APPLICATIONS OF ELECTROLYSIS IN METALLURGY AND INDUSTRY

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Electrolysis is a very important and useful phenomenon. The phenomenon of electrolysis has wide range of applications. It is used in large number of industrial manufacturing processes. The main practical applications of electrolysis are: 1. Extraction of Metals 2. Refining of Metals 3. Production of Chemicals 4. Electroplating   5. Electro-Typing   6. Electro-Forming   7. Electro-Cleaning   8. Production of non metals.

1. Extraction of Metals

Electrometallurgy is the process of electrolysis for extracting metal from   the ore. There are two methods of metal extraction based on ore's physical state. The ore is treated with strong acid in the first method to   obtain a salt and such salt solution is electrolyzed to release the metal. The ore is in a   molten state in the second process and electrolysed in a furnace.

(i)   Extraction of Zinc:

The zinc ore is treated with sulphuric acid. The zinc sulphate solution which is obtained as a result of it is then electrolyted. In the electrolytic tank, the cathodes are of aluminium and the anodes are of lead. The current density is kept 1000 A/m^2 and zinc is deposited on cathode. The energy consumption is about 3000 to 5000 KWH per tonne.

(ii)   Extraction of Aluminium:

The ores of aluminium are bauxite and cryolite. These are treated chemically and reduced to aluminium oxide and then dissolved in fused cryolite and electrolysed in a furnace. Aluminium deposits at the cathode and settles down

at the bottom. To keep the electrolyte in a fused state the temperature of the furnace is about 1000°C. The current of about 4000 ampere is needed to complete the process and energy consumed is about 20,000 to 25,000 kWH per tonne.

2. Metal Refining

The main advantages of extraction of a metal by electrolytic processes are that the purity of product obtained is 98 to 99%. Further refining is done by electrolysis. , The anode is made of metal that has been extracted. Pure metal is deposited at the cathode. The electrolyte is made of the metal solution e.g. for copper, it is copper sulphate and for nickel, it is nickel chloride. Energy consumption in copper refining by electrolytic process is 150 to 300 kWH/tonne of refined copper. .Copper purity can be enhanced by electrorefining. The same electroplating or electro deposition principal is used in this case.

3. Production of chemicals

Many chemicals like caustic soda (NaOH) chlorine gas etc. are produced on a large scale through electrolysis. Large – scale electrolysis also produces potassium permanganate, hydrogen and oxygen etc.

4 .Electroplating:

Electroplating is used to coat one metal with another metal by using electrolysis. The process of coating an inferior metal with a superior metal by electrolysis is known as electroplating.

The aims of electroplating are:

- To prevent the inferior metal from corrosion.
- To make it more attractive in appearance.

The cathode is the object to be plated, while anode is the desired metal to coat the object. The electrolyte solution must contain ions of the same metal for plating. During electrolysis, the anode will dissolve into the solution. The ions produced will migrate to the cathode where they are discharged and deposited as a layer on the cathode. .

The following are the requirements for fine coating:

- The surface of the article should be free from greasy matter and its oxide layer. The surface is cleaned with chromic acid or detergents.
- The surface of the article should be rough so that the metal deposited sticks permanently.
- The concentration of the electrolyte should be so adjusted as to get smooth coating.
- Current density must be the same throughout.

5. Electro-Typing:

This is a process by which type wood cuts etc. are reproduced in copper by a process of electro-plating. In this process a mould is first made of the type in wax, then it is coated with black lead to give it metallic surface and then it is subjected to the process of electro-deposition. Thus, a film of copper is formed on the prepared surface.

5. Electro-forming:

Reproduction of objects by electro-deposition on some sort of a mould or form is known as electro-forming. This is another application of electro-deposition.

In the reproduction of coins, medals, engravings and the like, a mould is first made by impressing the object, say, in wax. The surface of the wax, which bears exact impressions of the object, is coated by powdered graphite in order to make conducting. The mould is then dipped in an electro-forming cell as a cathode. After obtaining coating of desired thickness, the article is removed and the wax core is melted out of the metal shell. The process is employed in the manufacture of gramophone records, in which the original recording is done on a record of wax composition. This mould is then coated with powdered gold to make it conducting and dipped into a blue vitriol electrolyte as cathode. The solutions kept saturated by using a copper anode. The plating of copper on to the wax record produces a negative master

plate which is used to stamp a large number of shellac discs.

7. Electro-Cleaning:

The article to be cleaned of oil and grease is made the cathode and the iron tank or vat filled with an electrolyte solution of the electrolyte and heavy current is passed through the solution. Caustic soda and hydrogen are produced at cathode which removes the grease from the surface of the article. The process is called cathodic cleaning and is applicable to zinc and aluminium. For anodic cleaning, article is made anode.

8 . Production of Non – Metals

Electrolysis is used to obtain non – metals such as hydrogen, fluorine, chlorine. Hydrogen is obtain in the presence of electrolytes such as H_2SO_4 and KNO_3 through the electrolysis of water.

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Made By Dr. Sapna Sharma

Electro Chemistry - 1

Conductivity, Equivalent Conductivity and Molar Conductivity

- Conductivity --- The reciprocal of resistivity is known as specific conductivity or simple conductivity . It is denoted by κ (kappa) or K. Thus if K is specific conductivity and C is the conductance of solution , then :--

- $R = 1/C$ and. $\rho = 1/K$

- $1/C = 1/K \times l/a$

- $K = C \times l/a$

- If $l = 1cm$ and $a = 1$ sq. Cm then $K = C$
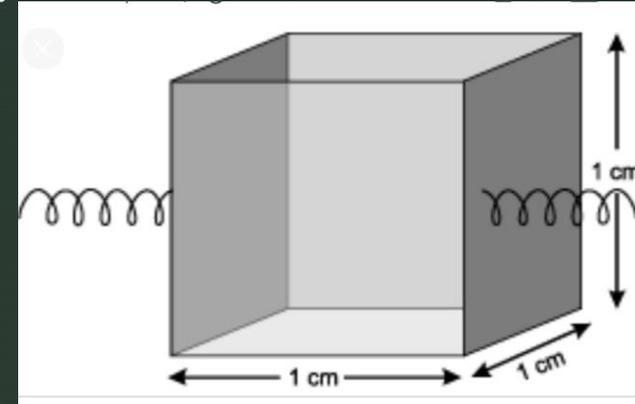
Hence Specific conductivity is defined as conductance of the solution of 1 cm length and having 1 sq.cm as the area of cross section or it is the conductance of 1cm cube of the solution of the electrolyte.

The unit of specific conductivity is --- S /m .

- Equivalent Conductivity --- Equivalent Conductivity of a solution at a dilution V is defined as the conductance of all the ions produced from 1 gram equivalent of the electrolyte dissolved in v cm cube of the solution when the distance between the electrodes is one cm and the areas of the electrodes is so large that whole of the solution is contained between them . It is denoted by Λeq.

- In general , if the volume of the solution containing 1 gram equivalent of the electrolyte is V cm cube then :-

. Equivalent Conductivity = Specific conductivity × V

. $$\Lambda eq = K \times V$$

In terms of concentration if the solution has a concentration of C gram equivalent per litre , then   the volume of the solution containing 1 gram equivalent will be 1000/ C .

$$\Lambda eq = K \times 1000 / normality$$

- Molar Conductivity --- The molar conductivity of the solution at a dilution V is the conductance of all the ions produced from 1 mole of electrolyte dissolved in v cm cube of solution when the electrodes are 1 cm apart and the area of electrode is so large that the whole of the solution is contained between them .

- It is denoted by - Λm

- Molar conductivity is related to specific conductivity by :-

- $\Lambda m = K \times V$

- $\Lambda m = K \times 1000/molarity$

Variation of Specific , Equivalent and Molar Conductivity with Dilution -

- The Equivalent Conductivity and Molar Conductivity increase with dilution whereas specific conductivity of an electrolytic solution decreases with dilution . This can be explained as the conductance of a solution is due to the presence of ion in the solution. The greater the no. of ion , the greater is the conductance . As on dilution more ions are produced in solution so the conductance should also increase on dilution. The specific conductivity of an electrolyte decreases with dilution because the no. of ions present per cm cube of the solution become less on dilution. However , the increase of equivalent and Molar Conductivity is due to the fact that these are the products of specific conductivity and volume of solution containing 1 gram equivalent or 1 mole of the electrolyte. As the decreasing value of specific conductivity is more than compensated by increasing value of V so these two increases with dilution.

Kohlrausch's Law

Kohlrausch studied the molar conductivity at infinite dilution Λm for a number of pairs of strong electrolytes , each pair having a common cation or anion . Then he calculated the differences of these Λm values for each pair. A few of these results are given in Table .

Electrolyte	λ_m° at 298 K	Difference	Electrolyte	λ_m° at 298 K	Difference
KCl	149·86	23·41	KBr	151·92	2·06
NaCl	126·45		KCl	149·86	
KBr	151·92	23·41	NaBr	128·51	2·06
NaBr	128·51		NaCl	126·45	
KNO_3	144·96	23·41	LiBr	117·09	2·06
$NaNO_3$	121·55		LiCl	115·03	

It is observed that the difference between $\Lambda m°$ values for each pair of sodium and potassium salts having a common anion was same , irrespective of what this anion was. Similarly , the difference in the $\Lambda m°$ values for each pair of salts having the same different anions and a common cation was same irrespective of what this cation was .

- On the basis of above observation , he concluded that each ion makes a definite contribution to the total molar conductivity of an electrolyte at an infinite dilution , irrespective of the nature of the other ion of the electrolyte . This individual contribution of an ion towards the total molar conductivity of the electrolyte is called Molar ionic conductivity . Kohlrausch in 1876 gave a law which can be stated as –

- The limiting molar conductivity of an electrolyte at infinite dilution is the sum of limiting ionic conductivities of the cation and anions each multiplied with the no. of ions present present in 1 formula unit of the electrolyte.

Mathematically, Λ°_m for $A_xB_y = x\lambda^\circ_{A^{y+}} + y\lambda^\circ_{B^{x-}}$

where Λ°_m is the limiting molar conductivity of the electrolyte, $\lambda^\circ_{A^{y+}}$ and $\lambda^\circ_{B^{x-}}$ are the limiting molar conductivities of the cation (A^{y+}) and the anion (B^{x-}) respectively.

For example, Λ°_m for $NaCl = \lambda^\circ_{Na+} + \lambda^\circ_{Cl-}$

$$\Lambda^\circ_m \text{ for } BaCl_2 = \lambda^\circ_{Ba+} + 2\lambda^\circ_{Cl^-}$$

$$\Lambda^\circ_m \text{ for } Al_2(SO_4)_3 = 2\lambda^\circ_{Al^{3+}} + 3\lambda^\circ_{SO_4^{2-}}$$

In terms of *equivalent conductivities*, Kohlrausch's law is defined as follows :—

The equivalent conductivity of an electrolyte at infinite dilution is the sum of two values one depending upon the cation and the other upon the anion.

i.e., $$\Lambda^\circ_{eq} = \lambda^\circ_c + \lambda^\circ_a$$

where λ°_c and λ°_a are called the *ionic conductivities* at infinite dilution for the cation and the anion respectively.

The above law is called the *law of independent* migration of ions because at infinite dilution, the dissociation of the electrolyte is complete and there are no interionic effects so that each ion migrates to the electrode independent of the nature of the other ion with which it is associated.

Transport Number

Transport Number – The fraction of the total current carried by an Ion is called its transport number or transference number or Hittorf's number, Greater the speed of the lion, greater the amount of current it will carry with it and hence greater will be its transport number.

Let ua and uc be the speeds of the anión and cation respectively . Then Current carried by the anion is directly proportional to ua = kua .Current caried by cation is directly proportional to uc = kuc

Total current carried = Current carried by anion + Current carried by cation.

i.e = kua +kuc = k(ua +uc)

Therefore transport number of cation nc =kuc / k(ua +uc) or nc = uc/ua+uc

1. na = ua/ua +uc is

   na +nc =1

Hittorf's Method

Determination of Transport Number

Hittorf's Method : - The method is based upon the principle that the fall' in concentration around an electrode is proportional to the speed of the moving ion away from it.

$$\frac{\text{Fall in concentration around cathode}}{\text{Fall in concentration around anode}} = \frac{\text{Speed of anion}}{\text{Speed of cation}} = \frac{u_a}{u_c}$$

Since transport no of cation,

$$t_C = \frac{\text{speed of the cation}}{\text{speed of the cation+speed of the anion}}$$

$$t_C = \frac{\text{Fall in concentration around anode}}{\text{Fall in concentration around anode+Fall in concentration around cathode}}$$

$$t_C = \frac{\text{Fall in concentration around anode}}{\text{Total fall in concentration around both the electrodes}}$$

If the concentration is measured in terms of gram equivalents, then

$$t_C = \frac{\text{No of gram equilants lost from the anodic compartment}}{\text{No of gram equilants lost from both the compartments}}$$

Since no of ions/gram equivalents lost from both the anodic and cathodic compartments is equal to the no of ions/gram equilants discharged/deposited on each electrode. Hence the transport no of cation is

$$t_C = \frac{\text{No of gram equilants lost from the anodic compartment}}{\text{No of gram equilants deposited on each electrode}}$$

FIGURE 11.13.

Hittorf's transport number apparatus for the determination of transport number.
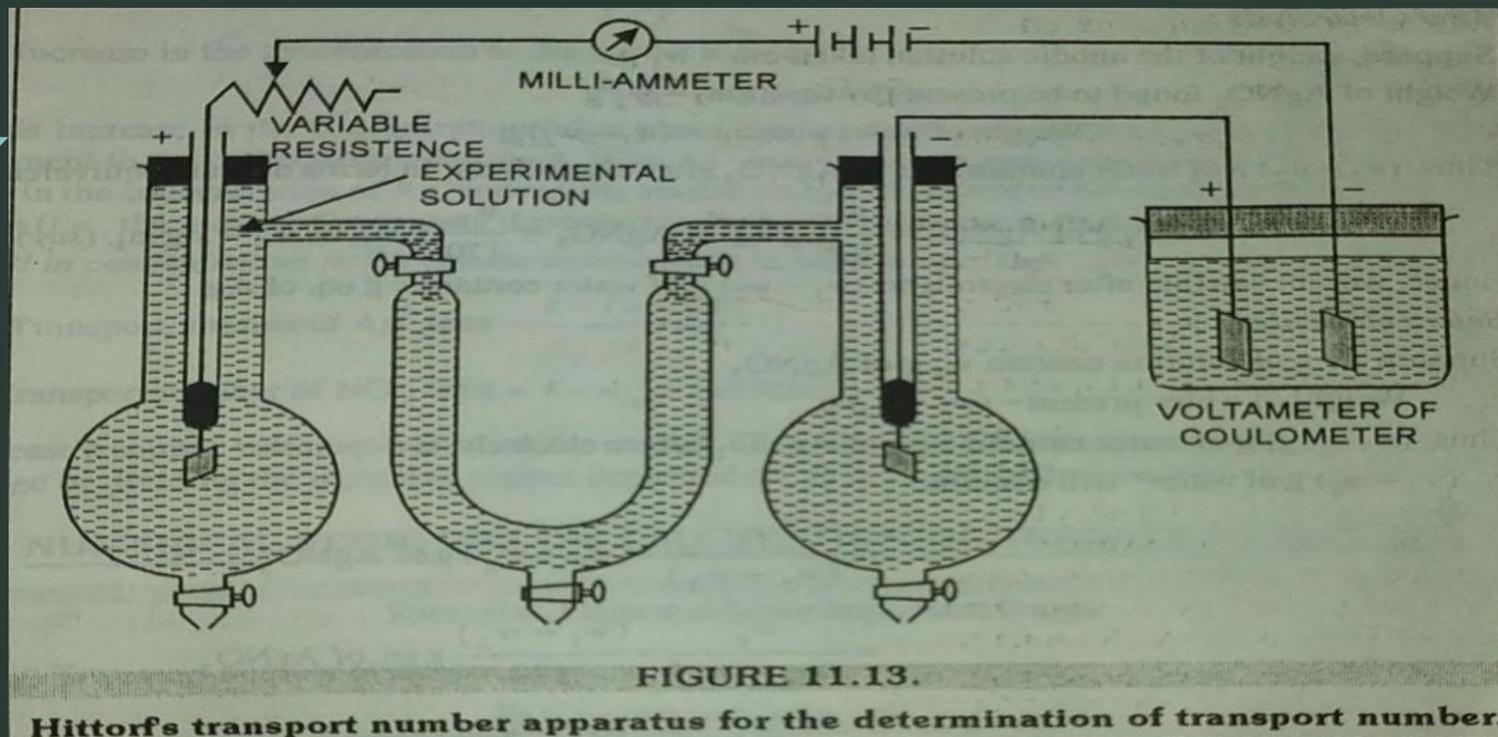
- Apparatus consists of 3 compartments, namely anodic, cathodic and the central compartment.

- The solution of these 3 compartments should not mix with each other on electrolysis.

- It should be possible to take out the solution of any compartment without disturbing the solution of other compartments.

Calculations :-

Calculations :- Taking example of $AgNO_3$ as the electrolyte and using silver voltameter in series

After electrolysis

Suppose wt. of the anodic solution taken out $= W_1 g$

Wt. of $AgNO_3$ found to be present (titration) $= W_2 g$

wt. of water present $= (W_1 - W_2) g$

Thus $(W_1 - W_2)$ of water contain $W_2 g$ of $AgNO_3$ after electrolysis. In terms of gram equivalents,

$W_2 g$ of $AgNO_3 = \dfrac{W_2}{170}$ g eq. of $AgNO_3 = \dfrac{W_2}{170}$ g eq. of Ag

$= x$ g eq. (say)

Hence we can say that after electrolysis $(W_1 - W_2) g$ of water contain x g eq. of Ag.

Before electrolysis

Suppose $W_3 g$ of solution contain $W_4 g$ of $AgNO_3$

$\therefore$ wt. of water present $= (W_3 - W_4) g$

Thus $(W_3 - W_4) g$ of water contain $W_4 g$ of $AgNO_3$ before electrolysis.

$\therefore (W_1 - W_2) g$ of water will contain

$= \dfrac{W_4}{(W_3 - W_4)} \times (W_1 - W_2) g$ of $AgNO_3$

$= \dfrac{W_4}{(W_3 - W_4)} \times \dfrac{(W_1 - W_2)}{170} g$ eq. of $AgNO_3$

$= \dfrac{W_4}{(W_3 - W_4)} \times \dfrac{(W_1 - W_2)}{170} g$ eq. of Ag

$= y$ g eq. (say)

when electrodes are not attacked

$x < y$

$\therefore$ Fall in conc. of the anodic compartment

$= (y - x) g$ eq. of Ag

Suppose the wt. of Ag deposited is the silver voltameter $= W g = \dfrac{W}{108} g$ eq. of Ag

$= z$ g eq. (say)

$\therefore$ Transport number of Ag^+ ion (n_{Ag^+}).

$= \dfrac{\text{Fall in conc. around anode in g.eq.}}{\text{Amount of Ag deposited in voltameter}}$

$= \dfrac{y - x}{z}$

Transport number of NO_3^- ions $(n_{NO_3^-}) = 1 - n_{Ag^+}$
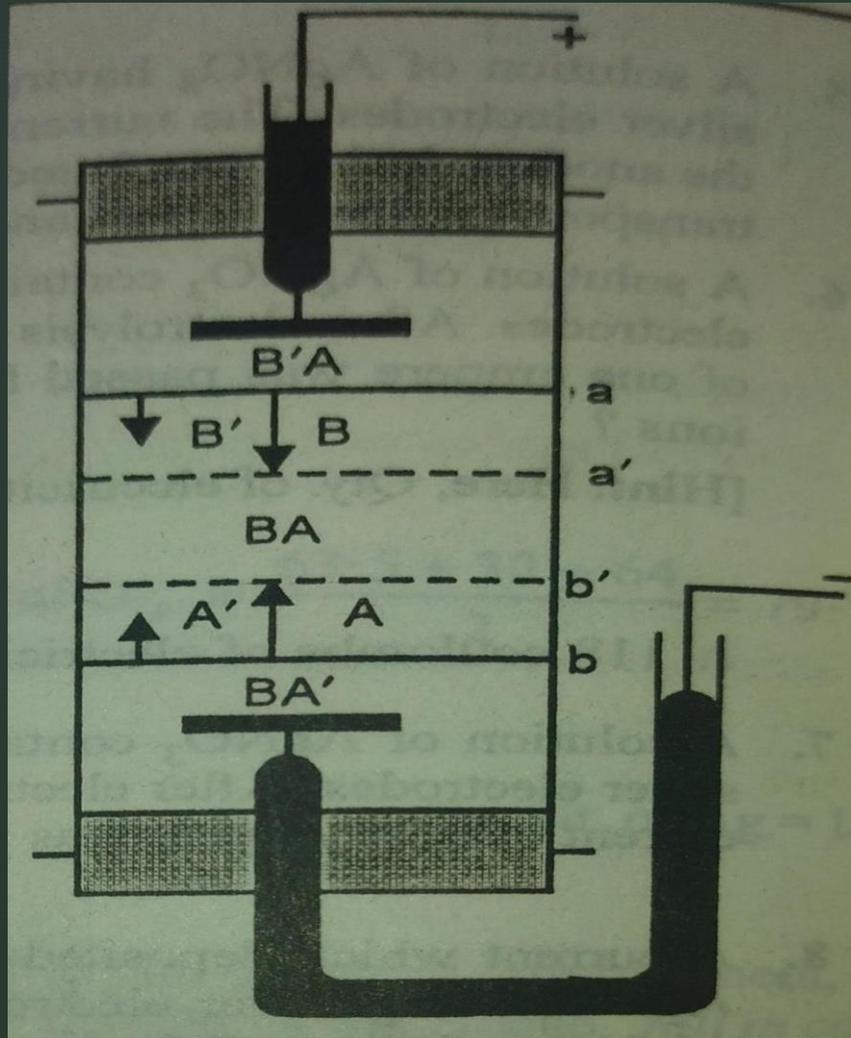
Moving Boundary method

Moving Boundary method – This method is based upon the fact that the transport number of the cation and anion are given by -----

$$n_c = \frac{u_c}{u_c + u_a} \quad \text{and} \quad n_a = \frac{u_a}{u_a + u_c}$$

Thus, by determining the speeds of the cation and the anion (uc and ua) the transport numbers can be calculated.The apparatus used is shown in Figure. It consists of a long tube mounted vertically and fitted with the platinum electrodes on two sides as shown in Figure. The salt BA under investigation is made into solution and then placed between the solutions of two other salts B'A and BA', one having a common cation and the other having common anion. For example, if BA is KCl, B'A may be LiCl and BA' may be CH3COOK. The three solutions are arranged in order of increasing density downwards to avoid mixing effects. The original boundaries are a and b. Even if the solutions are colourless, the boundaries can be observed because of the differences in the refractive indices of the solutions. In order that the boundaries may remain sharp throughout the experiment, B' and A' must have smaller velocities than B and A respectively so that B' does not overtake B and A' does not overtake A. When the current is passed, the boundaries move to a' and b'.

