Physical Chemistry
Past paper 2021

What is thixotropy phenomenon:

Thixotropy is a phenomenon where the viscosity of some fluids depend on the time of share rate. It is time dependent phenomenon.

Certain gels or fluids that are viscous under static condition will flow over time when shaken, or shear stressed.
PH, temperature or polymer concentration may are the factor of thixotropy.

What do you meant by CMC?

CMC stand for critical micelle concentration
The concentration of surfactants in solution above which micelles forms.

or

The concentration above which micelle formation occurs.

Temperature and electrolytes addition may affect the CMC.
It is essential for absorption of fatsoluble vitamins.

How tyndall effect observed. What is emulsification.

The scattering of light as light beam passes through colloid.
It is observed when light enters a dark room where the dust particles get scattered. It can be seen through the fog when torch is switched on.

The mixture of two or more liquids that are usually immiscible but under specific transforming processes will adopt a microscopic homogeneous aspect and microscopic heterogeneous one.

Define Zeta potential:

It is physical property which is exhibited by any particles in suspension macromolecul or material surface.

The potential difference between fixed charge layer and diffused layer having opposite charge.

Its unit is volts (V) or millivolts (mV).

Difference between electrosomsis and electrophorsis

• Electrophoresis is technique that is used to describe the motion of particles in fluid within a relatively uniform electric field.	Electrosmsis is phenomenon in which fluid moves through porous medium or charg surface under influence of applied electric field.
• The movement of charged particles can be fast.	The movement of liquid is generally slow.
• Solids and liquid both are separated.	Only liquid are separated.

Define enzyme catalysis with ex?

The increase in the rate of a process by biological molecule an enzyme.

Example: Lipases. It helps in gut to digest fats.

Amylase: In the salive, It help to change starches into sugar.

Physical adsorption	Chemical adsorption
• The force operating in this case are weak vander wall's force.	The force operating are chemical bonds (strong).
• The heat of adsorption is low about $20-40$ kjmol^{-1}	The heat of adsorption are high about $40-400$ kjmol^{-1}
• The process is reversible.	The process is irreversible.
• Monolayer or multilayer.	Monolayer only.
• It known as physisorption.	It known as chemisorption
• Non- activated	Activated.

Homogeneous Catalysis - ?

" In Homogeneous Catalysis reactants and Catalyst both are in the same phase "

Examples are as follows.
- Auto Catalysis
- Enzyme Catalysis
- Acid or base Catalysis

→ Auto catalysis:
In which None of the product formed act as a catalyst is auto catalysis
- The chemical reaction between acidified potassium permagnate ($KMnO_4$) & Oxalic acid is example of auto Catalyst.

→ Hydrogenation Reaction:

The addition of Hydrogen (H_2) to Unsaturated organic compounds like alkenes to form alkanes in the presence of Homogeneous Catalyst e.g Wilkinson's Catalyst.
In this catalyst dissolved in same Phas as reactants proceeding Hydrogenation reaction.

(q)

Two postulates of Langmuir Adsorption isotherm :-

(i) Each adsorbent has specific equivalent sites for adsorption

(ii) Rate of adsorption is relatively high as compared to rate of desorption at initial stages

(iii) One molecule of adsorbate can adsorb on one site of adsorbed.

(10)

Effect of Surface area on adsorption:

Surface area of the adsorbent has pronounced effect on the rate of adsorption.
Adsorbent with greater surface to Volume ratio possess greater extent of adsorption and vice versa. If substance is divided & Subdivided we get small Particles.

(12)

Enzymes as Catalyst are Specific in nature.

- Enzymes are bio organic catalyst which catalyze the chemical reaction occuring in human body
- Enzymes are highly specific catalyst due to their unique structural features, which arise from their complex protein nature

As,

Enzymes are macromolecules of protein in nature they are also called bipolymers. (enzyme as catalyst)

Due to following reasons they all imp in nature

→ Enzyme as a Catalyst act in all types of reaction (Redox, acid base and decomposition

→ Stereo specificity is basic character of enzymes.

→ Enzyme work on optimum PH or temperature

e.g
aerosols (fog, mist)
gels (jelly, agar)

(solid dispersed in liquid)
e.g paint, blood

(15)

Colloidal Dispersion:

A colloidal dispersion or Colloidal System is a mixture in which one substance (dispersed phase) is evenly distributed in another (dispersion medium) in the form of very small particles or droplets.

e.g   milk (liquid in Liquid)
       Fog (liquid in gas)
       Butter (Solid in Liquid)

Enzyme Inhibition:

The decrease in rate of enzyme catalyzed reaction as a result of complex formation of a foreign substance with enzyme is called enzyme inhibition.

• This is crucial in regulating metabolic pathways, drug action & toxin effects

→ Reversible E.I وقال ربّنا تبارك وتعالى

→ Irreversible E.I

Difference:

Colloids	Sols
Colloids are mixture where one substance is evenly distributed (the dispersed phase) in another (the dispersion medium)	A sol is a type of colloid where solid particles are dispersed in a liquid

PROPERTIES OF COLLOIDS

Color

Colloidal solutions are invariably colored. The color of the sol depends on the size and shape of the colloidal particles, the absorption power of the dispersed phase and dispersion medium and the wavelength of the light falling on it. For example a gold sol with different particle-size shows different colors.

Heterogeneity

Colloidal particles being larger than the molecules or ions, form heterogeneous mixtures consisting of particles of dispersed phase and dispersion medium.
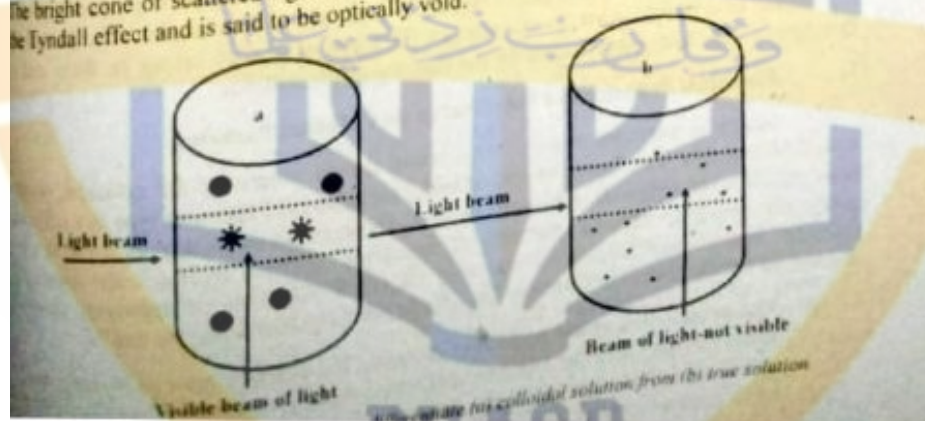
Non-Settling

Colloidal solutions are quite stable systems and the suspended particles remain suspended indefinitely. Only some large particles may settle but very slowly.

