing hydroxyl ions since it can lose a proton in aqueous solutions to OH^-.

$$NH_4^+ + OH^- \rightleftharpoons H_2O + NH_3$$

However NH_4^- is a weak acid producing only few hydrogen ions. Any ion or molecule that accepts a proton is called a base.

The following examples illustrate this clearly,

$$OH^- + H_3O^- \rightleftharpoons H_2O + H_2O$$

$$CO_3^{2-} + H_3O^+ \rightleftharpoons HCO_3^- + H_2O$$

$$NH_3 + H_3O^+ \rightleftharpoons NH_4^+ + H_2O$$

Thus *according to Bronsted all negative ions (anions) are classified as bases. In aqueous solutions hydroxide ion, chloride ion, acetate ion, and nitrate ion function as bases.*

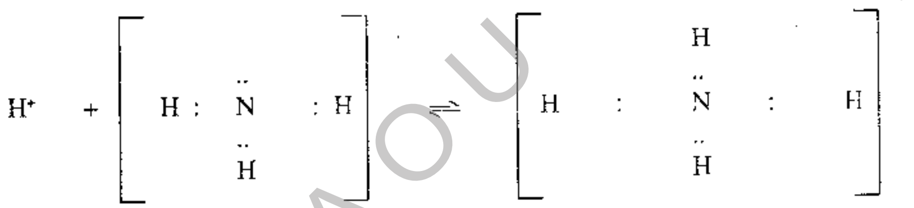
Even though Bronsted - Lowry concept of acids and bases is a much broader concept than the one proposed by Arrhenius, these acids and bases are still defined in terms of the substances themselves instead of their reactivity in aqueous solution. Further, the concept of Bronsted - Lowry recognises that acid-base behaviour is neither restricted nor dependent upon any particular solvent. Even though this concept possessed many advantages over the concept of Arrhenius, it is still handicapped by the undue emphasis placed upon proton exchange. Although a good number of acid-base reactions are characterized by transfer of protons, there are many reactions with acid-base characteristics in which no proton transfer is involved. Bronsted concept could not explain satisfactorily these non-protonic acid-base reactions.

29.6 LEWIS CONCEPT OF ACIDS AND BASES

In 1923 Lewis proposed a new concept of acids and bases. This concept was formulated on the basis of electronic theory of valency. Since it was not elaborated till 1938, Lewis concept was ignored for a long time. The theory provided much broader views than those of the earlier theories. Lewis attempted to explain the acid-base character in terms of chemical bond formation involving sharing or transfer of electrons. *A base is a substance that has a pair of electrons which it can donate to another molecule or an atom to form co-valent bond. An acid is a substance which can accept an electron pair from an atom or molecule to form co-valent bond.*

In other words it can be said that an acid is electron pair acceptor and a base is an electron pair donor in a process leading to co-valent bond formation.

The definition of bases introduced by Lewis is almost similar to that of Bronsted - Lowry since a molecule or an ion, which accepts protons does so due to the presence of lone pairs of electrons. This fact is illustrated by the reaction between a proton and ammonia.



$$H^+ + \left[H : \overset{\cdot\cdot}{\underset{\underset{H}{\cdot\cdot}}{N}} : H \right] \rightleftharpoons \left[H : \overset{\overset{H}{\cdot\cdot}}{\underset{\underset{H}{\cdot\cdot}}{N}} : H \right]^+$$

In this ammonia is a proton acceptor and according to Bronsted is a base. Since it is donating a lone pair of electrons to proton to form the ammonium ion (NH_4^+), it is termed as a base even Lewis concept. The two concepts thus appear identical except in the wording of the definitions of the concepts.

Check Your Progress - 1

Write the modern definition of acids and bases?

In a similar way let us examine the definitions proposed by Bronsted - Lowry and Lewis for acids. For convenience the substances classified as acids are divided into three types.

(1) The first type includes those molecules where the central atom has an uncompleted octet of electrons. Typical examples are boron trifluoride and sulphur trioxide. The reactions between these acids and typical bases are given in the following examples.

$$F_3B + :NH_3 \rightleftharpoons F_3B \leftarrow NH_3$$

$$O_3S + :OH_2 \rightleftharpoons O_3S \leftarrow OH_2$$

(2) The second type includes heavy metal ions with incompletely filled stable orbitals. For example silver and copper ions have such orbitals.

Following are the typical examples of such acids.

$$Ag^{+} \quad + \quad 2\ (:NH_3) \quad \rightleftharpoons \quad Ag\ (:NH_3)_2^{+}$$

$$Cu^{++} \quad + \quad 4\ (:OH_2) \quad \rightleftharpoons \quad Cu\ (:OH_2)_4^{++}$$

(3) The third type includes molecules containing double bonds (except C = C). A typical example is carbon dioxide and its reaction with water can be represented as follows :

$$O_2C \quad + \quad :OH_2 \quad \rightleftharpoons \quad O_2C \leftarrow OH_2$$

The Lewis concept of acids and bases thus may be considered an improvement over earlier views in as much as it recognises that the transfer of protons is only a particular form of acid-base behaviour. Lewis concept allows even other substances that do not involve proton transfer, to be considered as acids or bases. Thus Lewis concept appears superior to Bronsted - Lowry concept.