Thus ,

$$\text{Speed of the cation } (B^+), u_c \propto \text{length } aa'$$
$$\text{Speed of the anion } (A^-) \, u_a \propto \text{length } bb'$$
$$\text{Hence } n_c = \frac{aa'}{aa' + bb'} \quad \text{and} \quad n_a = \frac{bb'}{aa' + bb'}$$

Moving Boundary method for determination of Transport Number.

Applications of Conductance Measurements

1.Determination of degree of ionization (α) of weak electrolyte: The degree of ionization of a weak electrolyte at a particular concentration is equal to the ratio of actual number of ions formed due to partial ionization to the expected number of ions formed upon complete dissociation.

$$\alpha = \frac{\text{Actual no of ions formed due to partial dissociation}}{\text{Expected no of particles formed due to complete dissociation}}$$

Since the conductance is proportional to the number of ions in the solution, the degree of ionisation is equal to the conductance ratio as given below.

$$\alpha = \frac{\Lambda_c}{\Lambda_o} = \frac{\Lambda_c}{\lambda_o^+ + \lambda_o^-}$$

Where

Λ_c= equivalent conductivity at given concentration

.Λ_o= limiting equivalent conductivity.

λ_o^+ = limiting equivalent conductivity of cation

λ_o^- = limiting equivalent conductivity of anion.

- Calculation of Solubility And Solublity Product of Sparingly Soluble Salt

- Salts such as AgCl. BaSO4, PbSO4 etc which dissolve to a very small extent in water are called sparingly soluble salts.As they dissolve very little, their solutions are considered as infinitely dilute. Further as their solutions are saturated, their concentration is equal to their solubility.

- Thus by determining the specific conductivity (K) and the molar conductivity of such solutions , we have

$$\lambda_m^o = \kappa \times \frac{1000}{Molarity} = \kappa \times \frac{1000}{Solubility}$$

$$\Rightarrow Solubility = \frac{\kappa \times 1000}{\lambda_m^o}$$

Ionic Product of Water

- Pure water is a weak electrolyte and it undergo self ionization or auto-protolysis. In this process water molecules splits into hydrogen ion (H+) and hydroxide ion (OH-).

- The equation is shown as:
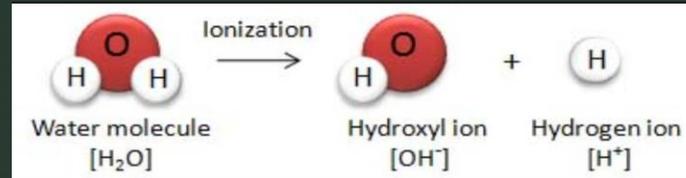
- Applying law of mass action at equilibrium, the value of dissociation constant, K comes to

- $\quad$ K = [H+] [OH-]/[H2O] or   [H+][OH-] = K[H2O]

- Since dissociation takes place to a very small extent, the concentration of undissociated water molecules, [H20], may be regarded as constant. Thus, the product K[H20] gives another constant which is designated as Kw. So,

- [H+][OH-] = Kw

- The constant, Kw, is termed as ionic product of water.

The values of $[H^+]$ and $[OH^-]$ in pure water at 25°C can be calculated from conductance measurements as follows :

Ionic conductance of H^+ ions and OH^- ions are found to be

$$\lambda_{H^+} = 349 \cdot 8 \text{ ohm}^{-1} \text{ cm}^2$$

$$\lambda_{OH^-} = 198 \cdot 5 \text{ ohm}^{-1} \text{ cm}^2$$

$\therefore$ $\qquad \Lambda_0 (H_2O) = \lambda_{H^+}^\circ + \lambda_{OH^-}^\circ \qquad$ (*By Kohlrausch's law*)

$$= 349 \cdot 8 + 198 \cdot 5 \text{ ohm}^{-1} \text{ cm}^2$$

$$= 548 \cdot 3 \text{ ohm}^{-1} \text{ cm}^2.$$

Specific conductance of pure water at 25°C is found to be

$$K = 5 \cdot 54 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}.$$

As water dissociates to a very small extent to give H^+ ions and OH^- ions, water may be considered to be very dilute solution of H^+ ions and OH^- ions in water so that we have

Eq. conductance of water = Specific conductance of water × Vol. in cc containing 1 g eq. of ions

$\therefore$ Volume in c.c. containing 1 g eq. of ions

$$= \frac{\text{Eq. conductance of water}}{\text{Sp. conductance of water}} = \frac{548 \cdot 3}{5 \cdot 54 \times 10^{-8}}$$

i.e., $\dfrac{548 \cdot 3}{5 \cdot 54 \times 10^{-8}}$ cc of water contain 1 g eq. of H^+ ions or OH^- ions.

$\therefore$ 1 cc of water contains H^+ ions or OH^- ions

$$= \frac{5 \cdot 54 \times 10^{-8}}{548 \cdot 3} = 1 \cdot 01 \times 10^{-10} \text{ g eq.}$$

or 1000 cc of water contains H^+ ions or OH^- ions

$$= 1 \cdot 01 \times 10^{-10} \times 1000$$

$$= 1 \cdot 01 \times 10^{-7} \text{ g eq.}$$

i.e., $[H^+]$ or $[OH^-] = 1 \cdot 01 \times 10^{-7}$ g eq per litre

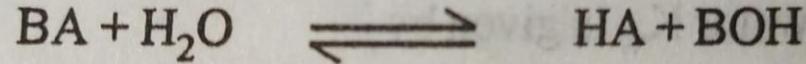$$= 1 \cdot 01 \times 10^{-7} \text{ moles/litre.}$$

As pure water dissociates to give equal number of H^+ ions and OH^- ions so that we have

$$[H^+] = [OH^-] = 1 \cdot 01 \times 10^{-7} \text{ M at 25°C}$$

Hence, $\qquad K_w = [H^+][OH^-]$

$$= (1 \cdot 0 \times 10^{-7}) \times (1 \cdot 01 \times 10^{-7})$$

$$= 1 \cdot 02 \times 10^{-14} \text{ at 25°C.}$$

Hydrolysis constant. The general equation for the hydrolysis of salt (BA) may be written as-- $$BA + H_2O \rightleftharpoons HA + BOH$$

Applying the law of chemical equilibrium, we get,

$$\frac{[HA][BOH]}{[BA][H_2O]} = K, \text{ the equilibrium constant.}$$

Since water is present in very large excess in the aqueous solution, its concentration (H20) may be regarded a constant so that we have, $$\frac{[HA][BOH]}{[BA]} = K[H_2O] = K_h$$

Where Kh is called the hydrolysis constant.

Since [HA] and (BOH) represent the molar concentrations of the free acid and the free base produced and [BA] represents the molar concentration of the unhydrolysed salt, the above expession for the hydrolysis constant may be written in a more general way as--

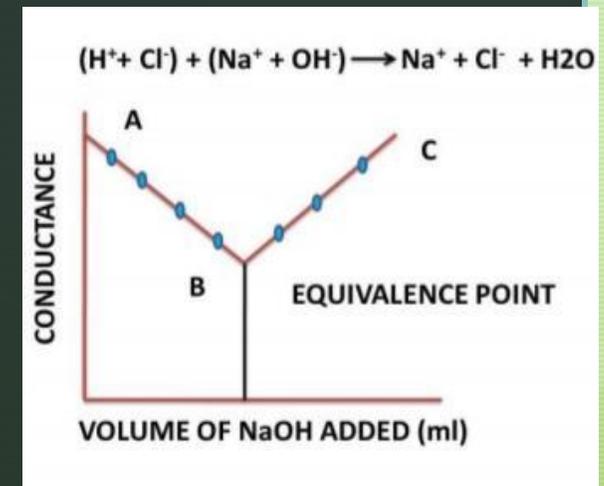$$K_h = \frac{[\text{Free Acid}][\text{Free Base}]}{[\text{Undyrolysed salt}]}$$

Conductometeric Titeration

Conductometric measurements are frequently employed to find the end points of the acid-base and other titrations. In such titrations variation of the equivalent conductance by the addition of titrant is measured. In conductometric titrations advantage is taken on the fact that conductivity of a solution is dependent upon the no of ions and their conductance.The addition of one electrolyte to the other one producing no appreciable change in volume will alter the conductance of the solution according to whether the ionic reactions are producing or not. If no ionic reaction takes place then the conductivity also does not change and if ionic reaction occurs, change in conductivity occurs.

- Strong acid Vs Strong base: Consider the titration of strong acid, like hydrochloric acid with a strong base such as sodium hydroxide. The acid is taken in a conductivity vessel and alkali in a burette. The conductance of hydrochloric acid is due to the presence of hydrogen an chloride ions. As the alkali is added gradually, the hydrogen ions are replaced by the slow moving sodium ions as represented below.
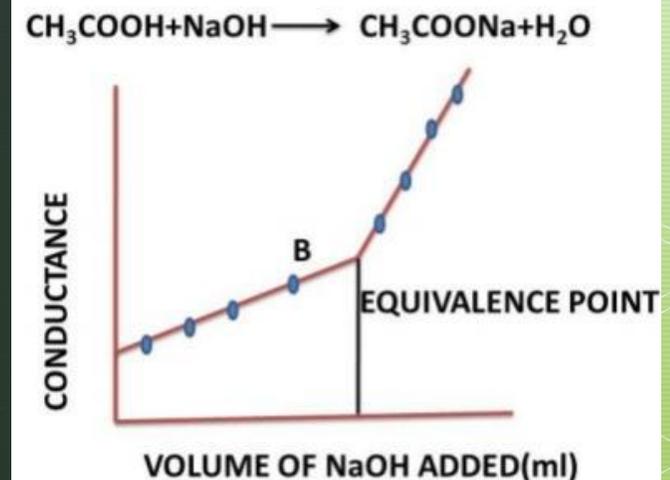
$$[H^+ (aq) + Cl^-(aq)] + [Na^+(aq) + OH^-(aq)] \longrightarrow Na^+(aq) + Cl^-(aq) + H_2O (l)$$
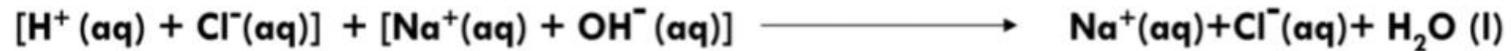
- As sodium hydroxide is added the H+ ions are removed as slightly ionized water. Therefore, the consductance will decrease as Na+ ions don't possesses much mobility. At the neutralization point the solution contains Na+ and Cl-ions and will have a considerably less conductance than the original value. Any subsequent addition of the alkali will result in introducing fast moving hydroxyl ions. The conductance will therefore begin to rise after reaching a certain minimum value. On plotting the conductance values as ordinate against mililitres of titrant added as abscissa, the points will lie on two straight lines, the point of intersection of which gives equilance point.

$(H^+ + Cl^-) + (Na^+ + OH^-) \longrightarrow Na^+ + Cl^- + H2O$

CONDUCTANCE

A

C

B

EQUIVALENCE POINT

VOLUME OF NaOH ADDED (ml)

- Weak acid Vs Strong base: The solution containing weak acid such as acetic acid has a very low conductance due to it poor dissociation. During the titration of acetic acid with a strong base such as sodium hydroxide, a high ionized salt such as sodium acetate is formed. Inspite of the common ion effect, neutral salt which is formed during first part of the titration tends to suppress the ionization of the acetic acid still present. The conductance increase because the conducting power of the highly ionized salt exceeds that of acid and the reaction may be represented as

$$CH_3COOH + Na^+(aq) + OH^-(aq) \longrightarrow CH_3COO^- + Na^+(aq) + H_2O\ (l)$$

- At end point when acid is completely neutralized further addition of alkali introduces the excess of fast moving hydroxyl ions, therefore, conductance increases rapidly. On plotting the conductance versus volume of the alkali added two straight lines are obtained and the pointwhere they meet give the end point of the titration.

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

CONDUCTANCE

B

EQUIVALENCE POINT

VOLUME OF NaOH ADDED(ml)

Strong acid Vs Weak base:

If we titrate strong acid like hydrochloric acid with a weak base such as ammonium hydroxide, then addition of weak base to a strong acid will cause the conductance to decrease first as H+ ions are replaced by slow moving ammonium ions.NH4. After neutralization of the acid, further addition of the weakly ionized ammonium hydroxide will cause no appreciable change in the conductance. The titration curves obtained are shown in figure below.

$$H^+Cl^- + NH_4OH \longrightarrow NH_4Cl^- + H_2O$$
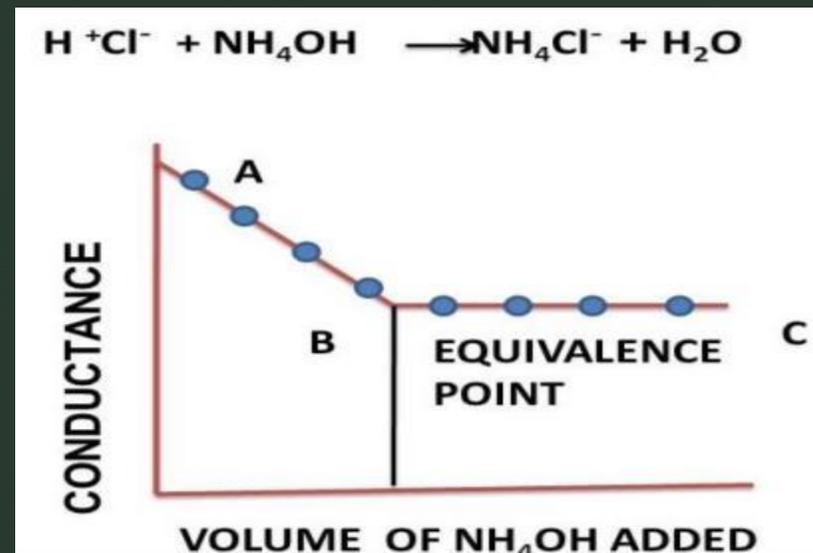
▪ Mixture of a Weak and a Strong acid Vs Strong base: When a mixture of weak and a strong acid like acetic acid and hydrochloric acid is titrated against a strong base like sodium hydroxide, a curve of the type shown in the figure below is obtained. In presence of a strong acid ionization of a weak acid is suppressed due to common ion effect. So strong acid is neutralized first followed by a weak acid. Therefore, first point of intersection, i.e point B refers to the neutralization of a strong acid and point C refers to the complete neutralization of an acid mixture.
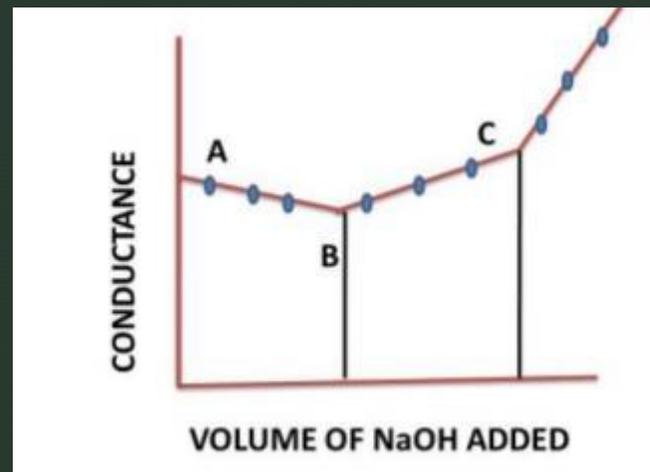
# BASIC CONCEPTS OF ELECTROCHEMISTRY

REDOX REACTIONS

- REDUCTION ------ GAINING ELECTRONS
  OXIDATION ------ LOOSING ELECTRONS,

- The reactions in which the oxidation occurs with reduction are called REDOX REACTIONS.

- The atom or molecule which loses electron is known as the reducing agent, or reductant and the substance which accepts the electrons is called the oxidizing agent or oxidant.

ELECTROCHEMICAL CELLS
(Galvanic cell)

- A device used to convert the chemical energy produced in a redox reaction into electrical energy is called **electrochemical cell** or simply **a chemical cell.** These are also known as **galvanic cells** or **voltaic cells a**fter the name of **Luigi Galvani (1780) or Alessandro Volta(1800)** who were the first to perform experiments on the conversion of chemical energy into electrical energy. In a Galvanic cell, two diferrent electrods are kept immersed in their respective salt solutions and connected by means of a salt bridge.
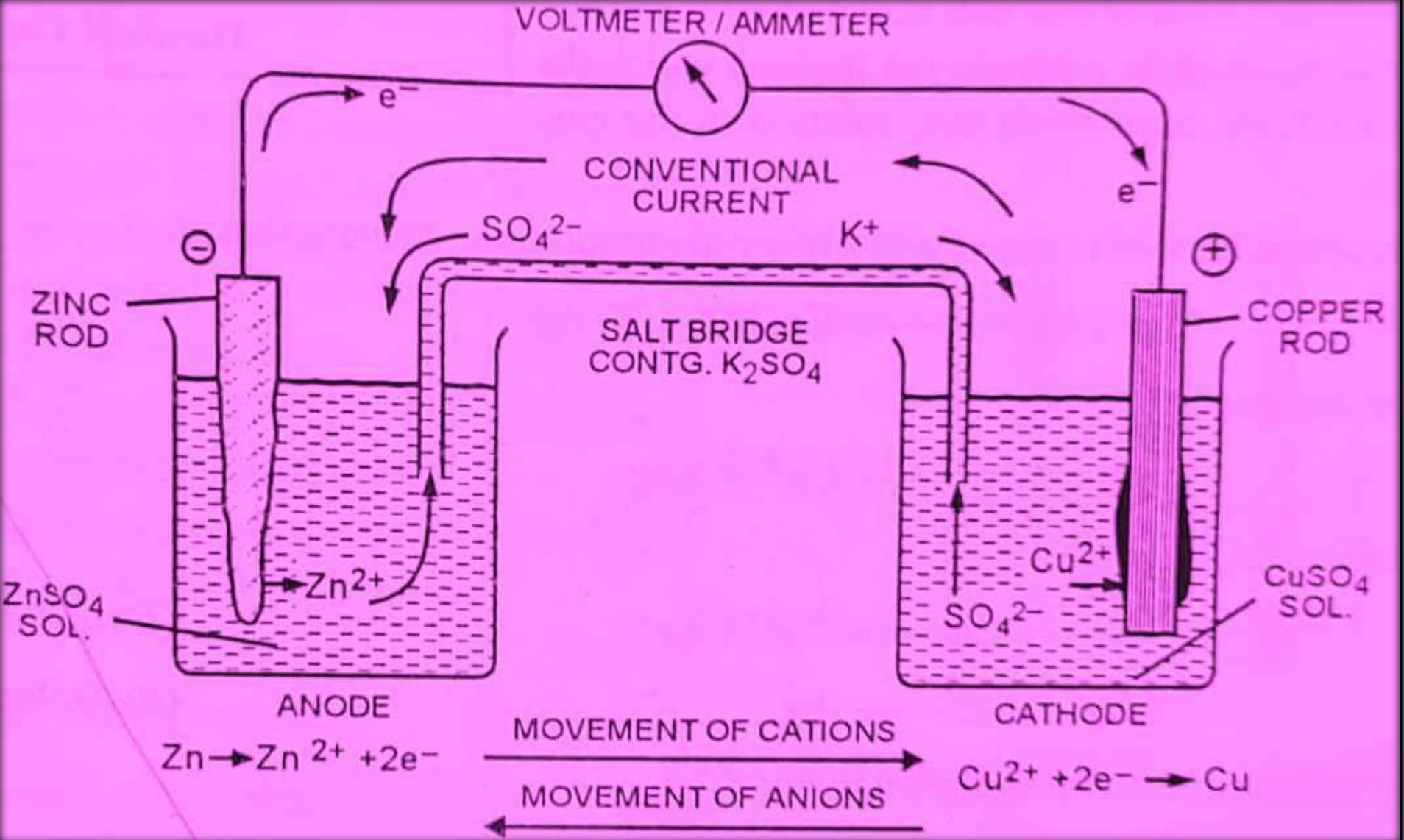
Electrochemical cell based on redox reaction

$$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$$
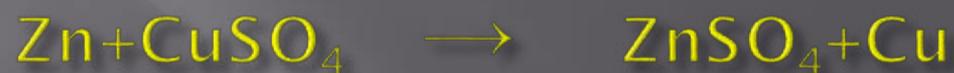
When a zinc rod in contact with 1M $ZnSO_4$, and a Cu rod in contact with 1M $CuSO_4$, are connected , Zn goes into the solution as Zn^{2+} ions and the electrons released flows through the external wire reaches the copper electrode where copper gets reduced .A salt bridge is used to maintain the electrical continuity between the two half cells, also it eliminates the liquid junction potential.

$$Zn \longrightarrow Zn^{2+} + 2e^-$$ **Oxidation half reaction**

$$Cu^{2+} + 2e^- \longrightarrow Cu$$ **Reduction half reaction**

Important Features

- The Zn electrode at which oxidation takes place acts as anode while the Cu electrode at which reduction takes place acts as cathode.

- At Zinc electrode , electrons are produced, so it is designated as negative pole while the copper electrode acts as positive pole.

- The electrons flow from negative pole (i.e Zn electrode) to positive pole (i.e Cu electrode) while the conventional current flows in the opposite direction.

- **Function of salt bridge** ; Due to the oxidation of Zn rod, there accumulates excess of Zn^{2+} in the oxidation half cell while reduction of Cu^{2+} in the reduction half cell leads to the accumulation of excess of SO_4^{2-} in right hand half cell . This accumulation of charge may lead to stop the flow of electrons from oxidation half cell to reduction half cell and hence the cell may stop functioning. To maintain the electrical neutrality of the solutions in the two half cells, salt bridge plays an important role. It pumps anions and cations of the inert electrolyte to the oxidation and reduction half cell respectively to balance the extra charges so produced.

- With the passage of time, the current falls to the deposition of Cu on the Cu – electrode form $CuSO_4$ solution and loss of Zn- electrode due to its dissolution to give Zn^{2+} ions.

Electrochemical / Galvanic Cell	Electrolytic Cell
Chemical energy is transformed into electrical energy in these electrochemical cells.	Electrical energy is transformed into chemical energy in these cells.
The redox reactions that take place in these cells are spontaneous in nature.	An input of energy is required for the redox reactions to proceed in these cells, i.e. the reactions are non-spontaneous.
In these electrochemical cells, the anode is negatively charged and the cathode is positively charged.	These cells feature a positively charged anode and a negatively charged cathode.
The electrons originate from the species that undergoes oxidation.	Electrons originate from an external source (such as a battery).