Filterability

Colloidal particles pass through an ordinary filter paper, which cannot, therefore, be used for removing the dispersed phase. Ultrafilters are used for the purpose. These are made up of unglazed porcelain which retain the colloidal particles and allow the molecules of dispersion medium to pass through.

Optical Properties of Sol (Tyndall effect)

An important characteristic of colloids is the scattering of light. If a beam of light is passed through a medium which is optically clear that is, it contains no particles of large size than the molecules of true solution; it is difficult to detect the path of light. But when light is passed through a colloidal system, in which the particle size is large, the rays are scattered. This phenomenon of scattering of light by particles was studied by Tyndall and is generally known as the *Tyndall Effect*. An illuminated light beam passing through a colloidal solution is visible while the same beam passing through true solution cannot be seen because solute molecules cannot scatter light as illustrated in Fig. 21.7. The bright cone of scattered light is called Tyndall cone. A true solution does not show the Tyndall effect and is said to be optically void.

If a beam of light is passed through a colloidal solution in a dark room, solution becomes luminescent when viewed through a microscopic at right angle to the path of incident light. Quantitative study of the Tyndall effect and other kinetic properties has been rendered possible with the help of ultra-microscope introduced by Richard Zsigmondy in 1903. The arrangement of the system is shown in Fig. 21.8.
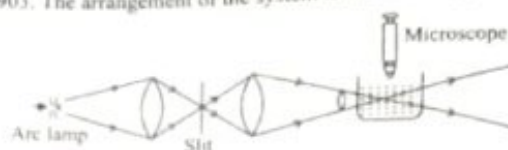

Fig. 21.8 Arrangement of ultra-microscope

A strong beam of light is passed through a cell containing colloidal solution and is viewed through a microscope. Zsigmondy showed that if the colloidal particles are seen from directions at right angles to the incident light, the colloidal particles appear as bright spot against a dark background.

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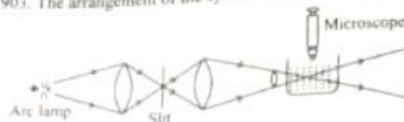

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6.   Kinetic Properties of Sol (Brownian movement)

Robert Brown (1927), a botanist, observed that pollen grains when suspended in a liquid and are observed under a microscope exhibit a ceaseless random motion and traveled a zig-zag path. It has been found that colloidal particles exhibit random zig-zag motion when seen under ultramicroscope. This random zig-zag motion of colloidal particles is known as *Brownian movement*. This movement is due to the bombardment of the colloidal particles by the molecules of the dispersion medium. When an

Fig. 21.9.Brownian movement

unequal number of molecules of the medium strike the colloidal particle from opposite directions, then the colloidal particle begins to start his random motion. The Brownian movement of colloidal particles counteracts the force of gravity acting on them and is thus responsible to a certain extent for the stability of the colloids.
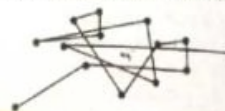
7.   Electrical Properties of Sol (Charge on Colloidal Particles)

Colloidal particles always carry some charge otherwise the colloidal system would be unstable. The charge on the colloidal particles is of the same type in a colloidal solution. Certain colloidal solutions such as those of ferric hydroxide hydrosol are positively charged, whereas particles of arsenious sulphide hydrosol are negatively charged. Proteins are amphoteric and may be either positively or negatively charged, depending on the pH of the solution. The charge on the particles may be due to:

(a) **The presence of acidic and basic groups.** The charge in case of proteins, amino acids, polypeptides etc. can be explained due to the presence of acidic ($-COOH$) and basic ($-NH_3$) groups in the molecule. In acidic solution, the molecules will have positive charge due to the protonation of basic groups, while in alkaline

solution the, molecules will be negatively charged due to the ionization of acidic groups as shown below.
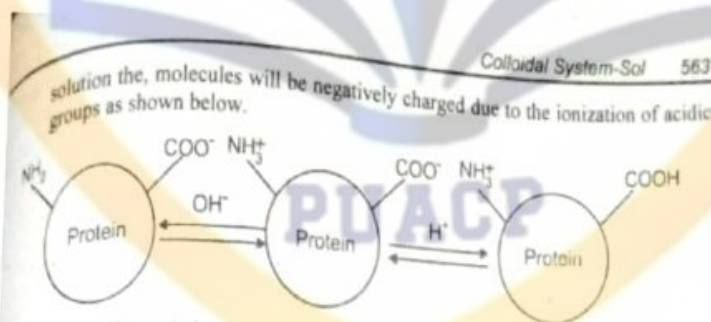

Fig. 21.10. The variation in charge of protein sol with change in pH of the medium.

It is clear that the charge in such cases is a function of pH of the medium. The pH at which the net charge on the molecule is zero is called the *isoelectric point*. The molecules at the isoelectric point exist as *Zwitter ions*. A lyophilic colloid has minimum stability at this pH. The direction of movement of protein sol particles in electrophoresis can be used for determination of sign of charge on protein particles.

(b) **Due to the formation of micelles of ionic surfactants.** Colloidal electrolytes such as soaps, $C_{15}H_{31}COO^-Na^+$ (sodium palmitate) dissociate in solution giving positively charged metal ions and negatively charged carboxylate ions with long hydrocarbon chain. The hydrocarbon parts of anions have a marked affinity for one another and they are drawn together in aqueous medium. Thus the negative ions (the palmitate ions) aggregate to form an ionic micelle which is of colloidal size. This accounts for the presence of negative charge on the colloidal soap

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Fig. 21.11 Micelle of anionic surfactant indicating negative charged on particle.

