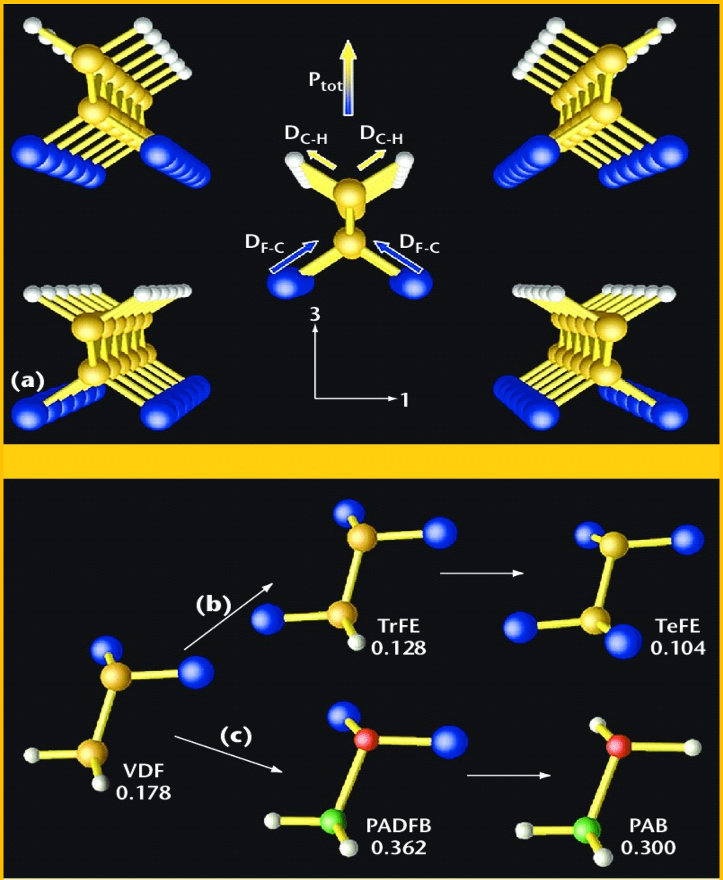
MSCCH-508
M.Sc II Semester
PHYSICAL CHEMISTRY-II



SCHOOL OF SCIENCE
DEPARTMENT OF CHEMISTRY
UTTARAKHAND OPEN UNIVERSITY,HALDWANI (NAINITAL)

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UNIT 1: SURFACE CHEMISTRY

Content

1.1 INTRODUCTION

In the world of chemistry many fascinating phenomena and chemical reactions occur at the surfaces which are unlikely to occur in the bulk phase of matter. Occurrence of such phenomena makes understanding of surface chemistry essential for their practical applications. Due to commercial, scientific and ecological importance of such interfacial phenomena, surface chemistry forms an importance part of physical chemistry.

Surface or interphase is the boundary of matter that separates two bulk phases. Surface is few molecules in thickness. It is represented by a hyphen (-) or solidus (/) inserted between two bulk phases. For example; gas – solid represents interphase between gas and solid phase. Two bulk phases present on each side of surface can be gas- liquid, gas- solid, liquid-liquid, liquid-solid or solid-solid. Gas and gas have no interphase due to their property to get diffuse into each other to form a homogeneous mixture.

Dear students you must have studied the presence of unbalanced residual forces at the surface of liquid which give rise to surface tension of liquid. Similar residual forces are also present at the surface of solid in the form of unbalanced intermolecular interactions or unbalanced valences of the surface atoms. The presence of these residual forces gives the surface of liquids and solids unusual properties which are not shown by the bulk phase. Such residual forces present at the surface of liquid phase are responsible for many properties of liquids viz. surface tension, capillarity, dissolution of gases etc. Similarly, many of the important fascinating phenomena occur at the solid surface due to presence of these unbalanced residual forces at the surface. These include catalysis, adsorption, electro-kinetics etc.

We are going to learn about one such phenomenon, adsorption of gases on solids, in detail in this unit.

1.2 OBJECTIVES

After you have studied this chapter, you should be able to:

1. Define adsorption, adsorbate, adsorbent, enthalpy of adsorption.
2. Differentiate adsorption from absorption and give examples of both.
3. Define adsorption isotherm and enlist different types of adsorption isotherms.
4. Explain Freundlich adsorption isotherm, its equation and validity.
5. Explain Langmuir adsorption theory, Langmuir adsorption isotherm, its equation and validity.
6. Derive Langmuir adsorption isotherm.
7. Explain multilayer adsorption, BET adsorption theory and BET equation.

8. Derive BET equation and determine the surface area of adsorbent using BET equation
9. Interpret different types of experimental adsorption isotherms
10. Explain Gibbs adsorption isotherm
11. Explain the mechanism of heterogeneous catalysis on the basis of adsorption.
12. Solve the numerical problems based on various adsorption isotherms.

1.3 ADSORPTION

1.3.1 Adsorption and absorption:

Let us begin this section with a discussion on a common day today observation. You must have used a piece of chalk to remove spilled ink from a surface. What happens when the cylindrical chalk piece comes in contact with the ink? The ink spontaneously passes to the chalk. If volume of ink is sufficient, the whole surface of chalk appears blue. If you break this chalk, you will notice that inner part of the chalk is still white i.e. ink has not been passed on to the interior of chalk. How can we explain this observation?

The chalk surface has certain residual forces through which it attracts the ink molecules, that’s why ink spontaneously passes to the surface. After attracting the molecules, they are retained at the surface and not passed to the bulk. As a result concentration of ink is more on the surface than bulk. This is an excellent example of adsorption in day today life.

Adsorption, thus, can be defined as a spontaneous phenomenon in which molecular species is attracted by a surface and retained there. As a result concentration of molecular species is higher at the surface than bulk. So adsorption is a *surface phenomenon*. Fig 1.1

Let us discuss the above example again. What happens when spilled ink is cleaned by using a piece of sponge? Sponge also attracts ink but it doesn’t retain ink at the surface, it passes the ink to its bulk. As a result, the piece of sponge becomes blue, out as well as inside. This is due to slightly different phenomenon of absorption.

Absorption is defined as spontaneous attraction of molecular species by a surface and passing it to the bulk phase.

So adsorption is different from absorption because the former is confined to the surface whereas the later is a bulk phenomenon.

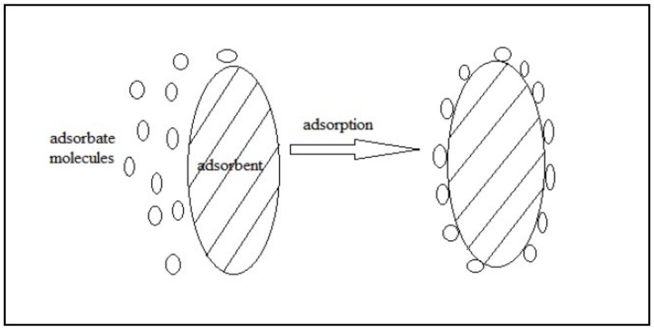


Fig.1.1: Adsorption of gas molecules by solid surface

There are examples where both the phenomena take place when molecular species come in contact with a surface i.e. they are adsorbed as well as absorbed. Mc Bain (1909) proposed the term *sorption* for such phenomenon. In an experiment, Mc Bain put some amount of charcoal in a container of hydrogen. 99% of hydrogen was taken up by charcoal in first two minutes whereas remaining 1% hydrogen was removed slowly by the charcoal. The faster up taking of hydrogen was due to adsorption and slow intake was due to diffusion of hydrogen into the bulk which could be termed as absorption. The whole phenomenon could be called as sorption.

1.3.2 Adsorbate and adsorbent:

There are two phases involved in the adsorption namely; adsorbate and adsorbent.

The bulk phase which provides its surface for adsorption is known as *adsorbent*. A solid or a liquid can act as adsorbent. Similarly, the bulk phase whose molecules are adsorbed on adsorbent is known as *adsorbate*. Gas or liquid can be adsorbate. Solids generally cannot act as adsorbate due to non-mobility of their constituent particles. Adsorptive removal of poisonous arsenic by ferric hydroxide is an important example of adsorption where ferric hydroxide acts as adsorbent and arsenic is adsorbate. It makes ferric hydroxide an antidote for arsenic poisoning. Decolourisation of water using charcoal, refining of sugar syrup by bone charcoal are some more examples of adsorption.

1.3.3 Enthalpy of Adsorption: Adsorption of gases on solids is always associated with change in enthalpy of the system. As we know, free gas molecules have higher randomness (entropy) than the adsorbed gas molecules. Or adsorption results into decrease in entropy of the system. Also, adsorption is a spontaneous behavior.

So, thermodynamically, for adsorption of gases on solid,

$\Delta S = -ve$ (Entropy decreases during adsorption)

Also, $\Delta G = -ve$ (adsorption is spontaneous in nature)

According to Gibbs equation,

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

ΔG can be $-ve$ inspite of $-ve$ value of ΔS only when ΔH has a higher $-ve$ value. This happens in adsorption. This means ΔH has $-ve$ value for adsorption of gases on solids. Or, adsorption is always an exothermic process.

The amount of heat evolved when one mole of gas is adsorbed on solid is generally called as heat of adsorption or enthalpy of adsorption.

Enthalpy of adsorption can be determined from the pressure data of gas adsorbed on solid at different temperatures. As adsorption is an exothermic phenomenon, extent of adsorption decreases with increase in temperature. If one wishes to attain same extent of adsorption at different temperatures, there will be different pressures required to do so. The relationship between these temperatures and pressures comes in the form of Clausius- Claypeyron equation which can be written as,

$$ln\frac{p_2}{p_1} = \frac{\Delta_{ads}H_v}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \qquad (1.1)$$

Where, p_1 and p_2 are the pressures required to achieve same extent of adsorption of a gas at temperatures T_1 and T_2 respectively. R is the universal gas constant and $\Delta_{ads}H$ is the enthalpy of adsorption.

1.4 ADSORPTION OF GASES ON SOLIDS

Adsorption of gases on solids is a common phenomenon. Many solids adsorb gases. In fact, adsorption of gases by charcoal was the observed by Scheeele as early as 1773. Gas masks work on the phenomenon of adsorption of poisonous gases by activated charcoal. Similarly, separation of noble gases by Dewar's method, involves their adsorption by activated coconut charcoal. Adsorption of gases on solids has its advantages, as well as disadvantages. Adsorption of atmospheric moisture by silica makes it imperative to heat the silica crucible to redness and cool it in desiccators so that the moisture gets removed. Otherwise, it may affect the weight of crucible.

1.4.1 Factors affecting adsorption of gases on solids:

Amount of gases adsorbed by solids depends upon a number of factors. These include:

1. Nature of gas
2. Surface area of adsorbent
3. Pressure of gas
4. Temperature

1.4.1.1. Effect of nature of gas: The gases which have higher interactions among the molecules are adsorbed to higher extent on a given surface in comparison to the gases which show ideal behavior. In other words, easily liquefiable gases like SO_2, NH_3, and HCl etc get adsorbed more readily in comparison to gases like H_2, N_2 which have lower critical temperature and get liquefied with difficulty. For example, 1 g of activated charcoal adsorbed 380 mL of SO_2 (critical temperature 157 ^{0}C) and only 4.5 mL of H_2 (critical temperature -200 ^{0}C).

1.4.1.2. Effect of surface area of adsorbent: Adsorption is a surface phenomenon. Extent of adsorption increases with increase in surface area of the adsorbent. It is the reason that adsorbent is usually taken in finely powdered form. Fine grinding leads to increase in total surface area and makes solid a better adsorbent. Heating of an adsorbent to a high temperature of 300-1000 ^{0}C removes the moisture, gases etc. adsorbed on its surface. As a result, it gets higher surface area after such heating. This process of heating an adsorbent to high temperature to get its surface free from adsorbed gases is known as activation of adsorbent.

1.4.1.3. Effect of pressure of a gas: At a given temperature, extent of adsorption of a gas increases with increase in pressure. This can be understood by considering the adsorption of gas on solid as a reversible process as follows:

$$G + S \leftrightarrow GS$$

where, G, S and GS are, respectively, free gas molecules, free site for adsorption on solid and adsorbed gas molecules on solid.

As the adsorption is reversible process, according to Le-Chatelier's principle, an increase in pressure will force the equilibrium in forward direction i.e. adsorption of more gas molecules on solid so as to reduce pressure and nullify the change due to increased pressure.

1.4.1.4. Effect of temperature: Extent of adsorption of gas on solids decreases with increase in temperature. This observation is also in agreement with Le Chatelier's principle. Adsorption is an exothermic phenomenon, i.e. heat is liberated when gases get adsorbed on solid surface. So, an increase in temperature will shift the equilibrium in a direction which will try to nullify the change in temperature i.e. in endothermic direction. In this case, backward direction is endothermic so increase in temperature will lead to desorption of gas from solid surface.

1.4.2 Adsorption Isotherms:

A number of researchers studied the adsorption of gases on solids and analyzed their observations. The plots between amount of gas adsorbed on solids and equilibrium pressure of gas at a given temperature is known as adsorption isotherms. Also, the mathematical relationships given to correlate amount of gas adsorbed on solids and the equilibrium pressure of gas at a given temperature are also termed as adsorption isotherms, though such isotherms are named after the scientists who proposed them.

Experimental results show that amount of gas adsorbed on solid at a given temperature increases with increase in its equilibrium pressure. The shape of a typical experimental adsorption isotherm is shown in Fig1.2

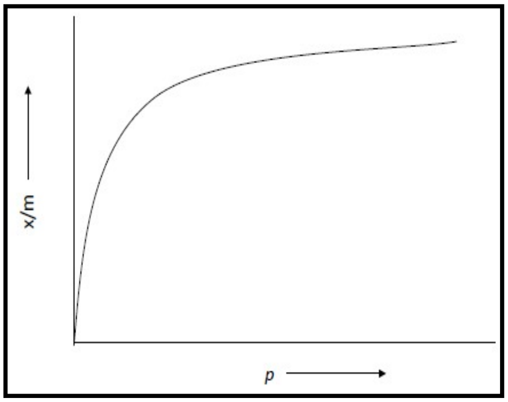


Fig.1.2:Adsorption isotherm of a gas on solid

Though, the shape of adsorption isotherm depends on choice of adsorbate, adsorbent and temperature. We can discern from the figure that the extent of adsorption is high at lower and moderate pressure values. It is reflected in the high slope of the curve in the beginning. As the pressure value increases further, the extent of adsorption increases but not to high extent. At high pressure values, extent of adsorption becomes free of increase in pressure. It is represented by the portion of the curve that becomes parallel to pressure axis.

Dear students, a number of attempts have been made by various scientists to explain the nature and shape of the adsorption isotherms obtained experimentally while studying the adsorption of gases on solids. These explanations are named after the scientists who proposed them. You must have read about Freundlich adsorption isotherm in your graduate course. We are going to learn about these isotherms in detail.

1.4.2.1 Freundlich Adsorption Isotherm: Freundlich adsorption isotherm is an empirical mathematical relationship between amount of gas adsorbed and equilibrium pressure of gas at a given temperature. Mathematically, Freundlich adsorption isotherm can be represented as:

$$\frac{x}{m} = kp^{\frac{1}{n}} \tag{1.2}$$

where, x = mass of the gas adsorbed

m = mass of the adsorbent (g)

p = pressure of gas

k and n = constants which depend on nature of adsorbate and adsorbent

The quantity $\frac{x}{m}$ in the above expression is termed as extent of adsorption or mass of gas adsorbed per unit mass of adsorbent.

As value of n is generally greater than 1 that means amount of gas adsorbed per unit mass of adsorbent doesn't increase as fast as increase in pressure.

Validity of Freundlich Adsorption Isotherm:

Equation 1.2 can be written as:

$$\log\frac{x}{m} = \log k + \frac{1}{n}\log p \tag{1.3}$$

This form of equation shows that a plot of $\log\frac{x}{m}$ is against $\log p$ would be a straight line. The slope of line will be equal to $\frac{1}{n}$ and intercept will be log k as shown in Fig 1.3

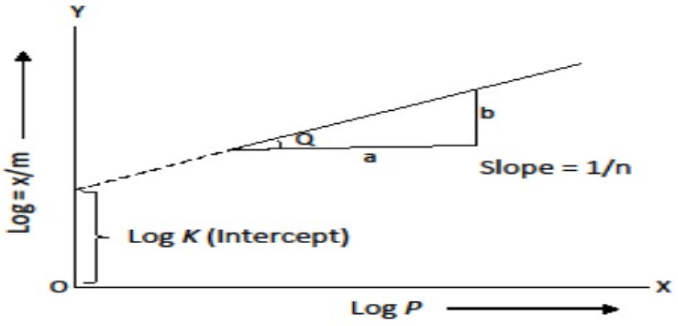


Fig. 1.3 Freundlich adsorption

When the experimental data is plotted according to this equation, straight line is obtained only for low pressure. The equation doesn't hold good for high pressure values. This shows that Freundlich adsorption isotherm can explain adsorption behavior of gases on solids only at low pressure and it is not suitable for high pressure adsorption.

1.4.2.2 Langmuir Adsorption Isotherm:

American Chemist Ervin Langmuir proposed his theory of adsorption in 1916.

1.4.2.2.1 Postulates of Langmuir adsorption theory:

Main assumptions of Langmuir's adsorption theory are:

1. Surface of the solid adsorbent consists of fixed number of adsorption sites.
2. Each site can hold only one gaseous molecule.
3. There is identical heat of adsorption for all the sites.
4. Only one layer of gaseous molecules can be formed on the solid surface i.e. adsorption of gases on solids is monolayer.
5. Gaseous molecules adsorbed on solid surface do not interact with each other.
6. There is a dynamic equilibrium between adsorption and desorption at the surface.

Based on these assumptions, Langmuir derived a simple mathematical expression for adsorption of gases on solids which is known as Langmuir adsorption isotherm. Langmuir adsorption isotherm can be represented as follows:

$$\theta = \frac{Kp}{1+Kp} \qquad (1.4)$$

Where, θ = fraction of surface covered with gas molecules

K = Langmuir's constant

p = Pressure of gas

1.4.2.2.2 Derivation of Langmuir Adsorption Isotherm:

Let, gaseous molecules are free to make contact with a solid surface than, gases molecules are spontaneously get adsorbed by the surface and soon the following equilibrium is established at the surface:

$$G + S \leftrightarrow GS$$

Where, G = free gas molecule

S = vacant adsorption site on solid surface

GS = adsorbed gas molecule

According to law of mass action,

Rate of forward reaction (i.e. adsorption) = $k_f\ [G][S]$ (1.5)

Rate of backward reaction (i.e. desorption) = $k_b\ [GS]$ (1.6)

At equilibrium,

Rate of forward reaction (i.e. adsorption) = Rate of backward reaction (i.e. desorption)

Or, $k_f\ [G][S] = k_b\ [GS]$

Or, $$K = \frac{k_f}{k_b} = \frac{[GS]}{[G][S]} \tag{1.7}$$

Where, K is the equilibrium constant.

The concentration of adsorbed molecules i.e. $[GS]$ is directly proportional to number of occupied adsorption sites or fraction of the surface of adsorbent covered with the gas molecules (θ).

So, from the equation (1.6), it can be written that,

Rate of backward reaction (i.e. desorption) $\propto\ [GS] \propto \theta$

Or, Rate of desorption $\propto \theta$

Or, Rate of desorption $= k_d\theta$ (1.8)

Similarly, the rate of adsorption is directly proportional to the fraction of surface free for adsorption and the concentration of free molecules is directly proportional to the pressure of gas (p).

Or, Rate of adsorption $\propto p\,(1-\theta)$

Or, Rate of adsorption $= k_a\, p\,(1-\theta)$ (1.9)

Since, at equilibrium,

Rate of forward reaction (i.e. adsorption) = Rate of backward reaction (i.e. desorption)

Or, $$k_a\, p\,(1-\theta) = k_d\theta \tag{1.10}$$

Or, $$\theta = \frac{k_a p}{k_d + k_a p} \tag{1.11}$$

Dividing (1.11) by k_d,

$$\theta = \frac{\frac{k_a}{k_d}p}{\frac{k_d}{k_d} + \frac{k_a}{k_d}p}$$

Or,

$$\theta = \frac{\frac{k_a}{k_d}p}{1 + \frac{k_a}{k_d}p}$$

Or,

$$\theta = \frac{Kp}{1+Kp} \qquad (1.12)$$

The equation (1.12) is known as Langmuir adsorption isotherm. In this expression the constant *K* is equilibrium constant, known as *distribution coefficient* which gives idea about distribution of gas molecules between adsorbent surface and free gaseous state.

From equation (1.12), *K* can be written as,

$$K = \left(\frac{\theta}{1-\theta}\right)\frac{1}{p}$$

(1.13)

Higher the value of *K*, higher is the extent of adsorption. Value of *K* depends only on temperature and it decreases with increase in temperature.

1.4.2.2.3 Relation between extent of adsorption of gas on solid and distribution coefficient:

Dear students, we can infer from Langmuir's theory, mass of gas adsorbed on unit mass of adsorbent ($\frac{x}{m}$) is proportional to the fraction of surface free for adsorption (θ)

Or,

$$\frac{x}{m} \propto \theta$$

Or,

$$\frac{x}{m} = k\,\theta \qquad (1.14)$$

Substituting value of θ from (1.12) to (1.14),

$$\frac{x}{m} = k\,\frac{Kp}{1+Kp}$$

(1.15

This expression correlates mass of gas adsorbed on unit mass of adsorbent ($\frac{x}{m}$) with the pressure of gas. It is also used to explain the experimental adsorption isotherm as shown in Fig.1.2, under different conditions of pressure.

(i). At low pressure:

At low pressure, the factor, $Kp \lll 1$,

So, denominator in the expression (1.15) $1 + Kp \approx 1$.

Or, the expression (1.15) becomes

$$\frac{x}{m} = k\,Kp$$

Or,

$$\frac{x}{m} \propto p$$

So, at low pressure, amount of gas adsorbed on solids is directly proportional to the pressure of gas. This statement correlates with the experimental adsorption isotherm.

(ii) At high pressure:

At high pressure, $Kp \ggg 1$,

So, denominator in the expression (1.15), $1 + Kp \approx Kp$.

Or, the expression (1.15) becomes

$$\frac{x}{m} \approx \frac{k\,Kp}{Kp} = \frac{k\,K}{K} = constant$$

Or, at high pressure, amount of gas adsorbed on solids becomes independent of the pressure of gas. This statement also correlates with the experimental adsorption isotherm.

(iii) At moderate pressure range:

As the denominator of expression (1.15) has pressure term p, the denominator increases faster than the numerator with value of p, so the increase in pressure of gas does not increase the amount of gas adsorbed on solid with same rate. Or, extent of adsorption is not directly proportional to increase in pressure of gas at moderate pressure range. It is in agreement of low slope value of experimental adsorption isotherm at intermediate pressure range.

1.4.2.2.4 Limitations of Langmuir Adsorption Isotherm

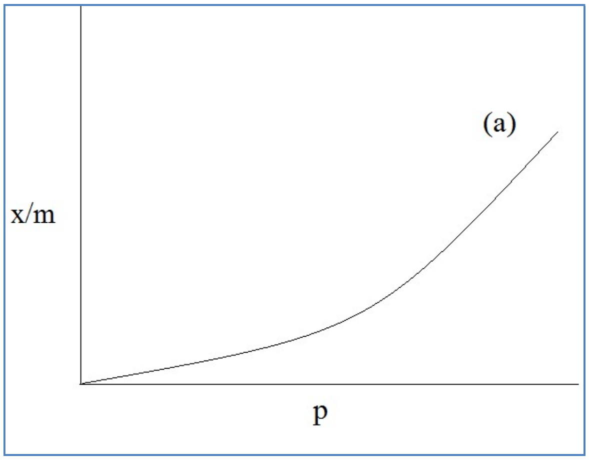
Langmuir adsorption isotherm is based on two important assumptions. These are:

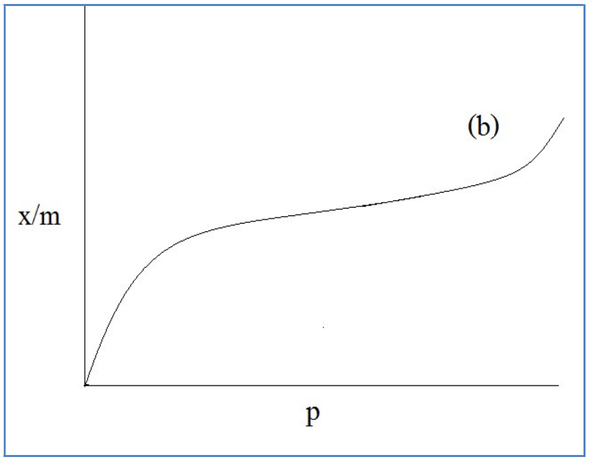
(i) Monolayer adsorption of gases on solids and
(ii) No interactions among the adsorbed gas molecules in the vicinity.

These conditions are expected to be obtained only at low gaseous pressure and moderate high temperature. As under low pressure and moderate temperature, intermolecular interactions among gas molecules are not strong enough to hold each other to form multilayer at the surface and also molecules do not interact with the other molecules adsorbed in vicinity. Under reverse conditions, i.e., if the experimental data is obtained under high pressure and low temperature, it readily deviates from Langmuir adsorption isotherm. Under high pressure, frequency of molecules approaching the surface is quite high and low temperature renders them with low thermal energy which is insufficient to skip from attraction of neighboring molecules. So Langmuir adsorption isotherm is expected to hold good only when adsorption experiments are conducted under low gaseous pressure and at moderate high temperature.

1.4.2.3 BET theory for multilayer adsorption

Owing to assumptions of monolayer formation of gas molecules on solid surfaces and no interactions among the adsorbed molecules, Langmuir adsorption isotherm is unable to explain many of the experimental adsorption isotherms. If the adsorption behavior of gases on solids is studied under high pressure and/or low temperature, experimental adsorption isotherms have shapes different from that of shown in Fig1.4. In fact, following four different types of experimental adsorption isotherms shown in Fig.1.4, are obtained apart form that shown in Fig.1.4. These observations cannot be explained on the basis of Langmuir adsorption isotherm.





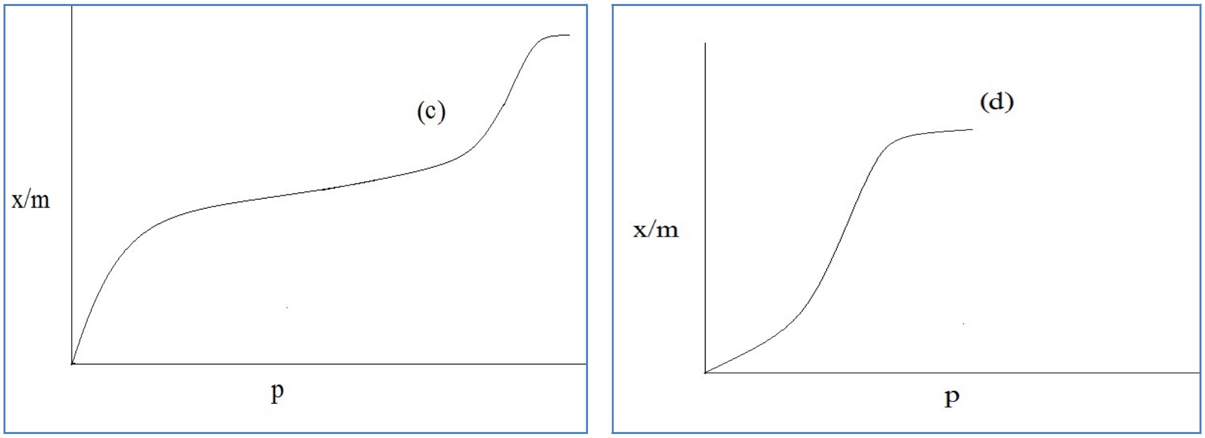


Fig 1.4: Different types of experimental adsorption isotherms

1.4.2.3.1 Postulates of BET Theory:

In 1938, Stephen Brunauer, Paul Emmett and Edward Teller proposed a theory of multilayer adsorption to explain these experimental adsorption isotherms. Their theory was based on the following assumptions:

(i) Gas molecules are reversibly adsorbed at the surface of solids.
(ii) Adsorbed molecules do not interact with the gas molecules adsorbed in vicinity.
(iii) Adsorbed gas molecule can act as a single adsorption site for the molecule of upper layer. Thus, adsorbed molecule interacts with free molecules to hold them leading to formation of second layer of gas molecules on the surface.
(iv) Molecules of second layer attract free molecules to form next layer of adsorbed molecules. As a result of the intermolecular interaction, multilayer formation takes place at the surface of solids. Thus, gas molecules are adsorbed on solid in layers infinitely.
(v) Langmuir theory can be applied to each layer.
(vi) The uppermost layer is in dynamic equilibrium with the gas phase.

Based on these assumptions, Brunauer, Emmett and Teller derived a theoretical relationship between total volume of gas adsorbed and gaseous pressure, known as Brunauer, Emmett and Teller (BET) adsorption isotherm.

1.4.2.3.2 Derivation of BET adsorption isotherm:

If G is a free gas molecule and S is the vacant adsorption site on solid surface then according to BET theory, gas molecules are adsorbed on solid in layers infinitely leading to multilayer formation and following equilibria exist at the surface:

$$G + S \rightleftharpoons GS$$

$$G + GS \rightleftharpoons G_2S$$

$$G + G_2S \rightleftharpoons G_3S$$

$$G + GS \rightleftharpoons G_2S$$

.

$$G + G_{n-1}S \rightleftharpoons G_nS$$

GS and G_2S are respectively, single and two gas molecules adsorbed per vacant site.

Equilibrium constant for each of the above equilibria can be written as:

$$K_1 = \frac{[GS]}{[G][S]} \tag{1.16}$$

$$K_2 = \frac{[G_2S]}{[G][GS]} \tag{1.17}$$

Or,

$$K_3 = \frac{[G_3S]}{[G][G_2S]} \tag{1.18}$$

…………………..etc

Since, $[G] \propto p$ where p is the pressure of the gas.

And, $[S] \propto \theta$ where, θ is the fraction surface free for adsorption.

Also, $[GS] \propto \theta_1$, where θ_1 is the fraction of surface covered with single molecule.

Similarly, $[G_2S] \propto \theta_2$, where θ_2 is the fraction of surface covered with two molecules.

These relations can be used to rewrite expressions for equilibrium constants of (1.16), (1.17) and (1.18) as,

$$K_1 = \frac{\theta_1}{p\theta} \tag{1.19}$$

$$K_2 = \frac{\theta_2}{p\theta_1} \tag{1.20}$$

$$K_3 = \frac{\theta_3}{p\theta_2}$$

………………………… and so on.

As the interactions between gas molecules and surface are quite strong in comparison to gas molecules of different layers so equilibrium constant (K_1) for the first layer will have much higher value than the equilibrium constants of the subsequent layers. In other words, difference in K_1 and other equilibrium constants will be more where as difference in the values of subsequent equilibrium constants would be very small.

Or, $K_2 \approx K_3 \approx K_4 \approx \cdots K_m$

where, K_m is the equilibrium constant of the equilibrium between adsorbed molecules and gaseous molecules. This equilibrium at the outermost layer can be assumed as equilibrium between saturated vapor and its liquid phase.

Or, Vapor $\rightleftharpoons$ Liquid

So,

$$K_m = \frac{1}{p_0} \tag{1.21}$$

Since, $K_2 \approx K_3 \approx K_4 \approx \cdots K_m$

So, K_1, K_2 and other equilibrium constants can be written as,

$$K_1 = \frac{\theta_1}{p\theta}$$

$$K_2 \approx K_m = \frac{\theta_2}{p\theta_1}$$

$$K_3 \approx K_m = \frac{\theta_3}{p\theta_2}$$

On rearrangement of these equations,

$$\theta_1 = K_1 p\theta \tag{1.22}$$

$$\theta_2 = K_m p\theta_1 \tag{1.23}$$

Substituting the value of K_m and θ_1 in the above equation,

$$\theta_2 = \frac{p}{p_0} K_1 p\theta \tag{1.24}$$

Similarly, values of θ_2, θ_3 etc can be written in terms of p and p_0.

Like,

$$\theta_3 = \left(\frac{p}{p_0}\right)^2 K_1 p\theta \tag{1.25}$$

When the whole surface of the solid adsorbent is covered with the gas molecules, then fraction of total covered surface can be given by,

$$\theta_{total} = \theta + \theta_1 + \theta_2 + \theta_3 + \cdots = 1 \tag{1.26}$$

Substituting values of $\theta_1, \theta_2, \theta_3$ etc from (1.22), (1.24), (1.25) in (1.26):

$$\theta_{total} = \theta + K_1 p\theta + \frac{p}{p_0} K_1 p\theta + \left(\frac{p}{p_0}\right)^2 K_1 p\theta + \cdots = 1$$

Or,

$$\theta_{total} = \theta\left[1 + K_1 p\left\{1 + \left(\frac{p}{p_0}\right) + \left(\frac{p}{p_0}\right)^2 + \cdots\right\}\right] = 1 \tag{1.27}$$

When $\frac{p}{p_0} \ll 1$, the expression within the curly bracket of equation (1.27) can be written as

$$1 + \left(\frac{p}{p_0}\right) + \left(\frac{p}{p_0}\right)^2 + \cdots \approx \frac{1}{1-\frac{p}{p_0}} \text{ Using Mclaurin's expression}$$

Substituting it in (1.27),

$$\theta_{total} = \theta\left[1 + K_1 p\left\{\frac{1}{1 - \frac{p}{p_0}}\right\}\right] = 1$$

Or,

$$\theta_{total} = \theta\left[1 + \frac{K_1 p}{1 - \frac{p}{p_0}}\right] = 1$$

Or,

$$\theta = \frac{1}{\left[1 + \frac{K_1 p}{1 - \frac{p}{p_0}}\right]}$$

Or,

$$\theta = \frac{1 - \frac{p}{p_0}}{\left[1 + K_1 p - \frac{p}{p_0}\right]} \tag{1.28}$$

Now let us discuss about the volume of gas adsorbed at different layers.

If v_m is the volume of gas needed to completely cover the solid surface to form a single layer, then,

Volume of gas adsorbed to cover θ_1 fraction of surface to form a monolayer = $\theta_1 v_m$

Volume of gas adsorbed to cover θ_2 fraction to form a belayed = 2 $\theta_2 v_m$

Also, Volume of gas adsorbed to cover θ_3 fraction to form a trilateral = 3 $\theta_3 v_m$

……. And so on.