Lewis concept however suffers from at least two disadvantages. 1. The strength of an acid has naturally to depend on the nature of the base and similarly the strength of a base has to depend on the nature of the acid. Consequently it is impreative to express the strength of an acid relative to a base and similarly the strength of a base relative to an acid. 2. The concept is broad based and suffers from many limitations.

Check your Progress - 2

What concept is taken into consideration to compare the strengths of acids?

29.7 SUMMARY

In this unit we have studied

i) Operational definition of acids and bases.

ii) Some earlier conceptional definition of acids and bases.

iii) Arrehenius theory of acids and bases.

iv) Bronsted and Lowry protonic concept of acids and bases as more broad based theory but with its own limitations.

v) Lewis electronic concept of acids and bases as the most broad based theory.

29.8 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines each.

1. Bring out clearly the drawbacks in the earlier concepts of acids and bases.
2. Compare and contrast the concepts of Bronsted-Lowry and Lewis for acids and bases.
3. How is the strength of an acid explained in each of the different theories of acids.

II. Answer the following in 30 lines each.

1. Give a critical account of the earlier views on acids and bases. Point out the drawbacks of these views.
2. Describe in detail with illustrations, the different concepts introduced to explain the behaviour of acids and bases.
3. Discuss with suitable examples, the modern views on acids and bases. How are these concepts able to overcome some of the drawbacks of the earlier views?

29.9 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. Lewis concept is the modern one to define acids and bases. Acid is a species (means an ion or molecule or an atom) that accepts an electron pair. Base is a species that donates electron pair for covalent formation.

2. Degree of dissociation is taken into consideration to compare the strengths of acids. The acid which undergoes more dissociation in water is a strong one.

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UNIT - 30 : IONIC EQUILIBRIUM

Contents

30.1 AIMS AND OBJECTIVES

This unit is mainly to describe you the ionic equilibrium that exists in solution when polar covalent substance or ionic substance is dissolved in water and to discuss the application of law of mass action to such an equilibrium.

At the end of this unit you must be able to understand that:

The process of splitting or dissociation of a polar co-valent molecule or an ionic substance in aqueous solution into the positive and negative ions is called **ionization.**

The substances capable of undergoing ionization in water give rise to solutions, which conduct electricity through them are called **electrolytes.**

Substances with low degree of ionization are called weak electrolytes and those with high degree of ionization are named as strong electrolyes.

The incomplete ionization results in the occurence of an equilibrium between the ionized parts (i.e., ions) and the unionized part.

$$MA \rightleftharpoons M^+ + A^-$$

Law of mass action can be applied to the equilibrium and equilibrium constant K evaluated by the equation,

$$K = \frac{[M^+]\ [A^-]}{[MA]}$$

The equilibrium constant is called ionization constant or dissociation constant.

The mathematical relation derived by the application of law of mass action to the ionic equilibrium is popularly known as **Ostwald's dilution law.**

30.2 INTRODUCTION

One of the most puzzling questions faced by **Arrhenius** and other chemists was "why do some substances exhibit acidic or basic properties to a greater degree than other subotances?" For example it was realised experimentally that hydrochloric acid solution exhibited stronger acidic character than acetic acid solution at the same concentration. Arrhenius tried to explain this observation in terms of the ability of the acids to part with the protons when dissolved in water. The extent to which an acid makes available the protons (H^+) in the aqueous solution of the acid is roughly compared to the strength of the acid character. This dissociation of acids into positively charged part (protons) and the negatively charged counterpart (counter ions) is termed by him as **ionization.** Thus hydrochloric acid (HCl) and acetic acid (CH_3COOH) undergo ionization in water to different extents.

$HCl \rightleftharpoons H^+ + Cl^-$ Ionization large

$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$ Ionization small

Hence HCl is called strong acid and acetic acid is called weak acid. Here the 'strong' and 'weak refer to the degree of ionization but not to the concentration of these acid solutions.

From the facts mentioned above it is thus clear that there exists an equilibrium between the ions and undissociated part of the acid in aqueous solutions of acids.

$HA \rightleftharpoons H^+ + A^-$

Undissociated acid $\rightleftharpoons$ Proton + Anion of the acid

Similar equilibrium exists in aqueous solutions of polar covalent molecules and salts. But in the case of salts, ions are known to exist in the salt even in the solid state. However these solid salts when dissolved in water will be present partly as **free ions** and partly as **ion pairs** in the associated form. The equilibrium existing in aqueous solutions of the polar covalent substances and the salts (ionic substances) can be illustrated with the help of hydrochloric acid and sodium chloride.

$HCl \rightleftharpoons H^+ + Cl^-$

Undissociated molecule

$Na^+Cl^- \rightleftharpoons Na^+ + Cl^-$
ion pair ions
[Solid] [In solution]

The progress of dissociation of the polar covalent molecule and ionic solid into the positive and negative ions in aqueous solutions is referred to as **ionization.** The equilibrium that exists between the ions and the undissociated molecule or ion pair is called **equilibrium.**

Check Your Progress - 1

What do you mean by ionisation?