(c) **Due to preferential adsorption of ions.** The charge on the colloidal particles in some cases results from adsorption of either positive or negative ions from the medium in which they are prepared. The particles constituting the dispersed phase of a colloidal solution adsorb those ions preferentially which are common with their own lattice ions. For example, ferric hydroxide red sol system is obtained by hydrolysis of $FeCl_3$ as shown below:

$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3HCl$$
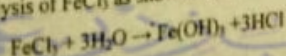
Ferric hydroxide red sol is positively charged because $Fe(OH)_3$ particles adsorb common ions (Fe^{3+} ions) from aqueous medium as shown in Fig. 21.12 (a). Similarly, arsenic sulfide sol is negatively charged because they adsorb S^{2-} ions (common ions) from medium as shown in Fig. 21.12 (b).
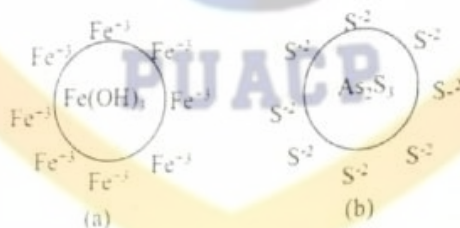
Fig. 21.12 (a) Positively charged $Fe(OH)_3$ sol and negatively charged As_2S_3 sol resulting from preferential adsorption of common cations and anions respectively

It is not necessary that a particular sol particles adsorb same kind of ions. Adsorption of ions on sol particles depends upon their concentration. The ions in excess are preferably adsorbed on sol particle surface. For example, if silver nitrate solution is added to potassium iodide solution, the precipitated silver iodide (AgI) will adsorb iodide ions (I^-) from the dispersion medium and negatively charged colloidal solution will result. However, if silver iodide is formed by adding potassium iodide to silver nitrate solution, we will get a positively charged suspension due to the preferential adsorption of silver ions (Ag^+) which are present in the dispersion medium. This phenomenon forms the basis of the use of adsorption indicators (e.g., eosin, fluorescein etc.) in volumetric analysis.

7.1 Electrical Double Layer and Zeta Potential

A charged colloidal particle is surrounded by ions of opposite kind. The ions of one type (+ve or –ve) get adsorbed and thus form a fixed charged layer on the colloidal particle. Fig. 21.13 (a) depicts the formation of +ve fixed layer at the solid-liquid interface. Ions of opposite charge from the liquid phase tend to approach this layer in

(b)

Michaelis - Menton mechanism for enzyme catalysis.

Enzymes Catalysis

"The catalysis brought about by enzymes are known as enzymes catalysis."

Enzymes: The reactions being slow remarkably catalysed by organic compounds called enzymes. Enzymes have been found to be complex protein molecules.

Michaelis-Menton Mechanism

Michaelis-Menton mechanism of enzyme catalysis obey lock and key model of enzyme functioning. An enzyme has specific site for adsorption of a particular substance.

⇒ According to this model, substrate can form a complex with enzyme by a reversible process, then substrate-enzyme complex is converted into product with regeneration of enzyme by irreversible process.

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \overset{k_2}{\longrightarrow} E + P$$
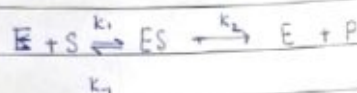
According to above equation, rate of R_n is:

$$u = k_2 [ES]$$

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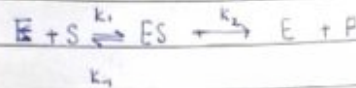
$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \overset{k_2}{\longrightarrow} E + P$$

According to above equation, rate of R_1 is:

$$u = k_2 [ES]$$

Net rate formation of enzyme-substrate complex can be written as.

$$\frac{d[ES]}{dt} = k_1[E][S] - k_{-1}[ES] - k_2[ES].$$

Applying steady-state approximation, because ES complex is formed and used during reaction and it is unstable. So, $d[ES]/dt = 0$

$$0 = k_1[E][S] - k_{-1}[ES] - k_2[ES]$$

$$k_{-1}[ES] + k_2[ES] = k_1[E][S]$$

$$[ES]\{k_{-1} + k_2\} = k_1[E][S].$$

$$[ES] = \frac{k_1[E][S]}{k_{-1} + k_2} \qquad (1)$$

Enzyme is present in vessel in free form as well as in ES complex form so,

$$[E]_o = [E] + [ES]$$

where $[E]_o$ is initial conc. of enzyme, $[E]$ is available conc. of free enzyme and $[ES]$ is conc. of enzyme-substrate complex.

$$[E] = [E]_o - [ES]$$

putting above eq in eq (1)

$$[ES] = \frac{k_1\{[E]_o - [ES]\}[S]}{k_{-1} + k_2}$$

when $[E]_0$ is initial conc. of enzyme.

$[E]$ is available conc. of free enzyme.

and $[ES]$ is conc. of enzyme-substrate complex.

$$[E] = [E]_0 - [ES]$$

putting above eq in eq (1)

$$[ES] = \frac{K_1 \{[E]_0 - [ES]\}[s]}{K_{-1} + K_2}$$

$$[ES] = \frac{\{[E_0] - [ES]\}[s]}{\frac{K_{-1} + K_2}{K_1}}$$

$$K_M = \frac{K_{-1} + K_2}{K_1}$$

$$[ES] = \frac{\{[E_0] - [ES]\}[s]}{K_M}$$

K_M = Michaelis - Menton constant.

$$[ES] = \frac{[E_0][s]}{K_M} - \frac{[ES][s]}{K_M}$$

$$[ES] + \frac{[ES][s]}{K_M} = \frac{[E_0][s]}{K_M}$$

Date / 20   M T W T F S

$$[ES] = \frac{[E_0][s]}{K_M + [s]}$$

putting value of $[ES]$ in eq (a)

$$\boxed{u = \frac{K_2[E_0][s]}{K_M + [s]}}$$

Result deduced are as follows:

(i) Rate of reaction is the function of concentration of substrate.

(ii) Rate of reaction is directly proportional to $[s]$ but upto certain limits only.

(iii) When $[s]$ is low, then $K_M + [s] \approx K_M$, so,

$$u = \frac{K_2[E_0][s]}{K_M}$$

$$u = \text{constant} \times [s]$$

$$u \propto [s]$$

$$u = \frac{k_2 [E_0][s]}{k_M + [s]}$$

Result deduced are as follows:

(i) Rate of reaction is the function of concentration of substrate.

(ii) Rate of reaction is directly proportional to $[s]$ but upto certain limits only.

(iii) When $[s]$ is low, then $k_M + [s] \approx k_m$, so,

$$u = k_2 \frac{[E_0][s]}{k_m}$$

$$u = \text{constant} \times [s]$$

$$u \propto [s]$$

so, rate of reaction is directly proportional to concentration of substrate.

Date: __/__/__

(iv) when $[s]$ is very high then $k_M + [s] \approx [s]$, so,

$$u = \frac{k_2 [E_0][s]}{[s]}$$

$$u = k_2 [E]_0 = u_{max}.$$

u_{max} is independant.

Fig. 21.4 Setup of Bredig's arc method used for preparation of metal particles.