So, total volume of gas adsorbed on solid surface to form multilayer

$$v_{total} = \theta_1 v_m + 2\,\theta_2 v_m + 3\,\theta_3 v_m + \cdots$$

Or,

$$v_{total} = v_m(\theta_1 + 2\,\theta_2 + 3\,\theta_3 + \cdots) \tag{1.29}$$

Substituting values of θ_1, θ_2, θ_3 etc from(1.22), (1.24), (1.25) in (1.29):

$$v_{total} = v_m\left(K_1 p\theta + 2\,\frac{p}{p_0} K_1 p\theta + 3\left(\frac{p}{p_0}\right)^2 K_1 p\theta + \cdots\right)$$

Or,

$$v_{total} = v_m K_1 p\theta \left(1 + 2\,\frac{p}{p_0} + 3\left(\frac{p}{p_0}\right)^2 + \ldots\right) \tag{1.30}$$

Since, the series,

$$1 + 2\frac{p}{p_0} + 3\left(\frac{p}{p_0}\right)^2 + \ \ldots \approx \frac{1}{\left(1 - \frac{p}{p_0}\right)^2}$$

So, substituting this value in (1.30),

$$v_{total} = \frac{v_m K_1 p \theta}{\left(1 - \frac{p}{p_0}\right)^2}$$

(1.31)

Substituting the value of θ from (1.28) in (1.31),

$$v_{total} = \frac{v_m k_1 p}{(1 - \frac{p}{p_0})^2} \cdot \frac{\left(1 - \frac{p}{p_0}\right)}{1 + k_1 p - \frac{p}{p_0}}$$

$$v_{total} = \frac{v_m K_1 p}{\left(\mathbf{1} - \frac{p}{p_0}\right)\left(1 + K_1 p - \frac{p}{p_0}\right)}$$

(1.32)

Since,

$$p = \frac{1}{K_m} \times \left(\frac{p}{p_0}\right)$$

(1.33)

Now, substituting the value from (1.33) to (1.32),

$$v_{total} = \frac{v_m K_1 \frac{1}{K_m} \times \left(\frac{p}{p_0}\right)}{\left(1 - \frac{p}{p_0}\right)\left(1 + K_1 \frac{1}{K_m} \times \left(\frac{p}{p_0}\right) - \left(\frac{p}{p_0}\right)\right)}$$

Or,

$$v_{total} = \frac{v_m \left(\frac{K_1}{K_m}\right) \times \left(\frac{p}{p_0}\right)}{\left(1 - \frac{p}{p_0}\right)\left[1 + \left(\frac{K_1}{K_m}\right) \times \left(\frac{p}{p_0}\right) - \left(\frac{p}{p_0}\right)\right]}$$

(1.34)

If, we write,

$$\frac{K_1}{K_m} = K$$

Then (1.34) becomes,

$$\boxed{v_{total} = \frac{v_m K\left(\frac{p}{p_0}\right)}{\left(1 - \frac{p}{p_0}\right)\left[1 + K\left(\frac{p}{p_0}\right) - \left(\frac{p}{p_0}\right)\right]}} \qquad (1.35)$$

The expression (1.35) is known as Brunauer, Emmett and Teller (BET) equation which is applicable to multilayer adsorption of gas molecules on solid surfaces.

1.4.2.3.3 Other form of BET equation:

On cross multiplication of (1.35), we get,

$$v_{total}\left(1 - \frac{p}{p_0}\right) = \frac{v_m K\left(\frac{p}{p_0}\right)}{\left[1 + K\left(\frac{p}{p_0}\right) - \left(\frac{p}{p_0}\right)\right]}$$

Or,

$$v_{total}\left(\frac{p_0 - p}{p_0}\right) = \frac{v_m K\left(\frac{p}{p_0}\right)}{\left[1 + K\left(\frac{p}{p_0}\right) - \left(\frac{p}{p_0}\right)\right]}$$

On taking reciprocal,

$$\frac{1}{v_{total}} \times \left(\frac{p_0}{p_0 - p}\right) = \frac{\left[1 + K\left(\frac{p}{p_0}\right) - \left(\frac{p}{p_0}\right)\right]}{v_m K\left(\frac{p}{p_0}\right)}$$

$$\frac{1}{v_{total}} \times \left(\frac{p_0}{p_0 - p}\right) \times \left(\frac{p}{p_0}\right) = \frac{\left[1 + K\left(\frac{p}{p_0}\right) - \left(\frac{p}{p_0}\right)\right]}{v_m K}$$

$$\frac{1}{v_{total}} \times \left(\frac{p}{p_0 - p}\right) = \frac{1}{v_m K} + \frac{K\left(\frac{p}{p_0}\right) - \left(\frac{p}{p_0}\right)}{v_m K}$$

$$\frac{p}{v_{total}(p_0 - p)} = \frac{1}{v_m K} + \frac{(K - 1)\left(\frac{p}{p_0}\right)}{v_m K}$$

$$\boxed{\frac{p}{v_{total}(p_0-p)}=\frac{1}{v_mK}+\frac{(K-1)}{v_mK}\left(\frac{p}{p_0}\right)} \tag{1.36}$$

The expression (1.36) is other form of BET equation. This form is helpful in determining the values of v_m and K. As the equation shows, a graph between $\frac{p}{v_{total}(p_0-p)}$ and $\left(\frac{p}{p_0}\right)$ should be a straight line with positive slope $\frac{(K-1)}{v_mK}$ and intercept $\frac{1}{v_mK}$. In actual experiments, values of slope and intercept help to calculate the values of these constantsv_m and K.

1.4.2.3.4 Determination of surface area of adsorbent using BET equation:

BET equation is highly useful in determination of surface area of the adsorbents. It is based on the assumption that when the molecules of a gas are adsorbed on the solid surface to from a monolayer, they occupy the whole surface without leaving any void between them. Its principle can be understood as follows:

Let, v_m is the volume in liter (at STP), of a nonreactive gas viz. N_2, to from a monolayer on the surface of solid.

Then, according to Gas laws, volume of 1 mol of an ideal gas at STP = 22.414 L

Number of molecules in 22.414 L of volume = $N_A = 6.022 \times 10^{23}$

So number of molecules of gas in volume v_m

$$=\frac{6.022\times10^{23}}{22.414}\times v_m \tag{1.37}$$

If cross sectional area of one molecule of gas is known, total surface area occupied by $\frac{6.022\times10^{23}}{22.414}\times v_m$ molecules can be determined.

For a solidified gas (adsorbate), volume of one molecule is determined by density formula as follows:

If M is the molar mass of gas and ρ is the density in solid state, then,

$$Density(\rho)=\frac{Molar\ mass}{Molar\ Volume}=\frac{M}{v\times N_A}$$

Where, v is the volume of one molecule.

So,

$$v = \frac{M}{\rho \times N_A} \qquad (1.38)$$

Since molecules are considered to be spherical, the volume of one molecule can be given as,

$$v = \frac{4\pi}{3} r^3 \qquad (1.39)$$

Equating (1.38) and (1.39), we get,

$$\frac{4\pi}{3} r^3 = \frac{M}{\rho \times N_A}$$

Or,

$$r = \left(\frac{3}{4\pi}\frac{M}{\rho \times N_A}\right)^{\frac{1}{3}}$$

And cross sectional area of a molecule,

$$A = \pi r^2 = \pi \left(\frac{3}{4\pi}\frac{M}{\rho \times N_A}\right)^{\frac{2}{3}} \qquad (1.40)$$

The equation gives cross sectional area of one molecule and substituting its value in (1.37) one can get the surface area of the adsorbent,

$$\begin{aligned}\text{Surface area of the adsorbent} &= \text{Number of molecules adsorbed to form a monolayer on whole surface} \\ &\times \text{cross sectional area of a molecule}\end{aligned}$$

$$\text{Surface area of the adsorbent} = \frac{6.022 \times 10^{23}}{22.414} \times v_m \times \pi \left(\frac{3}{4\pi}\frac{M}{\rho \times N_A}\right)^{\frac{2}{3}} \qquad (1.41)$$

This equation is theoretically used to determine surface area of the adsorbent.

v_m is determined from the equation (1.36) and its substitution in (1.41), along with density and molar mass of the gas used, gives surface area of the adsorbent.

1.4.2.3.5 Explanation of different types of experimental adsorption isotherms:

In the adsorption of gas molecules on solid surface, if $\frac{p}{p_0} \ll 1$ and $K \gg 1$ Then, BET equation is similar to Langmuir adsorption isotherm, which represents monolayer adsorption of gases on solids. Under these conditions, graph has the shape that is shown in Fig1.2.

If $K \lll\ll 1$ then, the adsorption graph in such cases has no part to show monolayer adsorption. It shows that in such cases, multilayer adsorption takes place from the start of adsorption of gas on solid. The graph is of the shape shown in Fig. 1.4(a).

On the other hand, If $K \ggg\gg 1$ then, graph like the one in Fig. 1.4(b), has intermediate flat portion that represents the monolayer adsorption which turns into multilayer with change in extent of adsorption.

In some experimental adsorptions, gases are adsorbed on solids forming monolayer like, but the adsorption attains a limiting value much before saturation vapor pressure. As a result, graph differs from that of in Fig. 1.4(b) due to formation of multilayer. Such graph has a shape as shown Fig. 1.4(c).

At times, adsorption isotherms represent a combination of Fig. 1.4(a) and 1.4(c). This graph is shown in Fig. 1.4(d). Such observation is explained on the basis of saturation of solid surface much before saturation vapor pressure.

1.4.2.4 Gibbs adsorption Isotherm:

Dear students, let us recall the definition of solution which states that a solution is a homogeneous mixture of two or more substances. A solution has two components, namely; solute and solvent. According to this definition of solution, the concentration of solute in a solution is same throughout. But it is not so always. In practice, the concentration of a solute at surface may be different from that in the bulk of the solution. J. Willard Gibbs, in 1878, theoretically showed that surface tension plays great role in deciding the relative concentration of solute at the surface and bulk of a solution. According to him, the solutes which lower the surface tension of the solvent get concentrated more at the surface than bulk and the solutes which raise the surface tension of the solvent become concentrated in the bulk than the surface of the solution. For example, detergents are the chemicals which lower the surface tension of water. According to Gibbs, when dissolved in water, detergents get concentrated more at surface than bulk of the solution. On the other hand, inorganic salts which increase the surface tension of ware get concentrated in the bulk of solution.

Gibbs derived a mathematical expression, to correlate the changes in concentration of a component of a solution in contact with the surface of solution with the change in the surface tension. This expression is known as Gibbs adsorption equation. It is represented as

$$-S = \frac{c}{RT}\frac{d\gamma}{dc} \tag{1.42}$$

where, S is the excess of solute present at the surface

c is the concentration solute in the bulk of the solution

γ is the surface tension

R is the universal gas constant

T is the absolute temperature

$\frac{d\gamma}{dc}$ is the change in surface tension with concentration of solution.

The negative sign in this equation indicates if there is actual excess of or deficit of solute on the surface.

The equation (1.42), also called as Gibbs adsorption isotherm, is applicable to the multicomponent solutions and it correlates the adsorption and change in surface tension of a solvent on addition of a solute.

The value of $\frac{d\gamma}{dc}$ can be obtained by plotting the value of surface tension (γ) against the concentration (c) of the solution. The slope of this curve gives the value of $\frac{d\gamma}{dc}$ i.e. variation of surface tension of solution with change in concentration.

Gibbs adsorption isotherm was first derived for the solution of gases in the liquids. According to it, a gas that increases the surface tension of a liquid gets concentrated more in the bulk than surface and vice versa. Gibbs adsorption isotherm for gases can be written like (1.42) just by replacing concentration (c) of solution by partial pressure of gas (p).

Gibbs adsorption isotherm was derived independently by J. J. Thomson in 1888 and its direct experimental proof was obtained by McBain and Swain who studied the solutions of phenol and hydrocinnamic acid and NaCl. They used rapidly moving microtome blade to remove the surface layer of the solution and determined the difference in solute concentration in the surface and bulk of the solution. The experimental findings were in agreement with Gibbs adsorption isotherm.

1.5 CATALYTIC ACTIVITY AT SURFACES

Dear students, you must be aware of two types of catalytic processes, namely; homogeneous and heterogeneous catalysis. Catalysis in which catalyst is in the same phase as that of the reactant/s is known as homogeneous catalysis whereas a catalytic process in which catalyst and reactants are in different phases is known as heterogeneous catalysis.

Most of the cases of heterogeneous catalytic reactions comprise of the reactions where solid surfaces act as catalyst. Uses of solid Fe in Haber's process, Ni in hydrogenation, Pt/Rh in Ostwald's process, V_2O_5 in Contact process are some of the popular examples of heterogeneous catalysis.

The most satisfactory explanation of the catalytic activity of solids is on the basis of adsorption of the reactant molecules on solid surfaces. According to this theory heterogeneous catalysis takes place in the following steps:

(i) Diffusion of reactant molecules (mostly gaseous) to the catalyst surface:

Heterogeneous catalysis begins only when reactant molecules reach the catalyst surface. Reactant molecules must have sufficient energy to diffuse and reach the solid catalyst surface for further catalysis. This is easy when reactants are either gaseous or liquids.

(ii) Adsorption of diffused reactant molecules on the solid surface: Solid catalyst surface has vacant active sites which can hold the reactant molecules with the residual forces. The enthalpy of such adsorption shows that the interaction between reactant molecules and surface is sufficiently high to be termed as chemisorption.

(iii) Interaction of molecules adsorbed in the vicinity to form product: The chemisorption of reactant molecules on catalyst surface result into weakening of already existing bonds in the reactant molecule. It activates the molecule which can interact with the activated molecules adsorbed in the vicinity resulting into formation of product. Heterogeneous catalysis, thus, works by decreasing the activation energy of reactant molecules.

(iv) Desorption of product molecules: Product molecules formed at the solid catalyst' surface are desorbed and are free to diffuse from the surface. Thereby, they vacate the active sites to adsorb other reactant molecules.

(v) Diffusion of product molecules from the surface: The product molecules diffuse from the catalyst surface which is engaged by the new diffusing molecules of the reactant/s.

Heterogeneous catalysis thus, is a surface phenomenon where surface area plays the crucial role and heterogeneous catalysts with large surface area are highly efficient. Therefore, heterogeneous catalysts are used in powdered forms which have larger surface area.

This theory is also able to explain the fact that once the whole surface area of the catalyst is covered with the reactant molecules, the rate of reaction becomes independent of the concentration of the reactants.

Heterogeneous catalysis thus, can be termed as a manifestation of gaseous molecules on the solid catalyst surfaces which result into their activation and lowering of activation energy.

1.6 SUMMARY

Adsorption is a surface phenomenon which is associated with evolution of heat. Adsorption of gases on solids at a given temperature depends on the equilibrium pressure of the gas. This graphical representation is known as adsorption isotherm. Several expressions have been given to explain the experimental adsorption isotherms. These have been named after the scientists who proposed them. Freundlich, Langmuir and BET adsorption isotherms are some of them. Each of them has their own limitation. Langmuir adsorption theory is based on monolayer adsorption of gas molecules on solid surfaces. It envisages no intermolecular interactions among the adsorbed molecules so it is experimentally obeyed only under low pressure and moderated temperature. BET on the other hand, tells about the multilayer adsorption of gases on solids. The BET equation can be used to determine the surface area of the adsorbent. Gibbs adsorption isotherm is also one important concept in surface chemistry which underlines the role of surface tension in the distribution of dissolved molecules at surface and in the bulk. Concepts of adsorption are helpful to understand the surface activity of the heterogeneous catalysts which catalyze by adsorbing the reacting species by chemisorption, thereby decreasing the activation energy. Adsorption phenomenon is also able to explain the fact that once the whole surface area of the catalyst is covered with the reactant molecules, the rate of reaction becomes independent of the concentration of the reactants.

1.7 TERMINAL QUESTIONS

1. How does adsorption differ from absorption?

2. Define the following terms: (i) adsorbent (ii) adsorbate (iii) sorption (iv) Enthalpy of adsorption

3. Prove that adsorption is always exothermic in nature.

4. What is Freundlich adsorption isotherm? What are its limitations?

5. What are the main postulates of Langmuir adsorption isotherm?

6. Whys is Langmuir adsorption isotherm obeyed only under low pressure and moderate temperature?

7. Derive Langmuir adsorption isotherm.

8. How does BET theory differ from that of Langmuir? How does it overcome limitations of Langmuir adsorption isotherm?

9. Drive BET equation mathematically.

10. Explain the principle of determination of surface area of adsorbent using BET equation.

11. What is Gibbs equation? How is change in surface tension of solution with concentration $(\frac{d\gamma}{dc})$ is determined experimentally?

12. What is the mechanism of heterogeneous catalysis? Explain with the help of suitable example.

1.8 REFERENCES

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UNIT 2: POLYMER CHEMISTRY

Contents:

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2.2 Objectives

2.3 Macromolecules

2.4 Polymers and their properties

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2.6 Configuration of polymers

2.7 Synthesis of some representative polymers

2.8 Applications of polymers

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2.12 Applications of liquid crystals

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2.15 Answers (MCQs)

2.16 References

2.1 INTRODUCTION:

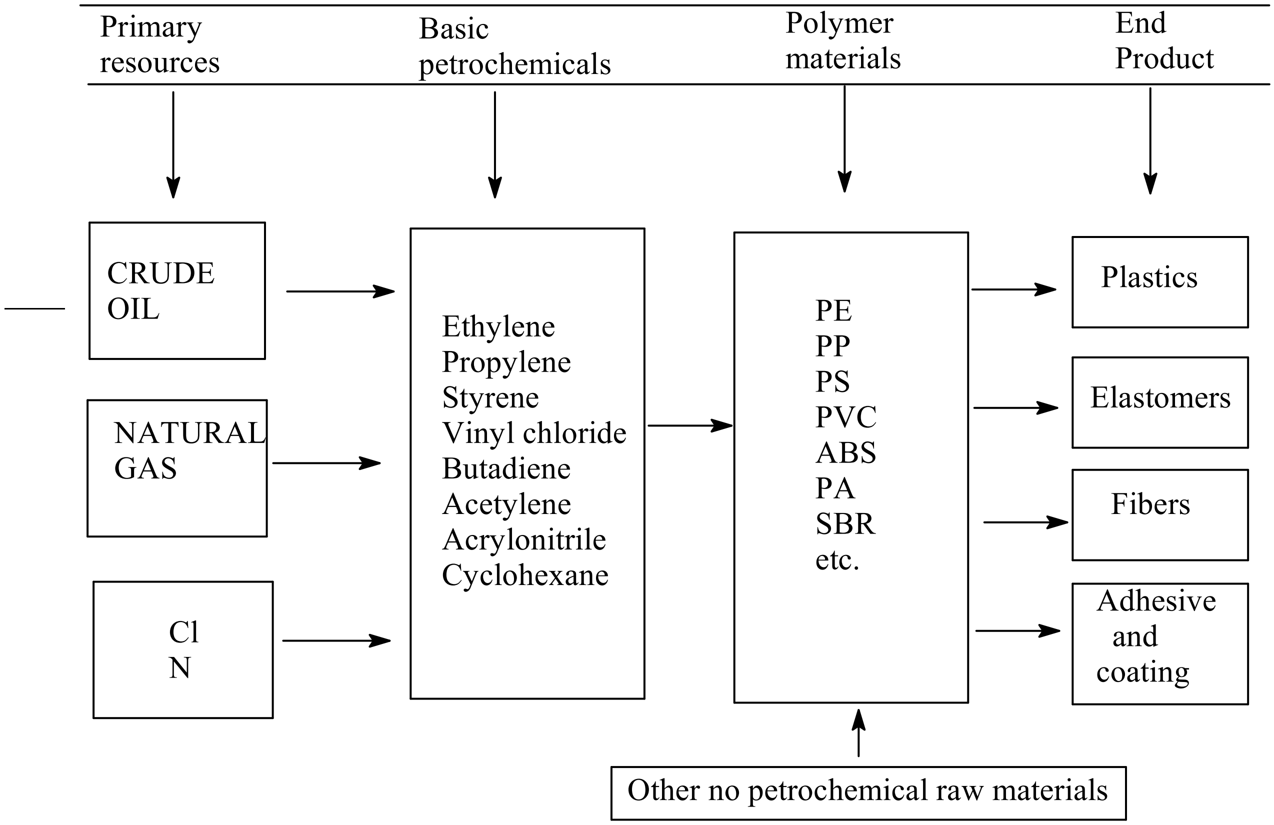
In present sinario polymers are an indispensible and integral part of human life style. The polymers have large diverse structural and applications which may ranges from simple domestic articles to sophisticated scientific and medical instruments. The polymeric material have incroached into about all the applications viz; construction, transportation, agriculture, industries, education i.e. almost in all the field of civilization. The polymeric materials are generally used as fibers, rubbers, plastics, adhesives, paints, conductors etc.

The formation, transformation, decomposition of biopolymers like proteins, polysaccharides (carbohydrates), polynucleotides (DNA, RNA, the genetic material) are related to the exsistance of life. In view of the importance of polymers right from origion of life till modern word it becomes very essential to understand the polymeric material properly.The polymers are obtained from petroleum or natural gas. The raw material from which polymers are obtained sumerized as follow Table 1:

2.2 OBJECTIVES:

The objectives of this unit are: To study polymers and their general applications and classification, to study the configuration of polymers, to study liquid crystals and their applications. To get aware about molecular mass, number and mass average molecular mass of polymers, to study molecular mass determination of polymers using osmometry, viscometry, diffusion and light scattering methods.

Table 1: Production of polymer- based products from raw materials



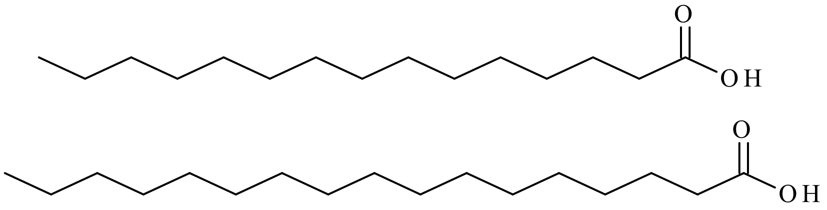
2.3 MACROMOLECULES:

Small molecules contain at least two, but less than ten atoms. Common examples of large molecules are the chlorophylls, whose molar mass is still less than 1000. Macromolecules have molar masses in excess of 10^3 or 10^4; there is no common definition. Naturally occurring acromolecules are cellulose, proteins and polypeptides (e.g. enzymes), and olynucleotides (e.g. DNA, deoxyribo nucleic acid). Artificial macromolecules include polymers such as Nylon, polyethylene, polystyrene or Teflon, which are made by joining smaller molecular groups, the monomers. Macromolecules can be also formed from smaller molecular groups by intermolecular forces as molecular clusters or inclusion compounds. The special supermolecules in biological systems with a specific function are called molecular functional units.

There are 4 basic types of macromolecules. They are:

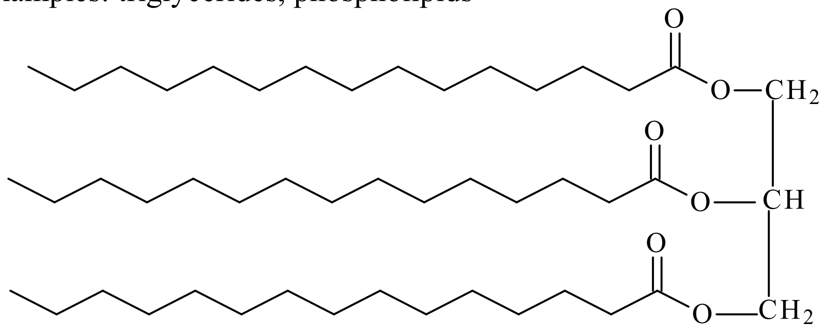
1. Lipids
2. Proteins
3. Carbohydrates
4. Nucleic Acids

   Lipids are made up of.Monomer (basic unit): fatty acids

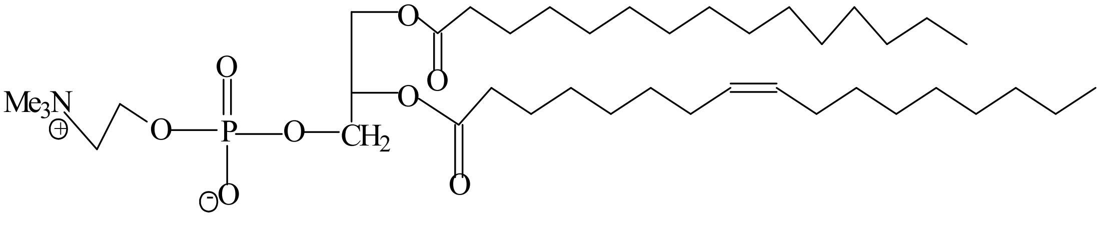


Polymer (chain of units): lipids

Specific examples: triglycerides, phospholipids



triglyceride

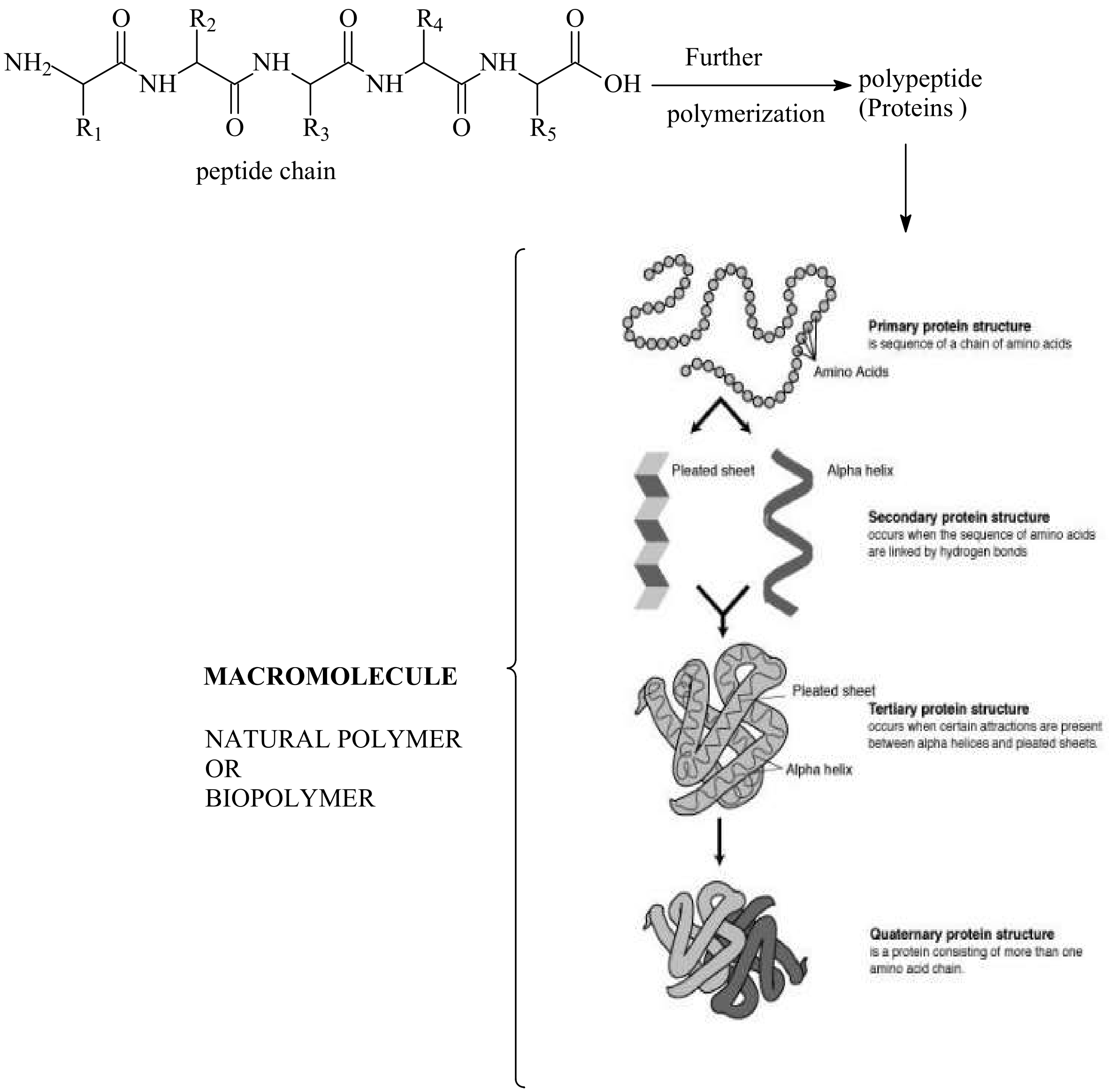


phospholipid

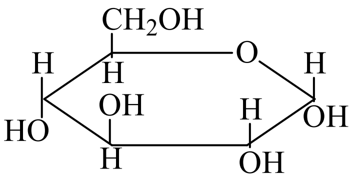
Proteins are made up of Monomer (basic unit): amino acids

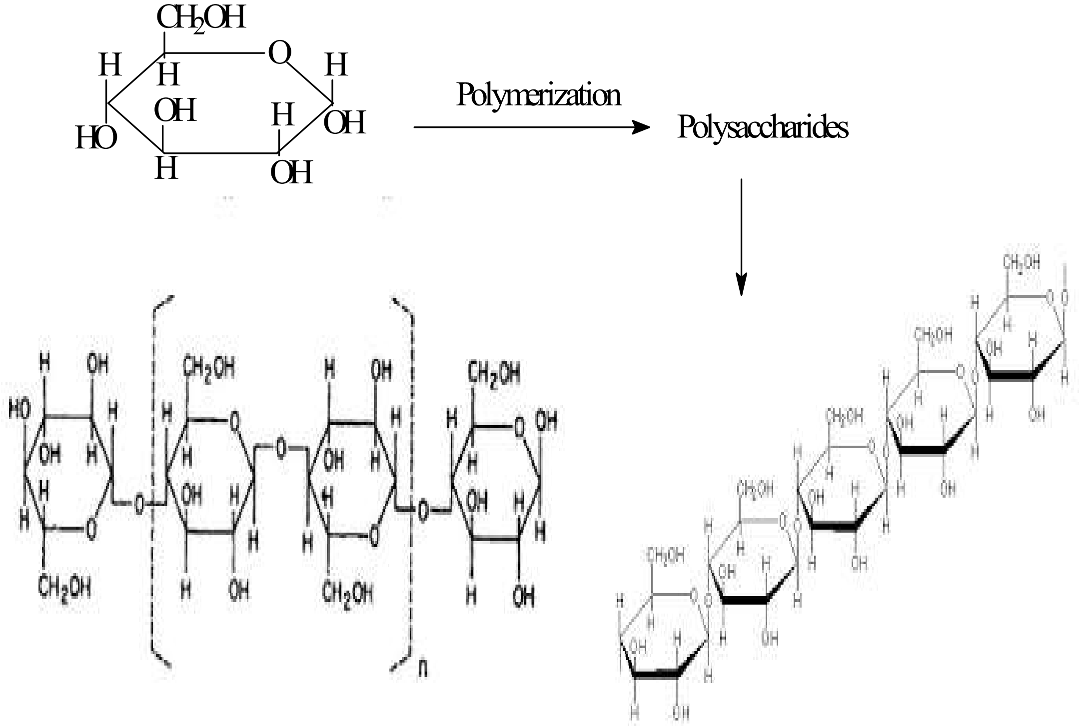
Polymer (chain of units):

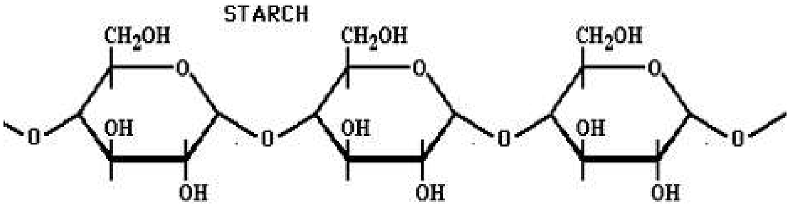
Protein More specifically polypeptides

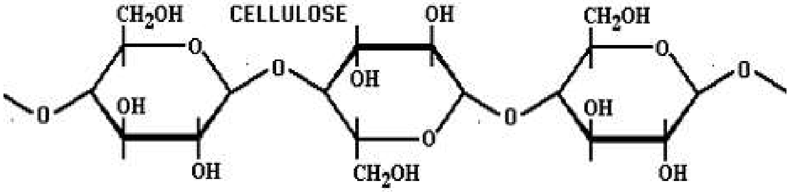


Carbohydrates are made up of Monomer (basic unit): simple sugars (or monosaccharides)

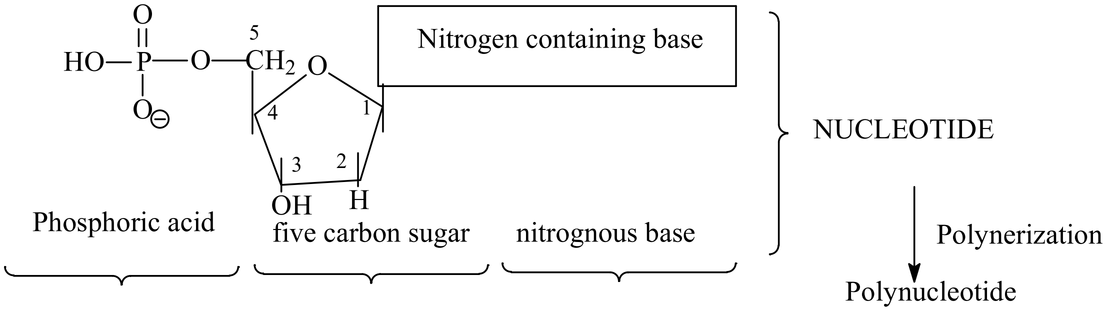


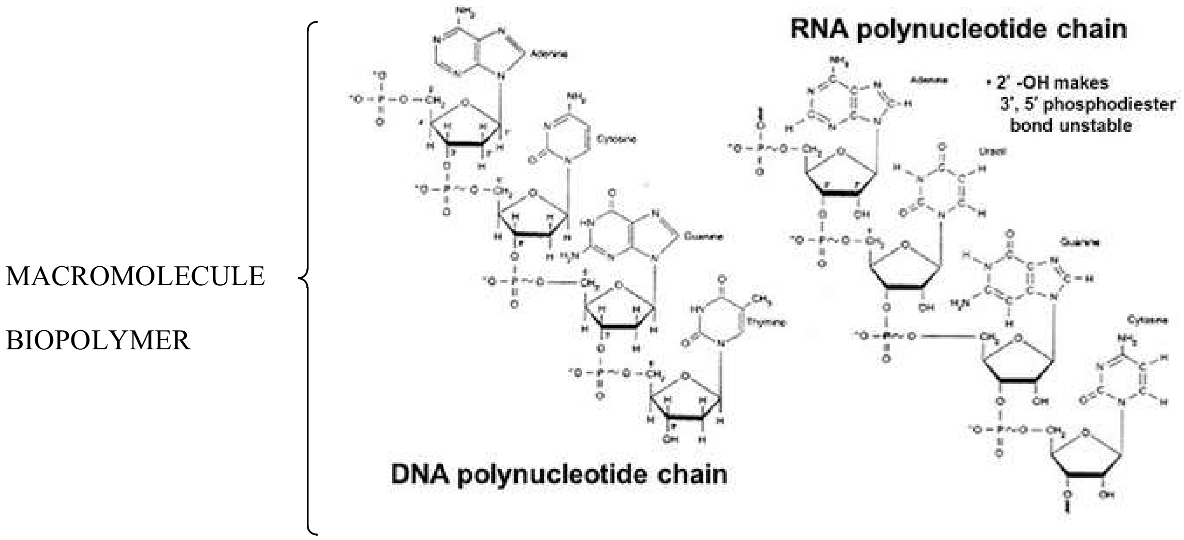






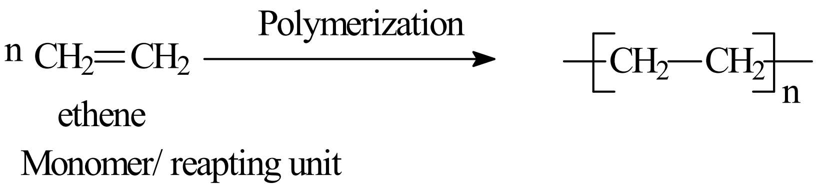
Nucleic Acids are made up of Monomers (basic unit): nucleotides





2.4 *POLYMERS AND THEIR PROPERTIES*:

A polymeric material is a large molecule, or macromolecule, composed of millions of repeated linked units, each a relatively light and simple molecule. Due to their large size they are sometimes called as macromolecules.