REPRESENTATION OF A GALVANIC CELL

These are the following conventions used in representing an electrochemical cell

❑ A galvanic cell is represented by writing the anode (where oxidation occurs) on the left hand side and cathode (where reduction occurs) on the right hand side.

Anode||Cathode

▣ The anode of the cell is represented by writing metal first and then the electrolyte (or the cation of the electrolyte

$Zn|Zn^{2+}$

❑ The cathode is represented by writing the electrolyte first and then metal.

$$\mathbf{Cu^{2+}} \mid Cu$$
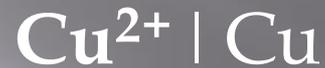
❑ The two half cells are separated by a salt bridge, which is indicated by two vertical lines.

$$Zn \mid ZnSO_4 \mid\mid CuSO_4 \mid Cu$$

Or

$$Zn \mid \mathbf{Zn^{2+}} \mid\mid \mathbf{Cu^{2+}} \mid Cu$$

ELECTROMOTIVE FORCE (EMF) OF A CELL AND ITS MEASUREMENT

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ELECTROMOTIVE FORCE(EMF) OF A CELL

Definition The difference between the electrode potentials of the two electrodes forming an electrochemical cell is known as electromotive force of a cell or cell potential.

OR

Electromotive force may also be defined as "The difference of potentials which causes the current to flow from an electrode at higher potential to an electrode at a lower potential. The electromotive force is commonly abbreviated as e.m.f and is expressed in volts. If all the reactants and products are present in their standard state at 25^{0}C, the e.m.f. is called standard e.m.f.

The e.m.f. of a cell may be expressed in terms of difference of the reduction potentials of the electrodes i.e e.m.f of a cell can be calculated as;

EMF= [Reduction potential of Right Hand Electrode] − [Reduction potential of Left Hand Electrode]

Or   EMF=$E_R - E_L$

Measurement of emf of a cell

The potential difference or emf of a cell can be measured on the basis of Poggendorff's compensation principle. In this method ,emf of a unknown cell is just opposed or balanced by an emf of a standard cell (external emf) until the two emf become equal and there is no net flow of current in the circuit. The whole assembly is known as potentiometer.
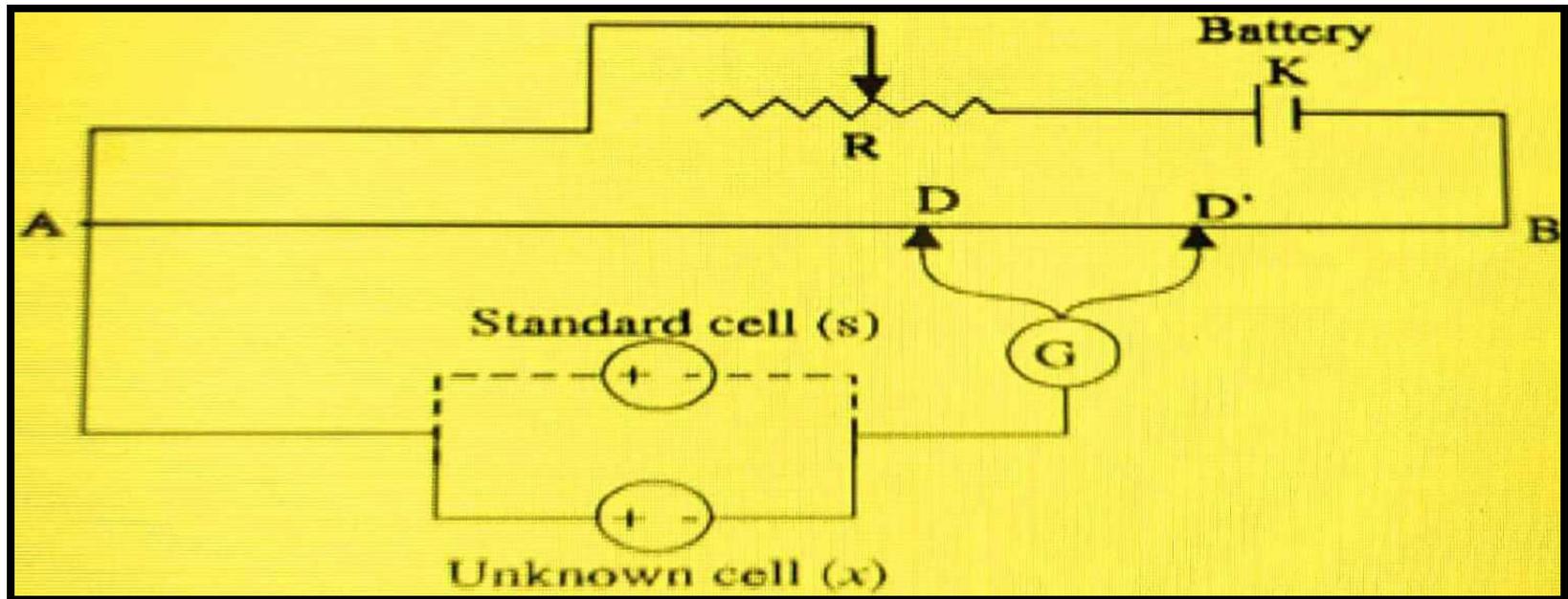
Poggendorff's compensation method for measuring EMF

The potentiometer consists of uniform wire AB of high resistance. A storage or working battery(K) of constant emf is connected to the ends A and B of the wire through a variable resistance R.

 The cell of unknown emf (x) is connected in the circuit by connecting its positive pole to A and the negative pole is connected to a sliding contact(D) through the Galvanometer G

 The sliding contact is freely moved along the wire AB till no current flows through the Galvanometer .Then the distance AD is measured. The emf of the unknown   cell E_x(say) is directly proportional to the distance AD.

$$E_x\ \alpha\ AD\ .$$

 Then the unknown cell(X) is replaced by standard cell(S) in the circuit. The sliding contact is again moved till there is null deflection in the Galvanometer. Then the distance AD' is measured.

 The emf of the standard cell E_s is directly proportional to the distance AD'.

$$E_s\ \alpha\ AD'.$$

Then, the emf of the unknown cell can be calculated from the following equation.

$$\frac{\text{EMF of the unknown cell X}}{\text{EMF of the standard cell S}} = \frac{\text{Length AD}}{\text{Length AD'.}}$$

$$\frac{\text{Ex}}{\text{Es}} = \frac{\text{AD}}{\text{AD'.}}$$

Therefore EMF of the unknown cell=$E_x = \frac{AD}{AD'.} \times E_s$

Thus knowing E_s, E_x can be calculated.

ELECTROCHEMICAL SERIES

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Electrochemical series:-

▸ By measuring the potentials of various electrodes versus standard hydrogen electrode (SHE), a series of standard electrode potentials has been established.

▸ When the electrodes (metals and non-metals) in contact with their ions are arranged on the basis of the values of their standard reduction potentials or standard oxidation potentials, the resulting series is called the **electrochemical** or **electromotive** or **activity series** of the elements.

- By international convention, the standard potentials of electrodes are tabulated for reduction half reactions, indicating the tendencies of the electrodes to behave as cathodes towards SHE

- Electrodes with positive $E°$ values for reduction half reactions do in fact act as cathodes versus SHE, while those with negative $E°$ values of reduction half reactions behave instead as anodes versus SHE. The electrochemical series is shown in the following table.

Standard Aqueous Electrode Potentials at 25°C 'The Electrochemical Series'

Element	Electrode Reaction (Reduction)	Standard Electrode Reduction potential E^o, volt
Li	$Li^+ + e^- \rightarrow Li$	-3.05
K	$K^+ + e^- \rightarrow K$	-2.925
Ca	$Ca^{2+} + 2e^- \rightarrow Ca$	-2.87
Na	$Na^+ + e^- \rightarrow Na$	-2.714
Mg	$Mg^{2+} + 2e^- \rightarrow Mg$	-2.37
Al	$Al^{3+} + 3e^- \rightarrow Al$	-1.66
Zn	$Zn^{2+} + 2e^- \rightarrow Zn$	-0.7628
Cr	$Cr^{3+} + 3e^- \rightarrow Cr$	-0.74
Fe	$Fe^{2+} + 2e^- \rightarrow Fe$	-0.44
Cd	$Cd^{2+} + 2e^- \rightarrow Cd$	-0.403
Ni	$Ni^{2+} + 2e^- \rightarrow Ni$	-0.25
Sn	$Sn^{2+} + 2e^- \rightarrow Sn$	-0.14
H_2	$2H^+ + 2e^- \rightarrow H_2$	0.00

H$_2$	$2H^+ + 2e^- \rightarrow H_2$	0.00
Cu	$Cu^{2+} + 2e^- \rightarrow Cu$	+0.337
I$_2$	$I_2 + 2e^- \rightarrow 2I^-$	+0.535
Ag	$Ag^+ + e^- \rightarrow Ag$	+0.799
Hg	$Hg^{2+} + 2e^- \rightarrow Hg$	+0.885
Br$_2$	$Br_2 + 2e^- \rightarrow 2Br^-$	+1.08
Cl$_2$	$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36
Au	$Au^{3+} + 3e^- \rightarrow Au$	+1.50
F$_2$	$F_2 + 2e^- \rightarrow 2F^-$	+2.87

- The negative sign of standard reduction potential indicates that an electrode when joined with SHE acts as anode and oxidation occurs on this electrode.

  For example, standard reduction potential of zinc is -0.76 volt.

- When zinc electrode is joined with SHE, it acts as anode (-ve electrode) i.e., oxidation occurs on this electrode. Similarly, the +ve sign of standard reduction potential indicates that the electrode when joined with SHE acts as cathode and reduction occurs on this electrode.

Characteristics of Electrochemical Series

- The substances which are stronger reducing agents than hydrogen are placed above hydrogen in the series and have negative values of standard reduction potentials.

- All those substances which have positive values of reduction potentials and placed below hydrogen in the series are weaker reducing agents than hydrogen.

- The substances which are stronger oxidising agents than H^+ ion are placed below hydrogen in the series.

- The metals on the top (having high negative values of standard reduction potentials) have the tendency to lose electrons readily. These are active metals.
- The activity of metals decreases from top to bottom.
- The non-metals on the bottom (having high positive values of standard reduction potentials)have the tendency to accept electrons readily. These are active non-metals.
- The activity of non-metals increases from top to bottom.

THANKYOU

SEMESTER IST
B.Sc. HONOURS (CHEMISTRY)
TITLE: PHYSICAL CHEMISTRY-I
COURSE CODE: 3CHMTC0102

UNIT II
GASEOUS STATE 2

Topics

1.   Behaviour of real gases: Deviations from ideal gas behaviour, compressibility factor, Z, and its variation with pressure and temperature for different gases.
2.   Causes of deviation from ideal behaviour.
3.   Van der Waals equation of state, its derivation.
4.   Application of Van der Waal's equation in explaining real gas behaviour.
5.   Calculation of Boyle temperature.
6.   Critical phenomena, Isotherms of real gases and continuity of states.
7.   Relation between critical constants and van der Waals constants
8.   Law of corresponding states

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Gaseous state 2

1. BEHAVIOUR OF REAL GASES

▶ A gas which obeys ideal gas equation (PV=nRT) and other gas laws at all temperatures and pressures is called an ideal gas.

▶ Real gases do not obey ideal gas equation under all conditions. They nearly obey ideal gas equation at higher temperatures and very low pressures.

▶ Real gases show deviation from ideal behaviour at low temperatures and high pressures.

▶ All the gases which are actually known to exist such as oxygen, nitrogen, carbon dioxide, etc. are real gases.

The deviations from ideal gas behaviour can be illustrated as follows:

The isotherms obtained by plotting pressure, P against volume, V for real gases do not coincide with that of ideal gas, as shown below.

positive deviation; when $V_{real} > V_{ideal}$

ideal behaviour; when $V_{real} = V_{ideal}$

negative deviation; when $V_{real} < V_{ideal}$
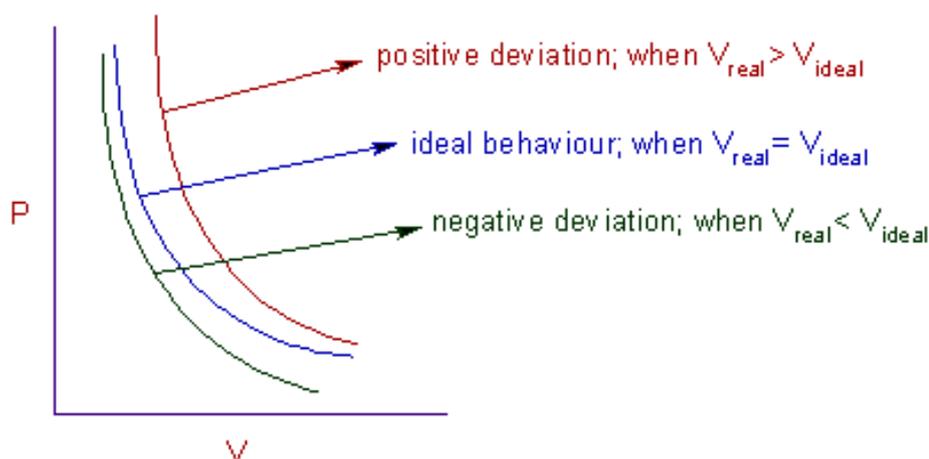
V_{real} = Volume of the real gas at given pressure.
V_{ideal} = Volume of the gas calculated by ideal gas equation at given pressure.

It is clear from above graphs that the volume of real gas is more than or less than expected in certain cases. The deviation from ideal gas behaviour can also be expressed by compressibility factor, Z.

1.1 EFFECT OF PRESSURE: COMPRESSIBILITY FACTOR(Z)

The ratio of PV to nRT is known as compressibility factor.

(or)

The ratio of volume of real gas, V_{real} to the ideal volume of that gas, V_{ideal} calculated by ideal gas equation is known as compressibility factor.

$$Z = \frac{PV_{real}}{nRT}$$

But from ideal gas equation: $PV_{ideal} = nRT$
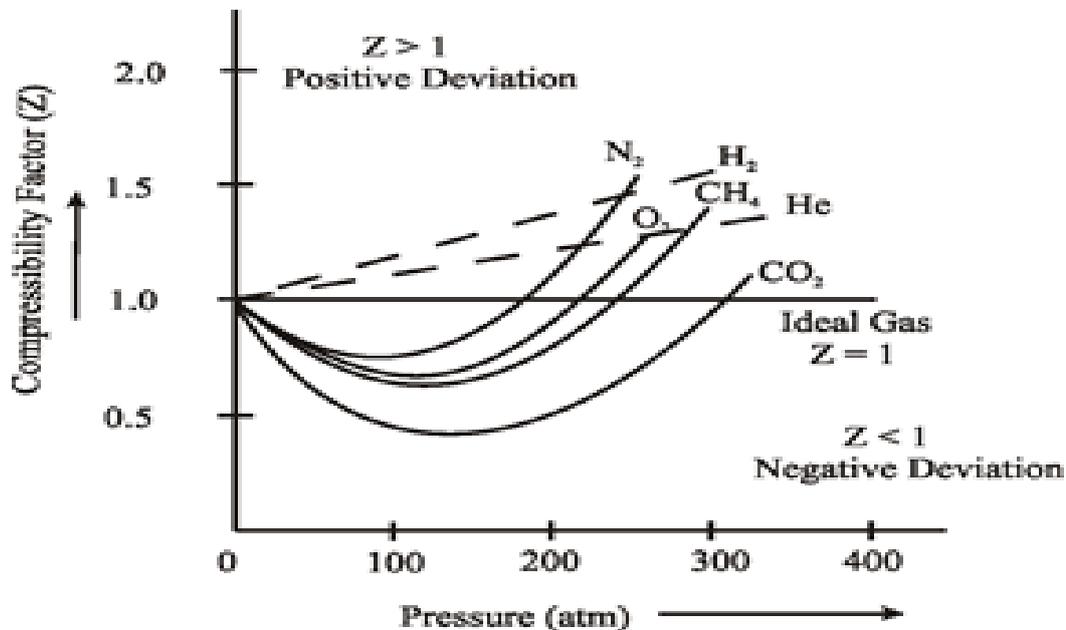
OR

$$V_{ideal} = \frac{nRT}{P}$$

Therefore

$$Z = \frac{PV_{real}}{nRT} = \frac{V_{real}}{V_{ideal}}$$

* For ideal or perfect gases, the compressibility factor, Z = 1.
* But for real gases, Z ≠ 1.

The isotherms for one mole of different gases, plotted against the Z value and pressure, P at 0 °C are shown below:

Gaseous state 2

Case-I : If Z>1, it indicates positive deviation

    1.1. $V_{real} > V_{ideal}$
    1.2.   The repulsive forces become more significant than the attractive forces.
    1.3.   The gas cannot be compressed easily.
    1.4.   Usually the Z > 1 for so called permanent gases like He, H_2 etc.

Case-II: If Z < 1, it indicates negative deviation

    1.5. $V_{real} < V_{ideal}$
    1.6.   The attractive forces are more significant than the repulsive forces.
    1.7.   The gas can be liquefied easily.
    1.8.   Usually the Z < 1 for gases like NH_3, CO_2, SO_2 etc.

- For gases like He, H_2 the Z value increases with increase in pressure (positive deviation). It is because, the repulsive forces become more significant and the attractive forces become less dominant. Hence these gases are difficult to be condensed.
- For gases like CH_4, CO_2, NH_3 etc., the Z value decreases initially (negative deviation) but increases at higher pressures. It is because: at low pressures, the attraction forces are more dominant over the repulsion forces, whereas at higher pressures the repulsion forces become significant as the molecules approach closer to each other.
- But for all the gases, the Z value approaches one at very low pressures, indicating the ideal behaviour.

1.2. EFFECT OF TEMPERATURE: BOYLE'S TEMPERATURE

Consider the following graphs of Z vs P for a real gas.
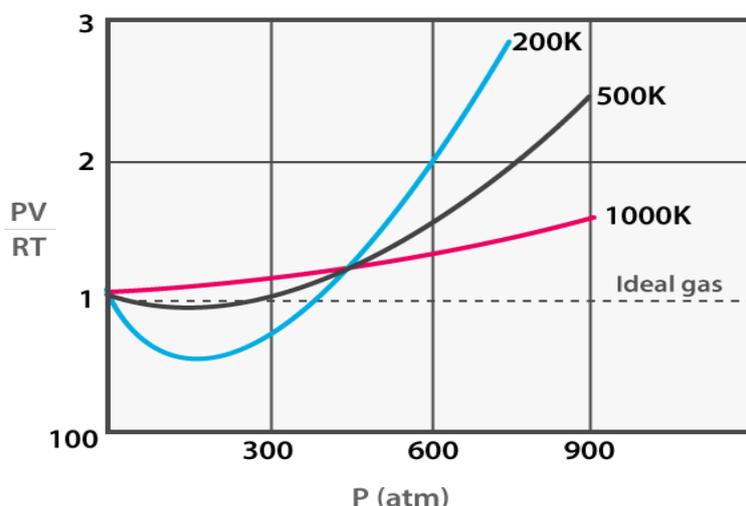
It is clear from the shape of the curves that the deviations from ideal gas behaviour become less and less with the increase in temperature.

At lower temperature, the dip in the curve is large and the slope of the curve is negative. As the temperature is raised, the dip in the curve decreases. At a certain temperature, the minimum in the curve vanishes and the curve remains horizontal for an appreciable range of pressures.

At this temperature, PV/RT is almost unity and the Boyle's law is obeyed.

This temperature at which a real gas behaves like an ideal gas for an appreciable range of pressure is called Boyle's temperature

Boyle's temperature is different for different gases e.g., for N_2 it is 50^oC whereas for H_2 it is -250^oC

CONCLUSIONS:

From the above discussions we conclude that :

(1) At low pressures and fairly high temperatures, real gases show nearly ideal behaviour and the ideal-gas equation is obeyed.

(2) At low temperatures and sufficiently high pressures, a real gas deviates significantly from ideality and the ideal-gas equation is no longer valid.

(3) The closer the gas is to the liquefaction point, the larger will be the deviation from the ideal behaviour.

2. REASONS OF DEVIATION FROM IDEAL BEHAVIOUR

This can be attributed to two wrong assumptions of <u>Kinetic molecular theory of gases</u>.

They are:

1) Volume of molecules The actual volume of the molecules is negligible as compared to the volume of the gas

2) Inter-Molecular forces of attraction There is no force of attraction or repulsion between the gas molecules.

These two assumptions become wrong when the temperature is low or Pressure is high.

2.1. EXPLANATION OF DEVIATION AT LOWER TEMPERATURE

At higher temperature, Kinetic energy of molecules is also high. As a result the attractive forces are negligible.

At lower temperature, kinetic energy of molecules is decreased. Molecules come closer to each other. At certain low temperature gases change into liquid state.

The intermolecular forces become significant near liquefying temperature.

For example SO_2 liquefies at 10^oC and H_2 liquefies at -252.7^oC.
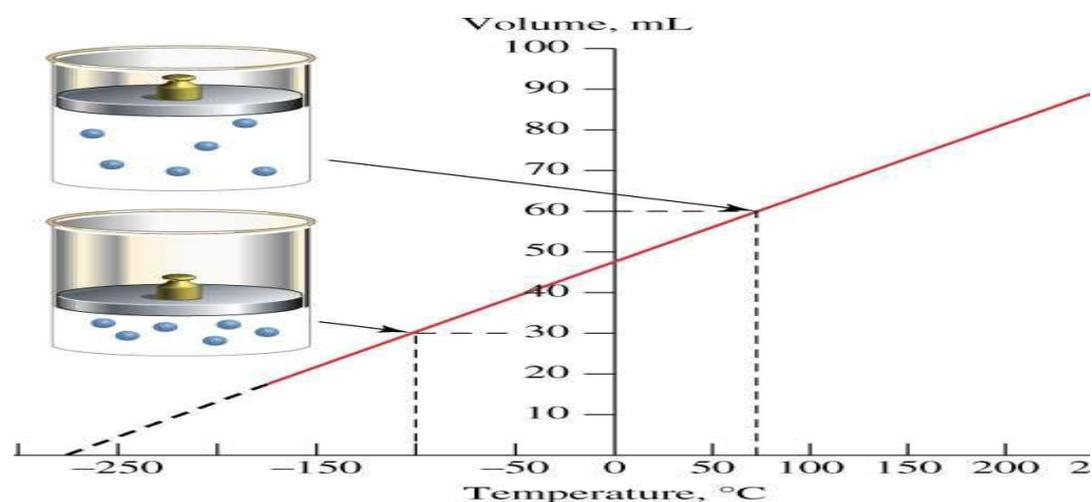
2.2 EXPLANATION OF DEVIATION AT HIGH PRESSURE

- At low pressure, the actual volume of the gas molecule is very small as compared to the volume of container.