PURIFICATION OF COLLOIDS

A sol prepared by any one of the above methods may often contain other materials besides the colloidal particles. It is often desirable to remove these impurities, particularly when they are electrolytes as they reduce the stability of the sol. The most commonly employed techniques are

(i) Dialysis   and   (ii) Ultrafiltration.

Dialysis

This method makes use of the fact that there is a significant difference in size between colloidal particles and the dissolved molecules or ions. The sol is filled in a porous membrane tubing and is suspended in a vessel containing distilled water. Crystalloid gets passed through the pores of membrane due to concentration gradient and the colloidal particles are retained within porous tubing due to large particle size. This process of removing crystalloids or other impurities from a sol by diffusion through a permeable membrane is known as *dialysis*. The process of purification of sol via dialysis is shown in Fig. 21.5.
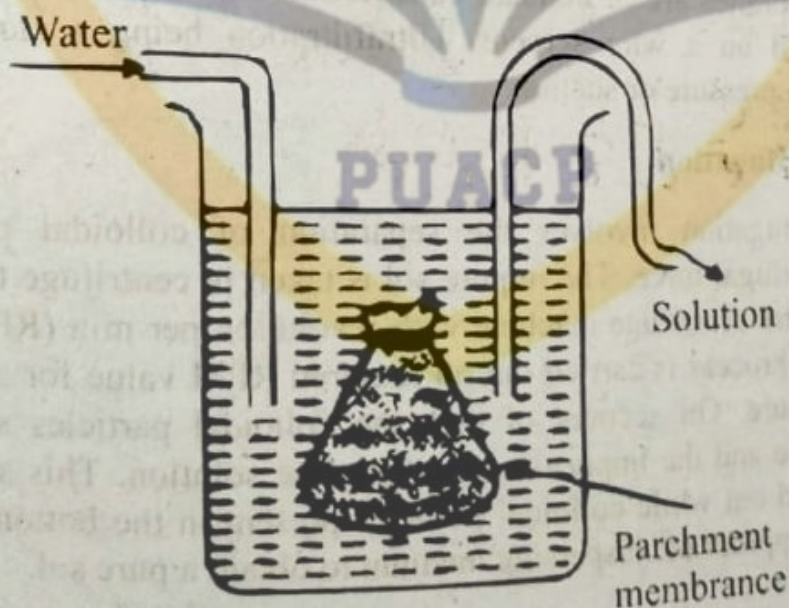

Fig. 21.5 Purification of sol via dialysis

The water in the tank is changed periodically. The process of dialysis can be quickened by applying an electric field. This process is called *electro-dialysis* and is shown in Fig.

A. Dispersion Method (Top down approach)
- Mechanical disintegration
- peptization.
- Bredig's Arc Method
- Ultrasonic dispersion method.

B. Condensation Method
- Reduction
- Oxidation
- hydrolysis
- double decomposition.

⟹ Purification

A sol prepared by any one of the above methods may often contain other materials beside the colloidal particles. It is often desirable to remove the impurities particularly when they are electrolytes as they reduce the stability of the sol. The most commonly employed techniques are :

→ Dialysis
→ Ultra filtration.
→ Ultracentrifugation

Colloids, how they are prepared & Purified.

Definition:

A homogeneous non-crystalline substance consisting of large molecules or ultramicroscopic particles of one substance dispersed through a second substance.

Colloids include, gel, sols and emulsions the particles do not settle and cannot be seperated out by ordinary filtering or centrifuging like those in a suspension.

⇒ Preparation Method:
Lyophilic & Lyophobic colloids

Lyophilic colloids can be prepared by just heating the solid with the liquid dispersion Medium.
whereas,

the Lyophobic colloids cannot be prepared just by heating, they need to be prepared by some special methods. Two methods by which Lyophobic colloids can be prepared as follow

(a)

What are colloids, kinetics properties of sols?

Colloids:

> "A colloid is a substance microscopically dispersed throughout another substance."

- The word colloid comes from a Greek word "Kolla" which means glue like thus colloidal particals are glue like substances.

- These particles pass through a filter paper but not through a semipermeable membrane.

> " The colloidal solutions are the intermediate b/w true solution and suspension."

- When the diameter of particles dispersed in a solution ranges from about $10 \overset{\circ}{A}$ to $2000 \overset{\circ}{A}$, the system is termed as colloid or colloidal solution.

Examples:
Milk, blood, fog, ice-cream

21.6. The colloidal solution along with unwanted electrolyte is placed between dialyzing membranes and pure water in a compartment on each side. When a potential is applied, the ions migrate into the water leaving behind the pure colloidal solutions. For effective separation a continuous supply of water should be maintained. The process of dialysis depends on the character of the aggregates involved, the nature of the fluid and semi-permeability of the membrane.
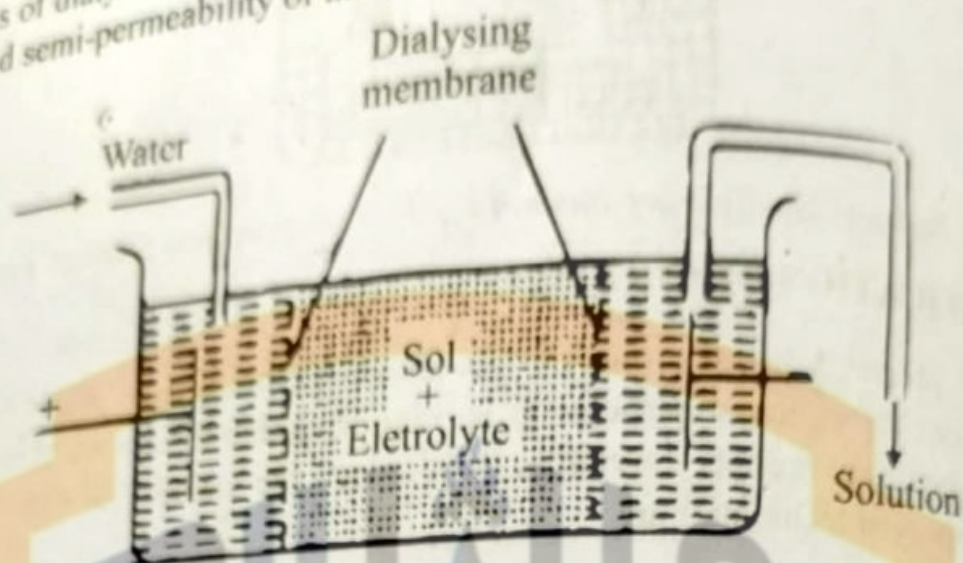

Fig. 21.6 Electro dialysis apparatus for rapid purification of sol.