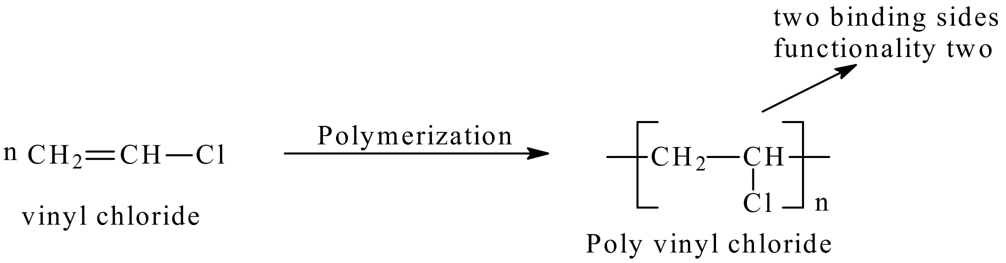
$$n\,CH_2{=}CH_2 \xrightarrow{\text{Polymerization}} -\!\!\left[CH_2-CH_2\right]_n\!\!-$$

n = degree of polymerization it can be 10^4 or more

Minimum value for degree of polymerization is 100

The chemical process involved in the formation of polymer is known as polymerization and the basic building block is called momoner or repearting unit. The number of mobnomeric units contained in apolymer is known as degree of polymerization viz;-

Functionality in monomers: Functionality in monomers reveals number of sites through which it can bind with other monomer to form polymers, viz in CH_2=CHCl the functionality of the monomer ie two as tits binds from two sides as follow :



$$n\,CH_2{=}CH-Cl \xrightarrow{\text{Polymerization}} -\!\!\left[CH_2-\underset{\displaystyle Cl}{\underset{|}{CH}}\right]_n\!\!-$$

The structure of the polymer largely depends upon the functionality of monomers viz:-

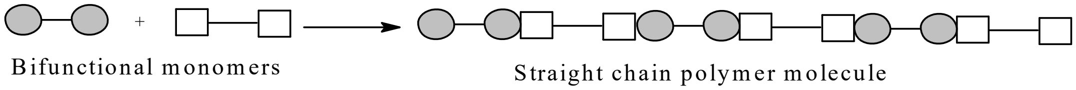
1. If the functionality is two, linear or straight- chain polymer molecule is formed. Examples are all vinyl polymers adipic acid, hexamethylene diamine, terephthalic acid, ethylene glycol, amino acids etc.

2. If the functionality is three, three dimensional network polymer molecules are formed. Examples are Phenol, melamine

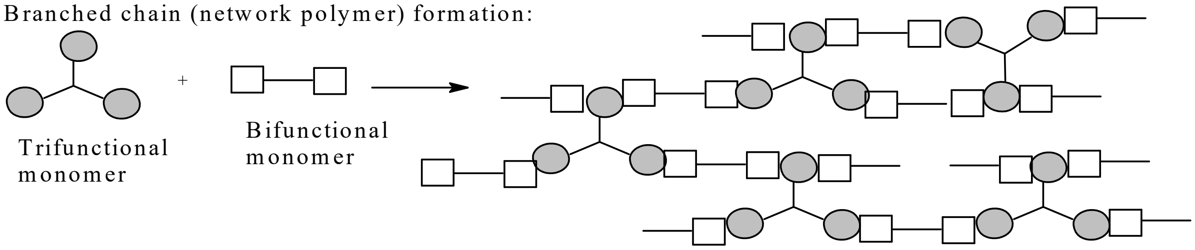
3. If a trifunctional monomer is mixed in small amounts with a bifunctional monomer, abranched chain polymer is formed

4. If a bifunctional monomer is mixed in small amounts with a trifunctional monomer, a three-dimensional network polymer is formed.

Linear chain formation



Branched chain (network polymer) formation:



Branched or cross linked polymer

Properties of polymers: The majority of manufactured polymers are thermoplastic, meaning that once the polymer is formed it can be heated and reformed over and over again. This property allows for easy processing and facilitates recycling. The other group, the thermosets, cannot be remelted. Once these polymers are formed, reheating will cause the material to ultimately degrade, but not melt.

Every polymer has very distinct property, but most polymers have the following general attributes.

1. **Polymers can be very resistant to chemicals.** Consider all the cleaning fluids in your home that are packaged in plastic. Reading the warning labels that describe what happens when the chemical comes in contact with skin or eyes or is ingested will emphasize the need for chemical resistance in the plastic packaging. While solvents easily dissolve some plastics, other plastics provide safe, non-breakable packages for aggressive solvents.

2. **Polymers can be both thermal and electrical insulators.** A walk through your house will reinforce this concept, as you consider all the appliances, cords, electrical outlets and wiring that are made or covered with polymeric materials. Thermal resistance is evident in the kitchen with pot and pan handles made of polymers, the coffee pot handles, the foam core of refrigerators and freezers, insulated cups, coolers, and microwave cookware. The thermal underwear that many skiers wear is made of polypropylene and the fiberfill in winter jackets is acrylic and polyester.

3. **Generally, polymers are very light in weight with significant degrees of strength.** Consider the range of applications, from toys to the frame structure of space stations, or from delicate nylon fiber in pantyhose to Kevlar, which is used in bulletproof vests. Some polymers float in water while others sink. But, compared to the density of stone, concrete, steel, copper, or aluminum, all plastics are lightweight materials.

4. **Polymers can be processed in various ways.** Extrusion produces thin fibers or heavy pipes or films or food bottles. Injection molding can produce very intricate parts or large car body panels. Plastics can be molded into drums or be mixed with solvents to become adhesives or paints. Elastomers and some plastics stretch and are very flexible. Some plastics are stretched in processing to hold their shape, such as soft drink bottles. Other polymers can be foamed like polystyrene, polyurethane and polyethylene.

5. **Polymers are materials with a seemingly limitless range of characteristics and colors.** Polymers have many inherent properties that can be further enhanced by a wide range of additives to broaden their uses and applications. Polymers can be made to mimic cotton, silk, and wool fibers; porcelain and marble; and aluminum and zinc. Polymers can also make possible products that do not readily come from the natural world, such as clear sheets and flexible films.

6. **Polymers are usually made of petroleum, but not always.** Many polymers are made of repeat units derived from natural gas or coal or crude oil. But building block repeat units can sometimes be made from renewable materials such as polylactic acid from corn or cellulosics from cotton linters. Some plastics have always been made from renewable materials such as

cellulose acetate used for screwdriver handles and gift ribbon. When the building blocks can be made more economically from renewable materials than from fossil fuels, either old plastics find new raw materials or new plastics are introduced.

7. **Polymers can be used to make items that have no alternatives from other materials.** Polymers can be made into clear, waterproof films. PVC is used to make medical tubing and blood bags that extend the shelf life of blood and blood products. PVC safely delivers flammable oxygen in non-burning flexible tubing. And anti-thrombogenic material, such as heparin, can be incorporated into flexible PVC catheters for open heart surgery, dialysis, and blood collection. Many medical devices rely on polymers to permit effective functioning.

2.5 CLASSIFICATION OF POLYMERS:

Polymers can be classified by various ways as summarized follow.

1. Classification based on origion: On the basis of origion there are three types of polymers

A. Natural polymers: Polymers obtained from nature are known as natural polymers Examples: Cellolose, cotton, protein, DNA, RNA, hoofs, horns, silk, starch, nail etc.

These polymers are biodegradable in nature; their properties are decided by nature and are mouldable

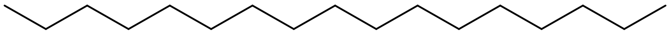
B. Seminatural/semisynthetic polymers: Polymers obtained naturally and then modified artificially are known as semisynthetic/ seminatural polymers:

Examples: Nitocellulose, cellulose acetate.

C. Synthetic polymers: Polymers synthesized artificially by using chemicals (monomers)

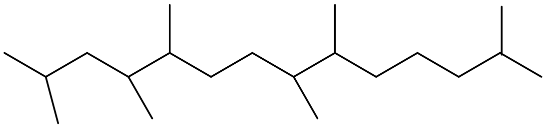
Examples: PE, PP, PVC, PS, BuNa-S, Bakelite, melmac, PMMA etc.

2. Classification based on structure: On the basis of structures the polymers may be of linear, branched or cross-linked as follow



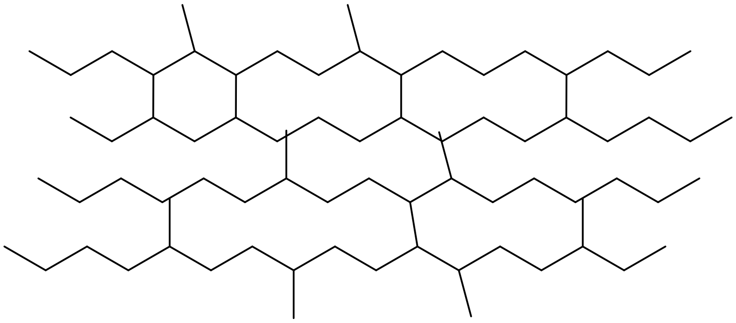
LINEAR

EXAMPLE HDPE
(high density polythene)



BRANCHED

EXAMPLE LDPE
(Low density polythene)



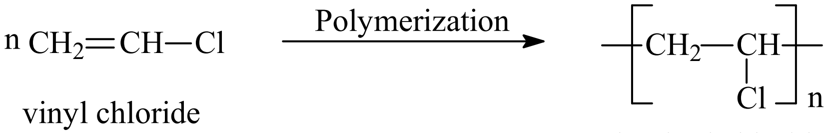
CROSS LINKED

EXAMPLE XLPE
(Cross linked polythene)
Rubbers, Thermoplastics

3. Classification based on physical state: On the basis of physical state polymeric material may be liquid (adhisives), solid like amorphous viz; LDPE, rubber etc) or semi crystalline (e.g. HDPE, nylon, polysters)

4. Classification based on chemical nature: On the basis of chemical nature polymers can be categorized as organic and inorganic polymers:

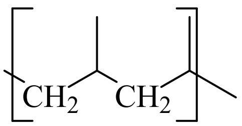
A. Organic polymers: The polymers in which the main back bone of the polymeric material is essentially made up of carbon are known as organic polymers viz; PP, PS, PE, PMMA, Bakelite



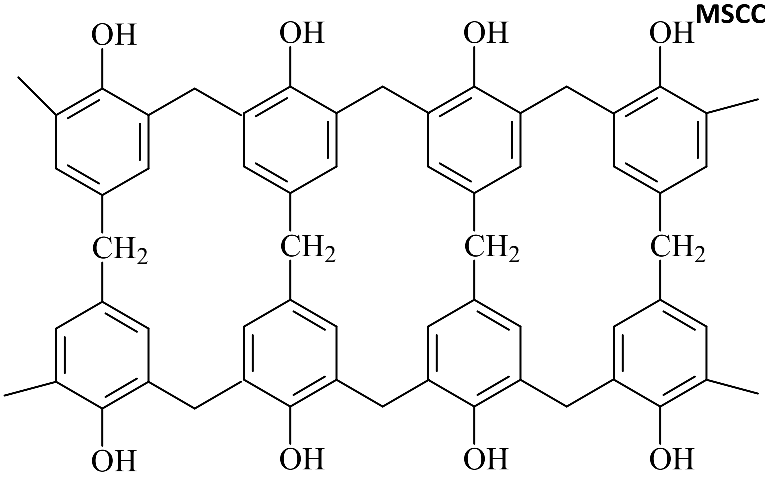
$$n\,CH_2{=}CH{-}Cl \xrightarrow{\text{Polymerization}} \left[CH_2{-}\underset{\displaystyle Cl}{\underset{|}{CH}} \right]_n$$

vinyl chloride

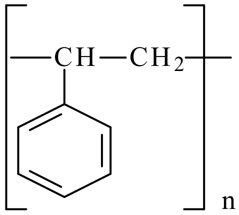
Poly vinyl chloride



PP

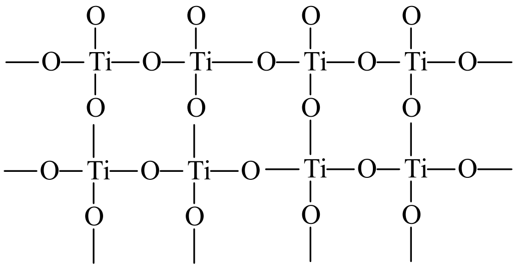


BAKELITE

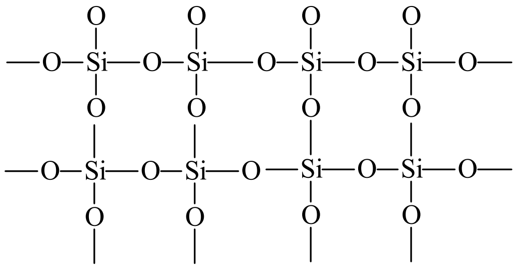


PS

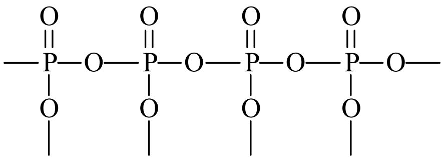
B. In-Organic polymers: Polymeric material in which the back bone of polymer contains heteroatoms in addition to carbon viz; polysiloxanes, polyphosphoric acid, polytitanoxanes etc.



Polytitanoxane



Polysiloxane



Polyphosphoric acid

5. Classification based on chemical thermal behaviour: on the basis of thermal behavior the plastics/polymers are categorized as thermoplastic and thermosetting plastics.

A. Thermoplastics: polymers which soften on heating and stiffen on cooling are known as thermoplastics viz, PE, PP, PVC, nylon, etc.

B. Thermosetting plastics: Polymers which undergo irreversible changes on the action of heat are known as thermosetting plastics viz; bakalite, epoxy resin etc.

6. Classification based on end use of the polymers: On the basis of their ultimate form and uses the polymeric materials are classified as:

A. Plastics: The polymers which can be shaped into tough utility articles by applying heat and pressure are called plastics. The plastics may be theromplastics or thermosetting plastic viz; PE, PVC, PMMA, urea formaldehyde resin, melamine etc

B. Elastomers: Polymeric material with rubber like elastic property and undergo reversible deformation/ elongation like natural rubber, synthetic rubber, silicon rubber. In these polymers the polymeric chains are held by weaker forces.

C. Fibers: Polymeric materials which can be drawn into a long filament like materials are called fibers viz; nylon-6, dacron, nylon-66, nylon-6 10, Terylene etc.

D. Liquid resins: Polymeric material having sticky nature like, epoxy resin, PAV

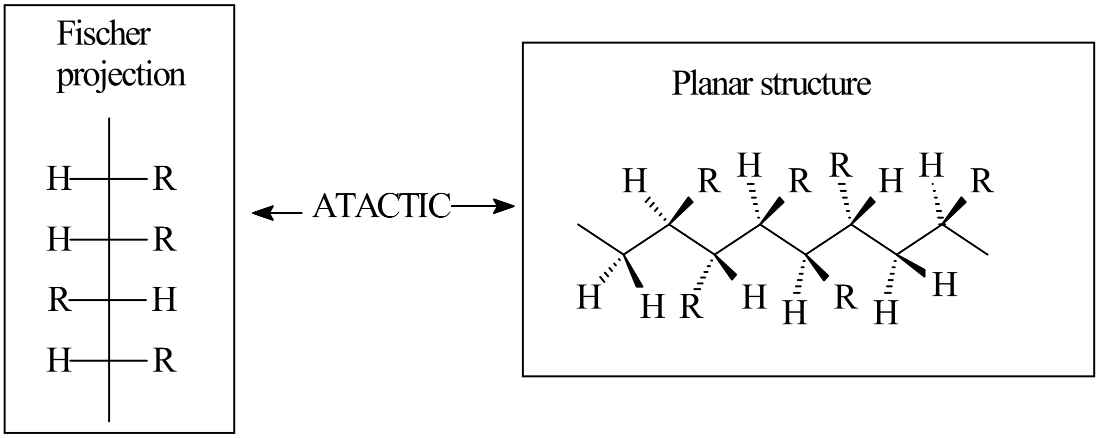
E. Film: Polymers that can be converted into film like PP, LDPE, HDPE, PVC, PET etc.

F. Paints: viz; epoxy

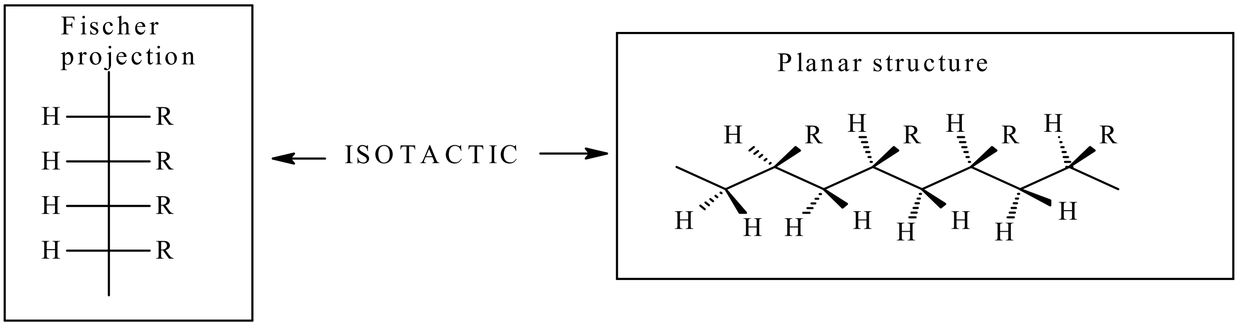
G. Membranes viz; polyacetylene, polyaniline etc

7. Classification based on tacticity: Based on tacticity (configuration), polymers are classified as:

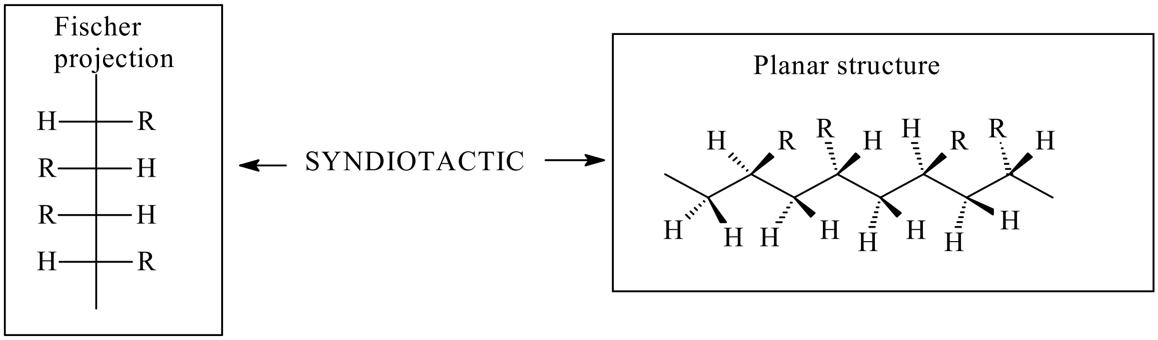
A. Atactic polymers: When the arrangement of side substituents(R) is random around the carbon back bone chain, such polymers are called atactic polymers.



B. Isotactic polymers: When the arrangement of side substituents(R) is on the same side of the carbon back bone, the polymers are called isoatactic polymers.

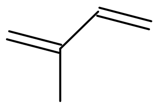
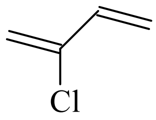
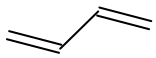
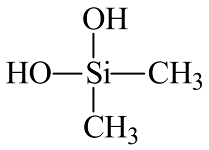


B. Syndiotactic polymers: When the arrangement of side substituents(R) is alternate around the carbon back bone chain, the polymers are called syndioatactic polymers.

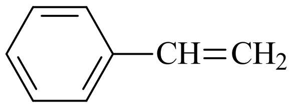


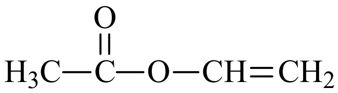
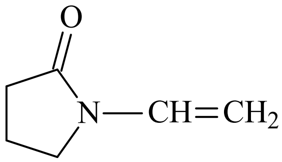
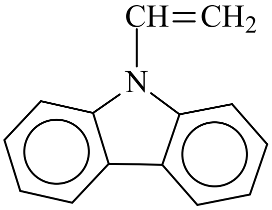
8. Classification based on chemical structure of monomeric unit: Based on the structures of repeating/ monomeric units polymeric materials can be categorized as:

A. Rubber and related polymers: The polymeric materials have following monomeric structural units

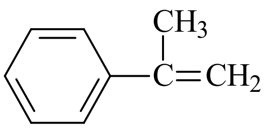
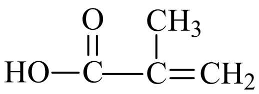
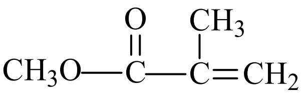
Structure of monomer	Polymeric material formed
	Polyisoperene, natural rubber
	polychloroperene
	Polybutadiene
 $HO{-}Si(OH)(CH_3){-}CH_3$	Polydimethylsiloxane

B.Vinyl polymers: Polymeric material having the vinyl (X- CH = CH_2) polymeric unit

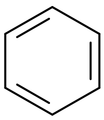
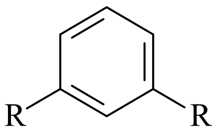
Monomeric unit	Polymer	Monomeric unit	Polymer
$H{-}CH{=}CH_2$	PE	$Cl{-}CH{=}CH_2$	PVC
$CH_3{-}CH{=}CH_2$	PP		PS
$HO{-}CH{=}CH_2$	Polyvinyl alcohol	$HOOC{-}CH{=}CH_2$	Polycarboxylic acid

$ROOC—CH{=}CH_2$	Polycarboxylic acid ester	 $H_3C—C(=O)—O—CH{=}CH_2$	Polyvinyl acetate
	Polyvinyl pyrolidone		Polyvinyl carbazole

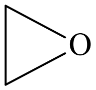
C. Vinyl polymer in which two or more ‘H’ are substituted:

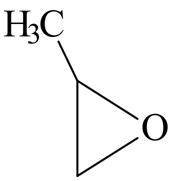
Monomer	**Polymer**	**Monomer**	**Polymer**
	Poly -α-methyl styrene	 $HO—C(=O)—C(CH_3){=}CH_2$	Polymethyl acrylic acid
 $CH_3O—C(=O)—C(CH_3){=}CH_2$	Polymethyl methacrylate(PMMA)	$CF_2{=}CF_2$	polytetrafluroethylene

D.Polyaromatics:

Monomer	**Polymer**	**Monomer**	**Polymer**
	**Polyphenyles**		**Sub. polyphenyles**

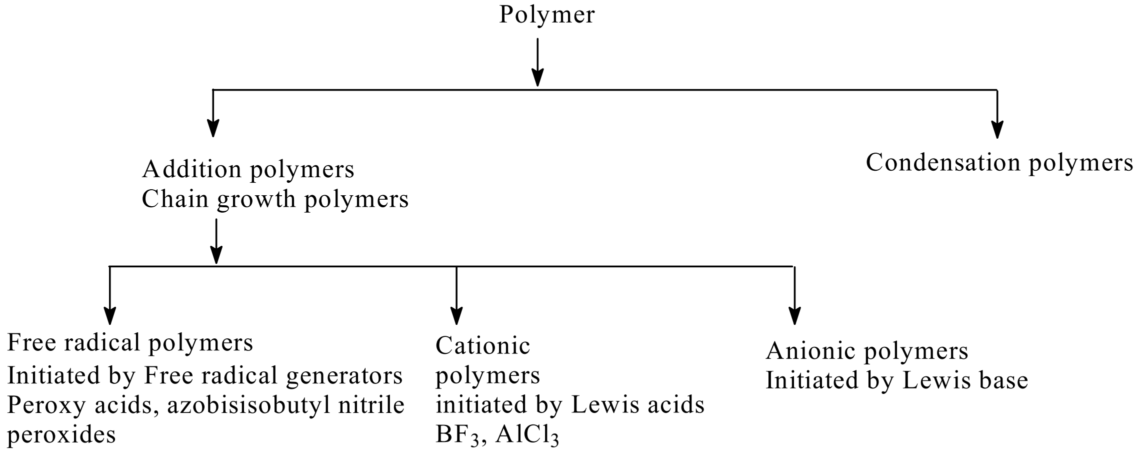
E. Polymers with ‘O’ in the main chain:

Monomer	**Polymer**	**Monomer**	**Polymer**
HCHO	Polyformaldehyde		Polyethylene oxide

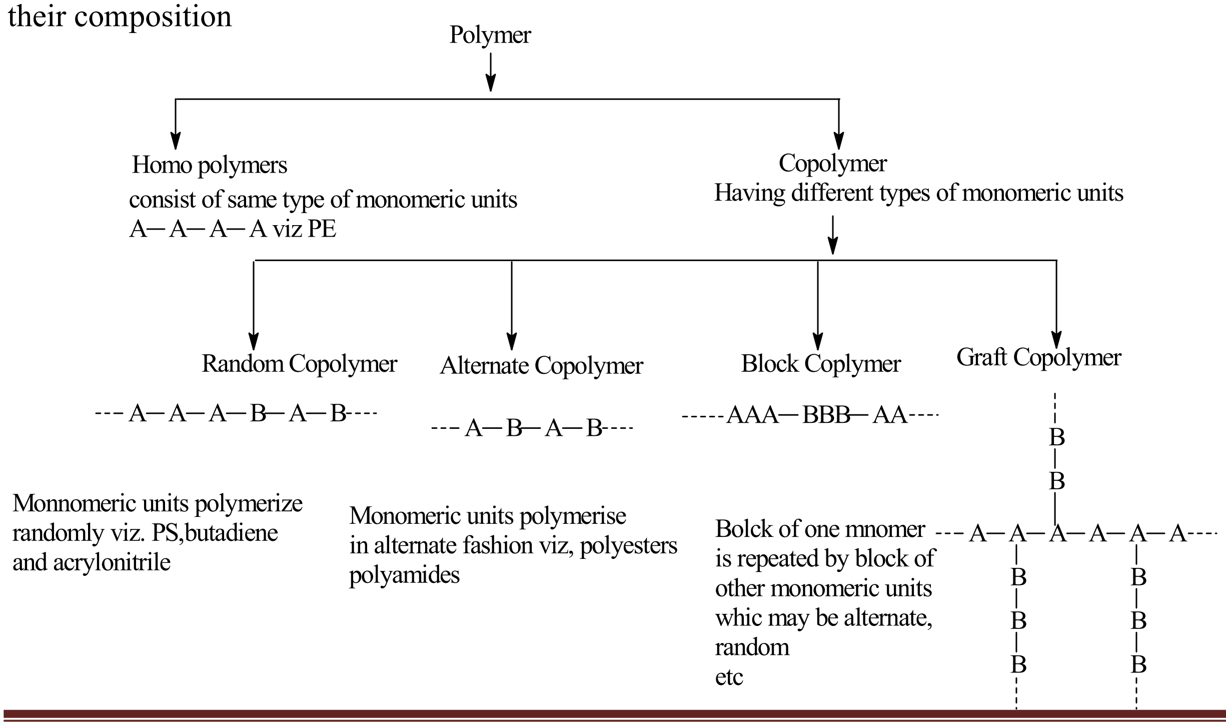


Polypropylene oxide

9. Classification based on polymerization techniques: On the basis of polymerization techniques used for the manufacture of polymeric material the polymers can be categorized as follow:



10. Classification based on composition: Polymers can be classified as follow on the basis of their composition

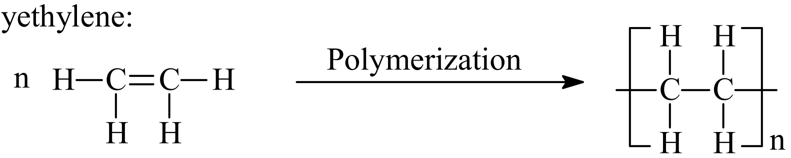


2.6 *CONFIGURATION OF POLYMERS*:

So far configuration is concern the polymers are categorized by Zeiglar and Natta on the basis of arrangement of substituents on main back bone of carbon chain. The term tacticity has been given to the polymers. It has already been discussed in point 7 of section 2.5.