- At high pressure this volume does not remain negligible.

- At 1 atm pressure, individual volume of molecule say 32 cm^3 is negligible as compared to total volume of gas 22400cm^3.

- At 100 atm pressure the volume of gas reduced to 224 cm^3, now the volume of individual molecule 32 cm^3 is not negligible as compared to the total volume.
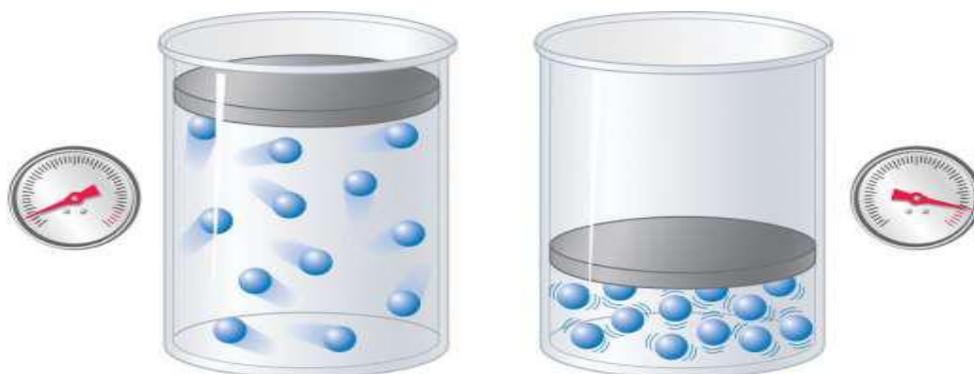
(a) Low pressure   (b) High pressure

3. **VAN DER WAALS EQUATION**:

van der Waals (1873) attributed the deviations of real gases from ideal behaviour to two wrong assumptions of the kinetic theory. These are :

(1) The actual volume of the molecules is negligible
(2) van der Waals attractive forces between them do not exist.

Therefore, the ideal gas equation (PV = nRT) derived from kinetic theory could not apply for real gases.

van der Waals pointed out that both the pressure (P) and volume (V) factors in the ideal gas equation needed correction in order to make it applicable for real gases.

Volume Correction:
van der Waals assumed that molecules of a real gas are rigid spherical particles which possess a definite volume.

The volume of a real gas = ideal volume - the volume occupied by gas molecules

If (b) is the effective volume of molecules per mole of the gas, the volume in the ideal gas equation is corrected as :

V(corrected)real = (Videal – b)
For (n) moles of the gas, the corrected volume is :
V(corrected)real = (Videal – nb)
Where (b) is termed the excluded volume which is constant and characteristic for each gas.

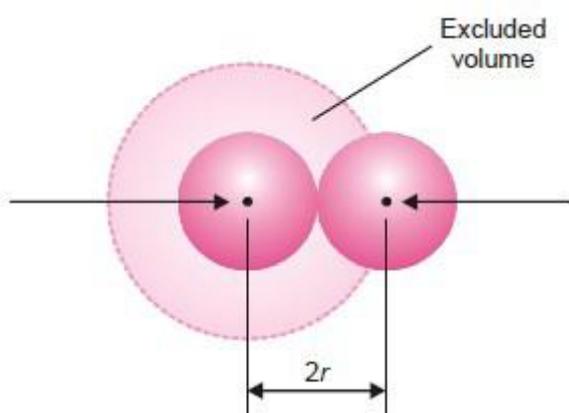Excluded volume is four times the actual volume of molecules:

**Fig:Excluded volume for a pair of gas molecules.**

Consider two molecules of radius (r) colliding with each other .They cannot approach each other closer than a distance (2r).

Therefore, the space indicated by the dotted sphere having radius (2r) will not be available to all other molecules of the gas. In other words the dotted spherical space is excluded volume per pair of molecules

$$\text{excluded volume for two molecules} = \frac{4}{3}\pi(2r)^3$$

$$= 8\left(\frac{4}{3}\pi r^3\right)$$

$$\text{excluded volume per molecule } (V_e) = \frac{1}{2} \times 8\left(\frac{4}{3}\pi r^3\right)$$

$$= 4 V_m$$

where V_m is the actual volume of a single molecule.

Pressure Correction:

(a) Low pressure   (b) High pressure
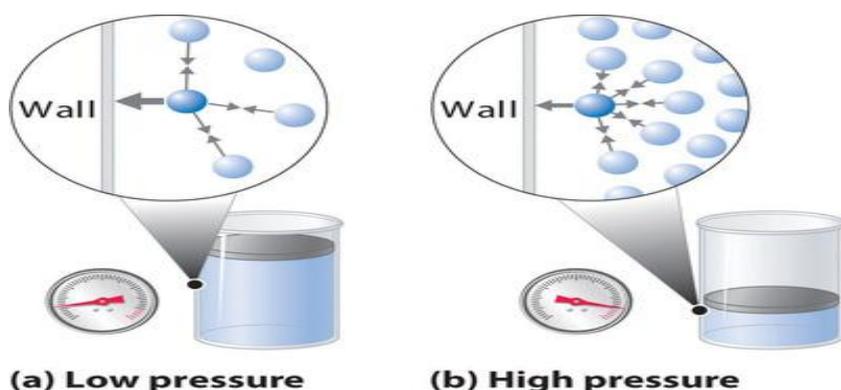
The pressure of the real gas is less than the expected pressure due to attractions between the molecules. These attractions slow down the motion of gas molecules and result in:

i) reduction of frequency of collissions over the walls and

ii) reduction in the force with which the molecules strike the walls.

Hence

$P_{ideal} = P_{real} + p$

Where p = reduction in pressure

However the reduction in pressure is proportional to the square of molar concentration, n/V.

$$\text{The reduction in pressure } (p) \propto \frac{n}{V} \times \frac{n}{V}$$

One factor for reduction in frequency of collisions and the second factor for reduction in strength of their impulses on the walls.

or

$$\text{Reduction in pressure (p)} = a\left(\frac{n}{V}\right)^2$$

where 'a' is a proportionality constant characteristic of a gas.

Therefore:

$$P_{ideal} = P_{real} + p = \left(P + a\frac{n^2}{V^2}\right)$$

Now the ideal gas equation can be modified once again by introducing this pressure correction as:

$$\left(P + a\frac{n^2}{V^2}\right)(V - nb) = nRT$$

This is known as van der Waals equation of state.

For one mole of a gas, the equation can be written as:

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

Where V_m = volume occupied by one mole of a real gas

Units of 'a' and 'b':

For 'a' ----------- atm L^2 mol^{-2}

For 'b' ----------- L. mol^{-1}

4. EXPLANATION OF BEHAVIOUR OF REAL GASES UNDER DIFFERENT CONDITIONS USING VAN DER WAAL'S EQUATION

At low pressures: Since V is large and therefore 'b' is negligible compared to V, the van der Waals equation for one mole of a gas is reduced to:

$$\left(P + \frac{a}{V^2}\right)V = RT$$

$$PV + \frac{a}{V} = RT$$

$$PV = RT - \frac{a}{V}$$

* $V = V_m$ = molar volume.

Therefore: PV < RT at lower pressures. This is the reason for decrease in the Z value at low pressures.

By dividing with RT on each side, the above equation can be written as:

$$\frac{PV}{RT} = 1 - \frac{a}{RTV}$$

or

$$Z = 1 - \frac{a}{RTV}$$

At very low pressures: Since V is very large and therefore both 'b' and 'a/V^2' values become negligible. Hence the van der Waals equation for one mole of gas is reduced to:

PV = RT

Therefore, at very low pressures all the gases obey the ideal gas equation.

At high pressures: Since the volume of the gas is small, the value of 'b' cannot be neglected. Although a/V^2 is also large its value may be neglected in comparison with very high value of P. Hence the van der Waals equation is reduced to:

P(V - b) = RT

PV - Pb = RT

PV = RT + Pb

Therefore: at high pressures, PV > RT. This explains the raising parts of the isotherms, at high pressures, plotted between Z vs P.

By dividing with RT on each side, the above equation can be written as:

$$\frac{PV}{RT} = 1 + \frac{Pb}{RT}$$

or

$$Z = 1 + \frac{Pb}{RT}$$

At high temperatures: In this case, V is very large and attractions are negligible. Hence both 'b' and 'a/V^2' are negligible. This reduces the van der Waals equation to:

PV = RT for one mole

For H_2 and He gases: Since the actual volume of these gas molecules is very small, the intermolecular forces of attractions are very small. i.e., a/V^2 can be ignored. Thus the van der Waals equation is reduced to:
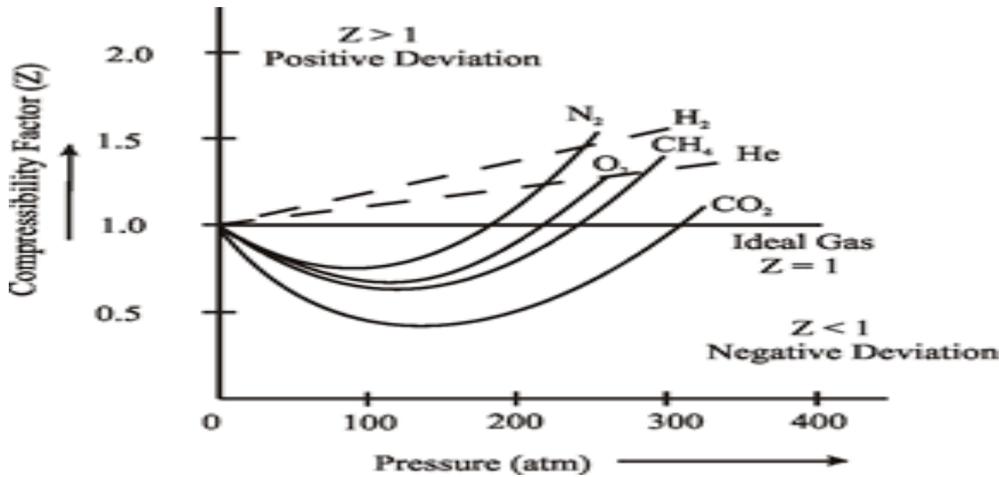
P(V - b) = RT
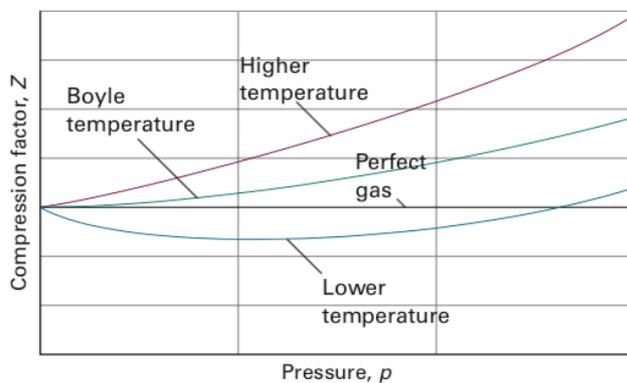
PV - Pb = RT

PV = RT + Pb

Therefore, for H_2 and He gases, PV > RT. Hence for these gases, the Z value is always greater than one as evident from the isotherms plotted between Z vs P.

5. CALCULATION OF BOYLE'S TEMPERATURE

It can be seen that Z vs P curves for all gases near zero pressure meet the curve for the ideal gas.

It is because at very low pressure, gases are expected to behave ideally.

For a characteristic temperature, the curve for Z remains almost horizontal over an appreciable range of pressures.

Within this range, Boyle's law is obeyed.

This temperature is called Boyle's temperature.

Mathematically, the Boyle temperature may be defined as the temperature at which $\text{limit}_{P \to 0} \left[\frac{\partial (PV)}{\partial P} \right] = 0$

The Boyle temperature T_B can be obtained by using Van der Waal's equation.

The Van der Waal's equation for 1 mole of a gas is

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \tag{1}$$

Rearranging the equation in the from

$$P = \frac{RT}{(V-b)} - \frac{a}{V^2} \tag{2}$$

And multiplying eqn (2) throughout by V, we get

$$PV = RT\left(\frac{V}{V-b}\right) - \frac{a}{V} \tag{3}$$

Differentiating eqn (3) with respect to P at constant temperature

$$\left[\frac{\partial(PV)}{\partial P}\right]_T = RT\left[\frac{1}{V-b}\left(\frac{\partial V}{\partial P}\right)_T + \frac{V(-1)}{(V-b)^2}\left(\frac{\partial V}{\partial P}\right)_T\right] + \frac{a}{V^2}\left(\frac{\partial V}{\partial P}\right)_T$$

$$\left[\frac{\partial(PV)}{\partial P}\right]_T = \left[\frac{RT}{V-b} - \frac{RTV}{(V-b)^2} + \frac{a}{V^2}\right]\left(\frac{\partial V}{\partial P}\right)_T \tag{4}$$

At Boyle temperature the above expression must be equal to zero. i.e.

$$\left[\frac{\partial(PV)}{\partial P}\right]_T = \left[\frac{RT}{V-b} - \frac{RTV}{(V-b)^2} + \frac{a}{V^2}\right]\left(\frac{\partial V}{\partial P}\right)_T = 0 \tag{5}$$

Since $\left(\frac{\partial V}{\partial P}\right)_T$ is always negative therefore in the equation (5) the term in square brackets on RHS is equal to zero. Thus,

$$\left[\frac{RT}{V-b} - \frac{RTV}{(V-b)^2} + \frac{a}{V^2}\right] = 0 \tag{6}$$

or $RT\left[\frac{1}{V-b} - \frac{V}{(V-b)^2}\right] = -\frac{a}{V^2}$

or $RT\left[\frac{V-b-V}{(V-b)^2}\right] = -\frac{a}{V^2}$

or $RT\left[\frac{-b}{(V-b)^2}\right] = -\frac{a}{V^2}$

or $RT = \frac{a}{b}\left(\frac{V-b}{V}\right)^2$

or $T = \frac{a}{Rb}\left(1 - \frac{b}{V}\right)^2 \tag{7}$

since at Boyle temperature, T=T$_B$

$$\therefore \quad T_B = \frac{a}{Rb}\left(1 - \frac{b}{V}\right)^2 \tag{8}$$

Where $P \to 0$, the volume V will be infinite, thus the equation reduces to $T_B = \frac{a}{Rb}$

6. THE CRITICAL PHENOMENON

The deviation of real gases from ideal behaviour becomes more and more significant at high pressures and low temperatures.

All the gases can be converted to liquids at sufficiently high pressures and low temperatures.

On cooling, the kinetic energy of the molecules decreases thus the volume occupied by the gas also decreases. The intermolecular force of attraction increases and at a sufficiently low temperature the gas converts into liquid.

Similarly the increase of pressure also brings the gas molecules closer and gets converted into liquid.

The gas does not liquefy above a characteristic temperature however high pressure may be applied. This temperature is called as **critical temperature** of the gas (Tc)

The **critical pressure (Pc)** is the minimum pressure which is just sufficient to liquefy the gas at critical temperature.

The **critical volume (Vc)** is the volume occupied by one mole of a gas at critical temperature and critical pressure.

Tc, Pc and Vc are called critical constants of the gas.

6.1 Andrew's study on critical phenomenon: Isotherms of CO_2

Carbon dioxide has been studied in detail by Andrews. at different temperatures, he studied the behaviour of the gas. keeping temperature constant, the various pressures were plotted against volumes, as obtained from his experiments. These Pas V plots at constant temperature are called isotherms. Andrews obtained a number of typical isotherms from his experiments on carbon dioxide as shown below. These isotherms can be roughly classified as follows:
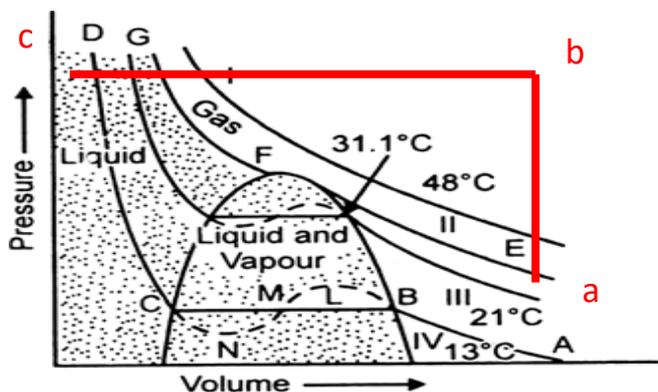
A) Isotherms at a temperature much above the critical temperature ($31.1^{o}C$): These are very much like the ideal gas isotherms (isotherm I)
B) Isotherms at a temperature just above the critical temperature: They have a point of inflexion which is not found in the ideal gas isotherms (Isotherm II)
C) Isotherms at a temperature just above the critical temperature: These show a straight horizontal part along which the gas gets converted to the liquid state(Isotherms III and IV)
This is the case of discontinuous liquefaction as the properties of the substance in the gaseous and liquid forms are markedly different from each other.

In each of these isotherms, like isotherm (IV) at $13^{o}C$, it is clear that with the increase of pressure, the volume of the gas decreases along AB according to Boyle's law and at B, the liquefaction starts. On decreasing the volume further, there is no change of pressure (along BC) until point C is reached where the whole of the gas has been liquefied.
Curve CD is almost vertical showing that liquid is obtained is slightly compressible.
At higher temperature, say $21^{o}C$, curve III is similar isotherm except that horizontal portion is shorter. If the temperature is further raised, the horizontal part of the isotherm becomes shorter and shorter until it is reduced to a point F as in curve II at the critical temperature.
Liquefaction of a gas does not occur at all along the isotherm above the critical temperature. It is only along the critical temperature isotherm that a gas indistinguishably continues into the liquid state.
All the gases behave similarly except that the length of horizontal portions and peak of the dotted parabola (F) are different depending upon the nature of the gas.

6.2 PRINCIPLE OF CONTINUITY OF STATE

When the ends of the horizontal portion of isotherms are joined, a dotted parabolic curve is obtained. The peak of the parabola represents the critical point. Outside the parabola on the right side only gaseous carbon dioxide exists and on the left hand side only liquid carbon dioxide exists. Within the parabola liquid and gaseous carbon dioxide exist together in equilibrium.
Andrew suggested that below the critical temperature it is possible to change from gaseous to liquid state without having both states together at any stage i.e. the change from gaseous to liquid state can be carried out without any sharp discontinuity.
This is explained by taking example of isotherm of CO_2. Consider a certain amount of gas at point 'a' keeping the volume constant, gaseous CO_2 is heated till it goes above the critical temperature and pressure, say till point 'b'. Now keeping the pressure constant, the gas is cooled and its volume decreases along path bc. At point c, CO_2 exists as liquid. It can be seen that along the path abc, the substance remains either in gaseous phase or in liquid phase. Nowhere along abc more than one phase is present. This is called continuity of state.

7. VAN DER WAAL'S EQUATION AND CRITICAL CONSTANTS

Thomson (1871) studied the isotherm of CO_2 drawn by Andrews. He suggested that there should be no sharp points in the isotherms below the critical temperature. These isotherms should really exhibit a complete continuity of state from gas to liquid. This, he showed as a theoretical wavy curve. The curve MLB in Fig.
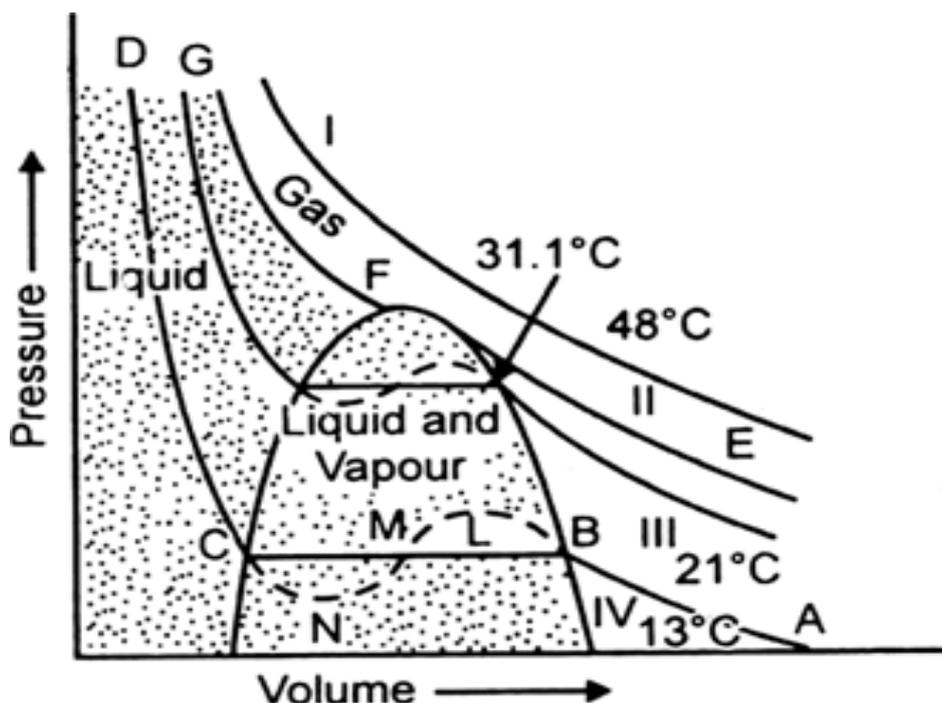
According to Van der Waals cubic equation, for any given calues of P and T there should be 3 values of V. These values are indicated by points B, M and C on the wavy curve

The three values of (V) become closer as the horizontal part of the isotherm rises. At the critical point, these values become identical. This enables the calculation of (Tc), (Pc)and (Vc) in terms of van der Waals constants.

According to Van der Waals equation

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$PV - Pb + \frac{a}{V} - \frac{ab}{V^2} - RT = 0$$

Multiplying the whole equation by V^2

or
$$PV^3 - (RT + Pb)V^2 + aV - ab = 0$$

At the critical point

$$V^3 = V_c$$

$$(V - V_c)^3 = 0$$

or $\quad V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3 = 0 \qquad \qquad ...(1)$

Thus at the critical point van der Waals equation gives

$$V^3 - \left(\frac{RT_c}{P_c} + b\right)V^2 + \left(\frac{a}{P_c}\right)V - \left(\frac{ab}{P_c}\right) = 0 \qquad \qquad ...(2)$$

Equating coefficients in (1) and (2)

$$3V_c = \frac{RT_c}{P_c} + b \qquad \qquad ...(3)$$

$$3V_c^2 = \frac{a}{P_c} \qquad \qquad ...(4)$$

$$V_c^3 = \frac{ab}{P_c} \qquad \qquad ...(5)$$

From (4) and (5)

$$V_c = 3b \qquad \qquad ...(6)$$

Substituting the value in (4)

$$P_c = \frac{a}{27b^2} \qquad \qquad ...(7)$$

Substituting the values of V_c and P_c in (3)

$$T_c = \frac{8a}{27Rb} \qquad \qquad ...(8)$$

Knowing a and b which can be deduced from deviations of ideal gas equation, the critical constants can easily be calculated. Conversely, since P_c and T_c can often be determined experimentally with comparative ease, these values may be employed to calculate the constants a and b.

$$a = 3V_c^2 P_c \qquad b = \frac{V_c}{3}$$

8. LAW OF CORRESPONDING STATES:

If the values of pressure, volume and temperature be expressed as fractions of the corresponding critical values, we have:

$$\frac{P}{P_c} = \pi, \quad \frac{V}{V_c} = \phi, \quad \frac{T}{T_c} = \theta$$

where π, ϕ and θ are termed the **reduced pressure**, the **reduced volume**, and the **reduced temperature** respectively.