30.3 IONIC EQUILIBRIUM

The equilibrium can be written in the general form as

$$MA \rightleftharpoons M^+ + A^-$$

Where 'M' can be a metal or hydrogen. In the case of polar covalent substances MA represents unionized molecule present in equilibrium with the ions. In a similar way in the case of salts, (ionic substances), MA can be assumed to be an ion pair or undissociated part of the ionic substances. The above mentioned ionization equilibrium exists in aqueous solution. It is generally customary not to include water (H_2O) in the equilibrium reaction.

But it should not be mis-construed that ionization takes place in the absence of water.

Law of mass action can be applied to the equilibrium.

$$MA \rightleftharpoons M^+ + A^-$$

And the equilibrium constant is written as

$$K = \frac{[M^+]\ [A^-]}{[MA]}$$

The equilibrium constant 'K' is called **ionization constant** or sometimes referred to as dissociation constant.

30.4 IONIZATION OF WEAK ACIDS

Organic acids such as acetic acid in general exhibit only partial ionization at moderate concentrations. Such acids and substances which are ionized in aqueous solutions only partly are called weak acids or weak electrolytes.

The ionization equilibrium of a week acid can be represented as

$$HA \rightleftharpoons H^+ + A^-$$

The degree of ionization at a concentration is designed as α (alpha) and is always less than unity. It is observed that α indicates with dilution and the dilution where 'α' approaches unity is referred to as infinite dilution. The equilibrium constant k_a for the ionization of an acid can be written in terms of the equilibrium concentrations of the ions and the undissociated acid by the application of law of mass action.

$$HA \rightleftharpoons H^+ + A^-$$

$$K_a = \frac{[H^+]\ [A^-]}{[HA]}$$

The equilibrium constant K_a or otherwise referred as ionization constant or dissociation constant can be expressed in terms of equilibrium concentrations as shown below. Let the initial concentration of the acid be 'C' moles/litre. Let 'α' be the degree of ionization or dissociation at this concentration. At equilibrium, the concentration of the undissociated acid is C(1-α). Similarly the concentrations of the ions at equilibrium are Cα and Cα.

$$HA \rightleftharpoons H^+ + A^-$$

$$C(1-\alpha) \quad C\alpha \quad C\alpha$$

$$K_a = \frac{[H^+]\ [A^-]}{[HA]}$$

$$K_a = \frac{C\alpha \times C\alpha}{C(1-\alpha)}$$

$$K_a = \frac{C\alpha^2}{(1-\alpha)}$$

It is experimentally proved that K_a for different concentrations of the acid is constant provided the temperature is constant. The verbal statement of the above equation is known as **dilution law.** Since it has been worked out by Ostwald, it is more popularly known as **Ostwald's dilution law.** The strengths of two acids can be comparing the values of their ionization or dissociation constants. The acid with higher K_a is stronger than the one with lower K_a.

Check Your Progress - 2

How do you explain the degree of dissociation?

30.4.1 Problem

Calculate the dissociation constant or ionization constant (K_a) of an acid if the degree of ionization of the acid at 0.1 m is 0.001.

The initial concentration of the acid = 0.1 m

Degree of ionization, $\alpha = 0.001$ or 10^{-3}

The ionic equilibrium is written as $HA \rightleftharpoons H^+ + A^-$

At equilibrium $C(1-\alpha) \rightleftharpoons C\alpha + C\alpha$

Ionization constant $K_a = \dfrac{[H^+]\ [A^-]}{[HA]} = \dfrac{C\alpha \times C\alpha}{C(1-\alpha)}$

$$K_a = C\alpha^2/(1-\alpha)$$

$$K_a = \frac{0.1 \times 10^{-3} \times 10^{-3}}{(1-10^{-3})}$$

Neglecting 10^{-3} in the denominator $K_a = \dfrac{0.1 \times 10^{-3} \times 10^{-3}}{1}$

$$K_a = 10^{-7}$$

30.4.2 Problem

If the degrees of ionization of acids A and B are repectively 0.01 and 0.05 at 1 m concentrations, compare their strengths.

For acid A, $$K_a = \frac{0.01 \ X \ 0.01}{(1-0.01)} \simeq 10^{-4}$$

For acid B, $$K_a = \frac{0.05 \ X \ 0.05}{(1-0.05)} \simeq 2.5 \ X \ 10^{-3}$$

Therefore B is stronger than A

30.5 SUMMARY

In this unit we have studied

i) Ionic equilibrium i.e., the equilibrium state in aqueous solution which exists between the undissociated molecules of a solute and its ions.

ii) Evaluation of the ionisation constant

iii) Ionisation of weak acids (or bases) and Ostwald's dilution law.

30.6 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines each.

1. Write the ionization equilibrium for a weak acid and apply law of mass action to it.
2. Calculate degree of dissociation or ionization of 0.1 M acetic acid if its ionization constant is 1.8 X 10^{-5}.
3. The degree of ionization of acid A is 0.01 at 0.1 M concentration. Similarly the degree of ionization of acid B is 0.02 at 0.15 M concentration. Compare the strengths of acids.

II. Answer the following in 30 lines each.

1. State and explain Ostwald's dilution law. Discuss its significance in establishing the strength of an acid.
2. What is meant by ionic equilibrium? Discuss the application of law of mass action to the equilibrium.