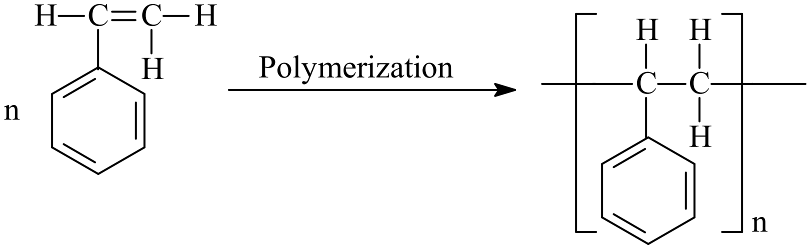
2.7 *SYNTHESIS OF SOME REPRESENTATIVE POLYMERS*:

Polyethylene:



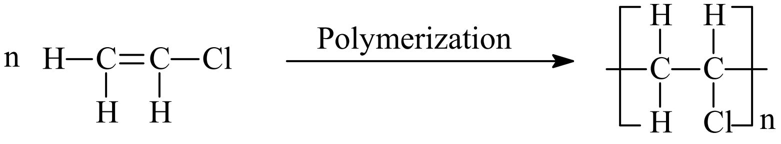
Ethylene Polythene

Polystyrene:



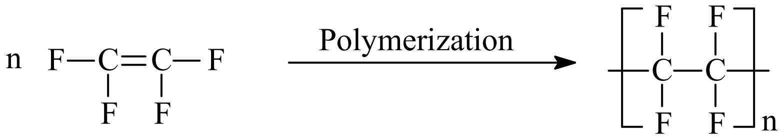
Styrene Polystyrene

Oplyvinyl chloride (PVC)



vinyl chloride PVC

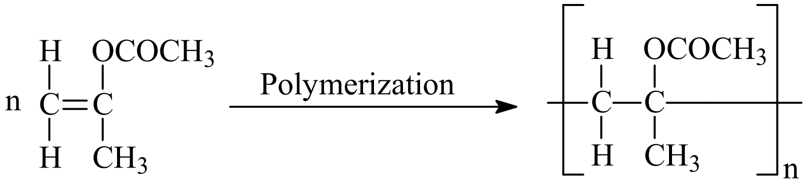
Polytetrafluoroethylene (PTFE):



$$n\ F-\underset{F}{C}=\underset{F}{C}-F \xrightarrow{\text{Polymerization}} \left[-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-\right]_n$$

TFE Teflon (PTFE)

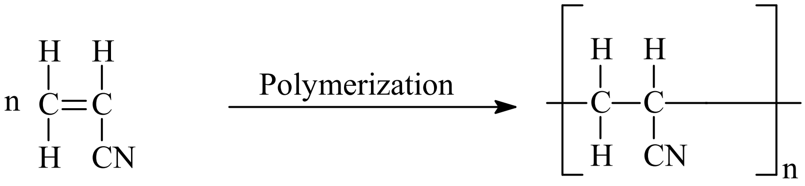
Polymethylmethacrylate (PMMA)



$$n\ \overset{H}{\underset{H}{C}}=\overset{OCOCH_3}{\underset{CH_3}{C}} \xrightarrow{\text{Polymerization}} \left[-\overset{H}{\underset{H}{C}}-\overset{OCOCH_3}{\underset{CH_3}{C}}-\right]_n$$

MMA PMMA

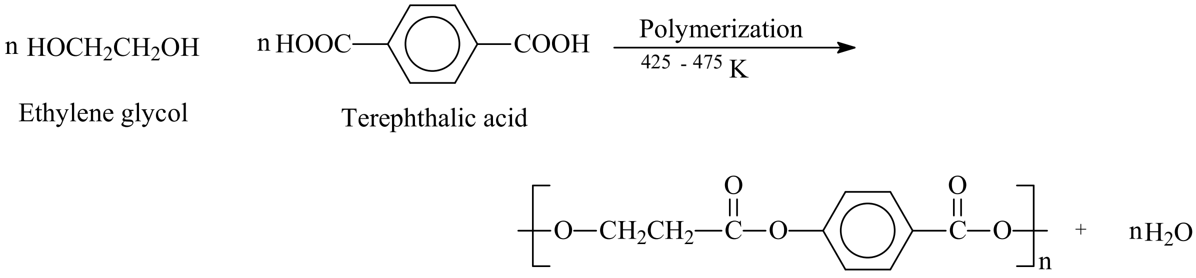
Polyacrylonitrile (PAN)



$$n\ \overset{H}{\underset{H}{C}}=\overset{H}{\underset{CN}{C}} \xrightarrow{\text{Polymerization}} \left[-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{CN}{C}}-\right]_n$$

Acrylonitrile polyacrylonitrile

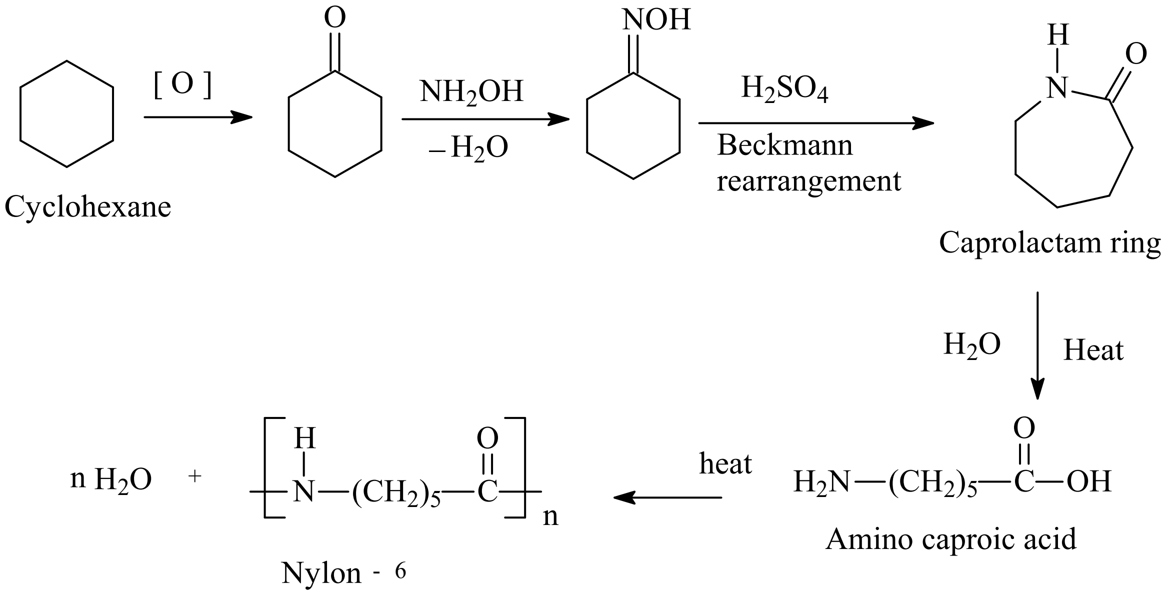
Terylene:



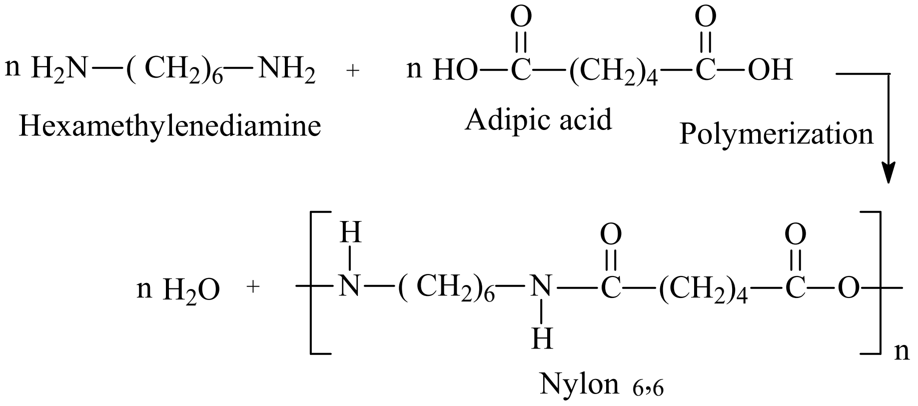
Ethylene glycol Terephthalic acid

Terylene

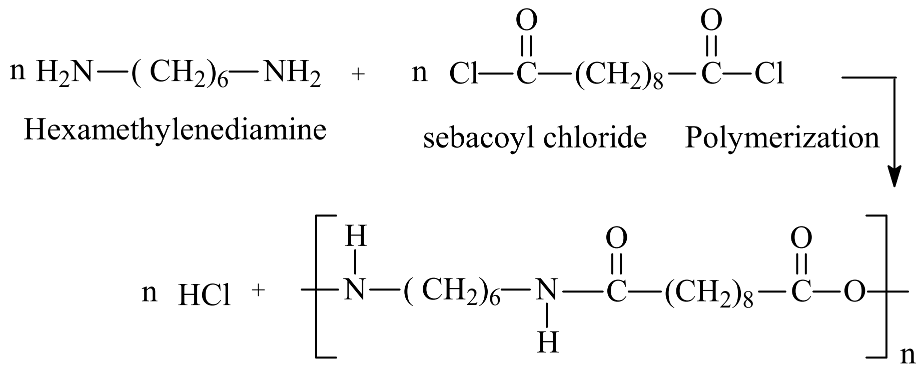
Nylon – 6:



Nylon -66



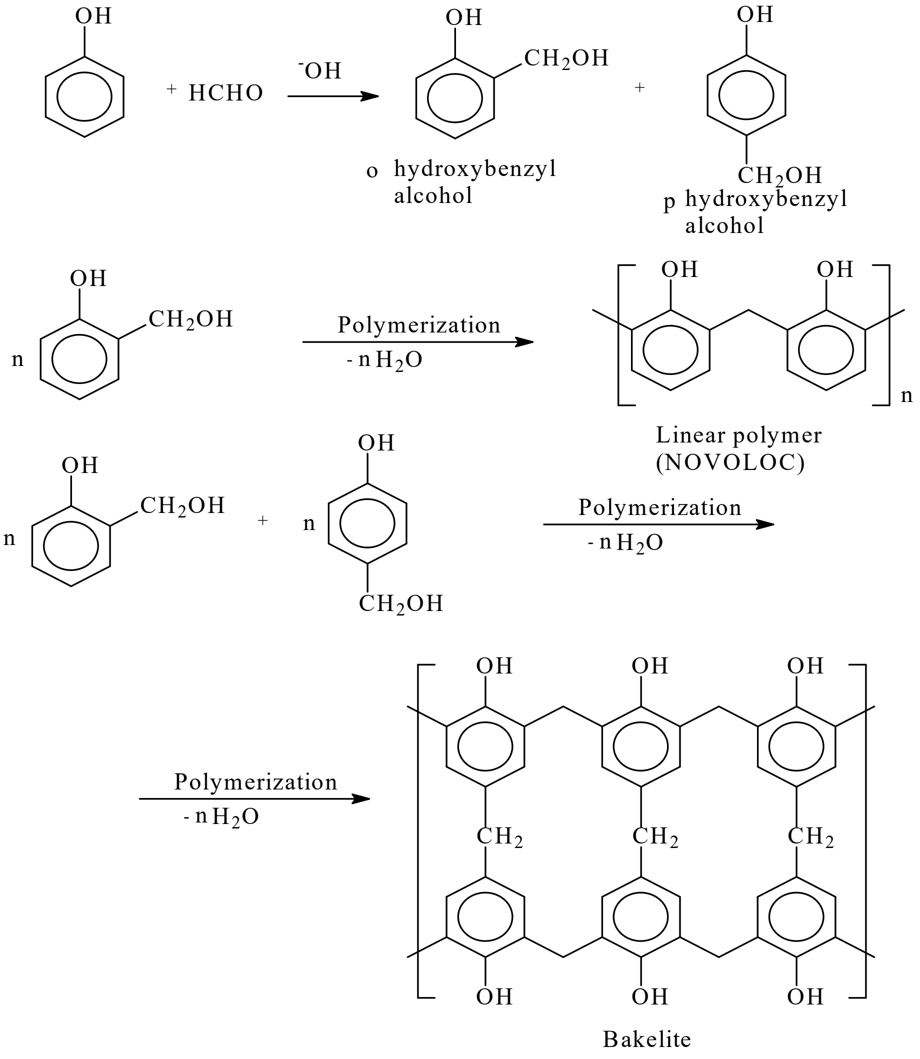
Nylon -6, 10



$$n\,H_2N-(CH_2)_6-NH_2 + n\,Cl-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{\text{Polymerization}} n\,HCl + \left[-\overset{H}{\overset{|}{N}}-(CH_2)_6-\underset{H}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-O-\right]_n$$

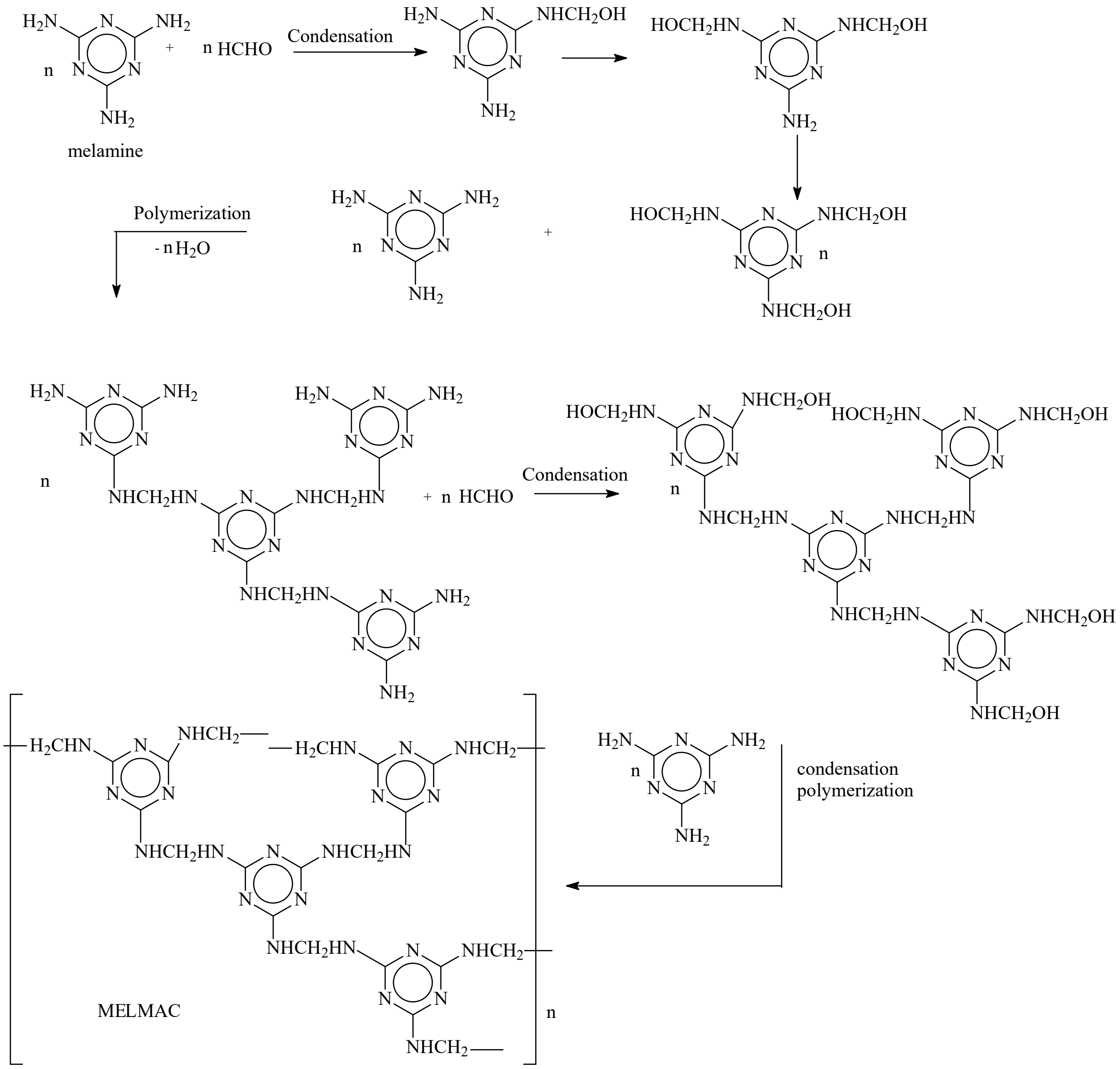
Nylon- 10, 6

Formaldehyde resins:Bakelite:

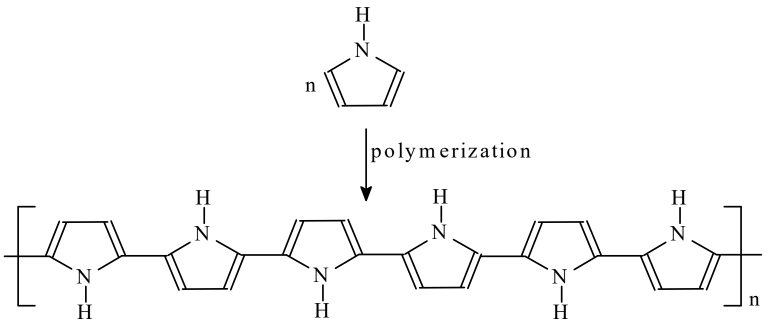


Bakelite

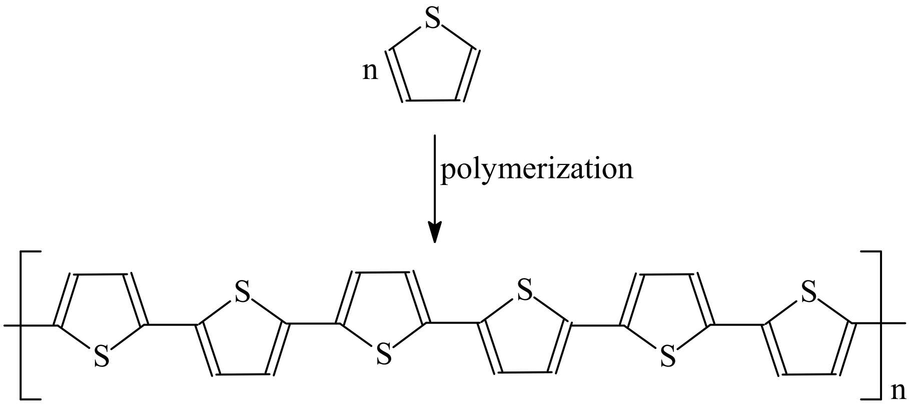
Melamine formaldehyde resin (MELMAC)



Conducting polymer: Polymers which are capable of conducting current through the chain of polymeric material because of conjugation present in the main back bone of the polymers. Further to make the polymer conductive they are doped with atoms that donate negative or positive charges (oxidizing or reducing agents) viz, polypyrrole, polythiophene etc.



Polypyrrole



Polythiophene

2.8 *APPLICATIONS OF POLYMERS*:

1. **Polymers can be very resistant to chemicals.** Consider all the cleaning fluids in your home that are packaged in plastic. Reading the warning labels that describe what happens when the chemical comes in contact with skin or eyes or is ingested will emphasize the need for chemical resistance in the plastic packaging. While solvents easily dissolve some plastics, other plastics provide safe, non-breakable packages for aggressive solvents.
2. **Polymers can be both thermal and electrical insulators.** A walk through your house will reinforce this concept, as you consider all the appliances, cords, electrical outlets and

wiring that are made or covered with polymeric materials. Thermal resistance is evident in the kitchen with pot and pan handles made of polymers, the coffee pot handles, the foam core of refrigerators and freezers, insulated cups, coolers, and microwave cookware. The thermal underwear that many skiers wear is made of polypropylene and the fiberfill in winter jackets is acrylic and polyester.

3. **Generally, polymers are very light in weight with significant degrees of strength.** Consider the range of applications, from toys to the frame structure of space stations, or from delicate nylon fiber in pantyhose to Kevlar, which is used in bulletproof vests. Some polymers float in water while others sink. But, compared to the density of stone, concrete, steel, copper, or aluminum, all plastics are lightweight materials.
4. **Polymers can be processed in various ways.** Extrusion produces thin fibers or heavy pipes or films or food bottles. Injection molding can produce very intricate parts or large car body panels. Plastics can be molded into drums or be mixed with solvents to become adhesives or paints. Elastomers and some plastics stretch and are very flexible. Some plastics are stretched in processing to hold their shape, such as soft drink bottles. Other polymers can be foamed like polystyrene (Styrofoam™), polyurethane and polyethylene.
5. **Polymers are materials with a seemingly limitless range of characteristics and colors.** Polymers have many inherent properties that can be further enhanced by a wide range of additives to broaden their uses and applications. Polymers can be made to mimic cotton, silk, and wool fibers; porcelain and marble; and aluminum and zinc. Polymers can also make possible products that do not readily come from the natural world, such as clear sheets and flexible films.
6. **Polymers are usually made of petroleum, but not always.** Many polymers are made of repeat units derived from natural gas or coal or crude oil. But building block repeat units can sometimes be made from renewable materials such as polylactic acid from corn or cellulosics from cotton linters. Some plastics have always been made from renewable materials such as cellulose acetate used for screwdriver handles and gift ribbon. When the building blocks can be made more economically from renewable materials than from fossil fuels, either old plastics find new raw materials or new plastics are introduced.

7. **Polymers can be used to make items that have no alternatives from other materials.** Polymers can be made into clear, waterproof films. PVC is used to make medical tubing and blood bags that extend the shelf life of blood and blood products. PVC safely delivers flammable oxygen in non-burning flexible tubing. And anti-thrombogenic material, such as heparin, can be incorporated into flexible PVC catheters for open heart surgery, dialysis, and blood collection. Many medical devices rely on polymers to permit effective functioning.

2.9 MOLECULAR MASSES OF POLYMERS:

The determination of molecular weight is of great importance in industry and research. The properties of polymers are influenced by molecular weight. As the intermolecular forces of attraction between different polymeric chains increase with the length of the polymeric chains.That's why the higher molecular weight polymers are tougher and more heat resistant. Their viscosity, solubility, softening temperature is also higher compared to the low molecular weight polymers. In industrial polymerization, control of molecular weight is very crucial. All the molecules of the polymer sample do not have identical molecular weight, hence polymers are polydispersed. This is the reason that in apolymerization reaction, the chain length of polymeric material is determined entirely by random events.. As there is spread in the molecular weight of the product, hence the molecular weight are average. Different methods of determination of molecular weight provide different average molecular weight.

Number-average molecular weight: When the total molecular weight of all the molecules of a sample is divided by the total number of molecules, the result obtained is called the number average molecular weight. For example, suppose in a particular sample

N_1 molecules have molecular weight M_1 each

N_2 molecules have molecular weight M_2 each

N_3 molecules have molecular weight M_3 each and so on.

Then we have

Total molecular weight of all the N_1 molecules = $N_1 M_1$

Total molecular weight of all the N_2 molecules = N_2M_2

Total molecular weight of all the N_3 molecules = $N_1 M_3$ and so on

Total molecular weight of all the molecules

$= N_1M_1 + N_2M_2 + N_3M_3 + \dots$

$= \Sigma N_iM_i$

Total number of all the molecules

$= N_1+N_2+N_3\dots$

$= \Sigma N_i$

Hence the number-average molecular weight will be given by

$\overline{M}$

$$\overline{M}n = \frac{N_1M_1+N_2M_2+N_3M_3+\cdots}{N_1+N_2+N_3+\cdots}$$

$$\overline{M}_n = \frac{\Sigma N_i M_i}{\Sigma N_i}$$

Weight-average molecular weight: When the total molecular weight of group of molecules having particular molecular weights are multiplied with their respective molecular weight, the products are added and the sum is divided by the total weight of the all the molecules, the result obtained is called the weight-average molecular weight. Supposing N_1, N_2 N_3 etc. molecules have molecular weights M_1, M_2, M_3 etc respectively.

Total molecular weight of N_1 molecules = N_1M_1

Total molecular weight of N_2 molecules = N_2M_2

Total molecular weight of N_3 molecules = N_3M_3 and so on.

The products with their respective molecular weight will be $N_1M_1 \times M_1$, $N_2M_2 \times M_2$, $N_3M_3 \times M_3$, etc. i.e. $N_1M_1^2$, $N_2M_2^2$, $N_3M_3^2$, etc.

Sum of the products = $N_1M_1^2+N_2M_2^2+N_3M_3^2=\dots$

$= \Sigma N_iM_i^2$

Total weight of all the molecules = $N_1M_1+N_2M_2+N_3M_3+\dots$

$= \Sigma N_iM_i$

Hence weight-average molecular weight is given by

$$\bar{M}_w = \frac{N_1M_1^2 + N_2M_2^2 + N_3M_3^2 + \cdots}{N_1M_1 + N_2M_2 + N_3M_3 + \cdots}$$

$$\bar{M}_w = \frac{\Sigma N_i M_i^2}{\Sigma N_i M_i}$$

Condition under which $\bar{M}_n = \bar{M}_w$:

$$\bar{M}_n = \frac{N_1M_1 + N_2M_2 + \cdots}{N_1 + N_2 + \cdots}$$

$$\bar{M}_w = \frac{N_1M_1^2 + N_2M_2^2 + \cdots}{N_1M_1 + N_2M_2 + \cdots}$$

If $\bar{M}_n = \bar{M}_w$ then

$$\bar{M}_n = \frac{N_1M_1 + N_2M_2 + \cdots}{N_1 + N_2 + \cdots} = \bar{M}_w = \frac{N_1M_1^2 + N_2M_2^2 + \cdots}{N_1M_1 + N_2M_2 + \cdots}$$

The two sides can be equal only if

$M_1 = M_2 = \ldots.$

i.e. all molecules should have the same molecular weight. In that case average has no significance.

2.10 MOLECULAR WEIGHT DETERMINATION:

The method for determining molecular weights of polymers is of two types viz.

- Primary or absolute methods, which are capable of determining molecular weights from first principles like colligative property measurements (which gives number-average molecular weight, light scattering measurements (which gives weight-average molecular weight).

- Secondary or relative method, which require calibration with samples of known molar mass. Example, viscosity measurement, osmotic pressure methods.

2.10.1 Scattering method: This method is based upon the phenomenon of 'scattering of light' by colloidal solutions because polymers are macromolecular colloids. The amount of light scattered depends directly on the size and number of particles present in the solution. When a light of intensity I_0 is passed through the solution contained in a cell of length l, the intensity of the transmitted light is reduced to I due to scattering. The relationship between I and I_0 is given by following equation (1)

$$\tau = \frac{1}{l} log \frac{I_0}{I}$$

where τ is called the turbidity of the scattering medium.

The turbidity τ is related to the apparent molecular weight of the polymer in the solution according to the following equation (2), given by Debye

$$\frac{HC}{\tau} = \frac{1}{M'} + AC + BC^2 + \cdots$$

where C = concentration of the solution in g/cm^3

A, B etc are constants and M$'$ is the apparent molecular weight of the polymer

$$H = \frac{32\pi^2 n_0^2 (dn/dc)^2}{3N\lambda_0^4}$$

It is equation (3)

where n_0 = refractive index of the solvent

dn/dc = variation of refractive index of the solution with concentration

λ_0 = wavelength in the vacuum of the light used

N = Avogadro's number

Eq. (2) leads to the following result, equation (4)

$$\lim_{c \to 0} \left(\frac{HC}{\tau}\right) = \frac{1}{M'}$$

Thus to get M' we should plot HC/τ versus C and then extrapolate the plot to zero concentration. Intercept gives 1/M' from which M' can be calculated (Fig2.1).

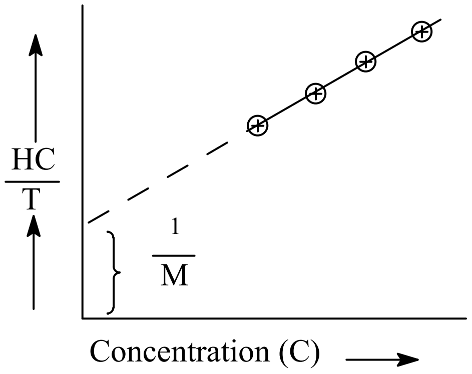


Fig 2.1. Plot of HC/τ Vs C

To get the value of HC/τ corresponding to different concentration C, solutions of experimental polymers in a particular suitable solvent are prepared. In each case, the turbidity τ is measured and the quantity H is calculated. To measure turbidity τ [using eq. (1)], the intensity of the light scattered at 90^0 to the direction of the incident beam is measured with simple photometer. To get the value of H, the quantities involved in eq. (3) have to the measured. The refraction index n_0 of the solvent is measured with refractometer; dn/dc is measured with special differential refractometers.

Further the apparent moleucular weight M' is related to a the molecular weight M by the relation

$$M = M' \alpha\beta \qquad \text{……(5)}$$

where α and β are corrections depending upon the size and the nature of the solute particles. A is called dissymmetry correction and β is called depolarization correction. The correction factor α is obtained by measuring the intensities of scattered light at angles of 45^0 and 135^0 to the primary beam and β is obtained from the ratio of the horizontal to the vertical components of the light scattered by the solute at 90^0 to the direction of the incident beam. It may be pointed out that the molecular weight obtained by this method is the weight average molecular weight, M_w.

***2.10.2* Osmometry *method*:** Osmosis is the phenomenon of the passage of solvent molecules into the solution through a semipermeable membrane. The hydrostatic pressure of the liquid column set up as a result of osmosis is called the osmotic pressure or osmotic pressure is the external pressure that has to be applied on the solution to prevent the entry of the solvent into the solution through the semipermeable membrane.

The solution of a polymer in a suitable solvent can be subjected to the phenomenon of osmosis because the size of the polymer molecules in the solution is large enough not to pass through the semipermeable membrane while the solvent molecules can easily pass through. If the solution were dilute, the osmotic pressure is given by the Van't Hoff equation viz.

$PV = nRT$

$$or \qquad P = \frac{n}{V}RT$$

It is equation (1)

Where P = osmotic pressure

N = number of moles of the polymer

V = volume of the polymer solution

T = absolute temperature at which measurements are made

R = solution constant or the gas constant

Substituting, n = w/M, eq. (1) reduces to following equation (2)

$$P = \frac{w}{M} \times \frac{1}{V}RT = \frac{w}{V}\frac{RT}{M} = C\,\frac{RT}{M}$$

where C = w/V is the concentration of the solution is grams/litre

Equation (2) may be rewritten as equation (3) as follow

$$\frac{P}{C} = \frac{RT}{M}$$

According to this equation, P/C should be constant at constant temperature i.e., a plot of P/C vs C should be a straight line.

However this result is found to hold good only for dilute solutions of low molecular weight polymers. For high polymer solutions, it is observed that the osmotic pressure varies with concentration according to the following relationship, equation (4)

$$\frac{P}{C} = \frac{RT}{M} + AC + BC^2 + \cdots$$

Where A, B etc are constant. The quantity P/C is called reduced osmotic pressure.

From equation (iv), it is evident that

$$\frac{P}{C} = \frac{RT}{M}\ if\ C = 0$$

ie.

$$\lim_{c\to 0}\left(\frac{P}{C}\right) = \frac{RT}{M}$$

Thus if P/C values are plotted against C and the graph is extrapolated to C =0 then the intercept on the Y-axis is equal to RT/M (Fig2.2). From this the value of M can be calculated as:

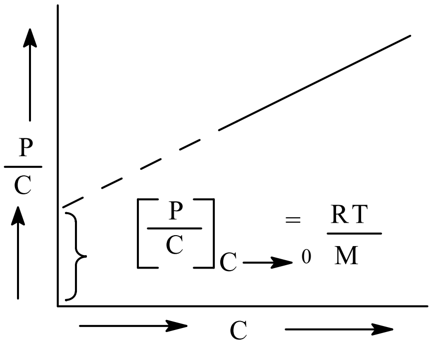


Fig.2.2

Variation of reduced osmotic pressure with concentration

$$M = \frac{RT}{\left(\frac{P}{C}\right)_{c \to 0}}$$

As osmotic pressure is a colligative properly i.e., it depends upon the number of particles present, therefore the molecular weight obtained by this method is the number-average molecular weight.

Thus to determine the molecular weight of a polymer, it is required to measure the osmotic pressure of solutions of several concentrations and extrapolate the line to zero concentration. The instruments used for determining the molecular weight by this method are called osmometers. Two different techniques are used:

(i) **Static method:** The solvent is allowed to enter the polymer solution through the semipermeable membrane till the level in the capillary tube stops rising.

(ii) **Dynamic method:** In this method, the rate of penetration of the solvent into the solution through the semipermeable membrane is noted under a known applied pressure. Dynamic method is preferred because it gives quick results.

***2.10.3. Viscometry method*:** This method requires the measurement of viscosities of polymer solutions of different concentrations which can be done easily with the help of Ostwald viscometer. However, this method is not an absolute method because it requires calibration using certain other substances of known molecular weights. The theory of the method is discussed below:

If η is the viscosity of a solution and η_0 that of pure solvent at the same temperature, the ratio η/η_0 is called the relative viscosity of the solution and is usually represented by η_r in following equation (1) i.e.

$$\frac{\eta}{\eta_0} = \eta_r$$

Another quantity specific viscosity η_{sp} is given by following equation (2)

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0}$$

Further, it is observed that the ratio η_{sp}/C where C is the concentration of the solution, generally expressed in grams per 100 ml of the solution, varies linearly with concentration. The extrapolation of η_{sp}/C value to zero concentration gives what is known as intrinsic viscosity, represented in following equation (3) usually by [η] i. e.,

$$[\eta] = \left(\frac{\eta_{sp}}{C}\right)_{c \to 0}$$

The intrinsic viscosity is found to be related to the molecular weight M by the expression

$[\eta] = kM^a$ .... Equation (4)

Where k and a are constants for the given polymer series in a particular solvent. Thus if k and a are known for a particular polymer series in a particular solvent, the value of M can be determined by finding [η] for the polymer under investigation.

[η] For the polymer under investigation can be found by plotting η_{sp}/C vs. C and extrapolating the result to zero concentration as shown in Fig.2.3 polyvinyl chloride in cyclohexane at 25^0C.

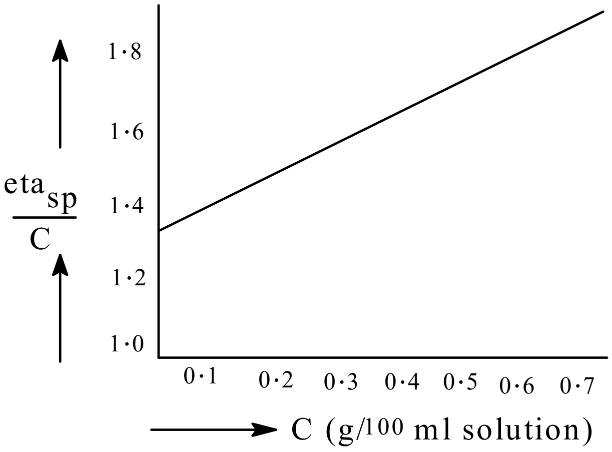


Fig 2.3 Plot of eta_{sp}/C (η_{sp}/C) vs C for PVC in cyclohexane at 25^0C

To determine k and a, a number of samples of the same polymer series are taken whose molecular weight have been determined by other methods like osmometry or light scattering. Writing equation (iv) in the form

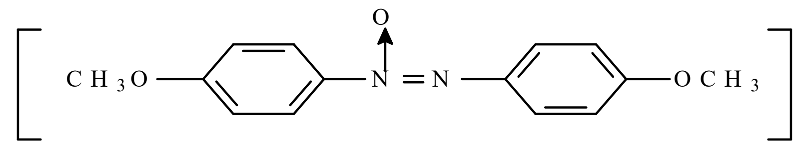
$$\log \eta = \log k + a \log M$$

a plot of log η vs. log M will be a straight line with slope a and intercept log k. Thus the values of k and a can be obtained for the given polymer series in a particular solvent.

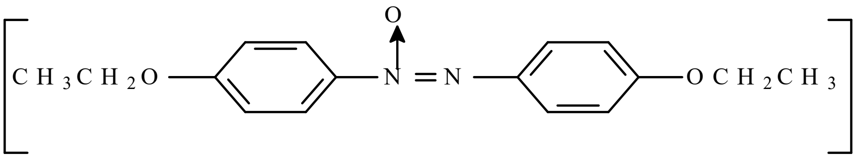
The molecular weight $\overline{M}_w$ obtained by this method is called viscosity $(\overline{M}_V)$ average molecular weight If $\alpha = 1$, it is equal to the weight-average molecular weight. However as a usually lies between 0.5 to 1, the viscosity average molecular weight $(\overline{M}_V)$ usually lies between number-average molecular $\overline{M}_n$ weight Usually lies between number-average molecular weight , and weight-average molecular weight .