(ii) Ultrafiltration

This is another important method for purifying sols. The process of ultrafiltration is similar to the filtration of an ordinary precipitate except with the difference that the membrane used here is designed in such a way that it will permit the passage of only electrolytes and medium, and not of colloidal particles. Colloidal particles thus can be separated from the medium containing electrolytes. Such membranes are made by impregnating ordinary filter paper with collodion or a regenerated cellulose. Since ultrafiltration membranes are of delicate constitution and can be easily broken, they are generally supported on a wire screens. Ultrafiltration being a slow process can be quickened by using pressure or suction.

(iii) Ultracentrifugation

Ultracentrifugation involves the separation of colloidal particles from the impurities by centrifugal force. The impure sol is taken in centrifuge tubes and the tubes are placed in an ultra-centrifuge machine with revolution per min (RPM) value ≥ 15000. The centrifugation process is carried out on required RPM value for a specific period at particular temperature. On account of this, the colloidal particles settle down at the bottom of each tube and the impurities remain in the solution. This solution containing impurities is sucked out while colloidal particles present in the bottom of each tube are re-dispersed in an appropriate dispersing medium to obtain a pure sol.

Table 21.2. Classification of Colloidal Solutions

S.No.	Dispersion Medium	Dispersed Phase	Name	Examples
1.	Gas	Liquid	Aerosol	Fog, mist, clouds.
2.	"	Solid	Aerosol	Smoke, dust.
3.	Liquid	Gas	Foam	Froath, whipped cream
4.	"	Liquid	Emulsion	Milk, oil in water.
5.	"	Solid	Sols	AgCl, As_2S_3 in water.
6.	Solid	Gas	Solid foam	Pumice stone, ice cream
7.	"	Liquid	Gels	Jellies, curd.
8.	"	Solid	Solid sols	Ruby, gem.

(c) **Based on Interaction of Phases**

On the basis of affinity between the dispersed phase and the dispersion medium, sols can be divided into two categories, lyophobic and lyophilic sols. *Lyophobic (solvent hating)* sols have little attraction between the dispersed phase and dispersion medium.

Because of the poor interactions, lyophobic sols are less stable, precipitate out easily and are obtained with difficulty. On heating or cooling such a system, solids are obtained which cannot be reconverted into sols either by adding solvent or by warming. Typical examples of such colloids are sols of metals, sulphur and silver halides. *Lyophilic (solvent loving)* sols on the other hand are systems in which the dispersed phase shows some definite affinity for the medium. Lyophilic sols are easily formed and are generally reversible, e.g., gums, starch etc.

When the liquid dispersion medium is water, the terms employed are *hydrophobic* and *hydrophilic sols*. Other essential differences between the two types of sols are given in Table 21.3.

Table 21.3. Distinguishing Characteristics of Lyophobic and Lyophilic Sols

S. No.	Lyophobic Sols	Lyophilic Sols
1.	These are generally unstable, get easily coagulated on adding electrolytes.	These are very stable and are not easily coagulated by electrolytes.
2.	These are irreversible in character.	These are reversible in character.
3.	Prepared by indirect methods.	Usually prepared by simple solution methods.
4.	Viscosity of the colloidal dispersion is same as that of the solvent.	These are highly viscous systems.
S.No.	Lyophobic Sols	Lyophilic Sols
5.	These are generally inorganic materials i.e., metals sulphide and oxide sols.	Mostly organic materials, e.g., starch, gum and proteins.
6.	Surface tension is similar to that of the dispersion medium.	Surface tension is lower than that of the dispersion medium.
7.	Particles carry positive or negative charge.	Particles may have little or no charge at all.
8.	Particles are easily detected under an ultramicroscope.	The particles cannot be readily detected under an ultramicroscope.
9.	There is no solvation of the lyophobic sol particles.	Lyophilic sol particles are solvated due their interaction with solvent.
10.	Examples. Gold or As_2S_3 in water.	Examples: Gum, starch, proteins.

$$= \frac{100 \times 10^8 + 36 \times 10^8}{160,000} = \frac{136 \times 10^8}{16 \times 10^4}$$

$$= \frac{136}{16} \times 10^4$$

$$= 85,000$$

Thus the weight average molecular weight is **85,000**.

DETERMINATION OF MOLECULAR WEIGHTS OF MACROMOLECULES

There are a number of methods available for the determination of molecular weight of macromolecules. Here, we will discuss the more important ones.
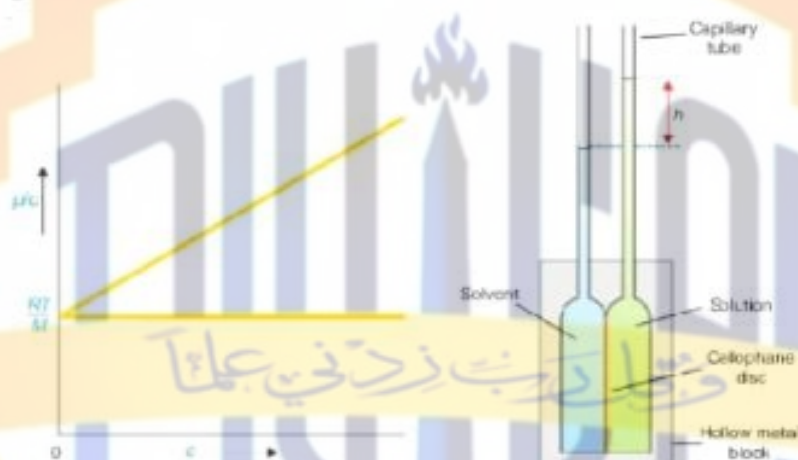
(1) Osmotic Pressure Method

The van't Hoff equation for dilute solutions may be written as :

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

or
$$\frac{P}{c} = \frac{RT}{M}$$

where p = osmotic pressure, atm ; c = concentration of solution gl^{-1} ; R = gas constant, 0.08205 l atm $deg^{-1} mol^{-1}$; T = kelvin temperature ; M = molecular weight of the solute (polymer).

In actual determination of molecular weight of a high polymer, osmotic pressure (p) of a series of small concentrations (c) is measured with the help of a special Osmometer shown in Fig. 22.35. The plot of p/c against c is a straight line (Fig. 22.34).

It is extrapolated to zero concentration. This gives RT/M as the intercept from which the molecular weight can be calculated .

■ Figure 22.34
Plot p/c versus c : giving intercept = $\frac{RT}{M}$

■ Figure 22.35
Fuos-Mead Osmometer for measuring osmotic pressure of polymer solution.