30.7 MODEL ANSWERS TO CHECK YOUR PROGRESS

I. Electrolytes on dissolving in polar solvents like water break into ions. Electrical conductivity proves the presence of these ions. This process of separation of electrolytes into ions in solution is known as ionisation.

II. Only a part of the weak electrolyte undergoes dissociation in water. Thus the fraction of the electrolyte which undergoes dissociation in water is called degree of dissociation. It is indicated by α.

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Block - 10 :

OXIDATION - REDUCTION

It has been able to penetrate deeply into the structure of the matter by studying the common features of chemical change. Matter is made up of atoms, which combine and recombine in various ways to form molecules, the characteristic of substances. Chemical reactions are visualised, described and explained quantitatively by means of these atomic and the molecular models. The number of chemical reactions are countless. Surprisingly enough, however, most of them can be understood in terms of few simple types. Actually, an understanding of what goes on when a candle burns in air and what happens when an acid is alkalised, forms good basis for an understanding of the great proportion of the chemical reactions. The burning of a candle is an example of what is called **an oxidation - reduction** reaction, while the alkalising of an acid is an example of the **acid-base** reaction.

UNIT - 31 : CLASSICAL AND MODERN CONCEPTS OF OXIDATION AND REDUCTION

Contents

31.1 AIMS AND OBJECTIVES

This unit aims to understand the phenomenon of chemical oxidation and reduction in terms of classical and modern definitions.

When you have worked through this unit you should be able to know that:

- Matter consists of generally molecules and the molecules are formed by combination of atoms.
- Chemical reactions are described and explained in terms of the atomic and molecular models.
- Burning of firewood and loss of metallic lustre when the latter is exposed to air, are examples of oxidation in common day to day experience.
- A direct chemical union of element or elements in a substance with oxygen is called oxidation.
- The compound that provides oxygen for an oxidation process is called an oxidant.
- The extraction of a metal from its oxide ore is a familiar example of reduction.
- Removal of oxygen from oxygen containing compound can be called reduction.
- In many instances removal of oxygen is effected through the addition of hydrogen, reduction can therefore be defined as addition of hydrogen.

- Addition of non metals such as oxygen, chlorine can be called oxidation while addition of hydrogen, metals etc., can be called reduction.

- Removal of electron is called oxidation addition of electron is called reduction.

- The chemical compound formation is also expalained in terms of a concept called, oxidation number.

31.2 INTRODUCTION

The burning of a piece of wood when placed in fire is a common example of chemical reaction. A great deal of heat is given off and the flame consumes the material, leaving only a small quantity of ashes. Similarly, when metals are heated in air, they lose their metallic character and are transformed into powdery substances of various colours. Thus iron is converted into red powder resembling iron rust. In a similar way tin is transformed into a black powder. All these reactions are examples of acid action reactions. A combustible substance such as wood when burnt in oxygen or air, combines chemically with oxygen. Thus the burning of a substance in oxygen or in air involves a direct chemical union of the element or elements in the substance with oxygen. This point is further confirmed by the fact that the weight of the product is the sum of the weights of the oxygen and the element or elements burning in it. For example, when carbon burns in oxygen, it combines chemically with the oxygen to form carbondioxide. it can be represented by the equation.

$$C + O_2 \rightarrow CO_2$$

Thus it can be shown that one mole of carbon atoms (12 gm) combines with one mole of oxygen (32 gm) to give one mole of carbon dioxide (44 gm).

Many non-metals and metals burn in oxygen, forming the corresponding oxides. For example, sulphur, phosphorus, iron magnesium etc., burn in oxygen giving off a great deal of heat and forming the corresponding oxygen compounds (oxides). Some of the metals rust forming essentially the oxides when exposed to oxygen or air for long periods. The processes can be represented by the following chemical equations.

$$\begin{aligned} S &+ O_2 \rightarrow 2P_2O_5 \\ 4P &+ 5O_2 \rightarrow 2P_2O_5 \\ 4Fe &+ 3O_2 \rightarrow 2Fe_2O_3 \\ 2Mg &+ O_2 \rightarrow 2MgO \\ 2Cu &+ O_2 \rightarrow 2CuO \end{aligned}$$

31.3 OXIDATION

The name **"Oxidation"** was given by **Lavoisier** to the chemical union of a substance with the oxygen and name **"oxide"** to the compound that is formed in the process. Thus, when carbon burns in oxygen to form carbon dioxide, it is said that carbon is oxidised to carbon dioxide.

The idea of oxidation can be extended even to compounds. For example petrol or kerosene (compounds of carbon and hydrogen) burns in oxygen, to form the oxide of carbon (CO_2) and the oxide of hydrogen (water).

$$C_{17}H_{36} + 26\,O_2 \dashrightarrow 17CO_2 + 18H_2O.$$

Many more examples of this type can be given. The processes involving burning elements or compounds in oxygen giving rise to the oxides are thus known as oxidations. In nature we come across a number of compounds of oxygen. For example, water is an oxide of hydrogen, sand is an oxide of silicon, rust is an oxide of iron. Good number of minerals are the oxides of the corresponding metals. hematite is an oxide of iron. Pyrolusite is an oxide of manganese. The idea of oxidation can be extended to explain other phenomena. For example, respiration of living things as well as the souring of wines involve oxidation.