2.11 LIQUID CRYSTALS:

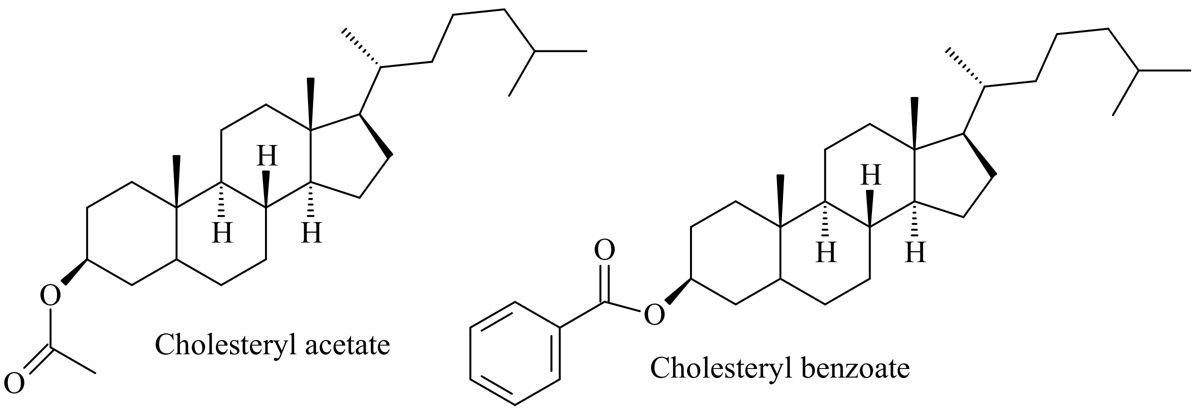
Liquid crystals (LCs) are matters which posses the properties between those of conventional liquids and solid crystals. A liquid crystal may flow like a liquid, but its molecules may be oriented in a crystal-like way. There are many types of liquid-crystal phases, which can be distinguished by their different optical properties like textures The contrasting areas in the textures correspond to domains where the liquid-crystal molecules are oriented in different directions. Within a domain, however, the molecules are well ordered. LC materials may not always be in a liquid-crystal phase (just as water may turn into ice or steam). Examples of liquid crystals are p-azoxyanisol and p-azoxyphenetole, cholesteryl acetate,cholesteryl benzoate,ammonium oleate as follow.



p - azoxyanisole

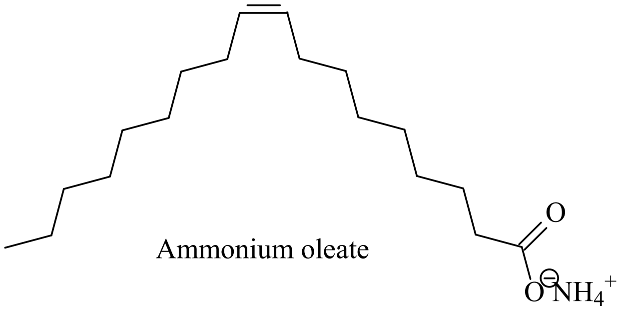


p - azoxy phenetole



Cholesteryl acetate

Cholesteryl benzoate



Ammonium oleate

Liquid crystals are of following types:

1. Smectic LC. The smectic liquid crystal (LC) has limited mobility. They flow in layers as if different sheets are gliding over one another. The distribution of velocity in different layers is different from that found in true liquid. The concept of viscosity is therefore not applicable to the LC of this type. When spread over aclean glass surfaces, they form a series of starta (Fig2.4)

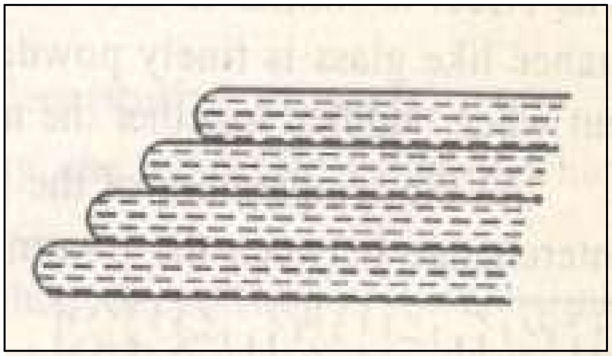
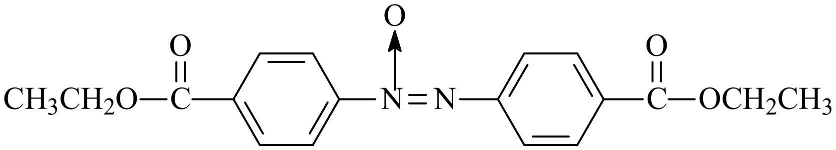


Fig 2.4 Layer structure of smectic liquid crystal

The smectic LC also give X-ray diffraction patterns like solid crystals nut it is in one direction only. Thus smectic phase has a complex internal structure. When viewed in polarized light, smectic phases appear to have fan like appearance. They are always uniaxial and are not affected by a magnetic field.

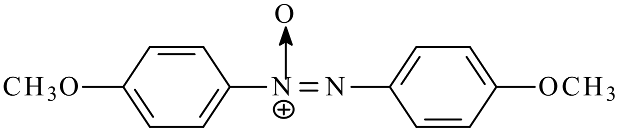
Ethyl –p –azoxy benzoate, ethyl-p-azoxy cinnamate are some examples of this class of liquid crystals.



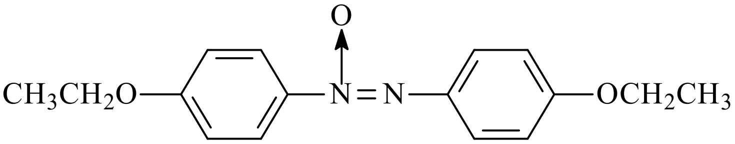
ethyl - p - azoxy benzoate

(ii) Nematic Liquid Crystals: Nematic type of liquid crystals show near normal flow behavior of liquids. They flow more readily than the smectic liquid crystals. Their flow is also Newtonian and the concept of viscosity is applicable to their flow. Their viscosity, however, is rather low as compared to that of liquids. Thus, nematic phases have o=liquid-like character and yet being turbid and anisotropic, they are unlike true liquids. This type is, therefore, regarded less truly anisotropic than the smectic type.

In polarized light, substances in nematic phase appear to have thread-like structures. They are uniaxial like smectic substances, but unlike the latter, they are affected by a strong magnetic field. Thus, when viewed in the direction of the lines of force of a magnetic field, the turbid liquid appears quite clear. If the magnetic field is cut off, the liquid appears turbid again. P-azoxy anisole and p-azoxy phenetole are some examples of these type.



p - azoxy anisol



p - azoxy phenetole

(iii) Cholesteric Liquid Crystals: Certain optically active compounds show many characteristics of nematic behavior but at the same time hey show strong colour effects in polarized light. This indicates that they have a layer structure like smectic liquid crystals. But hey differfrom smectic liquid crystals in having much thicker layers which are of the order of 500 to 5000 molecules thick. Such liquid crystals having some nematic and some smectic characters are called cholesteric liquid crystals. The first substance in shich this type of mesomorphism was detected was cholesteryl benzoate. Its transition point is 145^0 and melting point 178^0 C. i-cholesteryl formate is another example of this type of liquid crystals.

Theory of liquid crystal: The LC can be explained by the Swarm Theory proposed by Bose. According to this theory, since mesomorphic behavior is shown by substances having long chains, their free rotation is restricted and they tend to arrange themselves in parallel formations. In this way, number groups of swarms are obtained. The molecules in any one swarm are parallel to one another but may not be parallel to those present in another swarm. Fig 2.5 (I)

Each swarm consisting of several molecules, arranged parallel to one another, is taken as a small crystal. Thus a turbid liquid is viewed as consisting of a series of small crystals distributed at random in the body of the liquid. Lehmann actually found the each particular swarm appears as a transparent liquid crystal when viewed under a microscope. The turbidity of the liquid crystals is simply due to the scattering of light at the boundaries between the various swarms. The effect is similar to that observed when a transparent substance like galss is finely powdered. Each piece is transparent but when huddled together the mass appears someshat opaque.

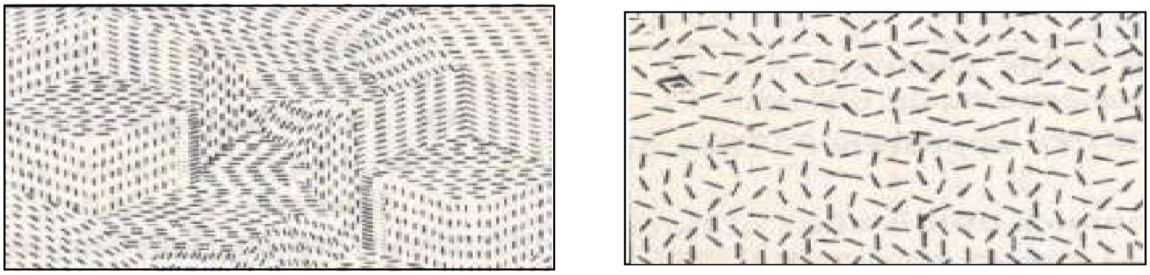

I II

Fig 2.5.I. Arrangement of molecules: I in anisotropic liquids. II. In isotropic liquids.

As the temperature of the liquied crystals is raised, the molecular motion increases and an interchange between the swarm occur. The swarms become smaller and smaller with rise in temperature and ultimately at a certain temperature, the swarms become smaller than too small to scatter ight. The turbidity now disappears. The liquid becomes clear. The double refraction and other anisotropic properties due to orientation of molecules within the swarms disappear. The liquid becomes singly refracting and isotropic. This temperature is the melting pint of the substance. The arrangement of molecules in an isotropic liquid is depicted in Fig. 2.5. (II)

2.12 APPLICATIONS OF LIQUID CRYSTALS:

Liquid crystals find wide use in liquid crystal displays, which rely on the optical properties of certain liquid crystalline substances in the presence or absence of an electric field.

In a typical device, a liquid crystal layer (typically 4 μm thick) sits between two polarizers that are crossed (oriented at 90° to one another). The liquid crystal alignment is chosen so that its relaxed phase is a twisted one This twisted phase reorients light that has passed through the first polarizer, allowing its transmission through the second polarizer (and reflected back to the observer if a reflector is provided). The device thus appears transparent. When an electric field is applied to the LC layer, the long molecular axes tend to align parallel to the electric field thus gradually untwisting in the center of the liquid crystal layer. In this state, the LC molecules do not reorient light, so the light polarized at the first polarizer is absorbed at the second polarizer, and the device loses transparency with increasing voltage. In this way, the electric field can be used to make a pixel switch between transparent or opaque on command.

Color LCD systems use the same technique, with color filters used to generate red, green, and blue pixels. Chiral smectic liquid crystals are used in ferroelectric LCDs which are fast-switching binary light modulators. Similar principles can be used to make other liquid crystal based optical devices.

Liquid crystal tunable filters are used as electroopticale devices, e.g., in hyperspectral imaging. Thermotropic chiral LCs whose pitch varies strongly with temperature can be used as crude liquid crytal thermometers, since the color of the material will change as the pitch is changed.

Liquid crystal color transitions are used on many aquarium and pool thermometers as well as on thermometers for infants or baths. Other liquid crystal materials change color when stretched or stressed. Thus, liquid crystal sheets are often used in industry to look for hot spots, map heat flow, measure stress distribution patterns, and so on. Liquid crystal in fluid form is used to detect electrically generated hot spots for failure analysis in the semiconductor industry.

Liquid crytal lasers use a liquid crystal in the lasing medium as a distributed feedback mechanism instead of external mirrors. Emission at a photonic bandgap created by the periodic dielectric structure of the liquid crystal gives a low-threshold high-output device with stable monochromatic emission.

Polymer dispersed liquid crystal (PDLC)sheets and rolls are available as adhesive backed Smart film which can be applied to windows and electrically switched between transparent and opaque to provide privacy.

Many common fluids, such as sopy water,are in fact liquid crystals. Soap forms a variety of LC phases depending on its concentration in water Bowlic columns could be used for fast switches.

2.13 SUMMARY:

In this important unit we described the polymer, macromolecules, and properties of polymers. Classification of polymers on different basis has been discussed in detail. The stereochemistry which play very important role in the quality of polymeric material has been discussed in this unit.This unit also depicts the synthesis of some important representative industrial polymers.The applications of polymers has been given in detail. Properties of polymers largely dependes upon their molecular weight which is generally expressed as number average molecular weight and weight average molwcular weight. This part has been described in detail. There are different experimental methods for determining the molecular weight of polymers like, scattering method, osmometry method, viscometry method, diffusion method. These methods are described in this unit. This unit also makes aware the readers about liquid, crustal, their types, theory and applications.

2.14 *TERMINAL QUESTIONS*:

Q.1 Tick the appropriate answer.

i. The word 'polymer' meant for material made from

A. Single entity B. Two entities

C. Multiple entitie D. Any entity

ii. One of characteristic properties of polymer material.

A. High temperature stability B. Low hardness

C. High mechanical strength D. High elongation

iii. Kevlar is commercial name for ___________ .

A. Glass fibers B. Carbon fibers

C. Aramid fibers D. Cermets

iv. The polymers can not be recycled:

A. Thermoplasts B. Thermosets

C. Elastomers D. All polymers

v. Strong covalent bonds exists between polymer chains in:

A.Thermoplasts B. Thermosets

C. Elastomers D. All polymers

vi. Elastic deformation in polymers is due to:

A. Slight adjust of molecular chains B. Slippage of molecular chains

C. Straightening of molecular chains D. Severe of Covalent bonds

vii. Nematic is a type of liquid crystal which is based upon

A. Ordering B.Molecules

C. Surface area D.Surface tension

viii. Cholesteryl benzoate is milky liquid at

A.149 degree Celsius	B. 180 degree Celsius
C. 145 degree Celsius	D. 189 degree Celsius

ix. Turbid liquid phases have property to move as

A. Gases	B.Liquids
C.Sticky substances	D.Honey

x. The turbid liquid state has property of

A.Close packing	B.Vibrational motion
C.Surface tension	D.More spaces

xi. Polymer obtained by the polymerization of two or more different types of monomer molecules is

A.Homopolymer	B. Copolymer
C.Heteropolymer	D.Addition polyme

xii. Molecular crystals are generally

A.Hard	B.Soft
C.Unstable	D.Stable

xiii .Ionic crystals are

A.Hard	B.Soft
C.Brittle	D.Amorphou

xiv. A sample of atactic polystyrene is separated into 5 fractions

Fraction	Number of Moles	Molecular Weight
1	20	10,000
2	20	20,000
3	20	30,000
4	20	40,000
5	20	50,000

What is the number average molecular weight?

A. 2.33×10^4 B. 3.0×10^4

C. 3.66×10^4 D. 4.33×10^4

xv. The commonly used reagent in protonic acid doping is

A. H_2SO_4 & $(NH_4)_2SO_4$ B. HCl and $(NH_4)_2SO_4$

C. Na_2SO_4 in THF D. Iodine in CCl_4

Q.2. What are liquid crystal? Discuss their classification?

Q.3. Explain the theory of liquid crystals

Q.4. Discuss the classification of polymers.

Q.5. Write explainary note on

a. Viscometry method for the determination of mol.wt of polymer

b. Osmometry method for the determination of mol.wt of polymer

c. Light scattering method for the determination of mol.wt of polymer

Q.6.Discuss the synthesis of: 1. PMMA 2. Melmac 3. Nylons 4. Bakelite 5. Dacron

Q.7.In apolymer there are 100 molecules of molecular weight 100,200 molecules of molecular weight 1000 and 300 molecules of molecular weight 10,000. Find number average, weight average molecular weigt and PDI

Q.8.Explain atactic, isotactic and syndiotactic polymers.

Q.9.Bring out with example difference between thermoplastics and thermosetting plastics

Q.10.Give a detail account on molecular weight of polymers.

2.15 ANSWERS (MCQS):

i		ii		iii		iv		v	
vi		vii		viii		ix		x	
xi		xii		xiii		xiv		xv	

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Unit:3 QUANTUM CHEMISTRY – I

Content

3.1 INTRODUCTION

Classical mechanics is obeyed by microscopic particles such as planets and rigid bodies. It was formulated by Sir Isaac Newton (1642-1727) in the seventeenth century. However microscopic particles such as electrons, protons, atoms molecules show wave duality. They do not obey Newtonian dynamics. They obey quantum mechanics (wave mechanics) a key feature of which is quantization of energy and angular momentum.

From your earlier knowledge, you know that Bhor's theory of hydrogen atom enabled calculation of radii and energies associated with the permissible orbits in the hydrogen atom. The values calculated were found to be in good agreement with experimental values. However, the use of spectroscope of high resolving power reveals the presence of fine structures in the spectra of hydrogen. Bohr's theory could not explain the occurrence of these fine spectral lines

3.2 BLACK BODY RADIATION AND QUANTUM THEORY:

Radiation is defined as a wave that consists of oscillating electric and magnetic field; hence, it is also called electromagnetic wave. It is characterized by its wavelength λ and frequency ν (number of oscillations per second) which are related as $\lambda\nu = c$, where c is the velocity of the wave. The value of c is generally 3×10^8 ms^{-1}.

Radiation is emitted by any solid at any temperature as a result of the vibrations of its particles. At low temperature the emitted radiation is of low frequency (large wave length) infrared (human body also gives off infrared radiation but the amount of radiation is very small). As the temperature is raised, not only the amount of radiation increases but also more radiations of smaller frequencies are emitted. At any temperature the radiation from a solid has a continuous range of frequencies (in contrast to gases which produces line spectra).

Different solids emit radiation at different rate at the same temperature, the rate is maximum when the solid is perfectly black (black body). By definition, a black body can absorb all the radiations that falls on it. In practice, a hollow enclosure having a small hole is the nearest approach to a black body because the radiation entering the chamber through the hole is absorbed completely due to repeated reflections inside the enclosure. Radiations emerging from the small hole of such a hollow enclosure are, therefore, called 'black body radiation'. The intensity of radiation, i.e., that total radiation emitted per unit surface area, from a black body depends only on temperature (T) and is independent of the nature of the solid.

3.2.1 Distribution of Energy in the Black Body Radiation:

The radiation emitted by a black body is not confined to a single wavelength but is spread over a wide spectrum of wave lengths. the distribution of radiant energy over the different

frequencies is described in term of a function which denotes the radiant density (amount of radiation per unit volume of the black body chamber) in the frequency range, say ν and $\nu + d\nu$. Experimentally, it is found that any temperature T the energy density increases with wavelength A^0, reaches a maximum and then falls off to zero. As temperature increases the point of maximum shifts to higher frequency (shorter wavelength) side. The experimental dependence of the energy density on temperature and wave length (λ) is shown in Fig.3.1

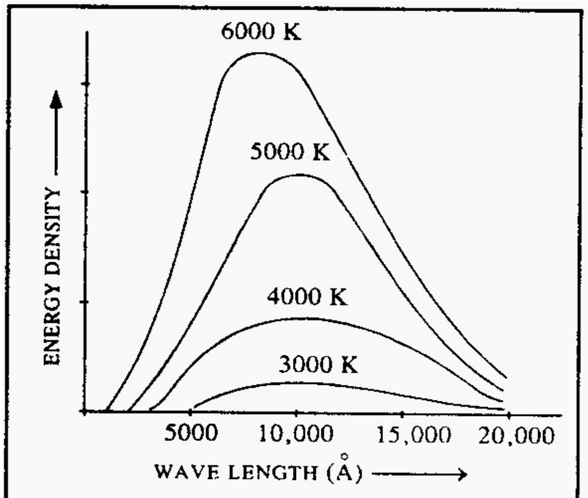

Fig. 1. Plots of energy density versus wave length for black body radiations at different temperatures.

Fig 3.1 Dependence of energy density on wavelength and temperature

The curves so obtained have the following characteristics.

The radiation emitted by a black body is not confined to a single wavelength but spread over a wide spectrum of wavelengths. The distribution of radiant energy over the different frequencies is described in terms of a function $\rho\ (\nu)d\nu$ which denotes the radiant energy density (amount of radiation per unit volume of the black body chamber) in the frequency range ν and $\nu + d\nu$.

(i) For each temperature, there is a particular wavelength at which the energy radiated is maximum.

(ii) The position of maximum shift toward lower wavelength with increase in temperature.

(iii) The higher the temperature, the more pronounced is the maximum.

These curves are usually referred to the black body radiation curves. A perfect absorber is also a perfect emitter of radiation. Thus of all bodies heated to a given temperature, maximum energy is radiated by black body.

According to Wien's displacement law, $\lambda_m T = b$, where λ_m is the wavelength corresponding to maximum in the curve the wein constant $b = 0.0029\, mK$. wein, the german physicist, was awarded the 1911 Physics Nobel prize for his discovery concerning the laws governing the heat radiation.

3.3 QUANTUM THEORY OF RADIATION:

The energy distribution in black body radiation is could not be explained by the application of classical physics. The correct expression was derived by Plank on the basis of quantum theory of radiation. According to this theory,

(1) Radiant energy is emitted or absorbed discontinuously in the form of tiny bundles of energy known as quanta.

(2) Each quantum is associated with definite amount of energy E$(= h\nu)$ where E is energy in Joules, ν is frequency of radiation in reciprocal of second(s^{-1}) and h is fundamental constant known as Plank's constant. The numerical value of h is 6.626×10^{-24} Js.

The value of quantum energy is given by $hc\bar{\nu}$ where $\bar{\nu}$ is the wave number defined as reciprocal of wavelength i.e., $\bar{\nu} = \frac{1}{\lambda}$. Evidently, $\nu = \frac{c}{\lambda} = c\bar{\nu}$ and E$= hc\bar{\nu}$.
(3) A body can emit or absorb energy only in whole number of quantum. i.e., $1h\nu$, $2h\nu$, $3h\nu$……….…… $nh\nu$. Energy in fractions of quantum cannot be lost or absorbed. This is known as quantization of energy.

Based on this theory, Plank obtained the following expression for the energy density of black body radiation.

$$E(\nu)d\nu = \frac{8\pi h\nu^3}{c^3} \times \frac{d\nu}{exp\left(\frac{h\nu}{kt}\right) - 1} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.1)$$

3.4 PHOTOELECTRIC EFFECT :

J.J. Thomson observed that when a beam of light of sufficiently high frequency is allowed to strike a metal surface in vacuum, electron is ejected from the metal surface. This phenomenon is known as photoelectric effect and the ejected electron photoelectrons. Fig 3.2

A few metals show this effect under the action of visible light,butmany more show under the action of more energetic ultraviolet light Cesium, which amongst the alkali metals has the lowest ionization energy, is also the metal from which electrons are ejected most easily by light. This metal is, therefore, used largely in photoelectric cells.After making careful study of photoelectric effect under different conditions, the following observations were made:

(1) For each metal, a certain minimum frequency of incident light is needed to eject electrons. This is known as threshold frequency, ν_0. A light of lower frequency than this cannot eject electrons no matter how long it falls on metal surface or how long is its intensity. The threshold frequency is different for different metals.

(2) The kinetic energy of ejected electrons is independent of the intensity of incident light but varies linearly with its frequency.

(3) The number of ejected electrons from the metal surface depends upon the intensity of the incident radiation. The greater the intensity, the larger is the number of ejected electrons.

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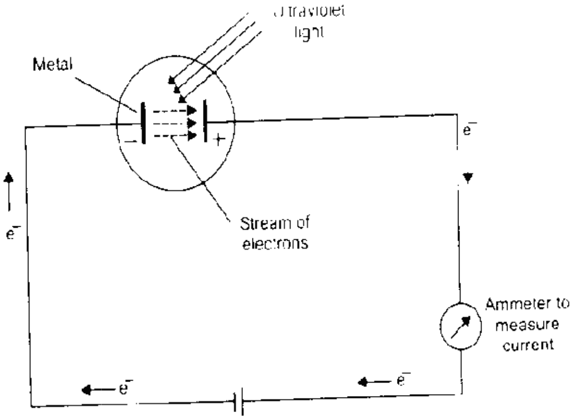

Fig.3.2 Photoelectric effect

3.4.1 Einstein's Photoelectric Equation:

The Photoelectric effect cannot be explained on the basis of the classical wave theory of light. According to the theory, energy of light depends on its intensity. If this view is correct, then the light of any frequency, if made sufficiently intense, can cause ejection of electrons. But this does not happen. The quantum theory of radiation affords an easy explanation for the photoelectric effect.

According to this theory, light consist of bundles of energy called photons. The energy of each photons being equal to $h\nu$ where ν is the frequency of light. When a photon of light of frequency ν_0 (threshold frequency) strikes on an electron in a metal, it imparts its entire energy $(= h\nu_0)$ to the electron. This energy enables the electron to break away from the atom by overcoming the attractive influence of the nucleus. Thus each photon can eject one electron. If the frequency of light is less then $\nu_{0,}$ there will be no ejection of electron. Now suppose frequency of the light falling on the metal surface is higher then the threshold frequency. Let it be ν. When the photon of this light strikes a metal surface, some of its energy (which is equal to the energy binding the electron with the nucleus) is consumed to separate the electron from the metal and the remaining energy will be imparted to the ejected electron to give it certain velocity u (i.e., kinetic energy $\frac{1}{2}mu^2$). Fig 3.3

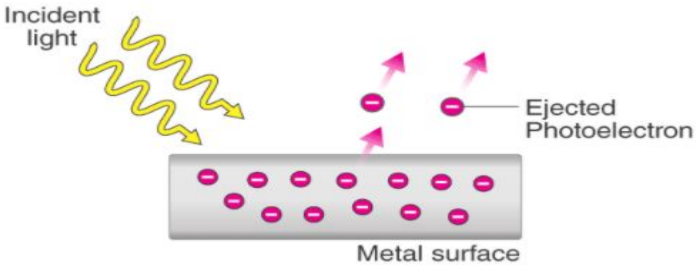

Fig 3.3 Photoelectric effect

Einstein, applying quantum theory, showed that :

$$h\nu = \phi + \frac{1}{2}mu^2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.2)$$

Where ϕ is threshold energy (or the work function) of the metal and ½mu^2 is the kinetic energy imparted to the ejected electron. Evidently,

$$\phi = h\nu_0 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.3)$$

Substituting the above value of ϕ in the equation (3.2) and rearranging, we get

$$\frac{1}{2}mu^2 = h(\nu - \nu_0) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.4)$$

Equation 4.4 is the Einstein photo electric equation. Albert Einstein (1879- 1955), the German physicist, won the noble prize in 1921 for explaining the photoelectric effect and other contribution to mathematical physics.

3.5 COMPTON EFFECT:

In 1923 Compton provided one more proof of quantum theory. The American physicist shared in 1927 Physics novel prize With Wilson, The British physicist Arthur Compton found that if monochromatic X-rays (i.e., X-rays having a particular wavelength) are allowed to fall on carbon or some other light element, the scattered X rays have wavelength lighter than the incident rays. In other words, the scattered X-rays have lower frequency, i.e., lower energy than the incident X-rays. Since the scattering is caused by electrons, it is evident that some interaction between X-rays and electrons has taken place and this is resulted in decrease in energy for the former. The decrease in energy or increase in wavelength of X-rays after scattering from the surface of an object is known as **Compton Effect.** Fig 3.4

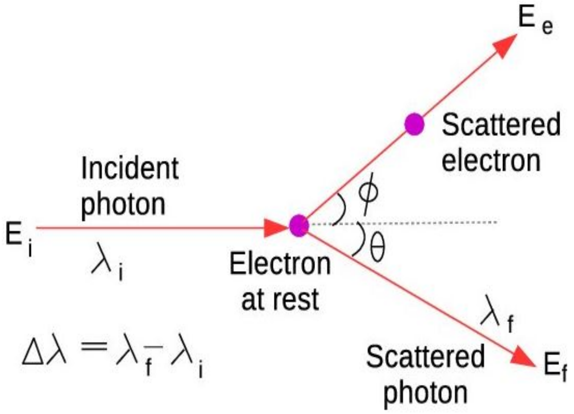

Fig 3.4 Compton Effect

Compton demonstrated that:

When X-rays of wavelength λ_i struck a sample of graphite, an electron was ejected and the X-ray scattered at an angle θ had longer wavelength λ_f.

By applying the law of conservation of energy and law of conservation of momentum and assuming X-ray to consist of photons, each possessing energy$h\nu$, Compton showed that

$$\triangle\lambda = \left(\frac{2h}{mc}\right) sin^2\frac{\theta}{2} \qquad \text{……………………….. (3.5)}$$

Where $\triangle\lambda = (\lambda_f - \lambda_i)$ is the increase in wavelength (termed as Compton shift) produced as a result of the collision, m is the rest mass of the electron, c is the velocity of light and θ is the angle between the incident and the scattered X-ray.

According to this equation, Compton shift should be independent of the wavelength of the incident X-ray. This has been found to be so experimentally. Further, the value of Compton shift, as obtained from the above equation, by substituting the values of h, c, m and θ have been found to be in close agreement with the experimental values.

Compton said that it was like a ball hitting a stationary ball which is pushed away while the energy of the striking ball decreased. Compton effect provides a good illustration of the uncertainty principle. Suppose X-rays are used to determine the position and momentum of an electron. As a result of mutual interaction of X-rays and electron the wavelength of X-rays increases, i.e., the frequency or energy of X-ray decreases. This energy must have been transferred to the electron and, therefore,the momentum of the electron must have changed during the process. Consequently, the momenof the electron cannot be determined with certainty.

Compton effect also provides for the photon nature of radiation. The Compton equation (a) can be written as

$$\triangle \lambda = \lambda_f - \lambda_i = \frac{h}{mc}(1 - \cos\theta) \qquad \text{……………………..} (3.6)$$

We see that the wavelength λ_f of scettered X-rays is always greater than the wavelength λ_i of the incident X-rays. The wavelength shift is independent of the nature of the substance and the wavelength of incident X-ray. It depends on the scattering angle θ only.

3.6 *THE SOMERFIELD EXTENSION OF BOHR’S THEORY*:

Bohr could not explain the presence of fine structure. The theory was extended by German mathematical physicist Arnold Somerfield (1868 – 1951), by putting forward the idea of elliptical orbits.

According to Somerfield, an electron revolving around a central positively charged nucleus is so influenced by the nucleus charge that is set into elliptical orbits with the nucleus situated at one of the foci (Fig.4.3) .That is clear that while according to Bohr’s theory electron move in circular orbits, according to Somerfield’s modification, electron move in elliptical orbits .In Somerfield modification, there will a major axis and a minor axis having different lengths. As the orbit broadens, the lengths of two axes become closer and they become circular as shown in Fig.3.5 Thus, the circular orbit is special case of elliptical orbit.

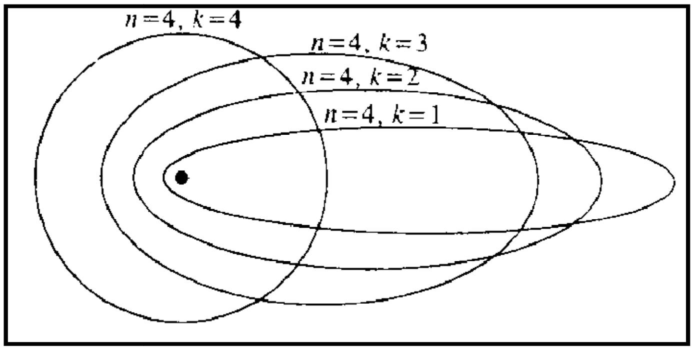

Fig. 3.5 Somerfield's elliptical electron orbit for n=4

3.7 WEAKNESS OF BOHR'S THEORY:

The Bohr's theory of the atom gave a surprisingly accurate quantitative explanation of the spectra of atom and ions with a single electron. However, with atom of two electrons [He], serious discrepancies with experiment were encountered. The main shortcomings of Bohr's theory are as follows:

1. Bohr's theory fails to explain spectra of multi electron atoms.

2. Bohr's atomic model fails to account for the effect of magnetic field on the spectra of atoms and ions. It is observed that when the source of spectrum is placed in a strong magnetic field, each spectral line is further split into numbers of lines, this is called Zeeman effect. This observation cannot be explained on the basis of Bohr's model.

3. In 1923, de Broglie suggested that electron like light has a dual character. It has particle as well as wave character. Bohr's theory treats the electron as a particle.

4. According to Heisenberg's uncertainty principle, it is impossible to determine simultaneously the exact position and momentum of a small moving particle like electron. The postulate of Bohr that the electrons revolve in well defined orbit around the nucleus with well defined velocities is, not tenable. Now we shall discuss de Broglie's concept and Heisenberg's uncertainty principle in some details since these two concepts are mainly responsible for exposing the most serious shortcomings off Bohr's theory.

3.8 WAVE THEORY OF MATTER :

3.8.1 Particle and Wave Character of Electron:

de Broglie's Equation: In 1905 Einstein had suggested that light has a dual character ; as `wave' and also as `particle'. De Broglie in 1924 suggested that any moving material particle has associated wave properties. de Broglie deduced that the laws of optics differ from the laws of ordinary mechanics only because of the rest mass of photons is zero. Hence de Broglie reasoned particles with small masses such as electrons, protons, neutrons, atoms, molecules etc. shows dual character. de Broglie was awarded the Physics Noble prize in 1929.

According to de-Broglie's, an electron of mass 'm' moving with a velocity 'u' is associated with a wave having wave-length λ. The wavelength and velocity are related by the following mathematical equation

$$\lambda = \frac{h}{mu} \quad \text{.................................. (3.7)}$$

Where h is the Planck's constant and mu is the momentum 'P'.

Proof of de-Broglie's equation: consider the case of photon. If we consider it to be a wave of frequency 'v', its energy is given by

$$E = hv \quad \text{...................... (3.8)}$$

if we consider it as a particle of mass 'm', its energy is given by

$$E = mc^2 \quad \text{......................... (3.9)}$$

From equation 3.8 and 3.9 we get

$$hv = mc^2$$

Since we know $v = \frac{c}{\lambda}$

Then $\frac{hc}{\lambda} = mc^2$

$$\lambda = \frac{h}{mc} \quad \text{........................... (3.10)}$$

As $c = u$ for all moving particles

Then $\lambda = \frac{h}{mu}$ .... (3.11)

Example:

Calculate the de Broglie wavelength of electron moving with the velocity 1.2× 10^5 m/sec.

Solution:

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

$$= \frac{6.626 \times 10^{-3}\ \mathrm{JS}}{(9.1 \times 10^{-31}\mathrm{Kg})(1.2 \times 10^{5} ms^{-1})}$$

$$= 6.068 \times 10^{-9} m$$

$$= 6.068 \mathrm{A}^{0}$$

3.8.2 Heisenberg Uncertainty Principle:

Werner Heisenberg, in 1927 enunciated one of the most fundamental relationships of modern physics which is known as uncertainty principle. According this principle 'it is impossible to make simultaneously, the exact determination of the velocity of a particle and also its position.' In the word of British cosmologist Stephan Hawking, 'even god is bound by the uncertainty principle and cannot predict future exactly'. The uncertainties in the determination of these two quantities very inversely so that, if one is determined fairly accurately, the other must be correspondingly less accurate, this limitation is in no way dependent upon the accuracy of the observing instruments or the method of the measurements, but it an inherent relationship in nature applicable to all particles.

If p and x represents two conjugate variables, such as momentum and position of any particle, the product of the uncertainties Δp and Δx in the determation of their respective values is approximately given by the following relation,

$$(\Delta x)/(\Delta p) \geq h/4\pi \qquad \text{.......................... (3.12)}$$

Where Δx uncertainty with is regard to its position and Δp is the corresponding uncertainty with regard to its momentum. Evidently if (Δx) is very small, i.e. the position of the particle is known more or less exactly, Δp would be large, i.e., uncertainty with regard to momentum will be large. Similarly, if an attempt is made to measure exactly the momentum of the particle, the uncertainty with regard to position will become large. The German physicist, Werner Heisenberg (1900-1976) won the physics Noble prize in 1932.

If we measure the position to within 1.0 nm, about the resolving power of an electron microscope, $\Delta y = 10^{-7}$ and hence $\Delta v = 10^{-7}$ cms^{-1}, with this indeterminacy in velocity, the position one second later would be uncertain to within 2.0 nm. or about 0.2% of the diameter of the particle. Thus, even in the case of ordinary microscopic particle, indeterminacy may limit exact measurements. With particle of atomic or subatomic size, the effect will be much greater.