If now we replace P, V and T by πP_c, ϕV_c and θT_c respectively in van der Waals equation

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

we have,

$$\left(\pi P_c + \frac{a}{\phi^2 V_c^2}\right)(\phi V_c - b) = R\theta T_c$$

Substituting the values of P_c, V_c and T_c in terms of a, b and R as given in equation (6), (7) and (8), we get

$$\left(\frac{\pi a}{27b^2} + \frac{a}{9\phi^2 b^2}\right)(3\phi b - b) = R\theta \frac{8a}{27Rb}$$

Dividing this equation throughout by $\dfrac{a}{27b^2}$, we get

$$\left(\pi + \frac{3}{\phi^2}\right)(3\phi - 1) = 8\theta \qquad \qquad …(9)$$

This is known as van der Waals reduced equation of state. In this equation the quantities **a, b, Pc,Tc, Vc** which are characteristics of a given gas have cancelled out, thus making it applicable to all substances in the liquid or gaseous state.

From equation (9) it is clear that when two substances have the same reduced temperature and pressure, they will have the same reduced volume. This is known as the Law of Corresponding States.

Gaseous state 2

Introduction to Maxwell-Boltzmann Distribution of Molecular Velocities

A *Maxwell-Boltzmann Distribution* is a probability ***distribution*** used for describing the velocities and energies of gaseous molecules within a stationary container at a specific temperature. The **distribution** is often represented with a graph, as shown in the **Fig. 1**, with the y-axis defined as the number of molecules and the x-axis defined as the **velocity/or speed**.
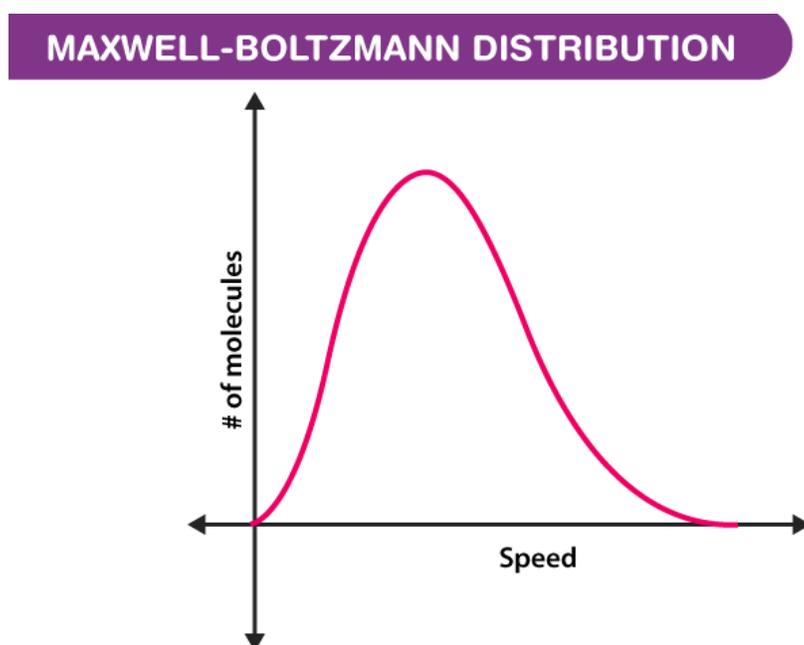
MAXWELL-BOLTZMANN DISTRIBUTION

# of molecules

Speed

Fig. 1

As per kinetic theory of gases, it was assumed that all gaseous molecules have the same velocity. But in actual it is not so. When any two gaseous molecules collide, one molecule transfer its kinetic energy to the other molecule. The velocity of the molecule which gains energy increases and that of the other decreases. Millions of such molecular collisions are taking place per second. Therefore, the velocities of the molecules changing constantly. Since the number of molecules is very large, only a small fraction of molecules will have the same particular velocity. In this there is a broad distributions of velocities over different fractions of molecules. The kinetic molecular theory is used to determine the motion of a molecule of an ideal gas under a certain set of conditions. However, when looking at a mole of ideal gas, it is impossible to measure the velocity of each molecule at every instant of time. Therefore, Maxwell-Boltzmann distribution which is based on the laws of probability is used to determine how many molecules are moving between velocities v and $v + dv$. Assuming that the one-dimensional distributions are independent of one another, that the velocity in the y and z directions does not affect the x velocity, for example, the Maxwell-Boltzmann distribution is given by the following relationship:

$$\frac{dN}{N} = 4\Pi \left(\frac{M}{2\Pi RT}\right)^{\frac{3}{2}} e^{\frac{-Mv^2}{2RT}} v^2 \, dv \quad \text{-----------(1)}$$

Where

- dN/N is the fraction of molecules moving between velocities v to $v + dv$,
- M is the mass of the molecule,
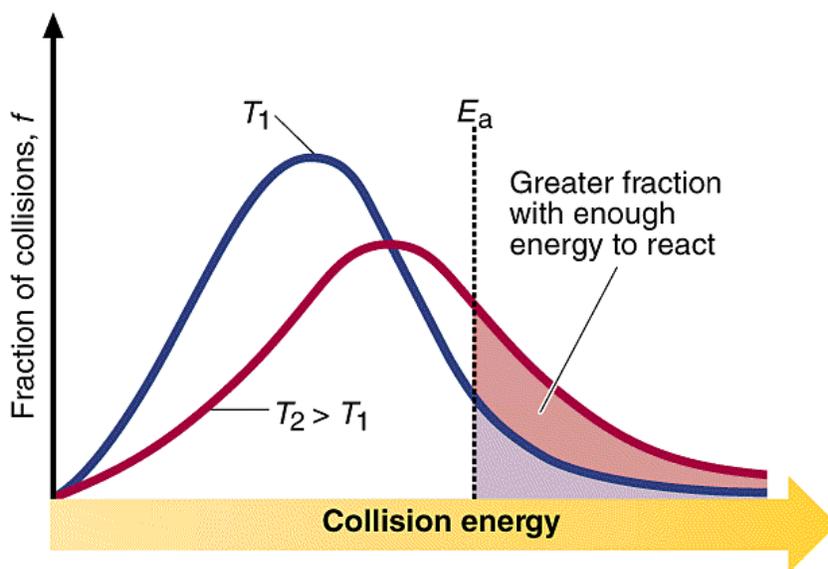- R is the gas constant, and
- T is the absolute temperature.

Fig. 2. Maxwell energy distribution and activation energy curve.

➢ *This is the graph of Boltzman energy distribution.*

• This graph is Number of particles against the kinetic energy.
• As the temperature increases the line moves to the right showing an increase in kinetic energy.
• The line also moves down which represents the number of gas particles which is always constant.
• Lines always start from the origin.

➢ *TEMPERATURE AND REACTION RATE*

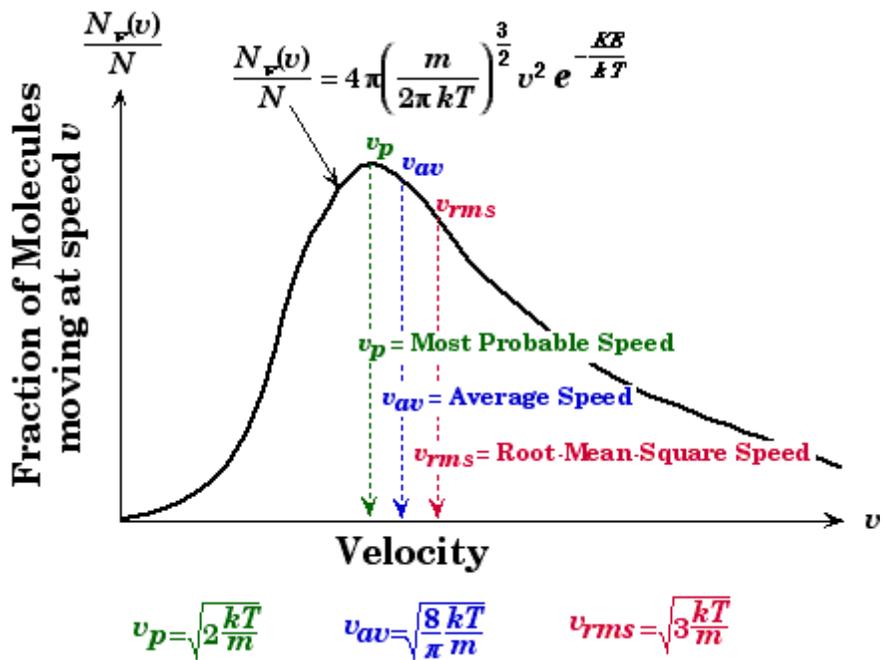❖ *What effect does temperature have on reaction rate?*

Higher temperature (faster reaction rate), lower temperature (slower reaction rate)

Explanation:

Increasing the temperature by definition is an increase in the average kinetic energy of the molecules. At higher temperature molecules get more energy that is greater than or equal to the activation energy (energy required to start the reaction). Therefore, they move faster and collide frequently. As a result, there is more successful collisions per unit time, that means an increased rate of reaction. When molecules are at lower temperature they move slower and do not collide with each other. If they do not collide they do not react. The red curve shows a higher temperature with a higher average kinetic energy. The molecules are moving faster so they collide harder and more often. Thus, less successful collisions per unit time and the reaction rate will be slower as shown in the **Fig.2**.

> ➤ *MAXWELL BOLTZMANN DISTRIBUTION OF MOLECULAR VELOCITIES*

The Maxwell-Boltzmann equation, which forms the basis of the kinetic theory of gases, defines the distribution of speeds for a gas at a certain temperature. From this distribution function, the most probable speed, the average speed, and the root-mean-square speed can be derived. The kinetic molecular theory is used to determine the motion of a molecule of an ideal gas under a certain set of conditions. However, when looking at a mole of ideal gas, it is impossible to measure the velocity of each molecule at every instant of time. Therefore, the Maxwell-Boltzmann distribution is used to determine how many molecules are moving between velocities v and $v + dv$. The Maxwell-Boltzmann distribution can be used to determine the distribution of the kinetic energy of for a set of molecules. The distribution of the kinetic energy is identical to the distribution of the speeds for a certain gas at any temperature.

The equation shown in the figure:

$$\frac{N_v(v)}{N} = 4\pi\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2\, e^{-\frac{KE}{kT}}$$

v_p = Most Probable Speed

v_{av} = Average Speed

v_{rms} = Root-Mean-Square Speed

$$v_p = \sqrt{2\frac{kT}{m}} \qquad v_{av} = \sqrt{\frac{8\,kT}{\pi\,m}} \qquad v_{rms} = \sqrt{3\frac{kT}{m}}$$

RELATIONSHIP BETWEEN DIFFERENT TYPES OF MOLECULAR SPEEDS

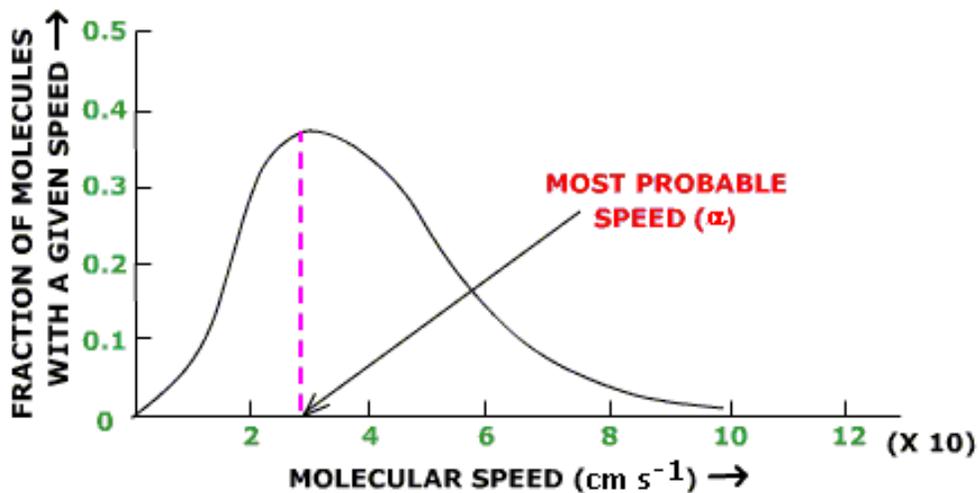**Fig.3** Maxwell Speed Distribution plot and typical velocities.

Fig.4 Most-probable speed correspond to the top of the Maxwell-Boltzmann distribution curve

When a gaseous system is in thermal equilibrium, we can use Maxwell-Boltzmann statistics which gives us the probability of particle being in an energy state at a particular temperature.

There are three ways to quantify typical velocities of a distribution of particles in thermal equilibrium.

1) MOST PROBABLE VELOCITY– DEFINITION

The first typical velocity is the easiest to calculate and termed as the **most probable velocity. It is denoted by** α/or v_p. The velocity at the top of the curve is the most probable velocity as the largest number of molecules have this velocity. The most probable speed is the speed most likely to be possessed by any molecule (of the same mass) in the system. This is indicated as green dotted line as shown in Fig. 3.

2) AVERAGE VELOCITY – DEFINITION

The second is the mean velocity or average velocity. It is denoted by v_{av}. **Average Velocity** is displacement over total time. We can calculate the expectation value of v

$$v_{av} = \int_0^\infty f(v)v\, dv \ldots\ldots\ldots\ldots(2)$$

It can be shown as v_{av} is slightly greater than the most probably velocity v_p. This is indicated as blue dotted line.

3) ROOT MEAN SQUARE VELOCITY – DEFINITION

The third is the root mean square velocity denoted by v_{rms}. It is defined through the expression

$$v_{rms}^2 = \int_0^\infty f(v)v^2\, dv \text{-------------}(3)$$

It can be shown as that root mean square velocity is greater than both the other two velocities. This is depicted as red dotted line.

➢ *"Collision number"*

Collision number is defined as the **"number of collisions"** per unit time. A collision is an interaction between two or more bodies in motion. There is a large volume of atoms or molecules are involved in the collisions. The collision number is indicated by the symbol of *Z*. When one molecule involved, the average number of collisions per unit time nearly one second per moles of reactant between reacting molecules is called collision number."

➢ *"Collision frequency"*

Collision frequency describes the rate of collisions between two molecules in a given volume, per unit time. In an ideal gas, assuming that the species behave like hard spheres, the collision frequency between *A* and *B* is given by the following expression:

$$Z_{AB} = N_A N_B (r_A + r_B)^2 \sqrt{\frac{8 \Pi k_B T}{\mu_{AB}}} \text{-----------------------------(4)}$$

Where:

N_A is the number density of *A* in the gas

N_B is the number density of *B* in the gas

$(r_A + r_B)^2$ is the collision cross section

k_B is the Boltzmann's constant

T is the absolute temperature

μ_{AB} is the reduced mass of the reactants *A* and *B*

The following assumptions are used when deriving and calculating the collision frequency:

- All molecules travel through space in straight lines.

- All molecules are hard, solid spheres.

- The reaction of interest is between only two molecules.

- Collisions are hit or miss only. They occur when distance between the center of the two reactants is less than or equal to the sum of their respective radii. Even if the two molecules barely miss each other, it is still considered a complete miss. The two molecules do not interact (in reality, their electron clouds would interact, but this has no bearing on the equation) as shown in the **Fig. 5**
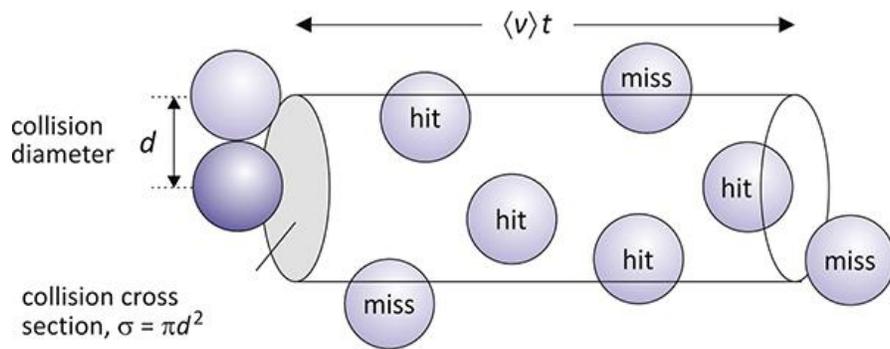

Fig. 5

➤ **"Collision Diameter"**

The distance between the centers of two molecules say A and B

taking part in a collision at the time of their closest approach as shown in **Fig.6**.

It is denoted by σ_{AB} and is given by the following relation:

$$\sigma_{AB} = \Pi \, (r_A + r_B)^2 \ldots\ldots\ldots\ldots\ldots\ldots.(5)$$

Where r_A and r_B are the atomic radii of the molecules A and B

Collision diameter

The closest distance of approach between the centres of the molecules taking part in a collision is called collision diameter. it is usally represented by σ.
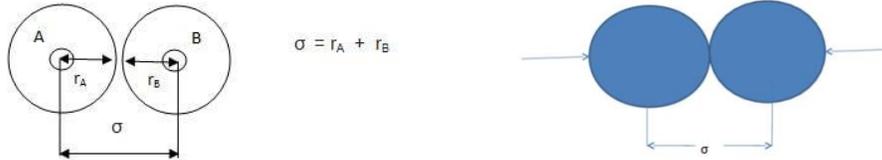
A   B

r_A r_B

σ

$\sigma = r_A + r_B$

σ

Fig.6

➢ *"Mean Free Path"*

The mean free path is the average distance traveled by a moving molecule between collisions as shown in **Fig. 7**. It is designated by λ. This can be imagine when gas leaking out of a pipe. It would take a while for the gas to diffuse and spread into the environment. This is because gas molecules collide with each other, causing them to change in speed and direction. Therefore, they can never move in a straight path without interruptions. Between every two consecutive collisions, a gas molecule travels a straight path. The average distance of all the paths of a molecule is the mean free path.
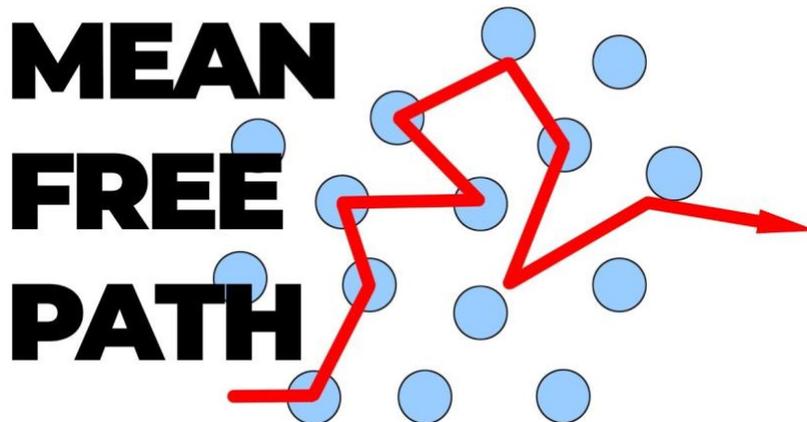
MEAN FREE PATH

Fig.7

Analogy

Imagine a ball traveling in a box; the ball represents a moving molecule. Every time the ball hits a wall, a collision occurs and the direction of the ball changes (**Fig. 8**). The ball hits the wall five times, causing five collisions. Between every two consecutive collisions, the ball travels an individual path. It travels a total of four paths between the five collisions; each path has a specific distance, *d*. The mean free path, λ, of this ball is the average length of all four paths.
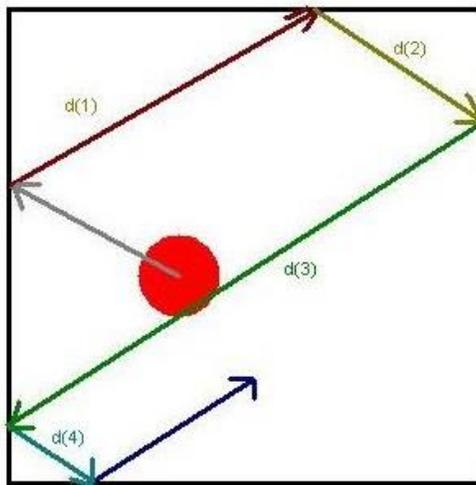

Fig. 8 This figure shows a ball traveling in a box.

Each path traveled by the ball has a distance, denoted d_n:

$$\lambda = \frac{d_1 + d_2 + d_3 + d_4}{4} \text{-----------------------(6)}$$

The mean free path cannot be calculated by taking the average of all the paths because it is impossible to know the distance of each path traveled by a molecule. However, we can calculate it from the average speed/velocity $\langle c \rangle$ of the molecule divided by the collision frequency (Z). The formula for this is:

$$\lambda = \frac{\langle c \rangle}{z}\text{---------------------(7)}$$

Factors affecting mean free path

- **Density**: As gas density increases, the molecules become closer to each other. Therefore, they are more likely to run into each other, so the mean free path decreases.

- Increasing the number of molecules or decreasing the volume causes density to increase. This decreases the mean free path.

- **Radius of molecule**: Increasing the radii of the molecules decreases the space between them, causing them to run into each other more often. Therefore, the mean free path decreases.

- **Pressure, temperature**, and other factors that affect density can indirectly affect mean free path.

❖ *Liquefaction of gases*

Liquefaction of gases is physical conversion of a gas into a liquid state (condensation). The liquefaction of gases is a complicated process that uses various compressions and expansions to achieve high pressures and very low temperatures, using, for example, turboexpanders.

❖ *Importance of Liquefaction of gases*

Liquefaction processes are used for scientific, industrial and commercial purposes. Many gases can be put into a liquid state at normal atmospheric pressure by simple cooling; a few, such as carbon dioxide, require pressurization as well. Liquefaction is used for analyzing the fundamental properties of gas molecules (intermolecular forces), or for the storage of gases, for example: LPG, and in refrigeration and air conditioning. There the gas is liquefied in the *condenser*, where the heat of vaporization is released, and evaporated in the *evaporator,* where the heat of vaporization is absorbed. Ammonia was the first such refrigerant, and is still in widespread use in industrial refrigeration, but it has largely been replaced by compounds derived from petroleum and halogens in residential and commercial applications.