Fuos-Mead Osmometer. It is a modern device for measuring the osmotic pressure of polymer solutions (Fig. 22.35). It consists of two hollow metal blocks holding a cellophane disc in between.

Each block carries a capillary tube. The hollow metal compartments are charged with solvent and solution through the side-tubes (not shown). Osmosis occurs across the semipermeable membrane (cellophane disc). The height of the solution in the capillary (h) is read off differentially to eliminate surface tension effect.

(2) Viscosity method

It is a very convenient method for determining the molecular weights of macromolecules in solution. The addition of macromolecules to a solvent increases its viscosity over that of pure solvent.

The **relative viscosity** of a solution of a polymer, denoted by η_r, is given by the expression

$$\eta_r = \frac{\eta}{\eta_0} \qquad (1)$$

where η is viscosity of solution and η_0 that of the solvent at the same temperature.

Each block carries a capillary tube. The hollow metal compartments are charged with solvent and solution through the side-tubes (not shown). Osmosis occurs across the semipermeable membrane (cellophane disc). The height of the solution in the capillary (h) is read off differentially to eliminate surface tension effect.

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where η is viscosity of solution and η_0 that of the solvent at the same temperature.

The **specific viscosity**, denoted by η_{sp}, is given by

$$\eta_{sp} = \eta_r - 1 \qquad ..(2)$$

In terms of (1) and (2), the intrinsic viscosity is defined as

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

where c is the concentration of the solute. The plot η_{sp}/c against η gives a straight line. Extrapolation to $c = 0$ yields the intrinsic viscosity.

It was shown by staudinger that an empirical relationship exists between intrinsic viscosity $[\eta]$ and the molecular weight $[M]$ of the high polymer.

$$[\eta] = kM^a$$

where k and a are constants for a specific polymer in a specific solvent. Once k and a are known for a polymer-solvent combination, M may be calculated from a determination of the value of intrinsic viscosity.

The viscosity measurements yield the weight average molecular weight of a macromolecular substance.

Figure 22.36
Plot of η_{sp}/c versus c.

(3) Svedberg's Sedimentation method

The rate of selling or sedimentation of polymer particles under the influence of gravitation force is very slow. Svedberg devised a centrifugal machine with the help of which macromolecules could be sedimented with speed. As a result, the particles move down in the containing tube. This causes a concentration gradient in the tube. The rate, dx/dt, at which the macromolecules sediment, is given in terms of the sedimentation constant S by the following expression :

$$S = \frac{dx}{dt} / \omega^2 x$$

where x is the distance of the solute species from the centre of rotation and ω is the angular velocity.

The sedimentation constant, S, is related to the molecular weight of the polymer by the expression :

$$M = \frac{SRT}{D(1 - \rho/\rho')}$$

where ρ and ρ' are the densities of the solvent and solute respectively. The rate at which sedimentation occurs, determined experimentally, can thus be used for finding the molecular weight of
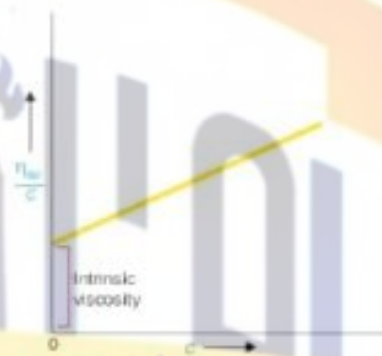
macromolecules. Since the rate of sedimentation depends on the mass of the particle undergoing sedimentation, the molecular weight obtained by this method is the *weight average molecular weight*, $\overline{M}_w$.

(4) Sedimentation Equilibrium method

$$S = \frac{dx}{dt} \Big/ \omega^2 x$$

where x is the distance of the solute species from the centre of rotation and ω is the angular velocity.

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(4) Sedimentation Equilibrium method

This method for determining molecular weight of a high polymer is quicker and convenient compared to method (3).

If a sol is whirled sufficiently long in an ultracentrifuge, a stage is reached at which the sol no longer settles. At this stage an equilibrium is reached between the centrifugal force and diffusion of the material in a direction opposite to the centrifugal force. If c_1 and c_2 be the concentrations of the particles at points x_1 and x_2 cm from the centre of rotation, the molecular weight, M, of the high polymer is given by the relation

$$\ln \frac{c_2}{c_1} = \frac{M\omega^2 (\rho - \rho')\,(x_2^2 + x_1^2)}{2RT\rho}$$

or

$$M = \frac{2RT\rho \ln c_2 / c_1}{\omega^2 (\rho - \rho')\,(x_1^2 - x_2^2)}$$

By determining the concentrations c_1 and c_2 at the two levels x_1 and x_2 in the settling cell at sedimentation equilibrium, M can be calculated.

$$P_{Almost} = \frac{1 + bP_B}{a}$$

$$P_{Almost} = \frac{1 + (0.35)(200)}{0.2} = 355 Pa$$

6.8.2 Eiley-Rideal Mechanism

Eiley-Rideal mechanism involves the following steps

(i) One reactant get adsorb on surface of catalyst.

(ii) Second reactant doesn't adsorb on catalyst surface. Instead it interact with adsorb reactant. In E-R mechanism, both reactants adsorb on catalyst surface. This is different from Langmuir-Hinshelwood mechanism. In L-H mechanism both reactants adsorb on catalyst surface.

(iii) After interaction products are formed. Later adsorbed product diffuses into reaction vessel after desorption.

However, product can remain in gaseous state d doesn't adsorb on catalyst surface in E-R mechanism.

Scheme of Eiley-Rideal (E-R) Mechanism

Reactant gases A and B are going to be converted into products C and D by following mechanism according to E-R mechanism.

$$A_{(gas)} \rightleftharpoons A_{1(Ads)}$$

$$A_{1(Ads)} + B_{(gas)} \rightleftharpoons C_{(gas)} + D_{(gas)}$$

According to E-R mechanism, rate of reaction is directly proportional to fraction of the surface covered by gas A and pressure of gas B, because adsorbed molecules of gas A interact with gaseous B to form product i.e.