The combination of oxygen with chemical elements namely oxidation can also take place when the elements or substances containing these elements are made to react with compounds containing oxygen instead with molecular oxygen. Such a compound containing oxygen is referred to as the oxidising agent. For example, if a jet of hot hydrogen is introduced into a flask of nitric oxide,. (NO) the hydrogen continues to burn in nitric oxide, with a hot flame producing water and nitrogen gas.

$$2H_2 + 2NO \longrightarrow 2H_2O + N_2$$

Another example is the burning of magnesium ribbon in steam. If a ribbon of magnesium is lighted in air and then immersed in steam, the magnesium continues to burn vigorously, extracting the oxygen from the steam, and forming magnesium oxide.

Check your Progress - 1

Write about the chemical process involved in the burning of firewood?

31.4 REDUCTION

Phenomena at first sight seem to be unrelated to burning were known in nature. For centuries metals have been obtained from their ores by a process that was termed "reduction of an ore to the metal". Since many ores are oxides (or complicated combinations of oxides), the process of reduction, is considered merely as removal of oxygen from the ore. For example, iron ore is reduced to metallic iron by mixing it with charcoal and heating to high temperatures.

$$2\,Fe_2O_3 + 3C \longrightarrow 4\,Fe + 3\,CO_2$$

In this reaction the carbon removes the oxygen from the iron oxide leaving the metal free. Reduction, thus is the opposite to oxidation. It could therefore be called deoxidation.

A number of the other substances can be used to reduce the ores to the respective metals. Hydrogen, carbondioxide or even other metals may be quoted as examples.

$$Fe_2O_3 + 3H_2 \longrightarrow 2Fe + 3H_2O$$
$$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$
$$Fe_2O_3 + 3Zn \longrightarrow 2Fe + 3ZnO$$
$$Fe_2O_3 + 2Al \longrightarrow 2Fe + Al_2O_3$$
$$CuO + H_2 \longrightarrow Cu + H_2O$$

In all these cases the oxide ore is reduced to the metal.

An examination of the above reactions reveals that one thing is common to all reactions. Every substance reducing the ore is removing oxygen from the ore. because of this, these substances are called "reducing agents". This shows that the reducing agents must be substances that have great affinity for oxygen.

31.5 OXIDATION - REDUCTION

An inspection of the oxidation reactions and the reductions described earlier reveals another important relation namely that both these processes take place in every reaction. Consider the following reaction:

$$2Fe_2O_3 + 3C \longrightarrow 4Fe + 3CO_2$$

In this iron oxide (F_2O_3) is reduced to iron, but at the same time carbon is oxidised to carbon dioxide (CO_2). It is clear that in all these reactions, there can be no reduction of an oxygen containing substance unless at the same time another substance combines with oxygen and is itself oxidised. In other words, oxidation and reduction take place simultaneously. The concept of oxidation and reduction as the chemical union and removal of oxygen respectively was extended to other elements showing chemical behaviour similiar to that of oxygen.

A good example is chlorine. It behaves in many ways like oxygen. For example, a jet of hydrogen lit in the air and then injected into a bottle of chlorine continues to burn in the chlorine with a hot pale-blue flame, forming hydrogen chloride. When hydrogen burns in oxygen it forms water and when it burns in chlorine, it forms hydrogen chloride. Not only the two phenomena are entirely similar but the chemical equations describing the phenomenon are also analogous. A comparison of the two equations emphasises this similarity.

$$2H_2 + O_2 \longrightarrow 2H_2O + \text{heat}$$

$$H_2 + Cl_2 \longrightarrow 2HCl + \text{heat}$$

Apart from hydrogen, many other elements burn in chlorine, more vigorously than in oxygen forming the corresponding chlorides. The examples are, the burning of copper and antimony, forming copper chloride ($CuCl_2$) and antimony chloride ($SbCl_2$) respectively.

The similarity of chlorine to oxygen is also observed in the reductionprocess. Just as oxygen can be removed from oxides, chlorine also can be removed from chlorides by reducing agents, resulting in the production of the free metal in each case. When hydrogen is passed over heated copper chloride ($CuCl_2$), hydrogen chloride is formed and the copper compound is reduced to the metal. It is similar to the reduction of copper oxide, by hydrogen, to copper. The reactions mentioned below explain the similarities.

$$CuO + H_2 \longrightarrow Cu + H_2O$$

$$CuCl_2 + H_2 \longrightarrow Cu + 2HCl$$

Because of these similarities in the chemical reactions of oxygen and chlorine, it may be concluded that the processes are fundamentally similar. Accordingly, the term "reduction" can be applied to the removal of either oxygen or chlorine. However, it may be odd if the same term 'oxdation' is used for the combination of an element with chlorine, but the two reactions are similar. The concept of oxidation can be extended to other elements too apart from chlorine which behave like oxygen. Among these elements are bromine, iodine, fluorine, sulphur and nitrogen. The chemical equations emphasise the similarity of the reactions.

$$2Cu + O_2 \longrightarrow 2CuO$$

$Cu + Cl_2 \longrightarrow CuCl_2$

$Cu + Br_2 \longrightarrow CuBr_2$

$Cu + I_2 \longrightarrow CuI_2$

$Mg + F_2 \longrightarrow MgF_2$

$Cu + S \longrightarrow CuS$

$3\,Mg + N_2 \longrightarrow Mg_3N_2$

There are many more elements besides those mentioned above which show reactions similar to those of oxygen. All these reactions are therefore called "oxidation" reactions.