When waves are associated with particles, an uncertainty principle is a necessary consequence. If the wavelength or frequency of an electron wave is to have a definitely fixed value, the wave must have an infinite event. Any attempt to confine a wave within boundaries requires destructive interference at the boundaries to reduce the amplitudes there to zero. It follows that an electron wave of perfectly fixed frequency, or momentum, must be infinitely extended and therefore must have a completely intermediate position. To fix the position, we require superimposed waves of different frequency and thus as the position becomes more closely defined, the frequency and hence momentum becomes less precisely specified.

The uncertainty principle relation can also be expressed in terms of energy and time. Thus,

$$\Delta\mathrm{E}.\,\Delta\mathrm{t} \geq \frac{h}{4\pi} \qquad \text{…………………………} (3.13)$$

$$h\Delta v.\,\Delta t \geq \frac{h}{4\pi} \qquad \text{…………………………..} (3.14)$$

To measure the energy of system with accuracy ΔE, the measurement must be extended over a period of time of order of magnitude$\frac{h}{\Delta\mathrm{E}}$. This equation is used to estimate the sharpness of spectral lines. In general, lines arising from transition from the ground state of an atom are sharp, because the optical electron spend a long time Δt in the ground state and ΔE the uncertainty in the energy level, is correspondingly small, the line breath is related to ΔE by $\Delta_v = \frac{\Delta\mathrm{E}}{h}$. The life time of excited states may sometimes be very short and transition between such states gives rise to diffuse lines as a result of the indeterminacy of the energy levels.

3.8.3 Physical Concept of Uncertainty Principle:

The physical concept of uncertainty principle becomes illustrated by considering an attempt to measure the position and momentum of an electron moving in Bohr’s orbit. To locate the position of the electron, we shall device an instrument ‘super microscope’ to see the electron. A substance is said to be seen only if it could reflect light or any other radiation from its surface. Because the size of electron is very small, its position in any instant may be determined by a super microscope employing light of very small wave length (such as x-rays or γ rays).

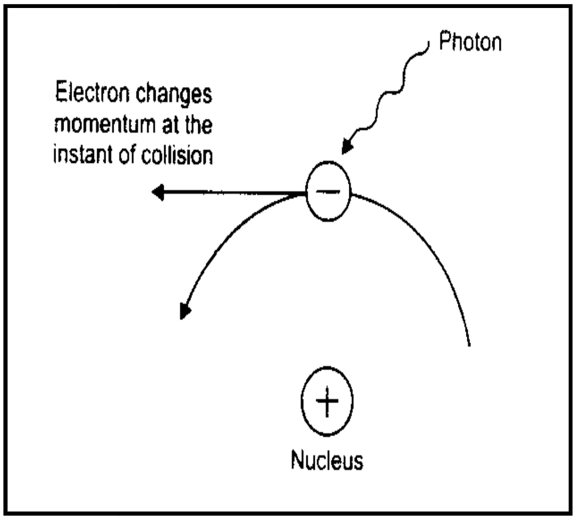

Fig 3.6 The momentum of electron changes when the photon of light strikes it, so does its position

A photon of such a radiation of small wave length λ, has great energy and therefore has large momentum. As one such photon strikes the electron and is reflected, its intensity changes the momentum of electron. Now the momentum gets changed and becomes more uncertain as the position of the electron is determined (Fig 3.6). Thus it is impossible to determine the exact position of an electron moving with a definite velocity (or possessing definite energy). It appears clear that Bohr's picture of as electrons moving in a orbit with fixed velocity (or energy) is completely untenable.

As it is impossible to know the position and velocity of any one electron on account of its small size, the best we can do is to speak of the probability or relative change of finding an electron with a probable velocity. The old classical concept of Bohr has now been discarded in favor of the probability approach.

Before we take on the detailed study of quantum mechanics let us study first that what are conservation laws and classical mechanics.

3.9 CONSERVATION LAWS AND CLASSICAL MECHANICS :

3.9.1 Newtonian Mechanics: For our purposes Newtonian mechanics consist of the verbal and mathematical statements of Newton's three laws of motion, which, together with a few definitions, allow us to derive the conservation laws.

3.9.2 First Law (Law of Inertia). Everybody tends to remain at rest or in uniform motion (constant velocity) in a straight line unless acted upon by a external force.

3.9.3 Second Law (Law of Force). The rate of change of momentum is proportional to the force producing it.

3.9.4 Third Law (Law of Action and Reaction). If body A exerts a force on a body B this is equivalent to body B exerting a force equal magnitude but opposite in sign on body A. the mathematical statement of the second law is:

$$\mathrm{F} = \frac{dp}{dt} \qquad \text{…………………………..} \qquad (3.15)$$

This leads directly to the important results of Newtonian mechanics. F is total force acting on the body and p is momentum of the body defined as

$$p = mv = m\frac{dr}{dt} \qquad \text{………………………} \qquad (3.16)$$

where m is the mass of the particle and v is the velocity and r is the radial vector from the origin to the position of the body.

3.10 DISTINCTION BETWEEN MATTER WAVES AND ELECTROMAGNETIC WAVES:

It should be carefully noted that matter waves are distinctly different from electromagnet waves. The speed of these waves is not the same as that of light; it is understandably, much less. These waves cannot be radiated in empty space. They are not emitted by the particle under consideration; they are simply associated with it. The wavelength of matter waves is generally very small as compared to wavelength of electromagnetic waves.

3.11 DERIVATION OF BOHR ANGULAR MOMENTUM POSTULATE FROM DE BROGLIE'S RELATION :

Consider an electron moving in a circular orbit of radius r around a nucleus. The wave train would be as shown in Fig. (3.7). Evidently, if the wave is to remain continually in phase Fig. (4.5a), the circumference of the circular orbit must be an integral multiple of wavelength λ, that is

$$2\pi r = n\lambda = \frac{nh}{mv} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.17)$$

Thus, angular momentum, $L = mvr = \frac{n\lambda}{2\pi}$ …………………….. (3.18)

This is Bohr's postulate.

Evidently, if the circumference is bigger or smaller then the value $\frac{nh}{2\pi}$, the wave will not longer remain in phase

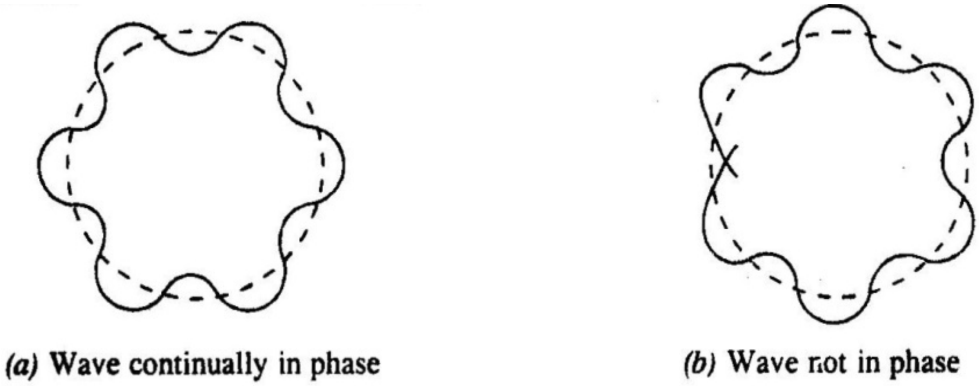

Fig. 3.7 The wave trains of an electron moving in a circular path around a nucleus

3.12 *QUANTUM MECHANICS*:

The microscopic particles such as protons, electrons, atoms and molecules show wave particle duality. They do not obey Newtonian dynamics. The laws of quantum mechanics (or wave mechanics) were formulated in 1925 by the German physicist. M. Born, W. Heisenberg and P. Jordon (in the formulation known as matrix mechanics) and in 1926 by Austrian physicist E. Schrodinger. Schrodinger formulation of quantum mechanics is more familiar to chemists than the Born Heisenberg–Jordon formulation of matrix mechanics through both are equivalent.

3.12.1 The Postulates of Quantum Mechanics :

The postulates of quantum mechanics for the mechanical treatment of the structure of atom rest upon a few postulates which, for a system moving in one dimension, say the x-coordinate are given below.

First postulate: The physical state of a system at time t is described by the wave function ψ (x, t).

Second postulate: The wave function ψ and its first and second derivative $\psi(x, t)/\delta x$ and $\delta^2\psi(x, t)/\delta x^2$ are continuous, finite and single valued for all values of x. And also the wave function ψ (x, t) is normalized, i.e.,

$$\int_{-\infty}^{+\infty} \psi^* (x, t)\psi (x, t)\, dx = 1 \qquad \text{………………… (3.19)}$$

Where ψ^* is complex conjugate of ψ formed by replacing i with –i wherever it occurs in the function ψ ($i=\sqrt{-1}$).

Third Postulate: A physically observable quantity can be represented by a Hermitian operator. An operator is said to be Hermitian operator Â, if it satisfies the following condition:

$$\int \psi_i^* \hat{A}\, \psi_j\, dx = \int \psi_j\, \hat{A}\, \psi_i^* dx \qquad \text{………………….. (3.20)}$$

Where ψ_i and ψ_j are the wave functions representing the physical states of the quantum system, i.e., a particle, an atom or molecule.

Fourth postulate: The observed value of an observable Â is the Eigen-value only if the function remains unchanged.

$$\hat{H}\boldsymbol{\psi} = \boldsymbol{E\psi} \qquad \text{…………………. (3.21)}$$

Eq. (3.21) is known as an Eigen-value equation. Here Ĥ is the operator for the observable (physical quantity) and $\boldsymbol{\psi}$ is an Eigen function. In other words, the measurement of the observable Ĥ yields the Eigen value E.

Fifth postulate:_ The average value (or expectation value), <Â> of an observable Â corresponding to the operator $\hat{A}$ is obtained from the relation

$$< \mathrm{A} > = \int_{-\infty}^{\infty} \psi^{*}.\ \hat{A}.\ \psi\, dx \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots..\ (3.22)$$

Where the function ψ is assumed to be normalized in accordance with Eq.3.19. The average value of, say, the x - coordinate is given by

$$< \hat{x} > = \int_{-\infty}^{\infty} \psi^{*}\ \hat{x}\ \psi\, dx \qquad \ldots\ldots..\ldots\ldots\ldots\ldots..(3.23)$$

Sixth postulate: The quantum mechanical operators corresponding to the observable are constructed by writing the classical expression in terms of the variables and covering the expressions to the operators, as shown in table below:

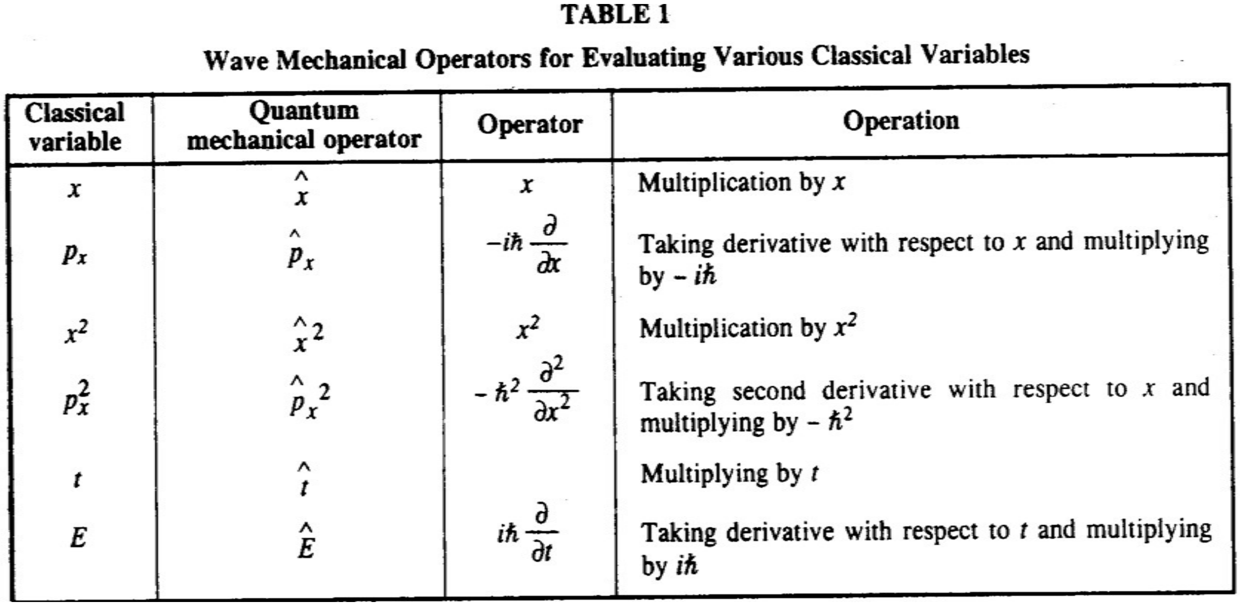

TABLE 1

Wave Mechanical Operators for Evaluating Various Classical Variables

Classical variable	Quantum mechanical operator	Operator	Operation
x	$\hat{x}$	x	Multiplication by x
p_x	$\hat{p}_x$	$-i\hbar \frac{\partial}{\partial x}$	Taking derivative with respect to x and multiplying by $-i\hbar$
x^2	$\hat{x}^2$	x^2	Multiplication by x^2
p_x^2	$\hat{p}_x^{\,2}$	$-\hbar^2 \frac{\partial^2}{\partial x^2}$	Taking second derivative with respect to x and multiplying by $-\hbar^2$
t	$\hat{t}$		Multiplying by t
E	$\hat{E}$	$i\hbar \frac{\partial}{\partial t}$	Taking derivative with respect to t and multiplying by $i\hbar$

Seventh postulate: The wave function $\psi(x, \mathrm{t})$ is a solution of the time-dependent equation

$$\hat{H}\ \psi(x,\mathrm{t}) = i\hbar\ \frac{\partial \psi(x,t)}{\partial t} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(3.24)$$

Where Ĥ is the Hamiltonian operator of the system.

3.12.2 Zero point energy: According to old quantum theory, the energy levels of harmonic oscillators were given by $E\upsilon = nh\upsilon$. If there were true the lowest energy level, with $\upsilon = 0$, would have zero energy. This would be a state of complete rest, represented by the minimum in the Fig.3.8.

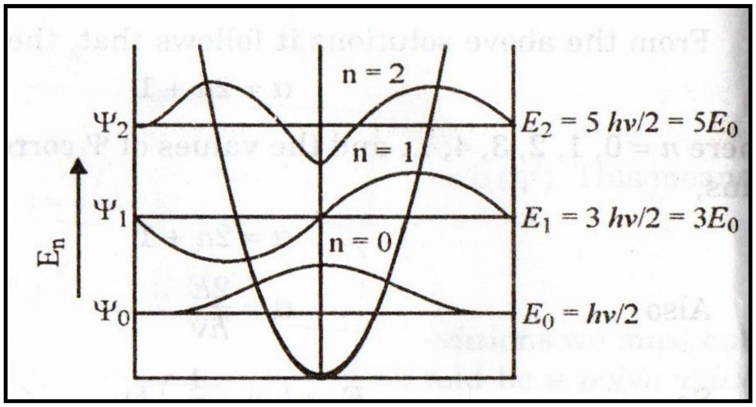

Fig.3.8 Various energy levels.

The uncertainty principle does not allow such a state of completely defined (in case of zero) momentum. Consequently, the wave treatment shows that the energy levels of the oscillators are given by

$$E\upsilon = (\upsilon + \frac{1}{2}h\upsilon) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.25)$$

Now when $v = 0$, the ground state, there is residual zero point energy amounting to

$$E_0 = \frac{1}{2}h\upsilon \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.26)$$

3.13 THE SCHRÖDINGER WAVE EQUATION:

3.13.1 Derivation of The Schrӧdinger Wave Equation

Ervin Schrӧdinger and Werner Heisenberg independently discovered the basic principles for a new kind of mechanics, which provided mathematical techniques competent to deal with the wave particle duality of matter and energy. The formalism of Schrӧdinger was called wave mechanics and that of Heisenberg matrix mechanics. Despite their quite different mathematical formalism, the two methods of essentially equivalent at the deeper level of their physical concepts. They represent two different forms of fundamental theory called quantum mechanics.

In the derivation of wave equation, Schrӧdinger made use of the de Broglie relationship between the momentum of a particle and the wavelength of the associated matter waves. This represents the essential postulatory basis of Schrӧdinger approach to the new mechanics. In Schrӧdinger wave model of an atom, the discrete energy levels or orbits proposed by Bohr are replaced by mathematical functions,ψ, which are related to the probability of finding electrons at various places around nucleus.

Consider a simple wave motion as that of the vibration of a stretched string. Let ω be the amplitude of this vibration of any point whose coordinate be x at time t. the equation of such a wave motion may be expressed as:

$$\frac{\partial^2\omega}{\partial x^2} = \frac{1}{u^2} \times \frac{\partial^2\omega}{\partial t^2} \qquad \text{…………………} (3.27)$$

Where u is the velocity with which the wave is propagating. There are two variables, x and t , in the above differential equation, i.e., the amplitude ω depends upon two variables x and t. This differential equation may be solved by separating the variables, thus ω may be expressed in the form

$$\omega = f(x)\mathrm{g}(t) \qquad \text{………………….}(3.28)$$

Where $f(x)$ is a function of coordinate x only and g(t) is a function of time t only. For stationary waves, such as which occurs in the stretched string, the function g(t) be represented by the expression

$$\mathrm{g}(t) = \mathrm{A}\sin(2\pi\nu \mathrm{t}) \qquad \text{…………………..}(3.29)$$

where ν is the vibrational frequency and A is a constant known as the maximum amplitude.

Hence the equation for ω may be written as,

$$\omega = \mathrm{f}(x)\,\mathrm{A}\sin(2\pi\nu t) \qquad \text{……………………..}(3.30)$$

Differentiating equation (3.30) with respect to t,

$$\frac{\partial\omega}{\partial t} = \mathrm{f(x)A}\cos(2\pi\nu t).2\pi\nu$$

And $\frac{\partial}{\partial t}(\frac{\partial\omega}{\partial t}) = -\,\mathrm{f}(x)\mathrm{A}\sin(2\pi\nu t).4\pi^2\nu^2$ ………………………(3.31)

or $\frac{\partial^2\omega}{\partial t^2} = -4\pi^2\nu^2\, \mathrm{f}(x)\mathrm{g(t)}$ ..…………………..…… (3.32)

Similarly from equation (3.28)

$$\frac{\partial^2\omega}{\partial x^2} = \frac{\partial^2 f(x)}{\partial x^2}\mathrm{g(t)} \qquad \text{……...…………… (3.33)}$$

From equations (3.27),(3.32) and (3.33), we

$$\frac{\partial^2\omega}{\partial x^2} = \frac{-4\pi^2\nu^2}{u^2} f(x) \qquad \text{…………………….. (3.34)}$$

The frequency of the vibrations, ν and the velocity, u are related by the expression

u = $\lambda\nu$, where λ is the corresponding wavelength. Hence from equation (3.34), we get

$$\frac{\partial^2 f(x)}{\partial x^2} = \frac{-4\pi^2}{\lambda^2} f(x) \qquad \text{……………………. (3.35)}$$

Now schrÖdinger wave may be formulated by combining two relationships. one is based on purely mathematical property of waves, namely equation (3.35) and the other is on the wave property of matter as represented by Broglie equation, (i.e., λ=h/mu).

The equation (3.35) represents wave motion in one direction only. It may be extended to movement in three directions represented by the coordinate x, y and z. if $f(x)$ for one co-ordinate is represented by $\psi(x.y,z)$which is amplitude function for three coordinate equations (3.35). Takes the form,

$$\frac{\partial^2\varphi}{\partial x^2} + \frac{\partial^2\varphi}{\partial y^2} + \frac{\partial^2\varphi}{\partial z^2} = \frac{-4\pi^2}{\lambda^2}\varphi \qquad \text{……………………. (3.36)}$$

Here φ is a function of Cartesan coordinates$(x.y,z)$. Replacing the symbol ∇^2 (pronounced as del square) for the differential (Laplacian) operator, i.e

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

We get $$\nabla^2\varphi = \frac{-4\pi^2}{\lambda^2}\varphi \qquad \text{………………….. (3.37)}$$

Following the de Broglie ideas, SchrÖdinger, the Austrian physicist, applied the above treatment to material waves associated with all particles including electrons, atoms and molecules. Upon introducing de Brogie relationship, λ =h/mu in equation (3.37)

$$\nabla^2\varphi = \frac{-4\pi^2 m^2 u^2}{h^2}\psi \qquad \text{………………….. (3.38)}$$

Where m is the mass and u is the velocity of the particle.

The kinetic energy of the particle given by ½mu^2, is equal to the total energy E minus the potential energy (V) of the particle,i.e.,

K.E.= ½mu^2=E-V

or mu^2= 2(E-V) …………………..(3.39)

Combining equation (3.38) and equation (3.39) we get

$$\frac{\partial^2\varphi}{\partial x^2} + \frac{\partial^2\varphi}{\partial y^2} + \frac{\partial^2\varphi}{\partial z^2} + \frac{8\pi^2 m(E-V)}{h^2}\varphi = 0 \qquad \text{………………….. (3.40)}$$

or $$\nabla^2\varphi + \frac{8\pi^2 m(E-V)}{h^2}\varphi = 0 \qquad \text{……………….….. (3.41)}$$

These two equations (3.40) and (3.41) are the wave equations for a simple particle. Either of these equations is called as Schrӧdinger wave equation which has been used to solve a number of problems related to the atomic and molecular structure.

Schrӧdinger shared the 1933 physics noble prize with Dirac for the discovery of new productive forms of atomic theory.

The Schrodinger’s Wave equation is a second degree differential equation. It has several solutions. Some of these are imaginary and not valid. If the potential energy is known, the total energy E and corresponding wave function φ can be evaluated.

The wave function is always finite, single valued and continuous. It is zero at infinite distance. Solutions that meet these requirements are only possible, if E is given certain characteristic values called **Eigen-values**. Corresponding to these values of E, we have certain characteristic values of wave function φ and are called **Eigen-functions.** As these Eigen-values correspond very nearly to the energy values associated with different Bohr-orbits, the Bohr model may be considered as a direct consequence of wave mechanical approach.

3.14 SIGNIFICANCE OF ψ AND ψ^2 :

In the Schrӧdinger wave equation we have used the function ψ as a quantity analogous to amplitude in classical wave. According to the theory of propogation of light and sound waves, the square of the amplitude of the wave is proportional to the intensity of sound or light. A similar concept, modified to meet the requirement of uncertainty principle, has been developed for the physical interpretation of wave function ψ.

A physical interpretation is given to ψ^2 rather than ψ it self. For an electromagnet wave, Einstein interpreted ψ^2 at a point as ‘probability density’, i.e., probability per unit space of finding the proton at that point. A simple interpretation was given by the Max Born to ψ^2 for a particle wave. If a particle is moving in one dirmension, ψ^2 or $\psi^*\psi$ represents probability of findings it within unit distance. Then in infinitesional dx around a point, the probability is $\psi^2\,dx$ or $\psi^*\psi dx$, ψ being a function of x only. In three dimentions space, the probability is $\psi^2 dx\,dy\,dz$ or $\psi^*\psi dx\,dy\,dz$ where $\psi = \psi(x, y, z)$ and it refers to the probability that the x, y and z coordinate of the particle lie within $x + dx$, $y + dy$ and $z + dz$ respectively. For a system of n particles in three dimensions, each will have its own set of coordinates the probability can be extended accordingly.

For an electron wave, an alternative and more useful interpretation of ψ^2or $\psi^*\psi$ is given in terms of "electron density, i.e., electronic charge per unit space". This arises from the concept that the electron being a wave may be supposed to behave like a cloud of negative electricity with non-uniform charge distribution.

The Schrodinger's wave equation is a second degree differential equation. It has several solutions. Some of these are imaginary and are not valid. If the potential energy term is known, the total energy E and corresponding wave function ψ can be evaluated.

The wave function is always finite, single valued and continuous. It is zero at infinite distance. Solutions that meet these requirements are only possible, if E is given certain characteristic values called **Eigen-values**. Corresponding to these values of E, we have certain characteristic values of wave function ψ and are called **Eigen- function**. As the Eigen-values correspond very nearly to the energy values associated with different Bohr-orbits, the Bohr model may be considered as a direct consequence of wave mechanical approach.

3.15 CONCLUSION:

In classical mechanics, the state of a system is defined by specifying all the forces acting and all the positions and velocities of the particles. Thus knowledge of the present state of a classical mechanical system allows its future state to be predicted with certainty. In quantum mechanism, as your have studied till now, the state of a system is defined by the wave function φ which is a function of the coordinates of the particles of the system and a function of time. The time-dependent Schrodinger Wave Equation is the quantum mechanical analogue of Newton's Second Law which allows the future state of a quantum mechanical system to be predicted from its present state. It should be clear to you that the knowledge of the state in quantum mechanism usually involves knowledge of only probabilities rather than certainties.

3.16 TERMINAL QUESTIONS :

1. What are the main Postulates of Quantum Mechanics .
2. Derive Bohr Angular Momentum Postulate from de Broglie's Relation .
3. Define de Broglie's Equation with proper derivation.
4. What is Schrödinger wave equation derive it and explain its significance?

5. What is Compton effect? How does Compton effect occur?

6. How does Planck's radiation law explain the spectral distribution of black body radiation?

7. How do you find the zero-point energy? Is zero-point energy infinite?

8. Outline the weaknesses of Bohr's model of atom?

9. What are the Conservation Laws and Classical Mechanics ?

10.Write a short notes on : (a) Eigen-values
(b) Eigen- function

1.8 REFERENCES

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UNIT :4 QUANTUM CHEMISTRY – I

Content

4.1 INTRODUCTION:

A statistical interpretation of the electron wave function was proposed by Max Born in 1926. This interpretation has been widely adopted since it has many advantages. According to this view, the electron is still considered as a particle and the value of ψ^2 at any point is taken to represent the probability of finding the electron at the point at any instant. It should be noted that consideration of the electron as a particle necessitate this statistical interpretation, for although a particle can only be in one position at a given instant, the Heisenberg uncertainty principle tells us that this position can never be precisely known. So, what we can do is only to state probability of the electron being found at a given point in space. Thus ψ^2 is interpreted as giving a direct measure of this probability. Consequently, the greater the wave amplitude, the greater is the probability of finding the electron at the point at a given instant or if a time interval is considered, the longer on an average is the total time the electron spends at that point.

4.2 INTERPRETATION OF SCHRÖDINGER WAVE EQUATION:

The Schrödinger equation can have several solutions, not all of which correspond to any physical or chemical reality. Such solutions or wave functions are, therefore not acceptable. The acceptable wave functions must satisfy the following conditions:

1. The wave function ψ is single valued, i.e., for each value of variables x, y, z there is one value of ψ. Suppose one of the variables is an angle θ then, single-valuedness of ψ requires that

$$\varphi(\theta) = \psi\ (\theta+2n\pi) \text{ where n is an integer.}$$

2. The wave function ψ and its first derivative with respect to its variables must be continuous, i.e., there must not be sudden change in ψ when its variables are changed.

Satisfying these conditions, Schrödinger equation yields significant solutions for certain definite values of total energy E. These values are called Eigen values.

4.3*EIGEN VALUES AND EIGEN FUNCTIONS:*

In unit 4 we have deduced the relation

$$\frac{\partial^2 f(x)}{\partial x^2} = \frac{-4\pi^2}{\lambda^2} f(x) \qquad \text{……………………. (4.1)}$$

In connection with the problems of standing waves in a stretched string, it is apparent that the solution $f(x)$ of equation (5.1) can have significance only for certain definite values of wavelength λ. These are the wavelengths corresponding to normal modes of vibration of the string. The values are referred to as Eigen values. The corresponding functions $f(x)$ which are the solutions of equation (5.1) are called Eigen functions or wave functions must satisfy certain conditions which in the case of stretched string are not difficult to understand. In the first place, $f(x)$ must be zero at each end of the string, since the system is fixed at these points and the vibration amplitude will be zero. In the second place, $f(x)$ must be single valued and finite between the limits of x represented by the two ends of the string. That means, at each point the vibrating string amplitude has a definite value at any given instant.

Just as the amplitude function, $f(x)$ in eqn. (5.1) has significance only for certain definite values of λ, so the functions ψ are satisfactory solutions of the wave equation only for certain values, the Eigen values, of total energy, E. For an atom these Eigen values are equivalent of discrete set of energy values postulated by Bohr's theory. The occurrence of definite energy levels of the atom is thus a direct consequence of wave mechanical treatment. The corresponding values of the function ψ are called as wave functions or Eigen functions of the Schrӧdinger equation. Like $f(x)$, the Eigen functions, ψ of this equation must also satisfy certain conditions; that is they must be single valued, finite and continuous throughout of the whole of the configuration space of the system under consideration, that is for all possible values of the coordinates x, y and z including infinity.

4.4 OPERATORS:

An operator is a mathematical instruction or procedure be carried out on a function. It is written in the form,

(Operator) (Function) = (another function)

The function on which the operator is carried out is called an operand. The left hand side of the above equation does not mean that the function is multiplied with the operator. Evidently, an operator written alone has no meaning.

A few examples of operator are given below:

(a) $\frac{d}{dx}(x^5) = 5x^4$. Here, $\frac{d}{dx}$ which stands for differentiation with respect to x is the operator. x^5 is the operand and $5x^4$ is the result of the operation.

(b) $\int x^2\, dx = \frac{x^3}{3}$ + C. Here $\int x^2\, dx$ which stands for the integration with respect to x is the operator, x^2 is the operand and $\frac{x^2}{3}$ + c is the result of the operation.

In case the symbol used for the operator is not self explanatory, a suitable letter or some symbol for the operator is used with the symbol ^ over it.

(c) Find the expression for the following operators

(i) $(\frac{d}{dx} + x)^2$

(ii) $(\frac{d}{dx} - x)(\frac{d}{dx} + x)$

Solution: let $\psi(x)$ be the operand.

$$(\frac{d}{dx} + x)^2\psi(x) = \left(\frac{d}{dx} + x\right)\left(\frac{d}{dx} + x\right)\psi(x)$$

$$= (\frac{d}{dx} + x)(\frac{d\psi}{dx} + x\psi)$$

$$= \frac{d^2\psi}{dx^2} + 2x\frac{d\psi}{dx} + x^2\psi + \psi$$

$$= (\frac{d^2}{dx^2} + 2x\frac{d}{dx} + x^2 + 1)\psi \qquad (\text{as } \frac{dx}{dx} = 1)$$

Removing ψ from both sides of this equation we get

$$(\frac{d}{dx} + x)^2 = \frac{d^2}{dx^2} + 2x\frac{d}{dx} + x^2 + 1$$

(ii) $(\frac{d}{dx} - x)(\frac{d}{dx} + x)\psi(x)$

$= (\frac{d}{dx} - x)(\frac{d\psi}{dx} + x\psi)$

$= \frac{d^2\psi}{dx^2} + \frac{d}{dx}(x\varphi) - x\frac{d\psi}{dx} - x^2\psi$

$= \frac{d^2\psi}{dx^2} + (x\frac{d\psi}{dx} + \psi\frac{dx}{dx}) - x\frac{d\psi}{dx} - x^2\psi$

$= \frac{d^2\psi}{dx^2} + \psi - x^2\psi$

$= (\frac{d^2}{dx^2} + 1 - x^2)\psi$

Removing ψ from both side of the equation, we get

$(\frac{d}{dx} - x)(\frac{d}{dx} + x) = \frac{d^2}{dx^2} + 1 - x^2$.

4.4.1 Algebra of Operators:

The operators follow certain rules similar to algebra. A few of those are given below:

(a) Addition and subtraction of operators:

If $\hat{A}$ and $\hat{B}$ are two different operators. And f is operand, then

$(\hat{A}+\hat{B}) f = \hat{A}f + \hat{B}f$ ……………………….(4.2)

(b) similarly $(\hat{A} - \hat{B})f = \hat{A}f - \hat{B}f$ ………………………(4.3)

4.4.2 Multiplication of Operators:

If $\hat{A}$ and $\hat{B}$ are two different operators and f is the operand then $\hat{A}\hat{B} f$ means that first f is operated by operator $\hat{B}$ to get the result, say f', and then f' is operated by $\hat{A}$ to get the final result, say f''. i.e. $\hat{A}\hat{B}f$ means that $\hat{B}f = f'$ and then $\hat{A}f' = f''$, so that we can write

$\hat{A}\hat{B}f = f''$ …….…………… (4.4)

It should be clear to you, that the order using the operator is from right to left, as written in the above equation. If the same operation is to be done a number of times in succession, it is written by the power of the operator. For example $\hat{A}\hat{A} f$ is written as $= \hat{A}^2 f$

That means $\hat{A}\hat{A} f = \hat{A}^2 f$ ……………………. (4.5)

It may be noted that usually $\hat{A}\hat{B} f \neq \hat{B}\hat{A} f$

4.4.3 Linear Operators:

An operator $\hat{A}$ is said to linear if the two functions f and g are related as $\hat{A}(f + g) = \hat{A}f + \hat{A}g$ ……………………..(4.6)

i.e., the operator on the sum of the two functions gives the same result as the sum of the two results obtained by carrying out the same operation on the two functions separately. For example $\frac{d}{dx}, \frac{d^2}{dx^2}$ etc. are linear operators, whereas "taking the square, square root" etc. are non linear.