Rate of reaction $\propto \theta_A$

Rate of reaction $\propto P_B$

Hence,

$$\text{Rate of reaction} = k_r \theta_A P_B \qquad (6.82)$$

Rate of reaction is independent of P_A, as θ_A depends upon P_A. For double system, we have

$$\theta_A = \frac{aP_A}{1 + aP_A + bP_B}$$

Then equation (6.82) will be

$$\text{Rate} = k_r \frac{aP_A P_B}{1 + aP_A + bP_B} \qquad (6.83)$$

This is a rate law expression for the catalytic reaction of two gases on solid surface following E-R mechanism. Since, B is not an adsorbing specie so, $b \approx 0$ then,

$$1 + aP_A + bP_B = 1 + aP_A$$

So, equation (6.83) will be,

$$\text{Rate} = k_r \frac{aP_A P_B}{1 + aP_A}$$

$$\text{Rate} = k_r \left(\frac{aP_A}{1 + aP_A} \right) P_B \qquad (6.84)$$

Terms in bracket is related to gas A, it has factor aP_A which can increase or decrease rate of reaction. We reach at following results

(i) When the partial pressure of gas A is very low then, $1 + aP_A \approx 1$. So, equation (6.84) will be,

$$\text{Rate} = k_r aP_A P_B$$

If partial pressure of gas A is low, then reaction will be 2nd order reaction.

When pressure of gas A is very high then, $1 + aP_A \approx aP_A$. So, equation (6.84) will be

One reactant get adsorb on surface of catalyst.

(ii)   Second reactant doesn't adsorb on catalyst surface. Instead it interact with adsorb reactant. In E-R mechanism, both reactants adsorb on catalyst surface. This is different from Langmuir-Hinshelwood mechanism. In L-H mechanism both reactants adsorb on catalyst surface.

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$$Rate = k_r aP_A P_B$$

If partial pressure of gas A is low, then reaction will be 2nd order reaction.

$$\Delta H_a = R\left(\frac{T_1 T_2}{T_2 - T_1}\right)\left(\ln\frac{P_2}{P_1}\right)$$

By putting values in above equation from given data we can find the isosteric enthalpy of adsorption as

$$\Delta H_a = 8.3143\left[\frac{(298)(323)}{323 - 298}\right]\left(\ln\frac{250}{350}\right) = -10.77 \text{kJmol}^{-1}$$

6.6.2   Catalytic Reaction of Gas Adsorbed on Solid Surface

The most important feature of Langmuir adsorption isotherm is its application to explain the catalytic reaction of a gas on solid surface. Catalytic reaction of gas on metal surface involve following steps

(a)   Diffusion of reactants towards catalyst surface.

(b)   Adsorption of reactants on solid surface.

(c)   Product formation on catalyst surface.

(d)   Desorption of product gas.

(e)   Diffusion of product gas into the reaction vessel from catalyst surface. This phenomenon is depicted by pictorial diagram as shown in Fig. 6.15.
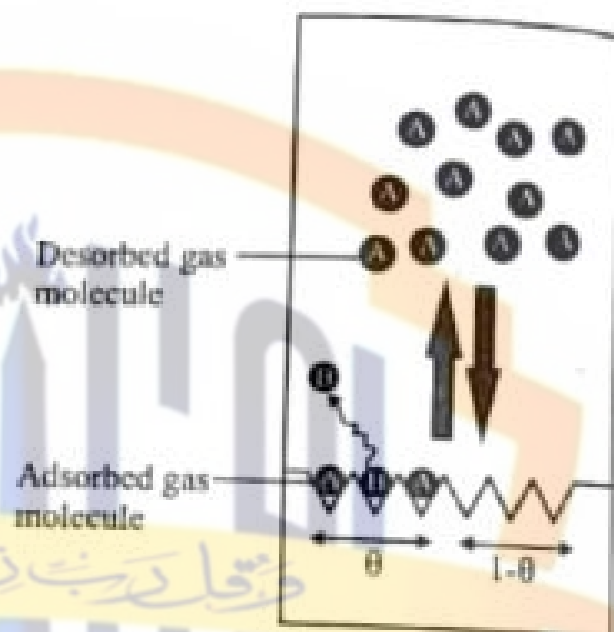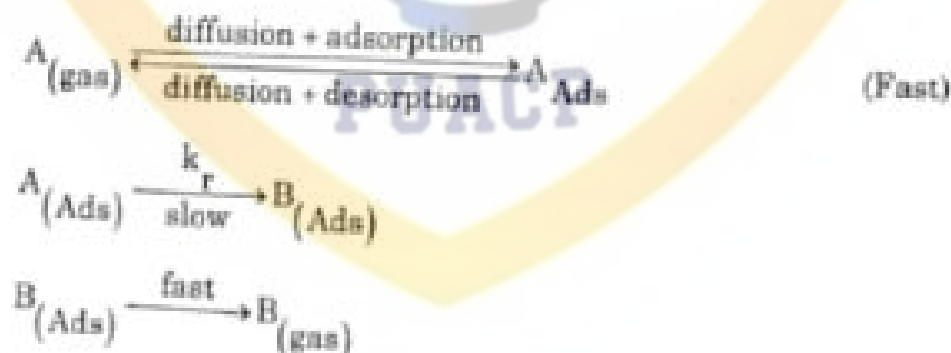

Fig. 6.15 Pictorial diagram of catalytic reaction of two gases on solid surface

According to above steps scheme of catalytic reaction of gas A to generate gas B can be written as

$$A_{(gas)} \underset{\text{diffusion + desorption}}{\overset{\text{diffusion + adsorption}}{\rightleftharpoons}} A_{\text{Ads}} \qquad \text{(Fast)}$$

$$A_{(Ads)} \xrightarrow[\text{slow}]{k_r} B_{(Ads)}$$

$$B_{(Ads)} \xrightarrow{\text{fast}} B_{(gas)}$$

Where, k_r is the heterogeneous rate constant.

Rate of reaction is directly proportional to fractional surface coverage of adsorbed gas A.

Rate of reaction $\propto \theta_a$

(ii)   Plot of $\ln P_i/P_A$ versus t as shown in Fig. 6.16.

(iii)   The value of k_r can be determined from slope i.e.

$$\text{Slope} = k_r b$$

$$k_r = \frac{\text{slope}}{b}$$

(iv)   Expression of half life of gas A can be derived as

$$t = t_{1/2} \text{ at } P_A = P_i/2$$

Applying this condition to equation (6.34), we get

$$\ln \frac{P_i}{P_i/2} = k_r b t_{1/2}$$

$$k_r b t_{1/2} = \ln 2$$

$$t_{1/2} = \frac{1}{k_r b} \ln 2$$

$$t_{1/2} = \frac{0.693}{k_r b} \qquad (6.35)$$

Fig. 6.16 $\ln P_i/P_A$ as a function of time

Results can be drawn from equation (6.35) as follows: $t_{1/2}$ is function of b, $t_{1/2}$ is inversely proportional to b and it is independent of P_A. With change in temperature, k_r and b changes which in turn causes a change in $t_{1/2}$.