From the above reactions a generalisation can be made. Oxygen is a non-metal. The other elements which behave like oxygen are also non-metals. Accordingly the concept of oxidation is extended to mean chemical union with any non metal. The non metals as a class can therefore be called oxidising agents.

The extension of the concept of oxidation is further justified by considering the reverse process - that is the removal of non-metals from their compounds by reducing agents. Thus, hydrogen reduces a large number of compounds of copper as shown by the following reactions to copper.

$CuO + H_2 \longrightarrow Cu + H_2O$

$CuCl_2 + H_2 \longrightarrow Cu + 2HCl$

$CuBr_2 + H_2 \longrightarrow Cu + 2HBr$

$CuS + H_2 \longrightarrow Cu + H_2S$

There are many other examples involving other metals. Accordingly the term reduction is extended to mean removal of a non-metal from a compound. The concepts mentioned earlier regarding 'oxidation' and 'reduction' may therefore be summarised as follows:

Oxidation is the union with oxygen or **any other nonmetal. Reduction is the removal of oxygen** or **any other non metal.** Oxidising agent is oxygen or any other non-metal.

31.6 MODERN CONCEPT OF OXIDATION - REDUCTION

It is found useful to extend the definition of oxidation to many reactions in which oxygen plays no part. Thus if, in a chemical reaction an element loses electrons, it has been oxidised. If an element gains electrons, it will be reduced. **Oxidation can therefore be referred to as process in which electrons are removed from an atom or a group of atoms. Reduction is a process in which electrons are added to an atom or a group of atoms.** The following examples explain the new concepts.

31.6.1 Oxidation Processes

$Na \longrightarrow Na^+ + e^-$

$Al \longrightarrow Al^{3+} + 3e^-$

$H_2 \longrightarrow 2H^+ + 2e^-$

$2Cl^- \longrightarrow Cl_2 + 2e^-$

31.6.2 Reduction Processes

$2H^+ + 2e \longrightarrow H_2$

$Cl_2 + 2e^- \longrightarrow 2Cl^-$

$Fe^{3+} + e^- \longrightarrow S^{2-}$

In the above examples, the atoms, molecules and ions in (31.6.1) are oxidised and the atoms, molecules and cations in (31.6.2) are reduced. The reactions in (31.6.1) are referred as **oxidation half reactions** and those in (31.6.2) are referred as **reduction half reactions.** An oxidation-reduction reaction is equal to the sum of the two half reactions namely the oxidation half reaction and reduction half reaction.

For example, consider the formation of sodium chloride when sodium metal is exposed to chlorine gas. This reaction can be written as a sum of the following two half reactions.

$$\begin{array}{llllll}
2\,Na & \longrightarrow & 2Na^+ & + & 2e^- & \text{(oxidation)} \\
Cl_2 + 2e^- & \longrightarrow & 2Cl^- & & & \text{(reduction)} \\
\hline
2Na + Cl_2 & \longrightarrow & 2Na^+ & + & 2\,Cl^- & \longrightarrow\ 2\,NaCl \\
\hline
\end{array}$$

Stannous chloride reduces mercuric chloride to mercurous chloride. This reaction can be split into two half reactions. i.e., oxidation of stannous tin (Sn^{2+}) to stannic in (Sn^{4+}). In the second half reaction, mercuric ion (Hg^{2+}) is reduced to mercurous ion (Hg_2^{2+}).

$$\begin{array}{llllll}
Sn^{2+} & & \longrightarrow & Sn^{4+} & + & 2e^- \\
2Hg^{2+} + & 2e^- & \longrightarrow & Hg_2^{2+} & & \\
\hline
Sn^{2+} + & 2Hg^{2+} & \longrightarrow & Sn^{4+} & + & Hg_2^{2+} \\
\hline
\end{array}$$

In the above example, mercuric chloride is called the oxidising agent and stannous chloride is called the reducing agent.

The combination of hydrogen and oxygen to produce water can be cited as another example for oxidation-reduction reaction.

$$2H_2 + O_2 \longrightarrow 2H_2O$$

However in this process the transfer of electrons is not so obvious as it is in other two reactions mentioned. However, there is definite shift of electrons from hydrogen towards oxygen. It can therefore be said that the hydrogen has been oxidised and the oxygen reduced. Hence there is a need to have a method to track this transfer of electrons. A convenient way to keep track of the shift of electrons is through the use of a concept called **oxidation numbers. Oxidation numbers,** since they deal with outer electrons, are closely related to **valencies.**

The following arbitrary rules will be helpful to understand the concept of oxidation number.

(1) The oxidation number, of an element in the uncombined state is O. This concept holds for diatomic molecules, such as hydrogen, for polyatomic molecules like S_8, and for mono-atomic molecules such as inert gases.