4.4.4 Vector Operators:

Operators are not necessarily limited to operate on function of one variable. The differential operator $\frac{d}{dx}$ can operate on function $f(x, y, z)$. An important group of operators are the vector operators. A vector operator ∇ ('del') is defined in Cartesian coordinates as:

$\nabla = i\frac{\partial}{\partial x} + j\frac{\partial}{\partial y} + k\frac{\partial}{\partial z}$ …………………….. (4.7)

Here i, j, k are unit vectors along the x, y, and z axes. Operating on a scalar function ϕ, operator generates a vector called the gradient of ϕ.

$$\nabla\phi = i\frac{\partial\phi}{\partial x} + j\frac{\partial\phi}{\partial y} + k\frac{\partial\phi}{\partial z} \qquad \text{………………………} (4.8)$$

4.4.5 Laplapcian operators:

Laplacian operators are a very common operator used in quantum mechanics. It is represented by ∇^2 (del squared). Mathematically this is defined as,

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

Schrödinger wave equation can be represented in term of Laplacian operators as,

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

$$\nabla^2\psi + \frac{8\pi^2 m(E-V)}{h^2}\psi = 0 \qquad \text{…..……………..} (4.9)$$

4.4.6 Hamiltonian Operators:

Schrödinger wave equation in terms of Laplacian operators is written as:

$$\nabla^2\psi = -\frac{8\pi^2 m(E-V)}{h^2}\psi$$

$$\nabla^2\psi = -\frac{8\pi^2 m}{h^2}(E\psi - V\psi)$$

or

$$-\frac{h^2}{8\pi^2 m} + \nabla^2\psi + V\psi = E\psi$$

or

$$\left(-\frac{h^2}{8\pi^2 m} + \nabla^2 + V\right)\psi = E\psi \qquad \text{……..…………..4.10}$$

This equation means that the operation $\left(-\frac{h^2}{8\pi^2 m}+\nabla^2+V\right)$ carried out on the function ψ, is equal to the total energy multiplied by the function ψ. The operator $\left(-\frac{h^2}{8\pi^2 m}+\nabla^2+V\right)$ is called Hamiltonian operator and is represented by Ĥ, so,

$$\hat{H} = -\frac{h^2}{8\pi^2 m}+\nabla^2+V$$

equation (5.10), thus can be written as

$$\hat{H}\psi = E\psi$$

This is another form of the Schrӧdinger wave equation.

4.5 MATHEMATICAL CONSIDERATION OF SCHRÖDINGER WAVE EQUATION:

4.5.1 Normalization

Till now you have studied that Schrӧdinger wave equation is a homogeneous differential equation whose solution gives a value of ψ, but when ψ is multiplied by a constant factor it would give the same differential equation. It is, therefore, necessary to find some conditions which will indicate which constant factor is to be used.

As the electron must be found somewhere, one can say that the probability of finding an electron in the whole of space considered in a particular problem is unity. This may mathematically be written as

$$\int |\psi^2|dx = 1 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (4.11)$$

Where dx is the volume of the whole space. This integral determines by what constant ψ must be multiplied for the solution of a particular problem. This constant is known as the **normalization** constant. An Eigen function which has to be completely evaluated in this manner is said to be **normalized**

The amplitude in the wave function is determined by using the normalization condition. For ψ to represent a wave packet (i.e., a group of waves), the above condition for normalization condition should be satisfied. The numerical coefficient inψ, the amplitude factor should be independent of time.

4.5.2 Orthogonality:

Suppose we have two wave functions $\psi_p$and $\psi_q$correspond to two values of the energy$E_p$and .E_q. If these two functions are separate solutions of the Schrödinger's equation, then $\int \psi_p \, \psi_q \, dx$ = 0 and the wave function ψ_p, ψ_q are said to **orthogonal**. This property will be proved for one-dimension only.

Now let us consider two Schrödinger equations which are written in one dimension only (for the motion of a particle in straight line).

$$\frac{d^2\psi_p}{dx^2} + \frac{8\pi^2 m}{h^2}(E_P - V_p)\psi_P = 0 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(4.12)$$

$$\frac{d^2\psi_q}{dx^2} + \frac{8\pi^2 m}{h^2}(E_q - V_q)\psi_q = 0 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(4.13)$$

Multiplying equation (5.12) by $\psi_q$and equation (5.13) by ψ_P and on subtracting we get

$$\frac{d}{dx}\left(\psi_q \frac{d\psi_p}{dx} - \psi_p \frac{d\psi_q}{dx}\right) + \frac{8\pi^2 m}{h^2}(E_P - E_q - V_p + V_q)\,\psi_p\psi_q = 0 \qquad \ldots\ldots\ldots\ldots\ldots\ldots(4.14)$$

Integrating equation (5.14) with respect to x over the whole of place from $-\infty$ to $+\infty$ and since ψ and V are zero at infinity the first term vanishes and the second term becomes

$$\frac{8\pi^2 m}{h^2}(E_P - E_q)\int_{-\infty}^{+\infty} \psi_p\psi_q \, dx = 0 \qquad \ldots\ldots\ldots\ldots\ldots(4.15)$$

As $E_p \neq E_q$

Hence $\int_{-\infty}^{+\infty} \psi_p\psi_q \, dx = 0$ ……………………(4.16)

It is possible to make a linear combination of orthogonal functions.

4.5.3 Degeneracy:

You have already proved that for every wave function ψ, there must be a corresponding energy value E, i.e., for every Eigen function there will be one Eigen value. That means each energy state must have a wave function which will be the characteristics of the system. If two different ψ's have the same value of energy then these two states of different ψ's are called degenerate state.

4.6 SOLUTION OF THE SCHRÖDINGER WAVE EQUATION FOR SOME SIMPLE SYSTEMS:

4.6.1 Particle in One–dimensional box:

We shall consider some model systems for which the Schrödinger wave equation can be solved exactly. First we will discuss particle in one-dimensional box. A particle whose potential energy is same everywhere is known as a free particle. A convenient choice is V=0. A system in which potential energy is zero with in a closed region and infinite (V=∞) everywhere else is known as a potential box. Fig.4.1

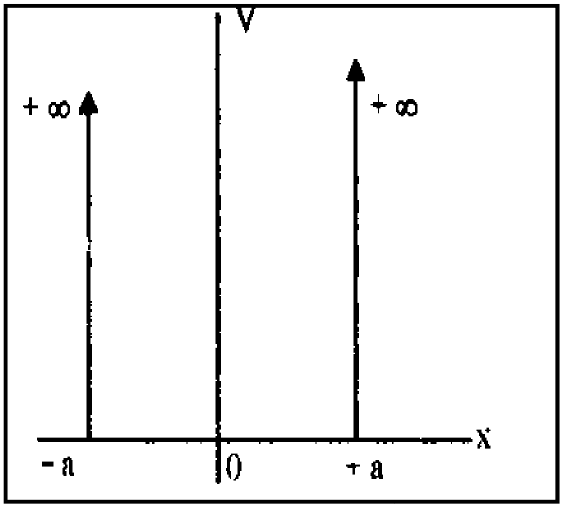

Fig 4.1 Particle in a box

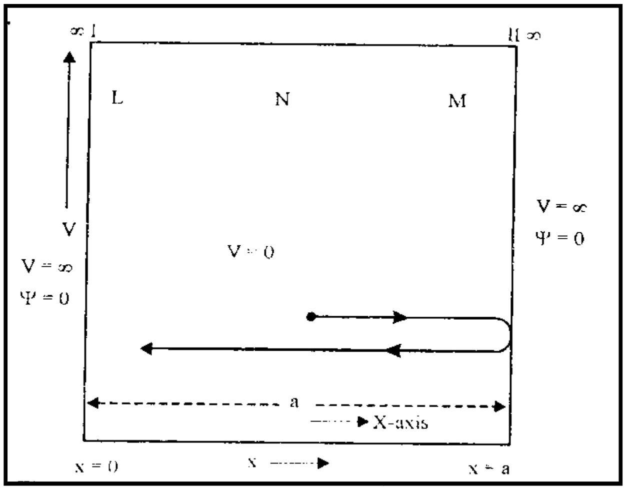

Fig. 4.2 Wave mechanical treatment of a particle in one-dimensional box

Now consider a particle of mass 'm' confined to move in a one–dimensional box of length a having infinitely high walls Fig.4.2.

It is simplest problem related to a particle in a microscopic system (say, electron in the atom) involves the calculation of the wave function and energy of the particle (electron) constrained to move in with in a certain distance in a given direction forward and backward.

Let us consider a particle (electron) in one dimensional box as shown in Fig.4.2. The particle is restricted to move along X-axis, forward or backward. Suppose that the particle does not lose energy when it collides against the wall of the box, so its energy remains constant. This box can then be represented by a potential box of width with potential walls of infinite (∞) height at x=0 and x=a. So potential energy (V) of the particle becomes infinity (V=∞) on the side

L (x=0) and M (x=a) of the box and is constant inside the box. For the sake of simplicity, it is assumed that the potential energy of the particle is zero everywhere inside the box, that is,

$$V = 0$$

However, outside the box the potential energy is infinity, i.e., V=∞ at $x < 0$ (i.e., negative side of X-axis) and at $x >$ a. Therefore, the wave function $\psi$and probability of finding the particle (i.e.,ψ^2) must be zero when $x < 0$, x=0 and $x \geq$ a. In other words, the particle is confined in the box and cannot escape the box, i.e., the particle do not exist outside the box. Now the Schrӧdinger's wave equation with respect to space is:

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(\mathrm{E} - \mathrm{V})\psi = 0 \qquad \text{……….………(4.17)}$$

For a particle moving in x- direction, this equation becomes

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2 m}{h^2}(\mathrm{E} - \mathrm{V})\psi = 0 \qquad \text{………………… (4.18)}$$

Now we know within the box, V= 0. Therefore we have

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2}{h^2}\mathrm{E}\psi = 0$$

Or $$\frac{\partial^2\psi}{\partial x^2} = -\frac{8\pi^2 m}{h^2}\mathrm{E}\psi \qquad \text{………………….(4.19)}$$

As π, m, E and h are constant, the equation (5.19) can be written as

$$\frac{\partial^2\psi}{\partial x^2} = -k^2\psi \qquad \text{…………………..(4.20)}$$

Where $\frac{8\pi^2 m}{h^2}\mathrm{E} = k^2$

Equation (5.20) is an ordinary second order differential equation which has the solution of the form

$$\psi = \mathrm{A}\sin(\mathrm{k}x) + \mathrm{B}\cos(\mathrm{k}x) \qquad \text{……..…………(4.21)}$$

Where A and B are constants

Equation (4.21) represents all the solutions of equation (4.20) which are mathematically satisfactory. However, these solutions (wave functions) do not necessarily satisfy our boundary conditions, and we should now examine equation (4.21) in view of these requirements. Differentiating equation (4.21) with respect to x, we get

$$\frac{\partial^2\psi}{\partial \mathrm{x}^2} = -\mathrm{k}^2(\mathrm{A}\sin \mathrm{k}x + \mathrm{B}\cos \mathrm{k}x) \qquad \text{…………………(4.22)}$$

The Schrödinger wave equation is satisfied if $\psi = 0$ everywhere outside the box, which means that the particle cannot be found outside the box, i.e., It is confined within the box. This implies that ψ must be zero at the walls of the box, i.e., at $x = 0$ and $x = a.$ Since ψ has to be a continuous function of x, it leads to the conclusion that in equation (4.21) B must be zero. Thus the solution of equation (4.20) is of the form

$$\psi = \text{A} \sin \text{k}x \qquad \text{…………………(4.23)}$$

Since $\psi = 0$ at $x = 0$ and at $x = a$,

hence $\text{A} \sin k\text{a} = 0,$

In this equation A cannot be zero so Sin ka = 0

$$\text{Sin } ka = \text{Sin } n\,\pi$$

Hence

$ka = n\pi$

$$k = \frac{n\pi}{a} \qquad \text{…….…………….(4..24)}$$

where n =(1,2,3…………………) is the quantum number. Putting the value of k from equation (4.24) in equation (4.23), we get

$$\psi = \text{A}\sin\left(\frac{n\pi x}{a}\right) \qquad \text{……..…………… (4.25)}$$

The probability of finding the particle within the box in a small length segment dx is $\psi^2\, dx$. Since the particle must be within the box, therefore,

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

Or

$$\int_0^a A^2 Sin^2 \frac{n\pi x}{a} dx = 1$$

The solution of the integral gives A as $\sqrt{\frac{2}{a}}$ so,

$$\psi = \sqrt{\frac{2}{a}} Sin \frac{n\pi x}{a}$$

4.6.2 Energy of the Particle:

From equation (4.21), (4.24) and (4.25) we can calculate the energy of the particle.

$$\text{Since} \quad k = \frac{n\pi}{a}$$

Hence $k^2 = \frac{n^2\pi^2}{a^2}$ Also from equation (4.20),

$$k^2 = \frac{8\pi^2 mE}{h^2}$$

$$\frac{8\pi^2 m\mathrm{E}}{h^2} = \frac{n^2\pi^2}{a^2}$$

$$0\mathrm{r}\ \ \mathrm{E} = \mathrm{E_n} = \frac{n^2h^2}{8ma^2} \text{ where } n = 1,2,3 \qquad \ldots\ldots\ldots\ldots\ldots\ldots \ (4.26)$$

This is the expression for energy of the particle in one-dimensional box. Since the energy depends upon the quantum number n, which can have any integral value. The energy levels of the particle in the box are quantized. The equation (4.26) gives permissible value of energy corresponding to n =1, n =2, n =3, n=4,…………etc. $\mathrm{E_n}$ stands for energy of the particle in n^{th} level. Fig 4.3 . Hence symbol $\mathrm{E_n}$ is used in the place of E. As already said that n is called quantum number, can assume only integral value. It is clear that the particle may have

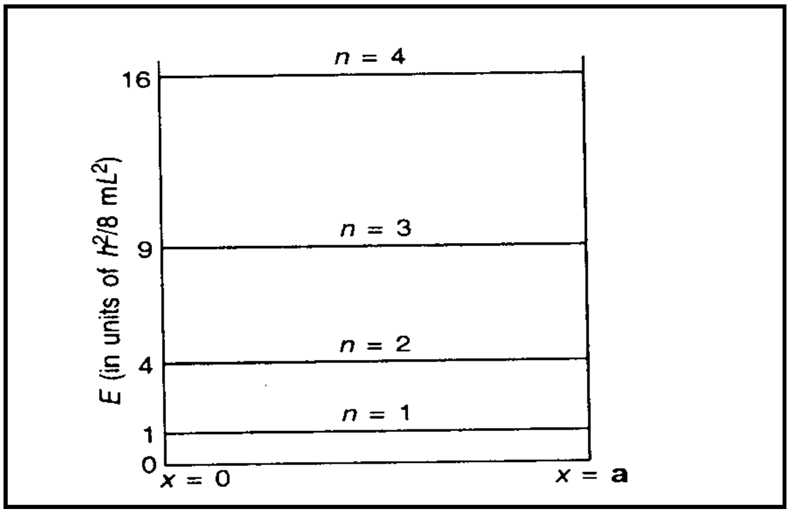

Fig 4.3 Energy levels in a particle

only certain discrete values of E. These are Eigen values of E .The value of E cannot be zero, because in that case,$\psi = \sin\ 0 = 0$, everywhere in the box. However, this is impossible, therefore, n =0 is not possible. Hence it is clear from the above discussion that the concept of energy quantization is inherent in the wave mechanics.

4.6.3 Calculation of Normalization Factor A:

The mathematical operation for calculating the value of A in equation (4.25) is called normalization. The process is given below.

$$\psi = \text{A} \sin \left(\frac{n\pi x}{a}\right) \qquad \text{…………………..} (4.27)$$

You know the probability that the particle within the space x and $x+dx$ for one dimensional box is given by $\psi^2 dx$. As a consequence of this assumption, we can write

$$\int_{-\infty}^{\infty} \psi^2\, dx = 1$$

Appling the condition that the probability of finding the particle with in a box, i.e., between $x = 0$ and $x = a$, is unity the above equation becomes

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

As we have already discussed above that $\psi = \text{A} \sin \text{k}x$

Then $\int_0^a \text{A}^2 \sin^2 \text{k}x dx = 1$

Hence $\text{A}^2 \int_0^a \sin^2 \text{k}x dx = 1$

As you know:

$$\sin^2 \text{k}x = \frac{1}{2}(1 - \cos 2\text{k}x)$$

So, $\frac{\text{A}^2}{2} \int_0^a (1 - \cos 2\text{k}x)\, dx = 1$

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

or $\frac{\text{A}^2}{2} \{[x]_0^a - \frac{1}{2\text{k}}[\sin 2\text{kx}]_0^a = 1$

or $\frac{\text{A}^2}{2} \left[a - \frac{1}{2\text{k}}(\sin 2\text{ka} - \sin 0)\right] = 1$

or $\frac{\text{A}^2}{2} \left[a - \frac{1}{2\text{k}} \sin 2\text{ka}\right] = 1$ (as sin0 =0)

as we know $\text{k} = \frac{\text{n}\pi}{\text{a}}$

or $\text{ka} = \text{n}\pi$

Hence $\frac{\text{A}^2}{2} \left[a - \frac{1}{2\text{k}} \sin 2\text{n}\ \right] = 1$

since $\sin 2n\pi = 0$

we get $\frac{A^2}{2}a = 1$

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

So, solution of Schrödinger's wave equation for a particle in one dimensional box can be written as

$$\psi = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right) \qquad \text{…………………(5.28)}$$

As $k = \frac{n\pi}{a}$

And $k = \sqrt{\frac{8\pi^2 mE}{h^2}}$

$\frac{n\pi}{a} = \sqrt{\frac{8\pi^2 mE}{h^2}}$

So $\psi_n = \sqrt{\frac{2}{a}}\sin\left(\sqrt{\frac{8\pi^2 mE}{h^2}}.x\right)$

The wave function ψ_n is said to be normalized and normalization factor is $\sqrt{2/a}$. The above equation is normalized wave function or normalized solution of Schrödinger wave equation for particle

4.7 SOME CONSEQUENCES OF ENERGY EQUATION:

4.7.1 Energy Levels:

You have just studied that the energy of the particle is: $E_n = \frac{n^2h^2}{8a^2m}$ where n is an integer, called quantum number and has the value n=1, 2, 3……….. It can never be zero or fractional. This means that the particle will have only discrete values for energy.

The above discussion means, the energy of the particle is quantized in the box and cannot change in a continuous manner. These permissible acceptable or discrete values of E depend upon n which are independent of x. These values are called Eigen values. So, a free particle, like electron, can have all values of energy but when it is confined with a certain range of space, the energy values (i.e., energy levels) become quantized. The greater the localization, the higher is the energy.

4.7.2 Zero Point Energy:

In any atom which is taken as a type of potential well or potential box, there are several discrete energy levels corresponding to n=1,2,3……………………,

when (a) n=1, $E_1 = \frac{h^2}{8ma^2}$

(b) n=2, $E_2 = \frac{4h^2}{8ma^2}$

so, $E_2 - E_1 = \frac{3h^2}{8ma^2}$

(c) n = 3, $E_3 = \frac{9h^2}{8ma^2}$

so, $E_3 - E_2 = \frac{5h^2}{8ma^2}$. and so on.

So, It is clear that energy difference between successive energy levels is not constant.

It is clear from above discussion that minimum value of n is, one, hence, energy corresponding to n=1will be minimum and is given by $E_{min} = \frac{h^2}{8ma^2}$

Hence when the particle is present in the potential box, the energy of the lowest level (n=1) is called zero point energy.

It is the characteristics of the systems executing to-and fro motion (vibration) that the energy of their lowest allowed state is greater than zero, i.e., a zero point energy exists.

It shows that:

(i) The energy of harmonic oscillator is quantized contrary to the classical view, and the result emerges from the solution of Schrödinger equation.

(ii) The energies are determined by the parameter n which is called "vibrational quantum number" of the oscillator

(iii) The lowest value of energy (when $n = 0$) is ½$h\nu$."This is the zero point energy" (in classical view it is zero).

(iv) As n increases by unity, the energy increases by $h\nu$ so the energy levels are equally spaced as shown in Fig.(4.4)

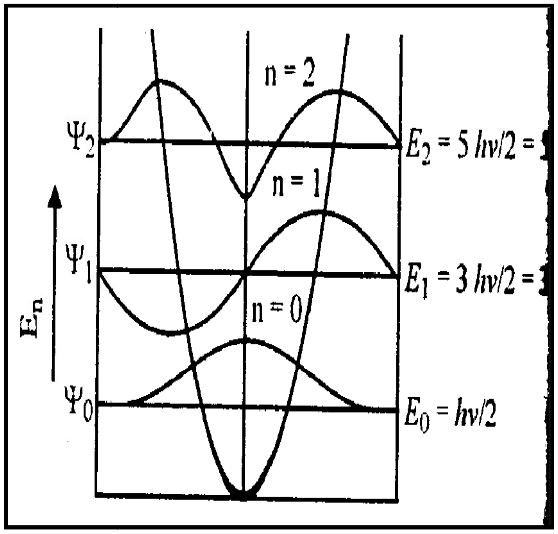

Fig.4.4 Plots of the wave function ψ and probability ψ^2 against x

4.8 PHYSICAL SIGNIFICANCE OF ψ AND ψ^2:

The plots of wave function (ψ) and probabilities (ψ^2) against x in Fig.4.4 reveals several interesting feature of quantum mechanical harmonic oscillator:

(i) The wave functions are either symmetric (even) or unsymmetrical (odd) with respect to x =0. We have seen that the exponential part of the wave function, is necessarily symmetric because of the quantity x^2, the polonomial part will be symmetric for x^0, x^2, x^4…………….and ant symmetric for x, x^3, x^5………..

(ii) The functions ψ^2 are never negative and hence necessarily symmetric.

(iii) In the ground state ($n = 0$) there are no nodes; and each successive state has one additional node.

(iv) The presence of nodes indicates the points of zero probability.

(v) Still more curious is the fact that ψ and $\psi^2$are non zero even for large values of x, i.e. beyond the classical turning point, i.e., the particle can penetrate the potential barrier.

(vi) The ψ^2 plot reveals the fact that the particle in the ground state has the maximum probability of being found at the central position ($x = 0$) while in the excited states the probability increases towards the classical turning points.

Example: An electron is confined in one dimensional box of length 1A^0. Calculate its ground state energy in electron volts (eV).

Solution: Ground state, n=1

$$E = \frac{n^2 h^2}{8ma^2}$$

$$= \frac{1^2(6.626\times10^{-34}\,\text{Js})^2}{8(9.109\times10^{-1}\ \text{Kg})^2\,(1.603\times10^{-1}\ \text{J/ev})}$$

$$= 37.6\ \text{ev}$$

4.9 *LINEAR HARMONIC OSCILLATOR*:

The quantum mechanical treatment of the simple harmonic oscillator is required for the clear cut understanding of molecular vibrations.

A point mass undergoing simple harmonic oscillations in one dimension, due to attraction by a force proportional to the displacement from the equilibration position, constitutes a linear harmonic oscillator. Before the quantum mechanical treatment is considered the classical treatment of the linear harmonic oscillator is attempted to provide a background.

As you know in a simple harmonic oscillator, the force tending to restore the particle to its equilibrium position is always directed towards equilibrium position, and is directly proportional to the displacement (x) from it.

Thus,

$$F = -kx \qquad \text{……………..……(4.29)}$$

Where k = force constant

x =displacement

The minus sign shows that restoring force is working in the opposite direction to the displacement.

If m is the mass of the particle, then

F = mass × acceleraton

$$= \mathrm{m}\times\left(\frac{\mathrm{d}^2x}{\mathrm{dt}^2}\right) \qquad \text{………………(4.30)}$$

From equation (4.29) and (4.30),

$$\mathrm{m}\times\left(\frac{\mathrm{d}^2x}{\mathrm{dt}^2}\right) = -\mathrm{k}x \qquad \text{………..………(4.31}$$

as the displacement (x) is harmonic, it can be written as,

$$x = \mathrm{A}\sin 2\pi\nu\mathrm{t} \qquad \text{….……………(4..32)}$$

Where A = amplitude of vibration

ν = frequency of oscillation

Double differentiating equation (5.32) with respect to t,

$$\frac{\mathrm{d}^2x}{\mathrm{dt}^2} = -\,4\pi^2\nu^2\,\mathrm{A}\sin 2\pi\nu\mathrm{t} \qquad \text{……..…………(4.33)}$$

From equation (5.31) and (5.33)

$$\mathrm{m}\,(-\,4\pi^2\nu^2\,\mathrm{A}\sin 2\pi\nu\mathrm{t}\,) = -\mathrm{k}x \qquad \text{...…………….(4.34)}$$

putting the value of x from equation (5.32)in equation (5.34), we get

$$4\pi^2\nu^2\,\mathrm{A}\sin 2\pi\nu\mathrm{t} = \mathrm{k}\,\mathrm{A}\sin 2\pi\nu\mathrm{t}$$

so $\mathrm{k} = 4\pi^2\mathrm{m}\nu^2$

hence:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{\mathrm{k}}{m}} \qquad \text{……………….(4.35)}$$

Equation (5.35) gives the frequency of the linear harmonic oscillator.

(a) Potential Energy (V) of the Linear Harmonic Oscillator:

Suppose the spring represents a chemical bond. The work done in stretching the spring increases the potential energy of the system. If the potential energy for the equilibrium length of the spring (or chemical bond) is assumed to be zero, that the other length is given by

$$\mathrm{V} = \int_0^x (-\mathrm{F}\,)\,dx$$

But $\mathrm{F} = -\,\mathrm{k}x$

$$\text{Hence V} = \int_0^x \mathrm{k}x\,dx$$

$$= \mathrm{k}\int_0^x x\,dx$$

$$= \frac{1}{2}\mathrm{k}\,x^2 \qquad \text{…...………..(4.36)}$$

Here $x =$ distortion from the equilibrium length. The plot of potential energy of a particle executing linear harmonic oscillation against displacement from the equilibrium position is shown in fig. 5.3

The Schrödinger wave equation in one dimension is given by,

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E - V)\boldsymbol{\psi} = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots(4.37)$$

The potential energy of a linear harmonic oscillator (i.e., simple harmonic oscillator executing motion in one dimension) is

$$V = \frac{1}{2}k\, x^2 \quad (k = \text{force constant})$$

$$\text{So,}\ \frac{d^2\psi}{dx^2} + \frac{8\pi^2 m}{h^2}\ (E - \frac{1}{2}k\, x^2)\psi = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots(4.38)$$

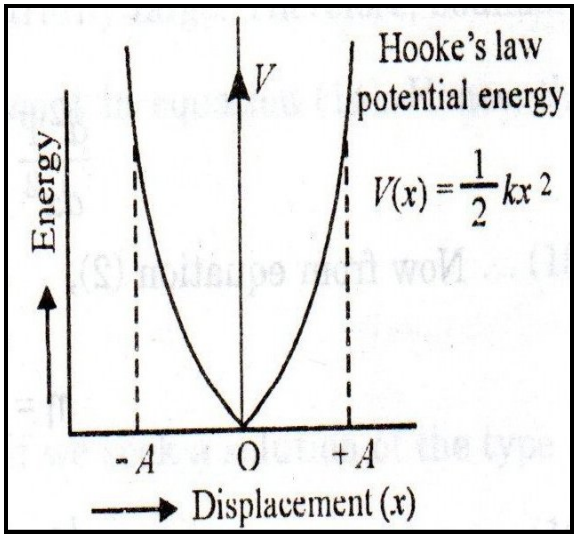

Fig.4.5 Potential energy diagram for a linear harmonic oscillator

If we change over to two new independent dimensionless variables η and α which are defined as,

$$\eta = \left(\frac{2\pi}{h}\sqrt{km}\right)^{1/2} x$$

but $k = 4\pi^2 m\nu^2$

$$\text{hence}\quad \eta = (\frac{2\pi}{h}\sqrt{4\pi^2 m\nu^2 m})^{1/2} x$$

$$= (\frac{4\pi^2 m\nu}{h})^{1/2} x \quad \ldots\ldots\ldots\ldots\ldots\ldots(4.39)$$

$$\text{And}\quad \alpha = \frac{4E\pi}{h}\sqrt{\frac{m}{k}}$$

$$= \frac{4E\pi}{h}\sqrt{\frac{m}{4\pi^2 m\nu^2}} \quad (\text{as } k = 4\pi^2 m\nu^2)$$

$$= \frac{4E\pi}{h}(\frac{1}{2\pi\nu})$$

$$\alpha = \frac{2E}{h\nu} \quad \ldots\ldots\ldots\ldots\ldots(4.40)$$

From equation (4.39),

$$\eta^2 = \frac{4\pi^2 \mathrm{m}\nu}{h} x^2$$

Hence $$x^2 = \frac{\eta^2 h}{4\pi^2 \mathrm{m}\nu} \qquad \text{……..……..……..(4.41)}$$

From equation (4.40),

$$\mathrm{E} = \frac{h\nu\alpha}{2} \qquad \text{..…..……….(4.42)}$$

Now $$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = \frac{\mathrm{d}}{\mathrm{d}x}\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right)$$

$$= \frac{\mathrm{d}}{\mathrm{d}x}\frac{\mathrm{d}\psi}{\mathrm{d}\eta}.\frac{\mathrm{d}\eta}{\mathrm{d}x}$$

$$= \frac{\mathrm{d}}{\mathrm{d}\eta}\frac{\mathrm{d}\psi}{\mathrm{d}x}\frac{\mathrm{d}\eta}{\mathrm{d}x}$$

$$= \frac{\mathrm{d}}{\mathrm{d}\eta}\left(\frac{\mathrm{d}\psi}{\mathrm{d}\eta}.\frac{\mathrm{d}\eta}{\mathrm{d}x}\right)\frac{\mathrm{d}\eta}{\mathrm{d}x}$$

So $$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = \frac{\mathrm{d}^2\psi}{\mathrm{d}\eta^2}\left(\frac{\mathrm{d}\eta}{\mathrm{d}x}\right)^2 \qquad \text{………………(4.43)}$$

From equation (4.39),

$$\eta = \left(\frac{4\pi^2 \mathrm{m}\nu}{h}\right)^{1/2} x$$

$$\frac{\mathrm{d}\eta}{\mathrm{d}x} = \left(\frac{4\pi^2 \mathrm{m}\nu}{h}\right)^{1/2}$$

On squiring both sides, we gets

$$\left(\frac{\mathrm{d}\eta}{\mathrm{d}x}\right)^2 = \frac{4\pi^2 \mathrm{m}\nu}{h} \qquad \text{………………….(4.44)}$$

Substituting this value in equation (4.43),

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = \frac{\mathrm{d}^2\psi}{\mathrm{d}\eta^2}\left(\frac{4\pi^2 \mathrm{m}\nu}{h}\right) \qquad \text{…………………(4.45)}$$

from (4.38), (4.40), (4.41) and (4.45)

$$\left(\frac{4\pi^2 \mathrm{m}\nu}{h}\right)\frac{\mathrm{d}^2\psi}{\mathrm{d}\eta^2} + \frac{8\pi^2 \mathrm{m}}{h^2}\left[\frac{h\nu\alpha}{2} - \left(\frac{1}{2}4\pi^2 \mathrm{m}\nu^2\right)\left(\frac{\eta^2 h}{4\pi^2 \mathrm{m}\nu}\right)\right]\psi = 0$$

Dividing both side by $\frac{4\pi^2 \mathrm{m}\nu}{h}$, we get,

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}\eta^2} + \frac{2}{h\nu}\left[\frac{h\nu\alpha}{2} - \frac{1}{2}\nu h\eta^2\right]\psi = 0$$

or $$\frac{d^2\psi}{d\eta^2} + (\alpha - \eta^2)\psi = 0 \qquad \text{…………(4.46)}$$

or $$\frac{d^2\psi}{d\eta^2} - (\eta^2 - \alpha)\psi = 0 \qquad \text{..…………(4.47)}$$

or $$\frac{\frac{d^2\psi}{d\eta^2}}{(\eta^2-\alpha)\psi} = 1 \qquad \text{……………(4.48)}$$

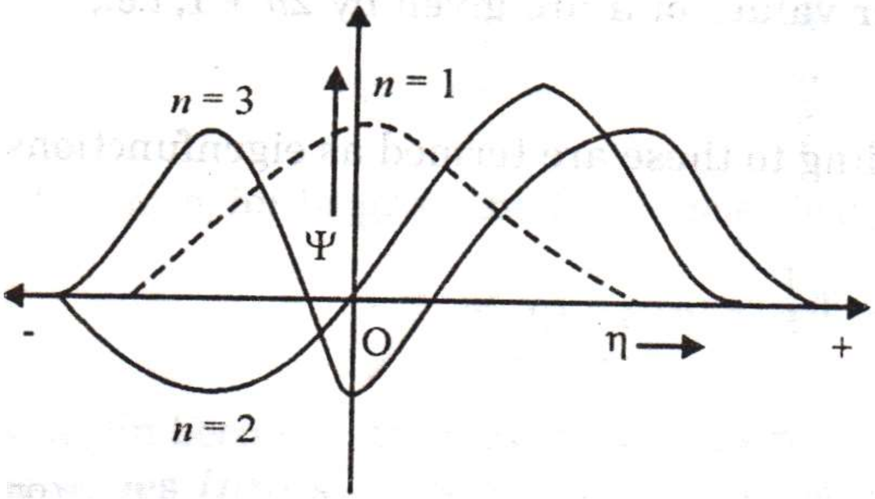

Fig 4.6 Characteristic wave functions of the linear harmonic oscillator.

Equation (4.45) (4.46) and (4.47) are the different forms of the wave equation for the linear harmonic oscillator.

4.10 EIGEN FUNCTION:

Consider the equation:

$$\frac{d^2\psi}{d\eta^2} = (\alpha - \eta^2)\psi = 0 \qquad \text{…………..(4.49)}$$

Suppose ψ should be finite, continuous and single valued at $\eta = 0$, the proper solution of the equation (equation-5.49) can be shown to be as follows:

When $\alpha = 1$, $\psi = \frac{1}{2}e^{-\eta^2/2}$

When $\alpha = 3$, $\psi = 2\eta e^{-\eta^2/2}$

When $\alpha = 5$, $\psi = (4\eta^2 - 2)e^{-\eta^2/2}$ and so on….

From the above discussion it follows that, the proper value of α is given by

$2\eta + 1$ i.e

$\alpha = 2n + 1$

Also we know $\alpha = \frac{2E}{h\nu}$

So,

so $\frac{2E}{h\nu} = 2n + 1$

or $E = (n + \frac{1}{2})h\nu$ ………………..(4.50)

Equation (4.50) gives the quantum states of liner harmonic oscillator.

For each value of α we get different wave functions ψ_n. Each ψ_n contains polynomial $H_n(\eta)$ generally called Hermite polynomial in either even or odd power of η remembering that for normalization, the condition is

$$\int_{-\infty}^{+\infty} |\psi_n|^2 d\eta = 1 \qquad (n = 0,1,2 \ldots\ldots\ldots\ldots\ldots)$$

The general formula for ψ_n is found to be

$$\psi_n = \left(\frac{4\pi n\nu}{h}\right)^{\frac{1}{4}} (2^n n!)^{-\frac{1}{2}} H_n(\eta) \exp\left(-\frac{\eta^2}{2}\right) \qquad \text{……………..(4.51)}$$

Where

$$\eta = x\sqrt{\beta}$$

n	$H_n(\eta)$	α	E_n,
0	1	1	$h\nu/2$
1	2η	3	$3h\nu/2$
2	$4\eta^2 - 2$	5	$5h\nu/2$
3	$8\eta^3 - 12\eta$	7	$7h\nu/2$
4	$16\eta^4 - 48\eta^2 + 12$	9	$9h\nu/2$
5	$32\eta^5 - 160\eta^3 + 120\eta$	11	$11h\nu/2$

Table 4.1 Hermite polynomials

The characteristics wave function corresponding to n=1,2,3………, for the linear harmonic oscillator are shown in Fig 4.7.