(v)   Units of k_r can be determined as

$$k_r = \frac{1}{bt} \ln \frac{P_i}{P_A}$$

$$k_r = Pa/s$$

(vi)   The pressure of gas as a function of time can be expressed as

$$\frac{P_i}{P_A} = e^{k_r bt}$$

$$\frac{P_A}{P_i} = e^{-k_r bt}$$

$$P_A = P_i e^{-k_r bt} \qquad (6.36)$$

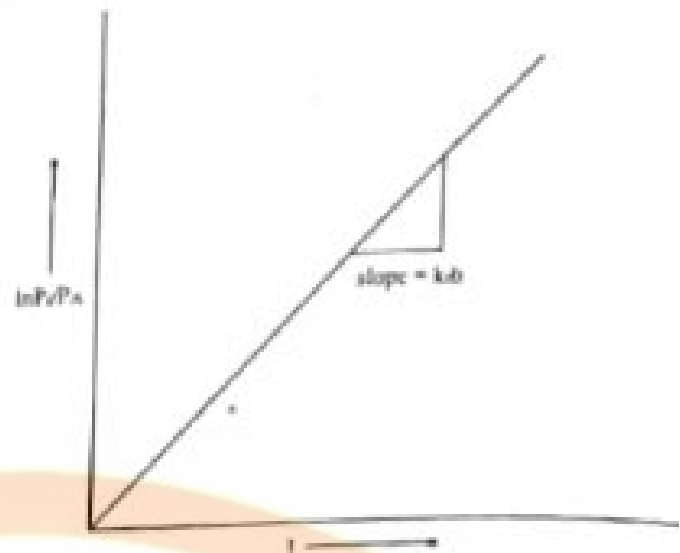According to equation (6.36), value of P_A decreases with increase of time exponentially as shown in Fig. 6.17.

$$\text{Rate} = k_r \theta_A \qquad (6.28)$$

According to Langmuir adsorption isotherm for non dissociative adsorption, we know $\theta_A = \dfrac{bP_A}{1 + bP_A}$. So, equation (6.28) will be

$$\text{Rate} = k_r = \frac{bP_A}{1 + bP_A} \qquad (6.29)$$

Nature of gas, whether it is strongly, moderately or weakly adsorbed on catalyst surface, highly affects kinetics of catalytic reactions. Thus kinetics of catalytic reaction can be discussed in two separate cases as given below

i) When Reactant Gas is Weakly Adsorbed

If gas is weakly adsorbed it means b is very low. So, $1 + bP_A = 1$ put this value in equation (6.29) we get,

$$\text{Rate} = k_r bP_A \qquad (6.30)$$

$$\text{Rate} \propto P_A$$

Hence, reaction is of first order, if b is very low.

$$-\frac{dP_A}{dt} = \text{Rate of consumption of gas A}$$

So, equation (6.30) can be written in terms of rate of consumption of gas A

$$-\frac{dP_A}{dt} = k_r bP_A \qquad (6.31)$$

By separating variables and integrating equation (6.31) we get,

$$-\int \frac{dP_A}{P_A} = k_r b \int dt \qquad (6.32)$$

$$-\ln P_A = k_r bt + c \qquad (6.33)$$

Applying boundary conditions, when $t = 0$ then $P_A = P_i$. Physically, it is said that when reaction just starts then pressure has its maximum value equal to initial pressure of gas.

So, $-\ln P_i = c$, by putting value of c in equation (6.33) we get,

$$-\ln P_A = k_r bt - \ln P_i$$

$$-\ln P_A + \ln P_i = k_r bt$$

$$\ln \frac{P_i}{P_A} = k_r bt \qquad (6.34)$$

Results concluded from equation (6.34) are as follows

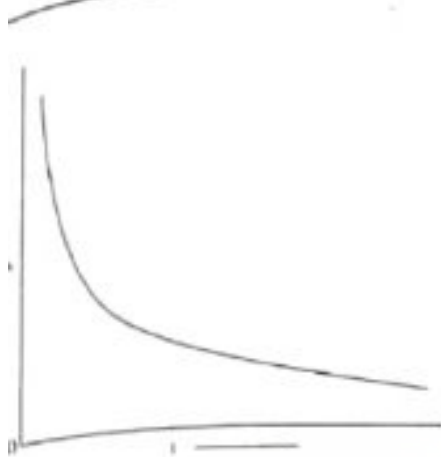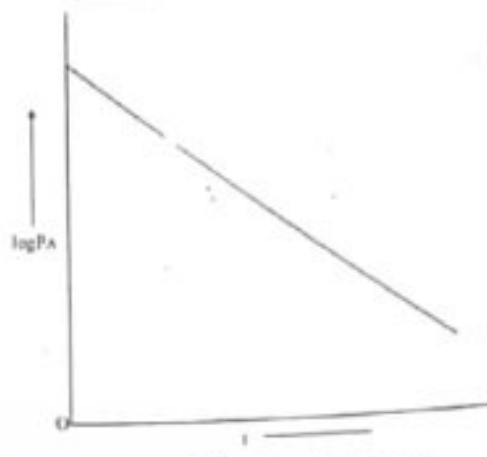(i)　　Equation (6.34) is straight line equation passing through origin.

Fig. 6.17 Plot of pressure of gas A versus   Fig. 6.18 Plot of log P_A versus t
t in exponential form

ii)   By converting natural logarithm into common log of equation (6.34), we get

$$2.303 \log \frac{P_i}{P_A} = k_r b t$$

$$\log \frac{P_i}{P_A} = \frac{k_r b t}{2.303}$$

$$\log P_i - \log P_A = \left(\frac{k_r b}{2.303} \right) t$$

$$\log P_A - \log P_i = -\left(\frac{k_r b}{2.303} \right) t$$

$$\log P_A = \log P_i - \left(\frac{k_r b}{2.303} \right) t$$

This is an equation of straight line with intercept and having negative slope as shown in Fig. 6.18. The slope of the plot can be used to determine the value of k_r and intercept can be used to determine the value of initial pressure.

Relation between Homogenous and Heterogeneous Rate Constants

The kinetic rate equation for homogeneous 1st order reaction is

$$\ln \frac{P_i}{P_A} = kt \qquad (6.37)$$

This is the rate law or kinetic rate equation for homogeneous 1st order reaction.

The kinetic rate equation for heterogeneous 1st order reaction is

$$\ln \frac{P_i}{P_A} = k_r b t \qquad (6.38)$$

By comparing equation (6.37) and (6.38), we get

$$k = k_r b \qquad (6.39)$$