Liquid oxygen is provided to hospitals for conversion to gas for patients with breathing problems, and liquid nitrogen is used in the medical field for cryosurgery, by inseminators to freeze semen, and by field and lab scientists to preserve samples. Liquefied chlorine is transported

for eventual solution in water, after which it is used for water purification, sanitation of industrial waste, sewage and swimming pools, bleaching of pulp and textiles and manufacture of carbon tetrachloride, glycol and numerous other organic compounds as well as phosgene gas.

Liquefaction of helium (^{4}He) with the precooled Hampson–Linde cycle led to a Nobel Prize for Heike Kamerlingh Onnes in 1913. At ambient pressure the boiling point of liquefied helium is 4.22 K (−268.93 °C). Below 2.17 K liquid ^{4}He becomes a superfluid and shows characteristic properties such as heat conduction through second sound, zero viscosity and the fountain effect among others.

The liquefaction of air is used to obtain nitrogen, oxygen, and argon and other atmospheric noble gases by separating the air components by fractional distillation in a cryogenic air separation unit.

❖ *Methods of Liquefaction of gases*

➢ *Linde's Method*

Air is liquefied by the Linde process, in which air is alternately compressed, cooled, and expanded, each expansion results in a considerable reduction in temperature. With the lower temperature the molecules move more slowly and occupy less space, so the air changes phase to become liquid.

➢ *Claude's Method*

Air can also be liquefied by Claude's process in which the gas is allowed to expand isentropically twice in two chambers. While expanding, the gas has to do work as it is led through an expansion turbine. The gas is not yet liquid, since that would destroy the turbine. Commercial air liquefaction plants bypass this problem by expanding the air

at supercritical pressures. Final liquefaction takes place by isenthalpic expansion in a thermal expansion valve.

❖ *Liquid crystal and their classification*

Liquid crystals (LCs) are a state of matter which has properties between those of conventional liquids and those of solid crystals. For instance, a liquid crystal may flow like a liquid, but its molecules may be oriented in a crystal-like way. There are many different types of liquid-crystal phases, which can be distinguished by their different optical properties (such as 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 state of matter (just as water may turn into ice or water vapor).

Examples of liquid crystals can be found both in the natural world and in technological applications. Widespread Liquid-crystal displays use liquid crystals. Lyotropic liquid-crystalline phases are abundant in living systems but can also be found in the mineral world. For example, many proteins and cell membranes are liquid crystals. Other well-known examples of liquid crystals are solutions of soap and various related detergents, as well as the tobacco mosaic virus, and some clays.

➢ *Liquid-crystal phases*

The various liquid-crystal phases can be characterized by the type of ordering. One can distinguish positional order (whether molecules are arranged in any sort of ordered lattice) and orientation order (whether molecules are mostly pointing in the same direction), and moreover order can be either short-range (only between molecules close to each other) or long-range (extending to larger, sometimes macroscopic, dimensions). Most thermotropic LCs will have an isotropic phase at high temperature. That is that heating will eventually drive them into a conventional liquid phase characterized by random and isotropic molecular ordering (little to no long-range order), and fluid-like flow behavior. Under other conditions (for instance, lower

temperature), a LC might inhabit one or more phases with significant anisotropic orientation structure and short-range orientation order while still having an ability to flow.

The ordering of liquid crystalline phases is extensive on the molecular scale. This order extends up to the entire domain size, which may be on the order of micrometers, but usually does not extend to the macroscopic scale as often occurs in classical crystalline solids. However some techniques, such as the use of boundaries or an applied electric field, can be used to enforce a single ordered domain in a macroscopic liquid crystal sample. The orientation ordering in a liquid crystal might extend along only one dimension, with the material being essentially disordered in the other two directions.

➢ *Nematic phase*

One of the most common LC phases is the nematic. The word *nematic* comes from the (*Greek: nema*), which means "thread". This term originates from the thread-like topological defects observed in nematics, which are formally called 'disclinations'. Nematics also exhibit so-called "hedgehog" topological defects. In a nematic phase, the *calamitic* or rod-shaped organic molecules have no positional order as shown in **Fig. (a)**, but they self-align to have long-range directional order with their long axes roughly parallel. Thus, the molecules are free to flow and their center of mass positions are randomly distributed as in a liquid, but still maintain their long-range directional order. Most nematics are uniaxial: they have one axis that is longer and preferred, with the other two being equivalent (can be approximated as cylinders or rods). However, some liquid crystals are biaxial nematics, meaning that in addition to orienting their long axis, they also orient along a secondary axis. Nematics have fluidity similar to that of ordinary (isotropic) liquids but they can be easily aligned by an external magnetic or electric field. Aligned nematics have the optical properties of uniaxial crystals and this makes them extremely useful in liquid-crystal displays (LCD).

Fig. (a) Alignment in a nematic phase.

➤ *Smectic phases*

The smectic phases, which are found at lower temperatures than the nematic, form well-defined layers that can slide over one another in a manner similar to that of soap. The word "smectic" originates from the Latin word "smecticus", meaning cleaning, or having soap-like properties. The smectics are thus positionally ordered along one direction. In the Smectic A phase, the molecules are oriented along the layer normal, while in the Smectic C phase they are tilted away from it as shown in **Fig. (b)**. These phases are liquid-like within the layers. There are many different smectic phases, all characterized by different types and degrees of positional and orientational order. Beyond organic molecules, Smectic ordering has also been reported to occur within colloidal suspensions of 2-D materials or nanosheets.
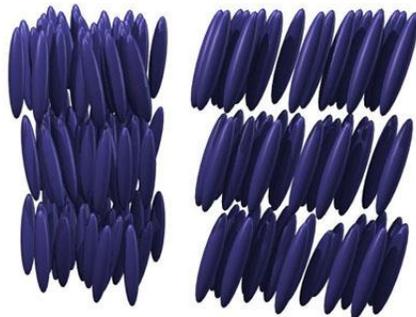

Fig. (b) Schematic of alignment in the smectic phases. The smectic A phase (left) has molecules organized into layers. In the smectic C phase (right), the molecules are tilted inside the layers.

➢ *Chiral phases or twisted nematics*

The chiral nematic phase exhibits chirality (handedness). This phase is often called the *cholesteric* phase because it was first observed for cholesterol derivatives. Only chiral molecules can give rise to such a phase. This phase exhibits a twisting of the molecules perpendicular to the director, with the molecular axis parallel to the director. The finite twist angle between adjacent molecules is due to their asymmetric packing, which results in longer-range chiral order. In the smectic C* phase (an asterisk denotes a chiral phase), the molecules have positional ordering in a layered structure (as in the other smectic phases), with the molecules tilted by a finite angle with respect to the layer normal as shown in **Fig. (c)**. The chirality induces a finite azimuthal twist from one layer to the next, producing a spiral twisting of the molecular axis along the layer normal.

Fig. (c) Schematic of ordering in chiral liquid crystal phases. The chiral nematic phase (left), also called the cholesteric phase, and the smectic C* phase (right).

Note: This e-content is submitted in original form.

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PHASE EQUILIBRIUM-2

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Assistant Professor of Chemistry

Govt. Degree College Kathua

- **NERNST DISTRIBUTION LAW/ PARTITION LAW**

- **CONDITIONS FOR THE VALIDITY OF LAW**

- **DERIVATION OF NERNST DISTRIBUTIONLAW.**

- **LIMITATIONS OF DISTRIBUTION LAW**

- **APPLICATIONS OF DISTRIBUTION LAW**
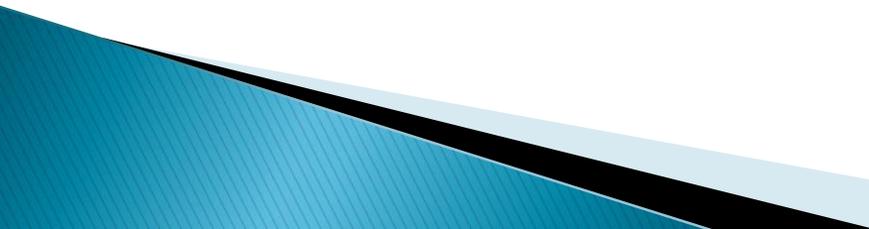
# NERNST DISTRIBUTION LAW

- Also known as **Nernst partition law.**

- To study the distribution of a solid or liquid (solute) between **two immiscible liquids/solvents**.

- The solute is **soluble** in both the solvents.

- For example **iodine** is added to **carbon disulphide and water** or **succinic acid** added to a mixture of **water and ether.**

- **<u>At constant temperature</u>**, when a solute is added to two immiscible solvents in contact with each other, the solute gets distributed between the two solvents in such a way that the ratio of concentrations of the solute in the two solvents is constant.

- Mathematically;

$$C_1/C_2 = K_d$$

Where C_1 and C_2 are the concentrations of solute in solvent 1 and 2 respectively.
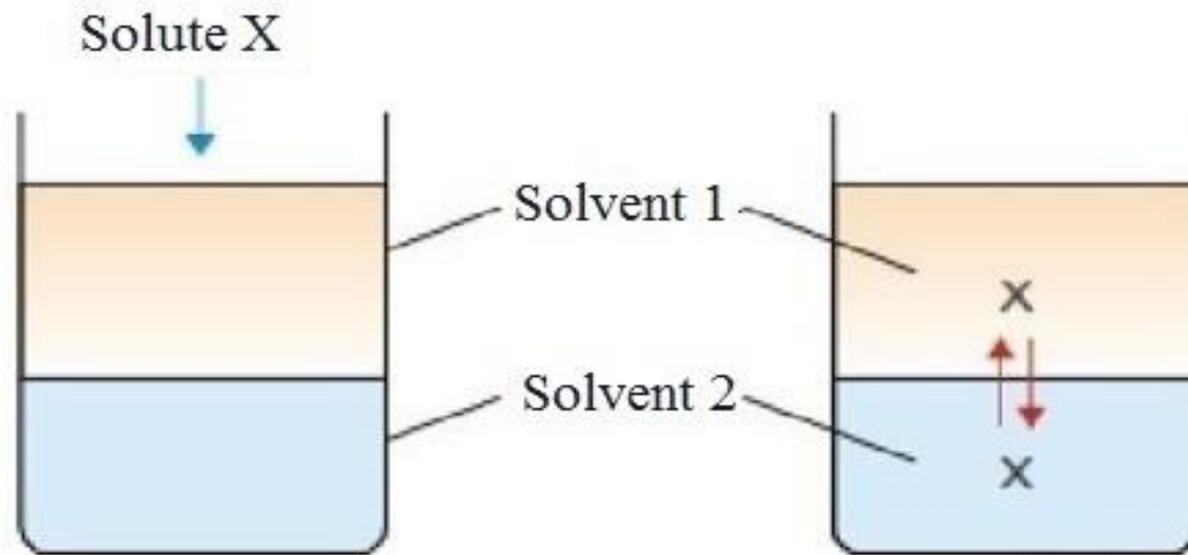
Distribution of solute X between solvent 1 and 2

And K_d is called the **distribution coefficient** or the **partition coefficient.**

- K_d depends only on the temperature of the system and is independent on the amount of solute taken.

- and also of the relative amounts of the two immiscible solvents.

- According to the phase rule, for a system of two immiscible liquids with a solute distributed between them and at equilibrium, the number of degrees of freedom:

- **F=C-P+2 =3-2+2=3**

The three variables required to define the system completely are temperature, pressure and concentration of the solute.

- **<u>Temperature and pressure are kept constant.</u>**

- The concentration of the solute is variable and can be varied within the limits.

- Thus **<u>if the concentration of the solute in one solvent is known</u>**, then concentration of the solute in other solvent can be evaluated and the ratio of the two concentrations thus will be constant.

CONDITIONS FOR THE VALIDITY OF THE DISTRIBUTION LAW

▶ The temperature must remain constant throughout the experiment.

▶ The two solvents should be immiscibe.

▶ The solution should be dilute, i.e., the amount of solute added should be small.

▶ the solute must have same molecular state in both the solvents, i.e., it should not undergo any association or dissociation in any of the solvents.

DERIVATION OF NERNST DISTRIBUTION LAW

▸ The thermodynamic derivation of Nernst distribution law is based upon the principle that:

"if there are two phases in equilibrium, the chemical potential (μ) of a substance present in them must be same in both the phases."

▸ Since the chemical potential (μ) of a substance present in the solution is given as:

$\mu = \mu^0 + RT \ln a$

- Where μ^0 is the standard chemical potential and 'a' is the activity of the solute in solution.

- Thus for solute in liquid A, the chemical potential of solute is:

$$\mu_A = \mu^0_A + RT \ln a_A$$

- Similarly for liquid B,

$$\mu_B = \mu^0_B + RT \ln a_B$$

- Since liquids A and B are in equilibrium, therefore

$$\mu^0_A + RT \ln a_A = \mu^0_B + RT \ln a_B \qquad (1)$$

or $\quad RT \ln a_A - RT \ln a_B = \mu^0_B - \mu^0_A \qquad (2)$

or $\quad \ln\dfrac{a_A}{a_B} = \dfrac{\mu^0_B - \mu^0_A}{RT} \qquad (3)$

- since **at constant temperature**, μ^0_A and μ^0_B are constant for a given substance. Therefore equation (3) can be written as:

or $\qquad \ln \dfrac{a_A}{a_B} = \text{constant}$ $\qquad\qquad$ (4)

Therefore, $\qquad \dfrac{a_A}{a_B} = \text{constant}$ $\qquad\qquad$ (5)

As the solution are dilute, activities of the solute are equal to their concentrations, therefore expression (5) is modified to:

$$\dfrac{C_A}{C_B} = \text{constant} \qquad\qquad (6)$$

Equation(6) is the original form of the distribution law.

LIMITATIONS OF THE DISTRIBUTION LAW

- Applicable only to **dilute solutions.**

- Fails to explain the distribution of solute among the two immiscible solvents under **variable temperature conditions.**

- Fails to explain the distribution of solute among the two immiscible solvents, if the solute dissolved undergoes **association or dissociation** in any of the solvents involved.

- Not applicable to **miscible solvent pairs.**

APPLICATIONS OF DISTRIBUTION LAW

▸ To calculate the **solubility of a solute** in a solvent.

▸ Study the extent of **association or dissociation** of the solute in the solvent.

▸ Study the **chemical equilibria** forming complex ions.

▸ To determine the **degree of hydrolysis of salts**.

▸ Used for the extraction of a compound present in a solvent (**solvent extraction**).

NERNST EQUATION AND
ITS IMPORTANCE

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- The Nernst equation provides a relation between the cell potential of an electrochemical cell, the standard cell potential, temperature, and the reaction quotient. Even under non-standard conditions, the cell potentials of electrochemical cells can be determined with the help of the Nernst equation.

- The **Nernst equation is often used to calculate the cell potential** of an electrochemical cell at any given temperature, pressure, and reactant concentration. The equation was named after <u>Walther Nernst</u>, a German <u>physical chemist</u> who formulated the equation.

DERIVATION

- Consider a metal in contact with its own salt aqueous solution. Reactions of metal losing an electron to become an ion and the ion gaining electron to return to the atomic state are equally feasible and are in an equilibrium state.

$$M^{n+} + ne^- \rightarrow M$$

$$K = \frac{[Product]}{[Reactant]}$$

$$K = [M]/[M^{n+}]$$

For this above reaction , maximum work done is given by

$$W_{max} = nFE_{cell} \quad \text{Where,}$$

F is Faraday = 96500 coulomb = electrical charge carried by one mole of electrons and E= cell potential

Change in the Gibbs free energy is an indication of the spontaneity and it is also equal to the maximum useful work done in a process.

Combining work done and Gibbs free energy change:

$$W_{max} = nFE_{cell} = - \Delta G \text{ or } \Delta G = - nFE_{cell}$$

Where, ΔG= Gibbs free energy.

- Change in the free energy at standard conditions of 298K and one molar /one atmospheric pressure conditions is ΔG°. From the above relation, it can be written that

$$\Delta G° = - nFE°_{cell}$$

Where, $E°_{cell}$ is the reduction potential measured at standard conditions.

During the reaction, concentration keeps changing and the potential also will decrease with the rate of reaction.

- To get the maximum work or maximum free energy change, the concentrations have to be maintained the same. This is possible only by carrying out the reaction under a reversible equilibrium condition.

- For a reversible equilibrium reaction, vant Hoff isotherm says:

$$\Delta G = \Delta G° + RT \ln K$$

Where,

K is the equilibrium constant

$K = Product/Reactant = [M]/[M]^{n+}$

R is the Gas constant $= 8.314 J/K$ mole

T is the temperature in Kelvin scale.

Substituting for free energy changes in vant Hoff equation,

$$-nFE_{cell} = -nFE°_{cell} + RT \ln [M]/[M^{n+}]$$
$$= -nFE°_{cell} + 2.303 RT \log [M]/[M^{n+}]$$

Dividing both sides by $-nF$

$E_{cell} = E°_{cell} - 2.303 \, RT/nF \, \log \, [M]/[M^{n+}]$

substituting for R,T and F,we get

$E_{cell} = E°_{cell} - 0.0591/n \, [M]/[M^{n+}]$ This is the nernst equation for a single electrode.

When $[M] = 1$,

$E_{cell} = E°_{cell} - 0.0591/n \, 1/[M^{n+}]$

This is called Nernst Equation for the calculation of EMF of cell.

IMPORTANCE

The Nernst equation can be used to calculate:

- Single electrode reduction or oxidation potential at any conditions

- Standard electrode potentials

- Comparing the relative ability as a reductive or oxidative agent.

- Finding the feasibility of the combination of such single electrodes to produce electric potential.

- Emf of an electrochemical cell

- Unknown ionic concentrations

- The pH of solutions and solubility of sparingly soluble salts can be measured with the help of the Nernst equation.

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PHASE EQUILIBRIUM

LECTURE -1

- Concept of Phase equilibrium, phase rule
- Phase
- Component
- Degree of freedom
- Criterion of phase equilbrium

Phase Equilibrium

PHASE EQUILIBRIUM IS THE STUDY OF THE EQUILIBRIUM WHICH EXISTS BETWEEN OR WITHIN DIFFERENT STATES OF MATTER NAMELY SOLID, LIQUID AND GAS. EQUILIBRIUM IS DEFINED AS A STAGE WHEN CHEMICAL POTENTIAL OF ANY COMPONENT PRESENT IN THE SYSTEM STAYS STEADY WITH TIME.

Phase Rule

- **Statement**
- Phase rule states that " *If the equilibrium between any number of phases is not influenced by gravity, or electrical, or magnetic forces, or by surface action but are influenced only by temperature, pressure and concentration , then the number of degrees of freedom (F) of the system is related to the number of components (C) and number of phases (P) by thefollowing phase rule equation :*

$$F = C - P + 2$$

Phase

- A **phase** is defined as *" an homogeneous, physically distinct and mechanically separable portion of system, which is separated from other such parts of the system by definite boundary surfaces"*
- *Example :*
- **Liquid phase :**

  Example : benzene and water

  Example : alcohol and water
-
- **Solid phase**

- *Example* : Many forms of sulphur can exist together, but these are all separate phases.
-
- **Gaseous phase**

- *Example :* a mixture of N_2 and H_2 forms one phase only.

- A heterogeneous mixture like:
- CaCO3 (s) $\longrightarrow$ CaO (s) + CO2 (g).

Component

Component is defined as " *the smallest number of independently variable constituents, by means of which the composition of each phase can be expressed in the form of a chemical equation".*

- Example :

- In the water system,

- Ice $_{(s)}$ Water $_{(l)}$ Water vapour $_{(g)}$

Degree of freedom

Degree of freedom is defined *as the minimum number of independent variable factors such as temperature, pressure and concentration of the phases, which must be fixed in order to define the condition of a system completely.*

or

2.5. CRITERIA OF PHASE EQUILIBRIUM

The following conditions must be satisfied for existence of equilibrium between various phases in a multi phase system.

1. **Thermal equilibrium :** All the phases of the system must have same temperature otherwise one or more phases may disappear from the equilibrium.

i.e.,
$$T_\alpha = T_\beta ;$$ where α and β are two phases and T is temperature.

2. **Mechanical equilibrium :** All the phases having equilibrium between them must be having same pressure otherwise volume of one phase will increase at the expense of another.

i.e.,
$$P_\alpha = P_\beta$$

3. **Chemical equilibrium :** For a system having many phases at equilibrium, the chemical potential (μ) of all the phases must be same.

Phase equilibrium

Lecture 2

Derivation of Gibbs phase rule

Gibbs phase Rule

Consider a heterogeneous system containing C components (C_1, C_2, C_3.................C_C) distributed among P phases (P_1, P_2, P_3.................P_P).

Number of degree of freedom (F) =

Total number of Variables – Number of variable Defined by the System because of its being in equilibrium.

Gibbs phase rule

Calculations of total number of variables:-

- Suppose a phase has two components then if the molar concentration of one of the components known then that of other can be calculated automatically since sum total of mole fraction of all the components is one. Therefore for C components if we know molar concentrations of (C-1) components then molar concentration of remaining one can be determined easily. For system consisting of P phases if concentrations P(C-1) components is known than that of other can be easily determined. Beside concentration variable other variables like temperature and pressure are same for all the phases in equilibrium. So total number of variable required to know properties of all the components are:

Total Number of Variable = P (C-1)+2

Here factor two is added for temperature and pressure.

Gibbs phase rule

Calculations of number of variables defined by the system because of its being in equilibrium:-

Contribution of any component in a mixture towards the total free energy of the system of a constant composition at constant temperature and pressure is termed chemical potential and it is denoted by μ, further chemical potential of any component is same in all the phases if there is a multiphase equilibrium.

Thus for a system consisting of three phases in equilibrium

The chemical potential of a component can be represented as:

$$(\mu_1)P_1 \quad = \quad (\mu_1)P_2 \quad = \quad (\mu_1)P_3$$

Now if we know

$$(\mu_1)P_1 \quad = \quad (\mu_1)P_2$$

$$(\mu_1)P_2 \quad = \quad (\mu_1)P_3$$

Then $(\mu_1)P_1 \quad = \quad (\mu_1)P_3$ need not to be specified so for one component system in three phases two relations or variables are required so for P number of phases (P-1) relations or variables are required and for C components in P phases C(P-1) relations are required. Thus total number of degree of freedom can be calculated easily

Gibbs phase rule

Number of degree of freedom (F) =

Total number of Variables – Number of variable Defined by the System because of its being in equilibrium.