(2) For ions consisting of a single atom (Cl^-, Ca^{++}) the oxidation number of the element of that atom is the charge on the ion. For example -1 for chlorine and +2 for calcium.

(3) Some elements exhibit the same oxidation number in ionic as well covalent compounds. For example the alkali metals, always exhibit +1, the alkaline earth metals show always +2. Oxygen (concept in peroxides H_2O_2) exhibits -2, hydrogen (except in hydrides with metals) shows +1, the halogens in binary compounds with metals and hydrogen show -1. Sulphur in binary compounds with metals or hydrogen exhibits -2, and carbon shows generally +4 or -4.

(4) In a neutral molecule, the sum of the oxidation number of all the atoms it contains is zero. For example in H_2O, the oxidation number of oxygen is -2 and the oxidation numbers of two hydrogens is +2(2 x 1).

(5) In complex ions containing more than one element, the sum of oxidation numbers of the atoms in it is equal to the charge on the ion. For example in NO^-_3 the oxidation number of nitrogen is +5 and the sum of the oxidation numbers of three oxygen atoms is –6 (3 x –2). The charge of the ion is therefore equal to +5-6 = -1. The rules mentioned above help to determine the oxidation number of an element in a molecule or ion.

Check Your Progress- 2

Offer modern definitions to oxidation and reduction.

31.7 OXIDATION - REDUCTION CONCEPT IN TERMS OF OXIDATION NUMBER

In checking the transfer of electrons in an oxidation - reduction reaction it is seen from the earlier discussions that if the oxidation number of an element is decreased the element is said to be reduced. Similarly if it is increased, the element is said to be oxidised. This can be explained by taking the example of the formation of sodium chloride from its elements.

The reaction is written along with the oxidation numbers of the elements involved in the reaction.

$$2\,Na^0 + Cl_2^0 \rightarrow 2\,Na^{+1}\,Cl^{-1}$$

The oxidation number of sodium is increased from 0 to +1 in the formation of the sodium ion and so it is oxidised.

Chlorine molecule suffers a change in the oxidation from 0 to -1 in the formation of chloride ion. Chlorine is therefore said to be reduced.

31.8 SUMMARY

In this unit we have studied

i) The traditional views of oxidation and reduction (i.e.,) oxidation is a process in which oxygen (electronegative element) is added to or hydrogen (or electro positive element) is removed from a substance. Reduction is a process in which hydrogen (or electro positive element) is added to or oxygen (or electro negative element) is removed from a substance.

ii) Oxidation and reduction take place simultaneously.

iii) Two modern concepts of oxidation and reduction:

(a) Electronic concept :
Loss of Electrons in a process is termed oxidation
Gain of Electrons in a process is termed reduction.

(b) Oxidation number concept :
The concept of oxidation number is a process in which oxidation number increase is called oxidation. A process in which oxidation number decrease is called reduction.

31.9 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines each.

1. Explain clearly the old concept in respect of oxidation and reduction.

2. Give a concise account of the modern concepts of oxidation and reduction.

II. Answer the following in 30 lines each.

1. Discuss critically the oxidation and reduction reactions with special reference to the old concept of these terms.

2. Explain the modern views on 'oxidation - reduction' reactions with specific illustrations.

31.10 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. In the burning of firewood mostly carbon and hydrogen of cellulose combine with oxygen and change into CO_2 and H_2O respectively. Therefore it is the oxidation process that takes place in the burning of firewood.

2. Increase of oxidation number is oxidation and the reverse process i.e., decrease of oxidation number is reduction. Renual of electrons is oxidation and addition of electrons in reduction.

Author : Dr. K. LAKSHMINARAYANA

BOOKS SUGGESTED FOR FURTHER READING

1. Text Book of Physical Chemistry by Samuel Glasstone
2. Physical Chemistry by Gardon, M. Barrow
3. Principles of physical Chemistry by S.H. Maron and C.F.Prutton
4. Physical Chemistry by W.J. Moore
5. Physical Chemistry by F. Daniels and R.A. Alberty
6. Physical Chemistry by Sheelan

SECTION-B PHYSICAL CHEMISTRY

Block - 5	**Behaviour of Gases**
Unit - 17	Gas laws
Unit - 18	Kinetic molecular theory
Unit - 19	Deviation of gas laws
Unit - 20	Critical phenomena
Block - 6	**Solutions**
Unit - 21	Gases in Liquids
Unit - 22	Liquids in liquids
Block - 7	**Colligtive properties**
Unit - 23	Lowering of vapour pressure
Unit - 24	Elevation of boiling point and depression of freeging point
Unit - 25	Osmosis
Unit - 26	Abnormal behaviour of Solutions
Block - 8	**Chemical Equilibrium**
Unit - 27	Reversible reactions
Unit - 28	Applications of law of mass action
Block - 9	**Acids and Bases**
Unit - 29	Concepts - classical and modern
Unit - 30	Ionic equilibrium
Block - 10	**Oxidation and Reduction**
Unit - 31	Concepts - classical and modern.