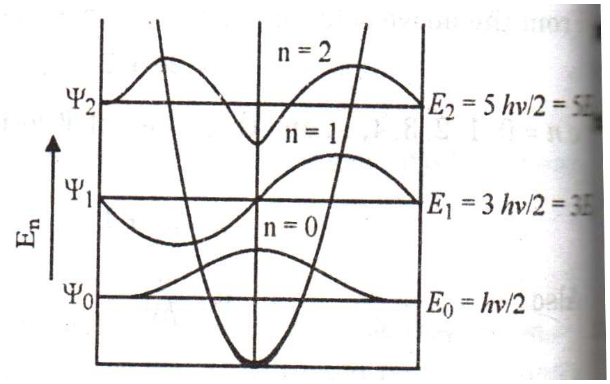

Fig 4.7 various energy levels

The curve shown in fig 4.7 shows that for small values of η the wave function becomes zero. This means that wave packet behaves very much like a particle with fizzy cages and associated wave packet is found only in the immediate neighborhood of the particle. The various energy levels are sketched in fig 4.7. These curves show that the wave functions are alternately symmetrical and unsymmetrical about the origin.

4.11 THE RIGID ROTOR (OR ROTATOR):

4.11.1 Introduction:

The rotational motion is of great interest in atomic and molecular problems. It crops up whenever we have to deal with motion of a particle under the influence of central field of force, for example, the motion of an electron around the nucleus of an atom.

For a single particle executing such a motion, the Schrödinger equation can be solved exactly. Now we shall describe first the rotational motion of a particle in a plane (particle in a ring) and then some other problems. We shall use the results for the case of a rotating diatomic molecule.

4.11.2 Rotational Energy of Rigid Rotator:

A diatomic molecule rotating about an axis perpendicular to the inter-nuclear axis and passing through the centre of gravity of the molecule, forms an example of a rigid rotor, it is being assumed that the inter-nuclear distance does not change during rotation. The kinetic energy (K.E) of the molecule is given by

$$\text{K.E.} \equiv \Gamma = \frac{1}{2}\mathrm{I}\omega^2 = \frac{\mathrm{L}^2}{2\mathrm{I}} \qquad \text{………………(4.52)}$$

Where ω is the angular velocity and I is the moment of inertia of the rotating molecule. The angular momentum $L = \mathrm{I}\omega$. If no force act on the rotor, we can put the potential energy $\mathrm{V} = 0$. Hence, the Hamiltonian is expressed as

$$\mathrm{H} = \mathrm{T} + \mathrm{V} = \mathrm{L}^2/2\mathrm{I} \qquad \text{………………4.53}$$

The equation for L^2 in spherical coordinates (r, θ and ϕ) is given by

$$L^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] \qquad \text{…………………..(.4.54)}$$

The Schrödinger equation $\hat{\mathrm{H}}\psi = \mathrm{E}\psi$ may be written as

$$\frac{1}{2I}\left[-\hbar^2\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right\}\right] = \mathrm{E}\psi \qquad \text{…….……………(.4.55)}$$

Equation 4.55 may be written as

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2\mathrm{I}}{h^2}\mathrm{E}\psi = 0 \qquad \text{……..……………(4.56)}$$

Equation 4.56 contains two angular variables θ and ϕ. It can be solved by the method of separation of variables, i.e., we look for a solution of the form

$$\psi(\theta,\phi) = (\mathrm{T}\theta)(\mathrm{F}\phi) \qquad \text{…………………(.4.57)}$$

Substituting equation (4.57) in equation (4.56), we get.

$$\frac{\sin\theta}{\mathrm{T}}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\mathrm{T}}{\partial\theta}\right) + \frac{8\pi^2\mathrm{IE}}{h^2}\sin^2\theta = -\frac{1}{F}\frac{\partial^2 F}{\partial\phi^2} \qquad \text{…………………(4.58)}$$

We can put both sides of equation 4.58 equal to a constant say, m^2, and obtain two differential equations each in one variable. These equations are given by

$$\frac{\partial^2 F}{\partial\phi^2} + \mathrm{m}^2(F) = 0 \qquad \text{………(.4.59)}$$

And

$$\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\mathrm{T}}{\partial\theta}\right) + \left(\beta - \frac{\mathrm{m}^2}{\sin^2\theta}\right)(\mathrm{T}) = 0 \qquad \text{………………..(4.60)}$$

where $\beta = \frac{8\pi^2\mathrm{IE}}{h^2}$

Equation (4.59) has the solution

$(F\phi) = N \exp(\pm im\phi)$ …..……………(4.61)

Where $i = \sqrt{-1}$ and N is normalization constant

This wave function is acceptable provided m is an integer. This condition arises because (F) must be single valued.

Therefore $(F\phi) = F(\phi + 2\pi)$

Hence , it follows that

$$\exp(2\pi mi) = 1$$

Since $e^{x} = \cos x + i \sin x$ (from Euler's relation)

$$\therefore \cos 2\pi m + i \sin 2\pi m = 1$$

This can be true only when if m=0, $\pm1, \pm2$ … … … …. etc. Let us normalize the wave function $F(\phi)$ to determine the normalization constant N.

$$\int_0^{2\pi} F^* F d\phi = 1 \quad (0 \le \phi \le 2\pi)$$

$$\text{or} \quad N^2 \int_0^{2\pi} e^{im\phi} \times e^{-im\phi} d\phi = 1$$

$$\text{or} \quad N^2 \int_0^{2\pi} d\phi = 1$$

$$\text{or} \quad N^2 (2\pi) = 1$$

So that $N = (2\pi)^{-½}$

Hence, the normalized wave function becomes

$$F_{\pm m}(\phi) = (2\pi)^{-½} exp(\pm im\phi); \ m = 0,1,2,3\ldots\ldots\ldots$$

Here we are not trying to obtain a complete solution of equation (4.60) but will merely state that if $\beta = \ell(\ell + 1)$ where ℓ is **rotational quantum number**, then this equation becomes a standard mathematical equation whose solutions are known to be associated Legendre polynomials $P_{\ell}^{|m|}(\cos\theta)$ where ℓ is either zero or a positive integer and $\ell > |m|$.

The normalized solutions are given by

$$T(\theta) = T_{\ell,\pm m,}(\theta) = \left[\frac{2\ell+1}{2} \times \frac{(\ell-|m|)!}{(\ell+|m|)!}\right]^{½} P_{\ell}^{|m|}(\cos\theta)$$

The energy eigen values of rigid rotor are obtained as follows:

$$\beta = 8\pi^2 IE/h^2 = \ell(\ell + 1)$$

Hence, $E = \frac{\ell(\ell+1)h^2}{8\pi^2 I}$ where ℓ= 0,1,2……………….

Normally we use the symbol J rather hen ℓ for the rotational quantum number, so the rotational energy levels are given by the equation

$EJ = \frac{J(J+1)h^2}{8\pi^2 I}$ where J = 0, 1, 2………………..…….

This is the equation for rotational energy levels.

4.12 PHYSICAL SIGNIFICANCE OF THE WAVE FUNCTION:

The only dependent variable in the Schrödinger wave equation is the wave amplitude of the wave function, ψ and it depends on the coordinate of the particle. In some cases, it may turn out to be a complex function of the form, $\psi = u + iv$, where u and v are the functions of the coordinates and $i = \sqrt{-1}$. The complex conjugate of ψ is $\psi^*= u - iv$. Their product $\psi\psi^*= u^2 + v^2$, and if ψ is real, $\psi\psi^*$is identical with ψ^2. Neither ψ nor ψ^* has any physical significance but $\psi\psi^*$(or ψ^2, when real) has. In dealing with all forms of wave motion, such as light waves, sound waves, electrical field or matter waves the square of the wave amplitude at any point is interpreted as the intensity of the effect at that point. So, the value of ψ^2 (ψ^2 can be used instead of $\psi\psi^*$, Since the most of the wave functions in atom or molecular structure problems contain real term only) at any point around the nucleus gives a measure of the electronic charge density at the point. This interpretation was originally suggested by SchrÖdinger. According to this view, the electron is to be regarded as smeared out forming a cloud of electricity, the density of which varies from point to point around the nucleus.

4.13 CONCLUSION:

Certain conclusions derived from the results described above bring the quantum mechanical harmonic oscillator into sharp contrast with the classical oscillator. In the first place, the energy of the former is quantized as in the case of particle in a box, and the energy levels are given by a vibrational quantum number. The energy of the classical harmonic oscillator on the other hand, is continuous. The occurrence of the vibrational energy levels is responsible for the vibrational spectra of molecules which the classical treatment could not explain.

The lowest energy (the zero point energy) of a quantum mechanical harmonic oscillator is ½ hν, while that of classical harmonic oscillator is zero (no zero point energy). This means that molecular vibrations around equilibrium bond distances will never stop, not even at absolute zero of temperature. This behavior is again similar to that of a particle in a box having infinite walls. In fact, the existence of zero point energy is characteristic of any quantum mechanical system executing to and fro motion.

Wave function (ψ and ψ^2) reveal still more interesting features. Probability calculations so that in the ground state, the most probable position of quantum harmonic oscillator is at the equilibrium point, while for a classical harmonic oscillator it lies at the maximum displacement points. The distinction gradually disappears as the quantum number increases i.e., in the excited states, when the points of maximum probability even for the former shift more and more towards the classical turning points, reaching these in the limiting case. This again is similar to the case of particle in a box.

4.14 TERMINAL QUESTIONS :

1. What is Eigen value and eigen function in chemistry?
2. Why is harmonic oscillator linear? What is the Potential Energy of linear harmonic oscillator?
3. Define the equation for Rotational Energy of Rigid Rotator ?
4. Derive Normalized solution of Schrödinger wave equation for particle one dimensional box?
5. What do you mean by normalization and orthogonality of wave function?
6. What is the significance of wave function in quantum mechanics?
7. An electron is confined in one dimensional box of length 2A^0. Calculate its ground state energy in electron volts (eV)?
8. What is Hermite polynomials in quantum mechanics?
9. Write the Physical significance of ψ and ψ^2 ?

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UNIT 5: *QUANTUM CHEMISTRY – I*

5.1 Introduction

5.2 Wave Mechanical Treatment of Hydrogen Atom

5.3 Schrödinger Wave Equation for Hydrogen Atom

5.4 Transformation of Coordinates of Equation 5.3

5.5 The Quantum Mechanical Model

5.6 Discussion

5.7 Conclusion

5.8 Terminal questions

5.9 References

SCHRÖDINGER WAVE EQUATION FOR HYDROGEN ATOM:

5.1 INTRODUCTION:

Hydrogen, being the simplest of all elements, provides a model for the study of elements in general. Moreover, it constitutes one of the basic examples of chemical systems exhibiting rotational motion. The spatial rotation of an electron around the nucleus in the hydrogen atom can be described in terms of electron's two angular variables θ (zenith angle) and ∅ (azimuthal angle) and its radial distance r from the nuclear centre. This system is equivalent to a particle moving in an infinite number of concentric spheres.

5.2 WAVE MECHANICAL TREATMENT OF HYDROGEN ATOM:

In the study of structure of atoms and molecules, the problem of structure of Hydrogen atom is regarded as very important because it forms the basis for the discussion of more complex atomic systems. The wave mechanics applied to hydrogen atom, is also used for hydrogen-like or closely related atoms.

Positive ions containing only one electron bound to a nucleus of charge Ze (e.g.,He^+,Li^{2+},B^{3+} etc.) may be treated quantum mechanically like a hydrogen atom and are called hydrogen like atoms.

5.3 SCHRÖDINGER WAVE EQUATION FOR HYDROGEN ATOM:

Hydrogen atom is a system of one proton (charge =+e) and one electron (charge = -e).

Assume that proton is stationary and the electron is moving about in its vicinity, common but cannot escape from the positive electronic field of nucleus.

The potential energy of the electron is the amount of work done in bringing the electron from infinity to the distance r is given by

$$V = \int_{\infty}^{r} \frac{Ze^2}{Ar^2} dr$$

$$V = \frac{-Ze^2}{Ar} \quad \text{(As Z= 1 for hydrogen)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(5.1)$$

Where ,

$\frac{1}{A} = \frac{1}{4\pi\in_0} = 9 \times 10^9\ Nm^2/C^2$

$\in_0$ = permittivity of vacuum

$=8.854 \times 10^{-12} c^2 N^{-1} m^{-2}$

On substituting the value of A in equation 5.1, we get

$$V = -\frac{e^2}{4\pi\epsilon_0 r} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(.5.2\ )$$

Here r is the distance between electron and nucleus.

The Schrödinger wave equation for three dimensions is:

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

putting the value of potential V from equation (5.2) , we get:

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial_{z^2}} + \frac{8\pi^2 m}{h^2}\left(E + \frac{e^2}{4\pi\epsilon_0 r}\right)\psi = 0 \qquad \ldots\ldots\ldots\ldots\ldots\ldots (5.3)$$

This is the Schrödinger wave equation for hydrogen atom in terms of Cartesian co-ordinates

It is convenient to solve this equation if we substitute polar co-ordinates r,θ and ϕ in place of Cartesian coordinate x, y and z. The correlation between the two types of coordinates is illustrated in Fig5.1

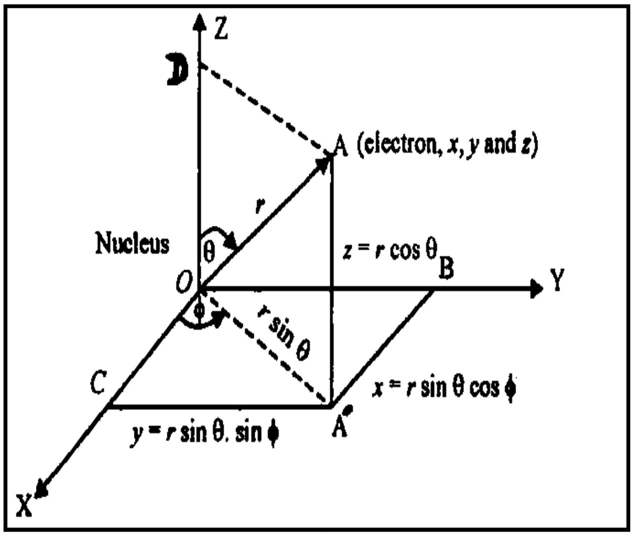

Fig. 5.1 Correlation between Cartesian coordinates (x, y and z) and polar coordinates (r,θ and ϕ)

5.4 TRANSFORMATION OF COORDINATES OF EQUATION :

The relation between Cartesian system and polar system is shown in Fig.5.1. It can be seen that:

(i) r is radial distance of point A(electron)from the origin O nucleus. The radial distance is given by

$$Z = \sqrt{x^2 + y^2 + z^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(.5.4\ )$$

(ii) θ is the angle between two radius vectors, OA and +z - axis (i.e., OZ-axis) which is the axis of sphere. This angle is called zenith angle and is given by Z = r cos θ

Hence $\cos\theta = \frac{z}{r} = \frac{z}{\sqrt{x^2+y^2+z^2}}$ ……………………(5.5)

(iii) The perpendicular AA^1 on the x, y - plane is such that OA^1 makes an angle ϕ with o x- axis, measured in the shown direction. This angle is called azimuthal angle or longitudinal angle and this is given by

$$\tan\phi = \frac{y}{x} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5.6)$$

Hence $\phi = \tan^{-1}(y/x)$

A^1B and A^1C are the normal drawn from A^1 on OY and OZ- axis, respectively.

(iv) Fig.5.1 also gives the following

$$z = \text{OD} = r\cos\theta \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5.7)$$

and OA^1 =AD= $r\cos\theta$

$$y = \text{OB} = \text{CA}^1 = r\sin\theta\sin\phi \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5.8)$$

$$x = \text{A}^1\text{B} = r\sin\theta\cos\Phi \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5.9)$$

On transforming equation 5.3 with the help of relation (5.7), (5.8) and (5.9),we get

$$\frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{\sin\theta}.\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}.\frac{\partial^2\psi}{\partial\Phi^2}\right]+\frac{8\pi^2m}{h^2}(E-V)\psi=0 \qquad \ldots\ldots\ldots\ (5.10)$$

Putting the value of V from equation (5.2), we get

$$\frac{1}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{\sin\theta}.\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin^2\theta}.\frac{\partial^2\psi}{\partial\Phi^2}\right]+\frac{8\pi^2m}{h^2}\left(E+\frac{e^2}{4\pi\epsilon_0 r}\right)\psi=0 \qquad \ldots\ldots\ldots(.5.11)$$

5.4.1 Separation of Variables:

Equation (5.10) or (5.11) is a second order partial differential equation. This contains three variables, r, ɵ and Φ. In order to separate these variables it is necessary to suppose that the wave functionψ, may be represented by the product of three wave functions, each having only one of the three variables namely r, θ and ϕ. Therefore,

$$\psi\,(r,\theta,\phi) = \text{R}\,(r).\text{T}\,(\theta).\text{F}\,(\phi) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(5.12)$$

Or we can write $\psi = \text{R}\,(r).\text{T}\theta).\text{F}(\phi)$ ……………………(5.13)

It should be clear that.

(i) R (r) is a function of r only which means that the function R depends upon r only and is independent of θ and ϕ.

(ii) $T(\theta)$ is a function of θ only which means that the wave function T depends on θ only and is independent of r, and ϕ.

(iii) $F(\phi)$ is a function of ϕ only which means that wave function F depends on ϕ only and is independent of r and θ .

Now $\psi\ (r, \theta, \phi)$ or simply ψ means that the wave function ψ depends on all the three variables r, θ and ϕ.

Now $\psi = R\ (r)\ T\ (\theta)\ F(\phi)$

Hence $\frac{\partial\psi}{\partial r} = T\ (\theta)\ F\phi \frac{\partial R(r)}{\partial r}$ ……………….(5.14)

$\frac{\partial\psi}{\partial\theta} = R\ (r)\ F\ (\phi) \frac{\partial}{\partial\theta} T(\theta)$ ……………….(5.15)

$\frac{\partial^2\psi}{\partial\phi^2} = R\ (r)\ T\ (\theta) \frac{\partial^2}{\partial\phi^2} F(\phi)$ ……………….(5.16)

Substituting these values from equations (5.12), (5.15), (5.16) in equation (5.10) and multiplying by $r^2 \sin^2\theta$ throughout,

We get:

$$sin^2\theta \left[\frac{\partial}{\partial r}\left(r^2 T(\theta).F(\Phi)\frac{\partial R(r)}{\partial r}\right) + \frac{1}{sin\,\theta}.\frac{\partial}{\partial\theta}\left(sin\,\theta\, R(r)F(\Phi)\frac{\partial T(\theta)}{\partial\theta}\right) + \frac{1}{sin^2\theta}.R(r)\,T(\theta).\frac{\partial^2 F(\Phi)}{\partial\Phi^2}\right] + \frac{8\pi^2 m}{h^2}\left(E + \frac{e^2}{4\pi \in_0 r}\right).r^2 sin^2\theta\, R(r)T(\theta)F(\Phi) = 0$$

On dividing by $R\ (r)\ T(\theta)\ F(\phi)$ and simplifying the bracket,

$$\frac{\sin^2\theta}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right) + \frac{\sin\theta}{T(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial T(\theta)}{\partial\theta}\right) + \frac{1}{F(\phi)}\frac{\partial^2 F(\phi)}{\partial\phi^2} + \frac{8\pi^2 m r^2 \sin^2\theta}{h^2}(E-V) = 0 \quad ……(5.17)$$

Or, $$\frac{\sin^2\theta}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right) + \frac{\sin\theta}{T(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial T(\theta)}{\partial\theta}\right) + \frac{8\pi^2 m r^2 \sin^2\theta}{h^2}(E-V) = -\frac{1}{F(\phi)}\frac{\partial^2 F(\phi)}{\partial\phi^2} \quad ……(5.18)$$

Left hand side of the equation (5.18) has two variables r and θ, where as the right hand side of the equation has only one variable $\emptyset$. If we put right hand side equal to m_l^2, then equation 5.18 becomes

$$\frac{\sin^2\theta}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right) + \frac{\sin\theta}{T(\theta)}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial T(\theta)}{\partial\theta}\right) + \frac{8\pi^2 m r^2 \sin^2\theta}{h^2}(E-V) = -m_l^2 \quad ……..(5.19)$$

And $$\frac{1}{F(\phi)}\frac{\partial^2 F(\phi)}{\partial\phi^2} = -m_l^2$$

Or, $$\frac{1}{F(\phi)}\frac{\partial^2 F(\phi)}{\partial\phi^2} + m_l^2 = 0 \quad …………(5.20)$$

Equation (5.20) is called $F(\emptyset)$ equation and contains only one variable $\emptyset$.

Equation 5.19 contains two variables r and θ. For the separation of the remaining two variables r and θ , we divide the equation (5.19) by $\sin^2\theta$ we get

$$\frac{1}{R(r)}\frac{\partial}{\partial r}\left(r^2\frac{\partial R(r)}{\partial r}\right) + \frac{1}{T(\theta)\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial T(\theta)}{\partial\theta}\right) + \frac{8\pi^2 m r^2}{h^2}(E-V) - \frac{m_l^2}{\sin^2\theta} = 0 \quad ……5.21$$

Rearrangement of equation (5.21) gives

$$\frac{1}{\mathrm{R}(r)}\ \frac{\partial}{\partial r}\left(r^2\,\frac{\partial \mathrm{R(r)}}{\partial r}\right) + \quad \frac{8\pi^2 \mathrm{mr}^2}{h^2}(\mathrm{E}-\mathrm{V})\ = \frac{\mathrm{m}_l^2}{\sin^2\theta} - \ \frac{1}{\mathrm{T}(\theta)\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial\ T(\theta)}{\partial\theta}\right) \qquad \text{…….(5.22)}$$

A close inspection of equation (5.22) shows that each side of the equation contains only one variable. Left hand side contains r only and the right hand side contains only θ. If we put right hand side equal to β, the equation 5.22 becomes.

$$\frac{1}{\mathrm{R(r)}}\ \frac{\partial}{\partial r}\left(r^2\,\frac{\partial}{\partial r}\,(\mathrm{R(r)}\right)\ +\ \frac{8\pi^2\mathrm{mr}^2}{h^2}(\mathrm{E}-\mathrm{V})\ =\ \beta \qquad \text{……………(5.23)}$$

Hence $$\frac{\mathrm{m}_l^2}{\sin^2\theta} - \ \frac{1}{\mathrm{T}(\theta)\mathrm{si}}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial\ T(\theta)}{\partial\theta}\right)\ =\ \beta \qquad \text{……………..(5.24)}$$

Multiplying equation (5.24) by T(θ), we get,

$$\frac{\mathrm{m}_l^2\mathrm{T}(\theta)}{\sin^2\theta} - \ \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial \mathrm{T}(\theta)}{\partial\theta}\right)\ -\beta\ \mathrm{T}(\theta) = 0 \qquad \text{…………..(5.25)}$$

This is a desired equation which is in terms of θ only

On combining equation (5.21) with equation (5.24) we get,

$$\frac{1}{\mathrm{R}(r)}\ \frac{\partial}{\partial r}\left(r^2\,\frac{\partial\ \mathrm{R(r)}}{\partial r}\right)\ -\beta + \ \frac{8\pi^2\mathrm{mr}^2}{h^2}(\mathrm{E}-\mathrm{V})\ = 0 \qquad \text{……………(5.26)}$$

Multiplying both sides of equation (5.26) by$\frac{\mathrm{R}(r)}{r^2}$, we get,

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\,\frac{\partial\ \mathrm{R(r)}}{\partial r}\right)\ -\beta\,\frac{\mathrm{R}(r)}{r^2} + \ \frac{8\pi^2\mathrm{m}}{h^2}(\mathrm{E}-\mathrm{V})\,\mathrm{R}(r) = 0 \qquad \text{…….……(5.27)}$$

It is the $\mathrm{R}(r)$ equation and contains only one variable r.

Thus the three variables (r, θ and ϕ) has been successfully separated, resulting into three independent differential equations. Therefore, the solution of the Schrödinger wave equation for hydrogen atom in terms of spherical coordinates are given by equations (5.20),(5.25) and (5.27). These equations are given below-

(i) $$\frac{\partial^2\mathrm{F}(\phi)}{\partial\emptyset^2} + \mathrm{m}_l^2\mathrm{F}(\phi) = 0 \qquad \text{……………(5.28)}$$

(ii) $$\frac{\mathrm{m}_l^2\mathrm{T}(\theta)}{\sin^2\theta} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial\mathrm{T}(\theta)}{\partial\theta}\right) - \beta\mathrm{T}\theta = 0 \qquad \text{…….……...(5.29)}$$

(iii) $$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\,\frac{\partial\ \mathrm{R(r)}}{\partial r}\right)\ -\beta\,\frac{\mathrm{R}(r)}{r^2} + \ \frac{8\pi^2\mathrm{m}}{h^2}(\mathrm{E}-\mathrm{V})\,\mathrm{R}(r) = 0 \qquad \text{…..………(5.30)}$$

It is clear from equation 5.28 that it is same wave equation for particle in one dimensional box. In term of sine and cosine functions, the solution of 5.28 is written as,

$$F\emptyset = Asin(m_\ell\emptyset) + Bcos(m_\ell\emptyset)$$

For a solution to be acceptable, the wave function should be single valued, continuous and finite. In order to meet the first condition (single valued), the function $F\emptyset$ should have the same value for $\emptyset = 0$, as it has $\emptyset = 2\pi$. Thus,
case I: when $\emptyset = 0$ then,

$$F(0) = Asin(m_\ell \times 0) + Bcos(m_\ell \times 0) = B$$

Case II: when $\emptyset = 2\pi$, then

$$F(2\pi) = Asin(m_\ell \times 2\pi) + Bcos(m_\ell \times 2\pi)$$

Under the above restrictions (single valued),

$$F(0) = F(2\pi)$$

$$B = Asin(m_\ell \times 2\pi) + Bcos(m_\ell \times 2\pi) \qquad \text{………………(5.31)}$$

Equation (5.31) is true only if $m_\ell = 0$, m_ℓ =positive integer or m_ℓ= negative integer. Such characteristics are those that would be expected of a quantum number and the particular restrictions on m_ℓ indicate that it is similar to magnetic quantum number of Bohr's -Somerfield atomic model.

In the normal practice, equation 5.28 is expressed in the exponential way, i.e.,

$$F(\emptyset) = \frac{1}{\sqrt{2\pi}} e^{\pm i m_\ell \emptyset}$$

where $m_\ell = 0, \pm 1, \pm 2$…………………..

In order $F(\emptyset)$ must be single valued, $F(\emptyset)$must have the same value after any number of whole revolutions, so,

$$e^{i m_\ell \emptyset} = e^{i m_\ell (\emptyset + 2\pi n)}$$

$$= e^{i(m_\ell \emptyset + 2\pi n m_\ell)}$$

Where n is a whole number and, therefore, the product nm must be a whole number, hence m must be a whole number. Possible values of m_ℓ are 0, ± 1, ± 2, ± 3 ....……..

Thus $m_\ell$is known as magnetic quantum number. This quantum number controls the direction of the angular momentum. That is magnetic quantum number describes the behavior of electron in the atom when it is placed in a magnetic field. In the same manner azimuthal quantum number can be described from Legendre polynomial.

Evaluation of Total Energy of Hydrogen Atom:

As we know that:

$$\alpha^2 = \frac{-8\pi^2 \mathrm{mE}}{h^2} \qquad \text{……………(5.32)}$$

$$\text{And} \quad \lambda = \frac{4\pi^2 \mathrm{mze}^2}{h^2 \alpha} \qquad \text{……………(5.33)}$$

Squaring both sides of equation (5.33),

$$\text{We get} \quad \lambda^2 = \frac{16 \ {}^4\mathrm{m}^2\mathrm{z}^2\mathrm{e}^4}{h^4 \alpha^2}$$

Hence $\alpha^2 = \frac{16\pi^4 m^2 z^2 e^4}{h^4 \alpha^2}$ ....(5.34)

Comparing equation (5.32) and (5.34), we get,

$$\frac{-8\pi^2 mE}{h^2} = \frac{16\ \ ^4 m^2 z^2 e^4}{h^4 \lambda^2}$$

Or,

$$E = -\frac{2\pi^2 m z^2 e^4}{\lambda^2 h^2} \qquad \text{..............(5.35)}$$

Putting n for λ, we get,

$$E = -\frac{2\pi^2 m z^2 e^4}{n^2 h^2}$$

For hydrogen atom $z = 1$

$$E = -\frac{2\pi^2 m e^4}{n^2 h^2}$$

This is the same result as is obtained from Bohr’s theory.

5.5 THE QUANTUM MECHANICAL MODEL:

Quantum mechanics provides a new model for representing the structure of hydrogen atom and hence of other atoms, with sound theoretical basis. The electron rotates round the nucleus but not in a well defined orbit, the rotation is three dimensions and motion is described by a wave equation- the Schrödinger equation. Rather than locating the electron in any instant exactly, this model provides the position of the electron in terms of a probability function, there being a finite, even through small, probability of its being found at all points in the infinite space outside the nucleus. The probability is maximum at a certain distance from the nucleus, interestingly in the ground state of H atom; this distance is the same as the radius (a_0) of the Bohr’s orbit which is:

$$\frac{h^2}{4\pi^2 m e^2}, \quad \text{i.e., } 0.529 A^0$$

The maximum probability is uniformly distributed in all direction at a distance of a_0 from the nucleus (i.e., it is spherically symmetrical). In excited states with non zero angular momentum of the electron ($l \neq 0$), the maximum lies in certain referred directions.

In each state one can visualize a three dimension surface encompassing the nucleus that encloses a large fraction (~ 90%) of the total probability; in other words, the electron may be supposed to spend 90% of its time inside this surface. This entire region within this surface is quantum mechanical analogue of classical orbit and is the physical representation of orbital.

There is an equivalent way of representing the probability distribution by considering the electron as a cloud of negative charge. The density of the electron cloud (probability density) in the ground state of the H atom is maximum at the nucleus and 90% of the charge of the cloud is contained within the surface of the orbital. Although the electron is most likely to be found at a distance a_0 from the nucleus, its average distance is $1.5a_0$.

As in the old planetary model, the stability of the atom, qualitatively, attributed to (i) a force tending to bring the nucleus and the electron together and (ii) an opposing force tending to keep the electron away from the nucleus. The former is electrostatic in nature ($F= \frac{ze^2}{r^2}$); for the latter quantum mechanics provides a more constant picture. We visualize the electron as diffuse cloud of matter and charge around nucleus. The former tends to make the electron cloud smaller and smaller. This makes the wavelength of the electron shorter and shorter and hence the energy greater. Rubinstein prefers to call it the "energy of confinement" (E_{conf}). Below the optimum distance (a_0) the confinement energy is sufficiently great for the nucleus to pull the electron cloud further toward itself. Equilibrium is ultimately established at the optimum distance for the atom to be stable when the two forces balance.

5.6 DISCUSSION:

The quantization of energy is shown in Fig. 5.2. The allowed energy levels are shown as horizontal lines.

That these lines are straight emphasizes the fact that energy (E) is the same irrespective of the position (x) of the particle. Since for a particular value of n, the energy E does not change with x, the latter is often termed as “constant motion.” Further, since $\widehat{H}$ or E is independent of time (t) the system under consideration is a good and simple example of “conservative system”.

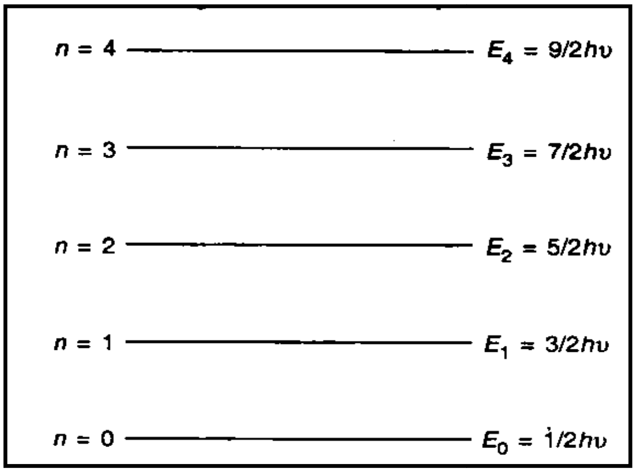

Fig 5.2 Quantization of energy

5.7 CONCLUSION:

The most important application of quantum mechanics to chemistry has been its explanation of the nature of covalent bond. G.N. Lewis, declared that this bond consists of a shared pair of electron. In 1927 Heitler and F. London applied quantum mechanism to give the first quantitative theory of the bond.

If two H atoms are brought together, the system consists of two protons and two electrons. If the atoms are far apart, there mutual interaction is effectively nil. In other words, the energy of interaction $U \to 0$ as the inter-nuclear distance $R \to \infty$. At the other extreme if two atom are forced closely together, there is a large repulsive force between the positive nuclei, so that $R \to 0$ $U \to \infty$. Experimentally we know that two hydrogen atoms can unite to form a stable hydrogen molecule, whose dissociation energy is 458.1 $kJ.mol^{-1}$. The equilibrium inter nuclear separation in the molecule is 0.0740 nm.

To sum up, the solution of the radial equation 5.30 gives the quantum numbers n and l. The solution of T (θ) equation (5.29) gives the quantum numbers n, l and m and the solution of F(ϕ) equation (5.28) gives the quantum number m. In other words the quantum numbers n, l and m follow directly from the wave mechanical treatment.

5.8 TERMINAL QUESTIONS :

1. Define the Schrödinger wave equation for hydrogen atom in terms of Cartesian co-ordinates .
2. What is the total energy of hydrogen atom according to Schrödinger wave equation.
3. What are the main variable in 2nd order partial differential equation . How wave function depended all these variable.
4. Explain quantization of energy if n= 0, 1,2,3,4 .
5. Why He^+,Li^{2+},B^{3+} etc are known as Hydrogen like atom .

5.9 REFERENCES:

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