$F = P(C-1) + 2 - C(P-1)$

$F = C-P + 2$

PHASE EQUILIBRIUM

Lecture 3

Derivation of Clasius clapeyron equation and its applications.

Clapeyron equation

Consider equilibrium of compound A as - $A_1 \rightleftharpoons A_2$

For which ΔG is given as- $\Delta G = G_2 - G_1$ \hfill (2)

Where, G_2 and G_1 are the molar free energies of the substances in final and initial states respectively.

At equilibrium state $\Delta G = 0$, at constant P and T

$$G_1 = G_2.$$

All such transformations will be in equilibrium at constant pressure and at constant temperature, when molar free energies of the substances are identical in both phases.

$$\Delta G = G_2 - G_1 = 0.$$

$$G_1 = G_2 \quad Or \quad dG_1 = dG_2 \tag{3}$$

The variation of free energies for pure substances with respect to P and T in single phase is given by the equation-

$$dG_1 = V_1 dP - S_1 dT \tag{4}$$

$$dG_2 = V_2 dP - S_2 dT \tag{5}$$

From equation (3), (4) and (5)-

$$V_2 dP - S_2 dT = V_1 dP - S_1 dT$$

$$(V_2 - V_1) dP = (S_2 - S_1) dT$$

$$dP/dT = (S_2 - S_1)/(V_2 - V_1) = \Delta S/\Delta V \tag{6}$$

But- $\Delta G = \Delta H - T\Delta S$ and at equilibrium, $\Delta G = 0$

$$\Delta H = T\Delta S \quad or \quad \Delta S = \Delta H/T \tag{7}$$

From equation (6) and (7)-

$$dP/dT = \Delta H/T.\Delta V \tag{8}$$

Where, ΔH is the change in enthalpy for reversible transformation occurring at temperature T. this equation is called as **Clapeyron equation.**

The Clapeyron equation gives **relation between the temperature and pressure** of the system **containing two phases of a pure substance** which are **in equilibrium** with each others.

This equation also shows that **dP/dT** is **directly proportional** to the **enthalpy** of the transition and **inversely proportional** to **temperature and the volume change** accompanying during the transition i.e. ΔH and ΔV are the functions of temperature and or pressure.

The equation (8) can be modified as-

$$(P_2 - P_1)/(T_2 - T_1) = \Delta H/T.\Delta V \tag{9}$$

Where, **T is taken as average of T_2 and T_1 or equation** (8) can be integrated with the proper limits of T and P by assuming that ΔH and ΔV are constant.

$$\int_{P_1}^{P_2} dP = \Delta H/\Delta V \int_{T_1}^{T_2} dT/T$$

$$(P_2 - P_1) = (\Delta H/\Delta V) \ln T_2/T_1.$$

$$(P_2 - P_1) = (2.303\Delta H/\Delta V) \ln T_2/T_1. \tag{10}$$

Clasius clapyeron equation

the *Clausius-Clapeyron equation*
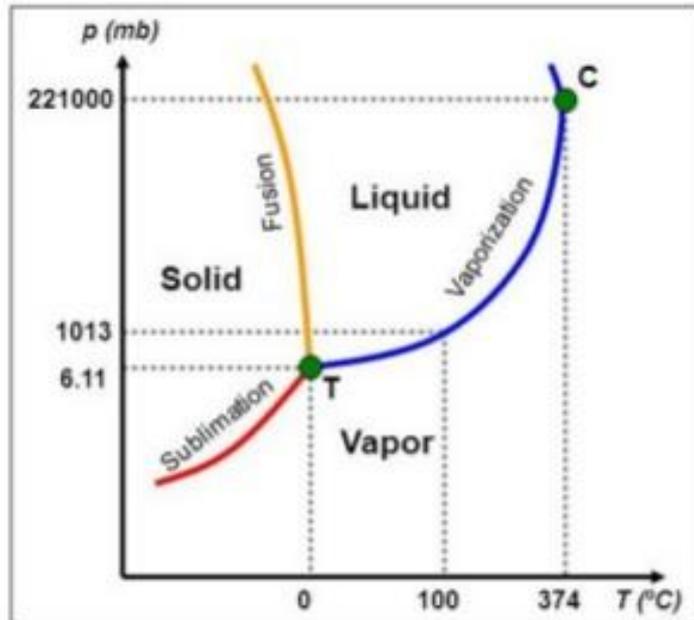
Vapour pressure of Liquid - the *Clausius-Clapeyron equation*

The *variation of vapour pressure with temperature* can be expressed thermodynamically by means of Clausius-Clapeyron equation.
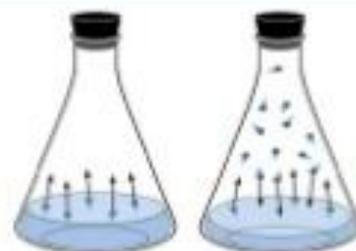
Let us consider a system- | Liquid ⇌ vapour |
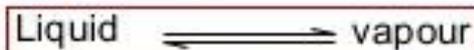
For the transition of liquid to vapour, P is the vapour pressure at given temperature T;

ΔH_v is the heat of vaporization of liquid.

The volume of given liquid is V_l and that of vapour is V_g.

Therefore, the Clepeyron equation can be written as- $dP/dT = [\Delta H_v /T(V_g - V_l)]$ (1)

But **molar volume of the substance in vapour phase** is **very large** as compared to **volume of same liquid in liquid state.** $(V_g - V_l) \approx V_g$. (18 ml water liquid = 22400 ml water vapour)

Therefore, the Clepeyron equation becomes- $dP/dT = \Delta H_v/TV_g$.   (2)

If we assume that the **vapour behaves ideally then V_g per mole of substance can be calculated as-**
$$V_g = RT/P \tag{3}$$

Substituting (3) in equation (2) as- $dP/dT = P\Delta H_v/RT^2$ (4)

$$dP/P = (\Delta H_v/R). \, dT/T^2 \tag{5}$$
$$d(\ln P) = (\Delta H_v/R). \, dT/T^2 \tag{6}$$

The equation (6) is known as *the Clausius-Clapeyron equation.* The heat of vaporization is a function of temperature. Assume that ΔH_v will be independent on the temperature (constant over the range of temperature and pressure).

Vapour pressure of Liquid
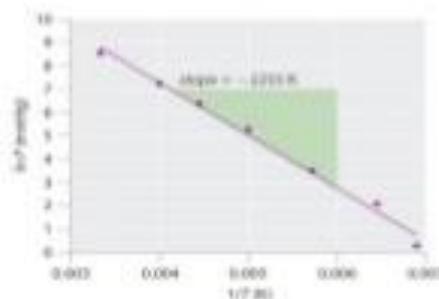
Then equation (6) can be integrated-

(a) **Integrated without limits of temperature and pressure:-**

$$\int d(\ln P) = (\Delta H_v/R) \int dT/T^2 + C \quad \text{(C is constant of integration)}$$

$$(\ln P) = (\Delta H_v/R) \cdot (-1/T) + C$$

$$(\log P) = (-\Delta H_v/2.303RT) + C' \tag{7}$$

The equation (7) - shows that logarithm of the vapour pressure should be a function of the reciprocal of the absolute temperature T. It is also a equation of straight line of the type, $y = -mx+c$; slope $= m = (-\Delta H_v/2.303R)$.

From the slope of the graph, heat of vaporization of the various liquids can be calculated as-

$$m = (-\Delta H_v/2.303R) \tag{8}$$

$$\Delta H_v = (-2.303R \cdot m) = -4.576 \cdot m \text{ cal/mol.}$$

(b) **Integration with limits:-**

Integrate equation (6) with the limits of pressure P_1 and P_2 corresponding to the temperature T_1 and T_2, then-

$$\int_{P_1}^{P_2} d(\ln P) = (\Delta H_v/R) \int_{T_1}^{T_2} dT/T^2$$

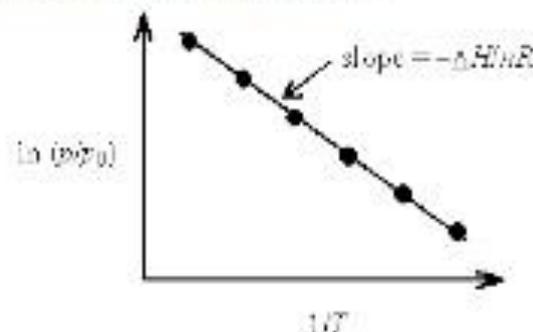$$[\ln P]_{P_1}^{P_2} = (\Delta H_v/R) [-1/T]_{T_1}^{T_2}$$

$$\ln(P_2/P_1) = (\Delta H_v/R) [(T_2 - T_1)/T_1 T_2] \tag{9}$$

$$\log(P_2/P_1) = (\Delta H_v/2.303R) [(T_2 - T_1)/T_1 T_2] \tag{10}$$

The equation (10) can be used **to calculated** ΔH_v from the values of the vapour pressure at any two temperatures or

PHASE EQUILIBRIUM

Lecture4

The water system

The Water System

How many components do you have?

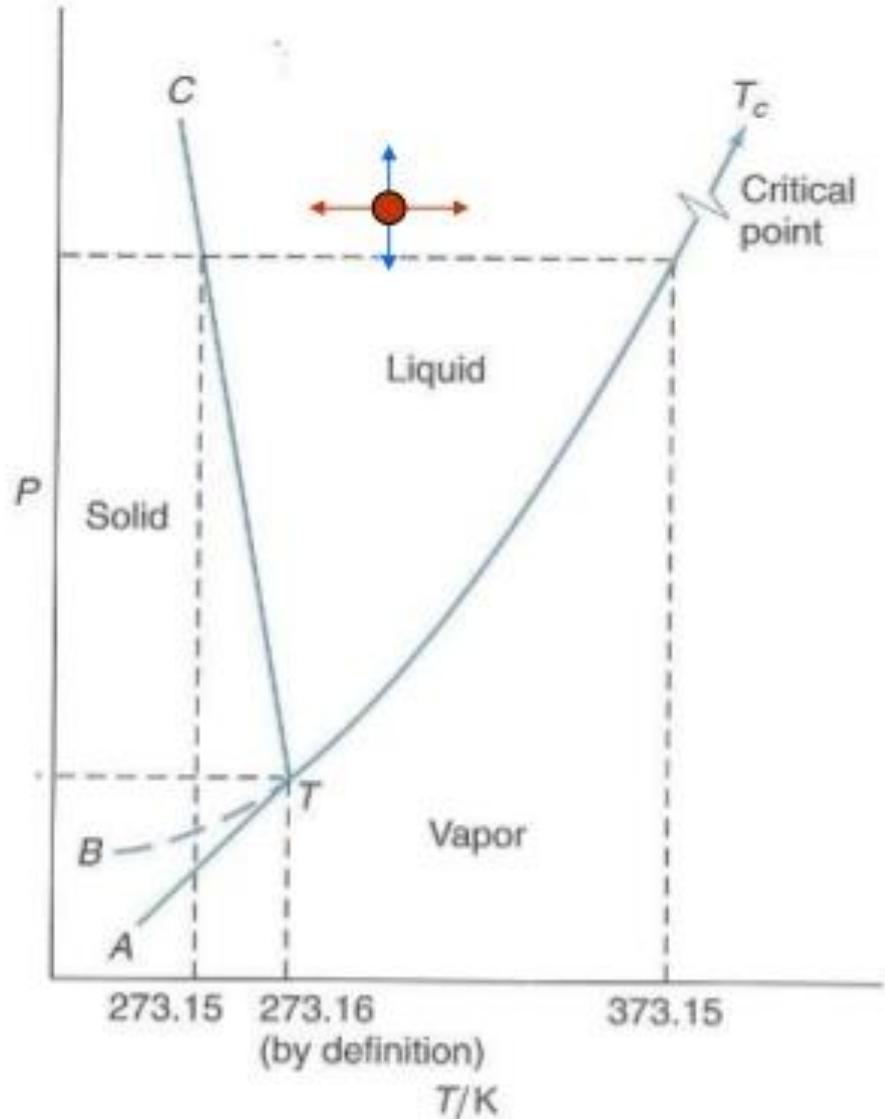We have only one component which is H_2O.

In the one-phase regions, one can vary either the temperature, or the pressure, or both (within limits) without crossing a phase line.
We say that in these regions:

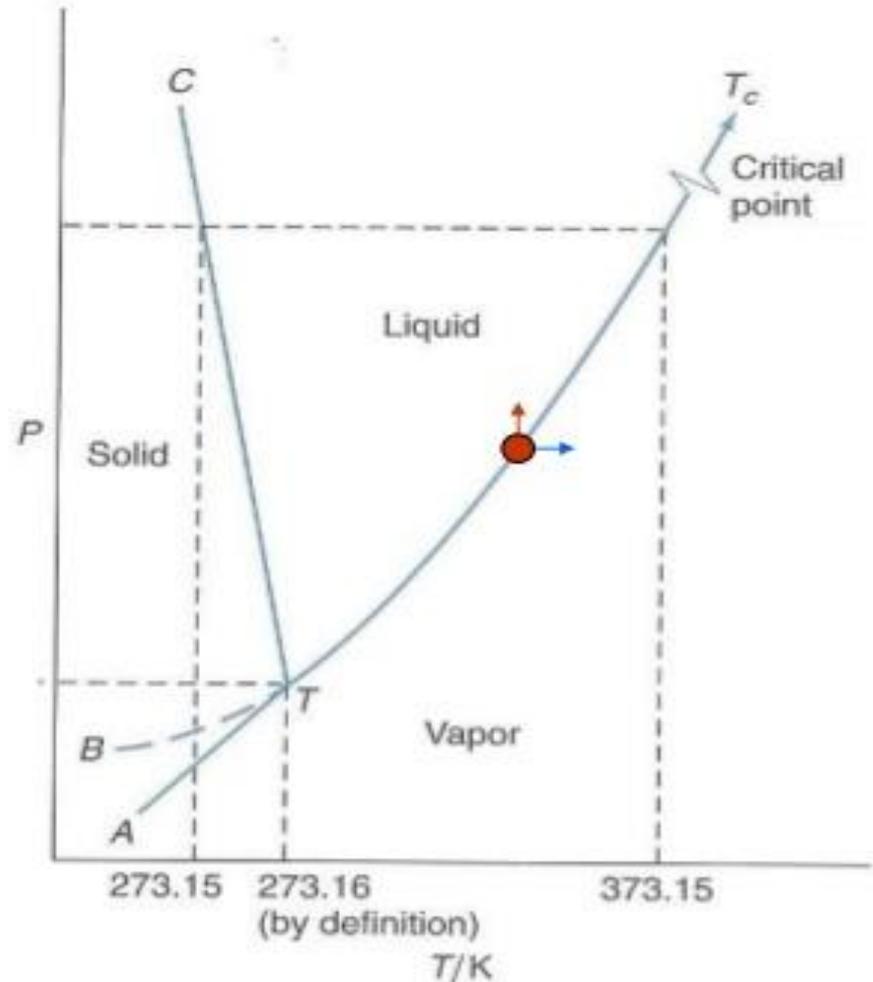$f = c - p + 2$

$\quad = 1 - 1 + 2$

$\quad = 2$ degrees of freedom.

Phase Diagram of Water

Along a phase line we have two phases in equilibrium with each other, so on a phase line the number of phases is 2.
If we want to stay on a phase line, we can't change the temperature and pressure independently.

We say that along a phase line:

$$f = c - p + 2$$
$$= 1 - 2 + 2$$
$$= 1 \text{ degree of freedom.}$$

The water system

At the triple point there are three phases in equilibrium, but there is only one point on the diagram where we can have three phases in equilibrium with each other.

We say that at the triple point:
$f = c - p + 2$
$= 1 - 3 + 2$
$= 0$ degrees of freedom.

Phase Equilibrium

Lecture- 5

The sulphur system

THE SULPHUR SYSTEM

It is a **one-component, four-phase system.**

The four phases are :

(**a**) Two solid polymorphic forms :

(*i*) Rhombic Sulphur (S_R)

(*ii*) Monoclinic Sulphur (S_M)

(**b**) Sulphur Liquid (S_L)

(**c**) Sulphur Vapour (S_V)

All the four phase can be represented by the only chemical individual 'sulphur' itself and hence one component of the system.

The two crystalline forms of sulphur S_R and S_M exhibit enantiotropy with a transition point at 95.6ºC. Below this temperature S_R is stable, while above it S_M is the stable variety. At 95.6ºC each form can be gradually transformed to the other and the two are in equilibrium. At 120ºC, S_M melts. Thus,

$$S_R \xrightleftharpoons{95.61°} S_M \xrightleftharpoons{120°} S_L$$
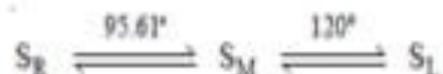
THE SULPHUR SYSTEM

The phase diagram for the sulphur system is shown in Figure . The **salient features of the phase diagram** are described below.

(*i*) The six curves *AB, BC, CD, BE, CE, EG*

(*ii*) The three Triple points *B, C, E*

(*iii*) The four areas:

> *ABG* marked 'solid Rhombic'
>
> *BEC* marked 'solid Monoclinic'
>
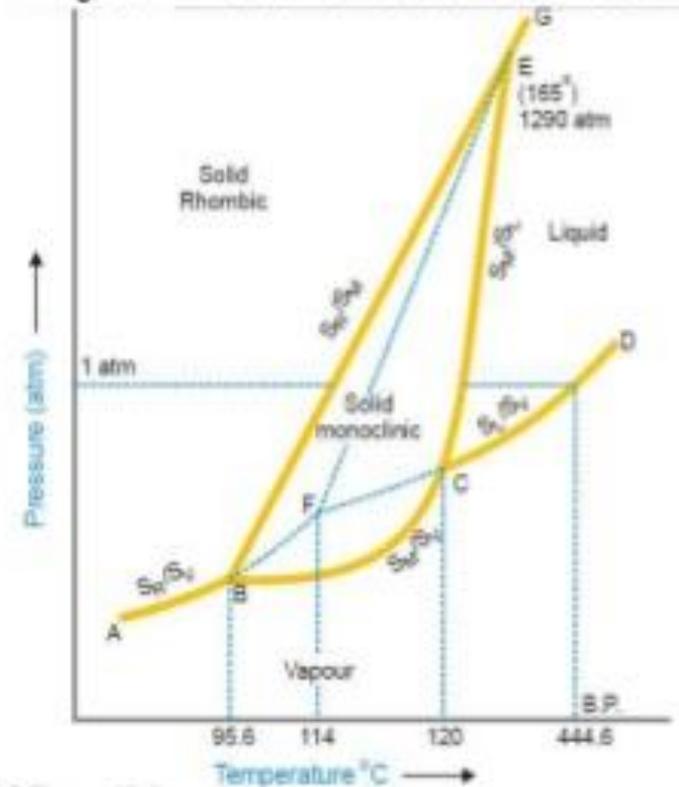> *GECD* marked 'liquid Sulphur'
>
> *ABCD* marked 'Sulphur vapour'

Let us now proceed to discuss the significance of these features :
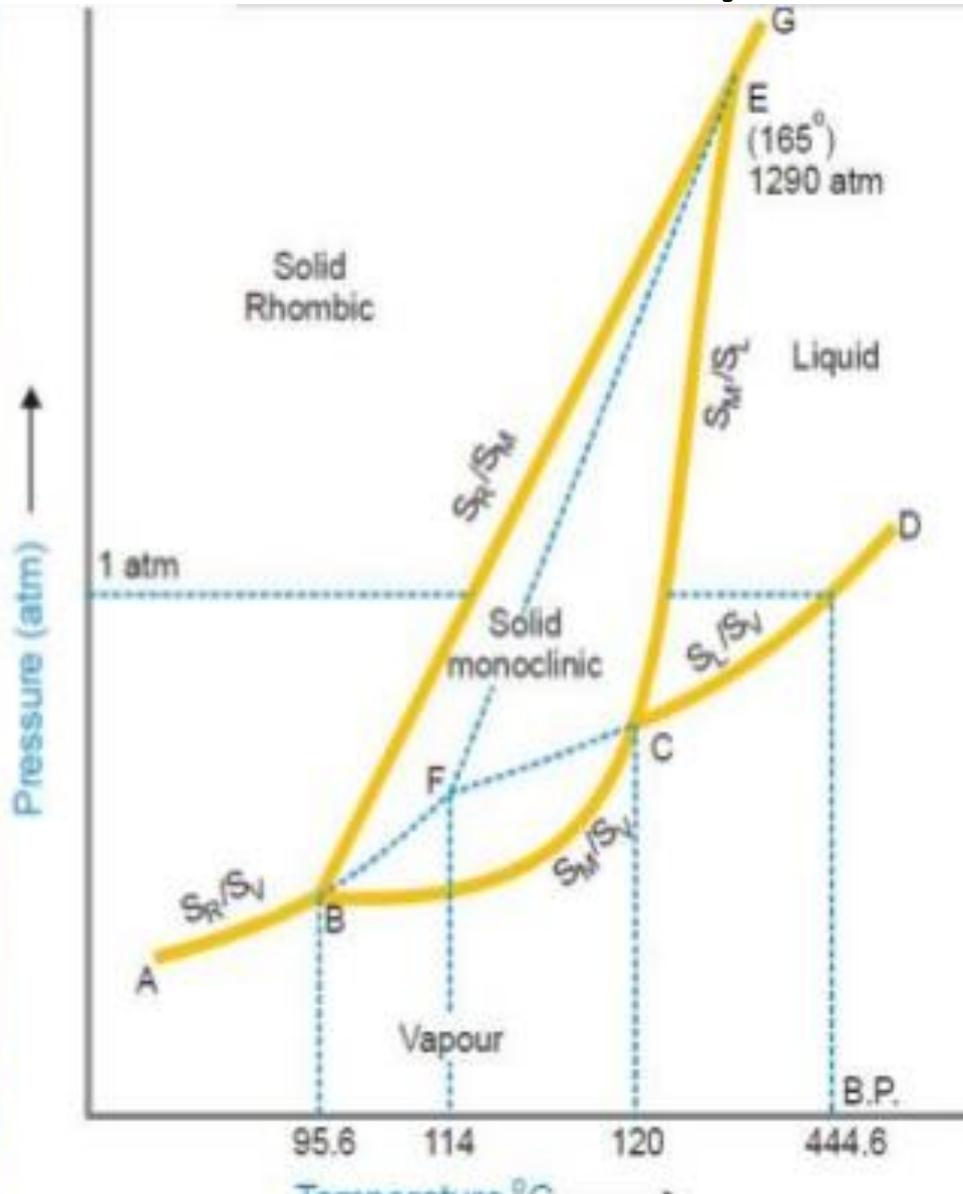

(1) The curves *AB, BC, CD, BE, CE, EG*

These *six curves* divide the diagram into *four* areas.