ANDHRA PRADESH OPEN UNIVERSITY
(Undergrduate Programmes)
SECOND YEAR SYLLABUS, 1989
CHEMISTRY - CORE -1

SECTION - A THEORETICAL CHEMISTRY

Block - 1	**Atomic Structure**
Unit - 1	Rutherford model of atom
Unit - 2	Planck's quantum theory
Unit - 3	Atomic spectra
Unit - 4	Quantum numbers
Unit - 5	Wave nature of electron
Unit - 6	Electronic configuration of atoms
Block - 2	**Chemical Bond**
Unit - 7	Ionic bond
Unit - 8	Covalent bond
Unit - 9	Other Chemical Bonds
Block - 3	**Molecular Structure**
Unit - 10	dipole moments
Unit - 11	Molecular spectra
Unit - 12	Simple applications of molecular spectra (qualitative)
Unit - 13	Application of visible absorption spectra (quantitative)
Block - 4	**Radioactivity**
Unit - 14	Discovery of Radioactivity
Unit - 15	Radioactive disintegration rate
Unit - 16	Radioactive disintegration series

Andhra Pradesh Open University
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II YEAR
CHEMISTRY COURSE - 1

Assignment - 1

N.B.:-

1. Do not copy the answer directly from any of the books.
2. As far as possible try to answer the questions independently in your own words.
3. If it is necessary to quote from any source give the correct reference.
4. Use your own fooscap pages for writting the assignment.
5. Leave sufficient margins for the comments of the evaluator.
6. Completion of this assignment normally should not take more than two hours time.

SECTION - A

Answer the following in 30 lines.

1. Discuss critically the drawbacks of Rutherford model of atom.
2. Write a concise account of valence bond theory of covalent bond.
3. What are quantum numbers ? State and explain Pauli exclusion principle.

SECTION - B

Answer the following in 10 lines.

1. Explain with suitable examples, how ionic bond is formed?
2. Write the electronic configurations of sodium, chlorine, nitrogen, chromium and copper atoms.
3. What are cathode rays? Describe their properties.

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II YEAR
CHEMISTRY COURSE - 1

Assignment - 2

N.B.:-

1. Do not copy the answer directly from any of the books.
2. As far as possible try to answer the questions independently in your own words.
3. If it is necessary to quote from any source give the correct reference.
4. Use your own fooscap pages for writting the assignment.
5. Leave sufficient margins for the comments of the evaluator.
6. Completion of this assignment normally should not take more than two hours time.

SECTION - A

Answer the following in 30 lines.

1. How is infrared spectroscopy useful in the elucidation of molecular structure?
2. Give a detailed account of radioactive disintegration series.
3. State kinetic gas equation and deduce any four gas laws from that equation.

SECTION - B

Answer the following in 10 lines.

1. Distinguish between an absorption spectrum and emission.
2. Describe the properties of α-rays.
3. Explain the reasons for the deviations of real gases from ideal behaviour.

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II YEAR
CHEMISTRY COURSE - 3

Assignment - 3

N.B.:-

1. Do not copy the answer directly from any of the books.
2. As far as possible try to answer the questions independently in your own words.
3. If it is necessary to quote from any source give the correct reference.
4. Use your own fooscap pages for writting the assignment.
5. Leave sufficient margins for the comments of the evaluator.
6. Completion of this assignment normally should not take more than two hours time.

SECTION - A

Answer the following in 30 lines.

1. Explain clearly the process of distillation of binary liquid mixtures.

2. Stae and explain law of mass action. Discuss its application to formation of ammonia from nitrogen and hydrogen.

3. Explain the modern views on oxidation reduction reactions with specific illustrations.

SECTION - B

Answer the following in 10 lines.

1. Taking suitable examples, explain Lewis concept of acids and bases.

2. Explain with a neat sketch, the phenomenon of osmosis.

3. Write expressions for equilibrium constants K_p and K_c for the reaction.

$$2SO_{2(g)} \quad + \quad O_{2(g)} \rightarrow \quad 2SO_{3(g)}$$

How they are related?

ANDHRA PRADESH OPEN UNIVERSITY
FACULTY OF SCIENCE

CHEMISTRY COURSE - I
MODEL QUESTION PAPER

Time : 3 Hours

Max. Marks: 75

SECTION - A

Answer any three of the following in 30 lines.

3 X 15 = 45.

1. State the drawbacks in Rutherford model of the atom. How are they set in Bohr's model ?
2. Describe the discovery and nature of radio activity.
3. Discuss the classical as well as modern concepts of oxidation and reduction with suitable illustrations.
4. Derive vander - Waals equation of state.
5. State law of mass action and apply the same to any three chemical equilibria.
6. Discuss about the formation and characteristics of ionic and covalent bonds with suitable examples.

SECTION - B

Answer any five of the following in 10 lines.

5 X 6 = 30

7. What are collegative properties? illustrate the same with suitable examples.
8. Explain Lewis concepts of acids and bases with illustrations.
9. State and explain Raoult's law.
10. Describe briefly Born Haber cycle.
11. Derive ideal gas equation.
12. Discuss the dual nature of light.
13. Define osmotic pressure, how is it determined experimentally?
14. State and explain Lechatelier's principle.
15. Give a detailed account of types and shapes of hybrid orbitals.
16. Describe briefly hydrogen bond formation and its applications.