Curve *AB*, the Vapour Pressure curve of S_R. It shows the vapour pressure of solid rhombic sulphur (S_R) . Along this curve the two phases S_R and sulphur vapour (S_V) are in equilibrium. The system S_R/S_V has one degree of freedom,

$F = C - P + 2 = 1 - 2 + 2 = 1$ *i.e.*, it is *monovariant*.

Sulphur system

Curve *BC*, the Vapour Pressure curve of S_M. It shows variation of the vapour pressure of monoclinic sulphur (S_M) with temperature. S_M and S_V coexist in equilibrium along this curve. The system S_M/S_V is *monovariant*.

Curve *CD*, the Vapour Pressure curve of S_L. It depicts the variation of the vapour pressure of liquid sulphur (S_L) with temperature. S_L and S_V are in equilibrium along *CD*. The two phase system S_L/S_V is monovariant. One atmosphere line meets this curve at a temperature (444.6°C) which is the boiling point of sulphur.

Sulphur system

Curve *BE*, the Transition curve. It shows the effect of pressure on the transition temperature for S_R and S_M. As two solid phases are in equilibrium along the curve, the system S_R/S_M is *monovariant*.
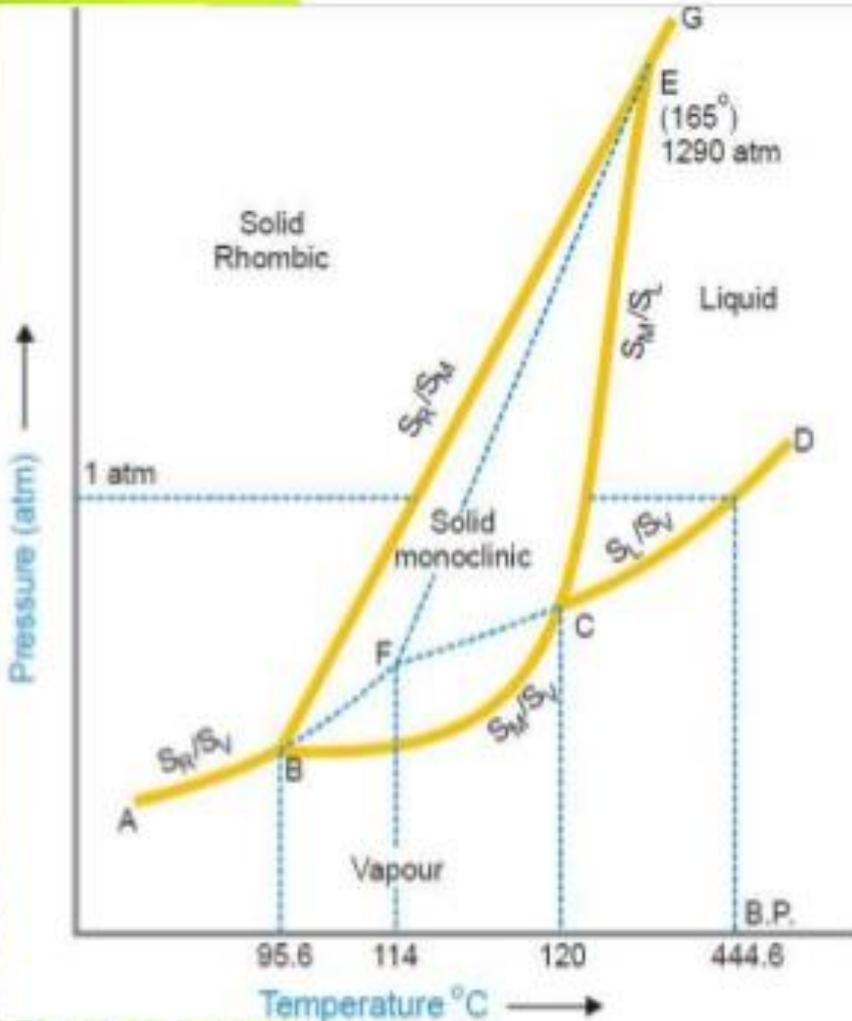
$S_R + Q$ (heat energy) $\rightleftharpoons S_M$
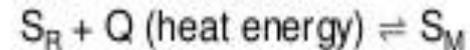
Thus, with the increase of pressure the transition temperature is raised .

Curve *CE*, the Fusion curve of S_M. It represents the effect of pressure on the melting point of S_M. The two phases in equilibrium along this curve are S_M and S_L. The system S_M/S_L is *monovariant*. With a slight increase of volume, the melting point will rise by increase of pressure .

Curve *EG*, the Fusion curve for SR. Here the two phases in equilibrium are SR and SL. The number of phases being two, the system SR/SL is *monovariant*.

Sulphur system

(diagram: Sulphur phase diagram)

Pressure (atm) ↑

G

E (165°) 1290 atm

Solid Rhombic

S_R/S_M

S_M/S_L Liquid

1 atm

Solid monoclinic

S_L/S_V

D

F

C

S_R/S_V

S_M/S_V

B

A

Vapour

B.P.

95.6   114   120   444.6

Temperature °C →

(2) The Triple points *B, C, E*

Triple point B. This is the meeting point of the three curves *AB, BC* and *BE*. Three phases, are in equilibrium at the point B. The system $S_R/S_M/S_v$ is *nonvariant*.

$$F = C - P + 2 = 1 - 3 + 2 = 0$$

At *B*, S_R is changed to S_M and the process is reversible. Thus the temperature corresponding to *B* is the *transition temperature* (95.6°C).

Triple point C. The curves *BC, CD, CE* meet at the point C. The three phases in equilibrium are S_M, S_L and S_V. The re being three phases and one component, the system $S_M/S_L/S_v$ is *nonvariant*. The temperature corresponding to *C* is 120°C. This is the melting point of S_M.

Triple point E. The two lines *CE* and *BE* meet at E where a third line *EG* also joins. The three phases S_R, S_M and S_L are in equilibrium at the point *E and is* is *nonvariant*. At this point gives the conditions of existence of the system $S_R/S_M/S_L$ at 155°C and 1290 atmospheres pressure.

sulphursystem

The sulphur system has **four areas** or **regions.** These are rhombic sulphur, monoclinic sulphur, liquid sulphur and vapour.

These represent single phase systems with two degrees of freedom,

$$F = C - P + 2 = 1 - 1 + 2 = 2$$

That is, each of the systems S_R, S_M, S_L, and S_V are *bivariant*.

Phase equilibrium

Lecture- 6

Two component system

Classification

System with eutectic melting point

Two component system

- **Reduced phase rule or condensed phase rule.**

- We know the phase-rule equation,

  $$F = C - P + 2 \ldots\ldots\ldots (1)$$

- For a two component system, $C = 2$ and hence the above equation becomes,

- $F = 2 - P + 2 = 4 - P \qquad \ldots\ldots\ldots (2)$

Congurent melting point system

- **a)Formation of compound with congruent melting point :**

- In this type of binary alloy system the two substances form one or more compounds with definite proportions. Of the compounds, a compound is said to possess congruent melting point, if it melts exactly at a constant temperature into liquid, having the same composition as that of the solid.

Classification of two component system

- The two component systems are classified into the following three types :
- Simple eutectic formation
- a) Formation of compound with congruent melting point.
- b) Formation of compound with incongruent melting point.
- Formation of solid solution

Eutectic system

- **Simple eutectic formation :**
- A system with two substances which are completely miscible in the liquid state , but completely immiscible in the solid state is known as **eutectic system.** In this system the substances do not react chemically.
- Among the mixtures of different proportions of two substances, the mixture which has the lowest melting point is known as the eutectic mixture.
- The temperature and composition corresponding to the point eutectic point is called eutectic temperature and eutectic composition respectively.

Incongurent melting point systems

- **b) Formation of compound with incongruent melting point :**

- Of the above compounds, a compound is said to possess incongruent melting point, if it decomposes completely at a temperature below it's melting point yielding a new solid phase with a composition different from that of the original.

Solid solution systems

- **Formation of solid solution :**

- In this type, when two substances, especially metals, are completely miscible in both the solid and liquid states, they form solid solutions where mixing takes place in the atomic levels. A solid solution can be formed only when the difference between the atomic radius of two metals is not greater than 15%.

Phase Equilibrium

Lecture-7

System with eutectic melting point

TWO COMPONENT SYSTEM - LEAD SILVER SYSTEM

- The Lead-Silver System Since the system is studied at constant pressure, the vapour phase is ignored and the condensed phase rule is used. F' = C – P + 1.

- The phase diagram of lead-silver system is shown.

- It contains lines, areas and the eutectic point.

Phase diagram of Lead - Silver system
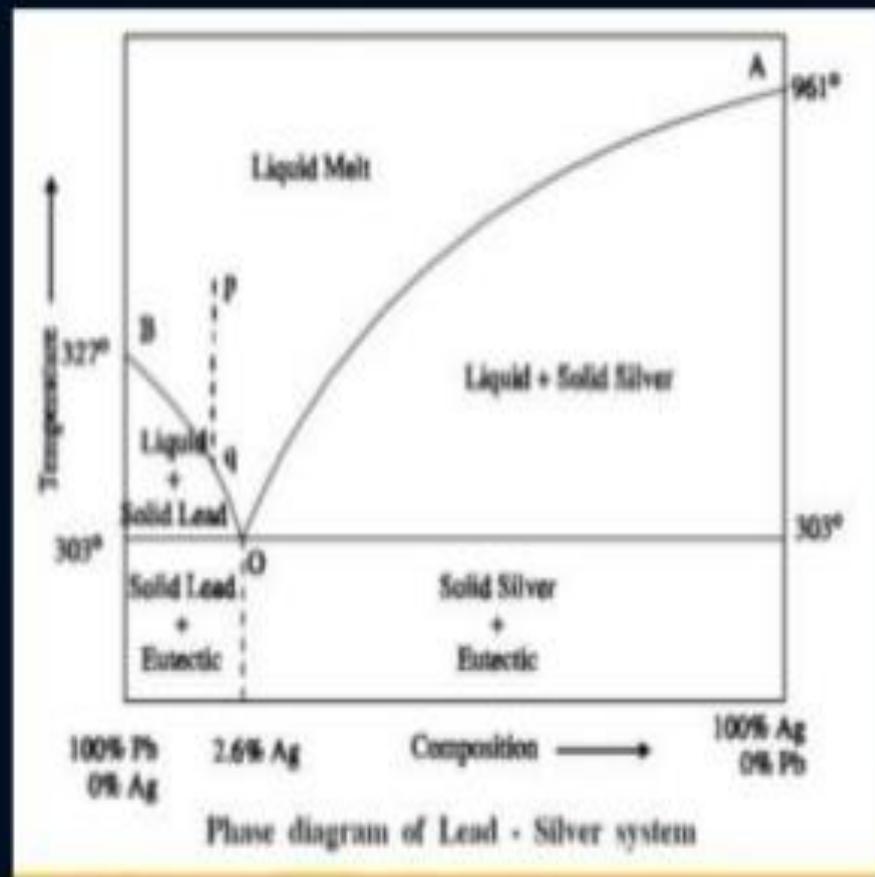
Curves :

- Curve AO : The curve AO is known as freezing point curve of silver. Point A is the melting point of pure Ag (961°C). The curve AO shows the melting point depression of Ag by the successive addition of Pb. Along this curve AO, solid Ag and the melt are in equilibrium.According to reduced phase rule equation.

$$F' = C - P + 1; F' = 2 - 2 + 1; F' = 1 \text{ (The system is univariant.)}$$

- Curve BO : The curve BO is known as freezing point curve of lead. Point B is the melting point of pure lead (327°C). The curve BO shows the melting point depression of 'Pb' by the successive addition of 'Ag'. Along this curve 'BO', solid 'Pb' and the melt are in equilibrium.According to reduced phase rule equation.

$$F' = C - P + 1; F' = 2 - 2 + 1; F' = 1 \text{ (The system is univariant)}$$

Areas :

- The area above the line AOB has a single phase (molten Pb + Ag).
  According to reduced phase rule equation.

    $F' = C - P + 1; F' = 2 - 1 + 1; F' = 2$ (The system is bivariant.)

- The area below the line AO (solid Ag + liquid melt), below the line BO
  (solid Pb + liquid melt) and below the point 'O' (Eutectic compound + solid
  Ag or solid Pb) have two phases.

    $F' = C - P + 1; F' = 2 - 2 + 1; F' = 1$ (The system is univariant.)

- Point 'O' (Eutectic point) : The curves AO and BO meet at point 'O' at a temperature of 303°C, where three phases (solid Ag, solid Pb and their liquid melt) are in equilibrium. According to reduced phase rule equation.

    F' = C – P + 1; F' = 2 – 3 + 1; F' = 0 (The system is non-variant.)

- The point 'O' is called eutectic point or eutectic temperature and its corresponding composition, 97.4%Pb + 2.6%Ag, is called eutectic composition. Below this point the eutectic compound and the metal solidify.

DIFFERENCES BETWEEN MELTING POINT, EUTECTIC POINT AND TRIPLE POINT

- 1. Melting Point : It is the temperature at which the solid and liquid phases, having the same composition, are in equilibrium. Solid A Liquid A.

- 2. Eutectic Point : It is the temperature at which two solids and a liquid phase are in equilibrium Solid A + Solid B Liquid.

- 3. Triple Point : It is the temperature at which three phases are in equilibrium Solid Liquid Vapour.

APPLICATION OF PATTINSON'S PROCESS FOR T
DESILVERISATION OF ARGENTIFEROUS LEAD

- The argentiferous lead, consisting of a very small amount of silver (say 0.1%), to a temperature above its melting point, so that the system consisting of onl phase represented by the point 'p' in the Figure. It is then allowed to cool.

- The temperature falls down along the line 'pq'. As soon as the point 'q' is read crystallised out and the solution will contain relatively increasing amount of ''

- On further cooling, more and more 'Pb' is separated along the line 'BO' the m continues to be richer and richer in silver until the point O is reached, where t percentage of Ag rises to 2.6%.

- Thus, the process of raising the relative proportion of Ag in the alloy is known Pattinson's process.

USES (OR) MERITS OF PHASE RULE:

- 1. It is applicable to both physical and chemical equilibria.

- 2. It is a convenient method of classifying the equilibrium states in terms of phases, components and degree of freedom.

- 3. It indicates that the different systems having the same degrees of freedom behave similarly.

- 4. It helps in deciding whether the given number

USES OF EUTECTIC SYSTEM

- 1. Suitable alloy composition can be predicted with the help of eutectic systems.

- 2. Eutectic systems are used in preparing solders, used for joining two metal pieces together.

LIMITATIONS OF PHASE RULE :

* 1. Phase rule can be applied only for the systems in equilibrium.

* 2. Only three variables like P, T & C are considered, but not electrical, magnetic and gravitational forces.

* 3. All the phases of the system must be present under the same conditions of pressure and temperature.

* 4. Solid and liquid phases must not be in finely divided state, otherwise deviations occur.

Phase Equilibrium

Lecture-8

System with congurent melting point

System with incongurent melting point

Ferric Chloride Water($FeCl_3$-H_2O) System:
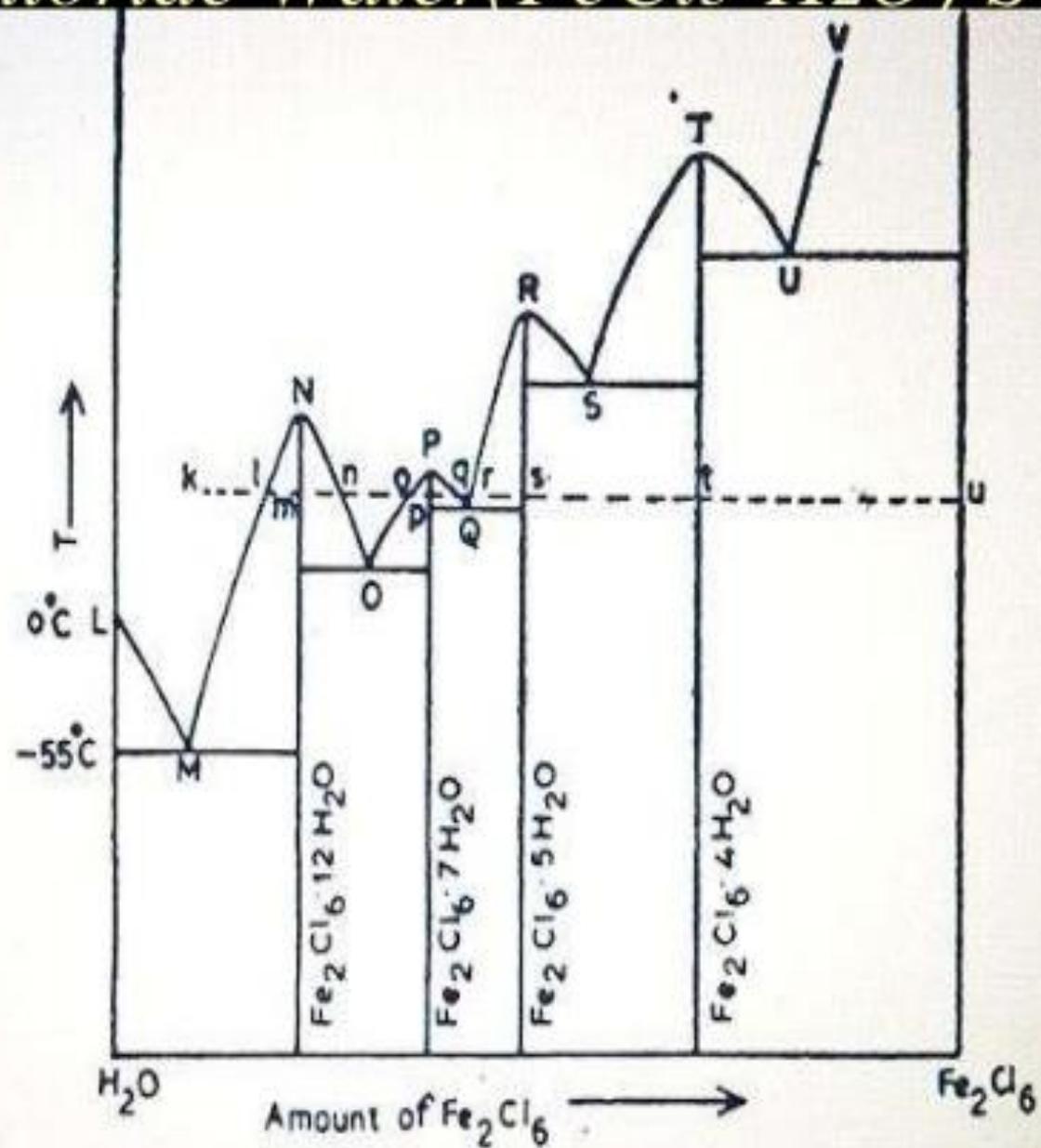
Ferric Chloride Water(FeCl3-H2O) System:

➤ In this system four congruently melting compounds are formed which are,

- dodecahydrate($Fe_2Cl_6.12H_2O$)

- heptahydrate($Fe_2Cl_6.7H_2O$)

- pentahydrate ($Fe_2Cl_6.5H2O$)

- tetrahydrate($Fe_2Cl_6.4H_2O$).

➤ The phase diagram consists of four maxima corresponding to the formation of these hydrates.

➤ Points N, P, R, T represents the congruent melting points of dodeca, hepta, penta and tetra hydrates respectively.

➤ The congruent melting point of a salt hydrate is also

Ferric Chloride Water($FeCl_3$-H_2O) System:

➤ There are five cryohydric points at M, O, Q, S and U.

➤ L is the melting point of ice.

➤ Addition of Fe_2Cl_6 lowers the melting point along LM.

➤ At the cryohydric point M the solution becomes saturated w.r.t dodecahydrate and represents the lowest temperature that can be attained with this system.

➤ Curves MNO, OPQ, QRS and STU represents the solubilities of *dodeca, hepta, penta and tetra* respectively while UV represents the solubility characteristic of the *anhydrous salt*.

➤ In the diagram the solubility of each hydrate increases with the rise of temperature.

Ferric Chloride Water(FeCl$_3$-H$_2$O) System:

➢ Now consider the phase changes that result when an unsaturated solution represented by point *k* is concentrated isothermally by adding anhydrous ferric chloride along *ku*.

➢ Firstly a saturated solution of dodecahydrate results at *l*.

➢ At *m* the whole mass solidifies to form dodecahydrate which melts when more of ferric chloride is added.

➢ Dodecahydrate disappears beyond *n* and between *n* and *o* an unsaturated solution exists.

➢ The solution becomes saturated with respect to heptahydrate at *o*.

Ferric Chloride-Water(FeCl₃-H₂O) System:

➢ *Further addition of ferric chloride increases the amount of solid heptahydrate in the solution and at p the whole solutions solidifies yielding heptahydrate.*

➢ *The heptahydrate persists upto q.*

➢ *Between q and r the solution remains unsaturated, at r the pentahydrate begins to crystallize out.*

➢ *At s solidification of whole mass into pentahydrate occurs.*

➢ *Between s and t a mixture of penta and tetrahydrate exists which is completely converted into tetrahydrate at t, beyond which tetrahydrate decomposes into anhydrous ferric chloride and at u only the anhydrous salt remains.*

Table 12.5 Salient Features of Ferric Chloride-Water System

	Point	Temperature (°C)	Phases in equilibrium	Moles of Fe_2Cl_4 per 100 moles of water
Freezing point of water	L	0.0	Ice and Water	0.0
Eutectic	M	−55.0	Ice, $Fe_2Cl_4.12H_2O(s)$, solution	3.10
Congruent m.pt.	N	37.0	$Fe_2Cl_4.12H_2O(s)$, solution	8.33 (1:12)
Eutectic	O	27.4	$Fe_2Cl_4.12H_2O(s)$, $Fe_2Cl_4.7H_2O(s)$, solution	12.20
Congruent m.pt.	P	32.5	$Fe_2Cl_4.7H_2O(s)$, solution	14.25 (1:7)
Eutectic	Q	30.0	$Fe_2Cl_4.7H_2O(s)$, $Fe_2Cl_4.5H_2O(s)$, solution	15.10
Congruent m.pt.	R	56.0	$Fe_2Cl_4.5H_2O(s)$, solution	20.00 (1:5)
Eutectic	S	55.0	$Fe_2Cl_4.5H_2O(s)$, $Fe_2Cl_4.4H_2O(s)$, solution	20.40
Congruent m.pt.	T	73.5	$Fe_2Cl_4.4H_2O(s)$, solution	25.00 (1:4)
Eutectic	U	66.0	$Fe_2Cl_4.4H_2O(s)$, $Fe_2Cl_4(s)$, solution	29.90

System with incogurent melting point

Formation of compound with incongurent melting point.
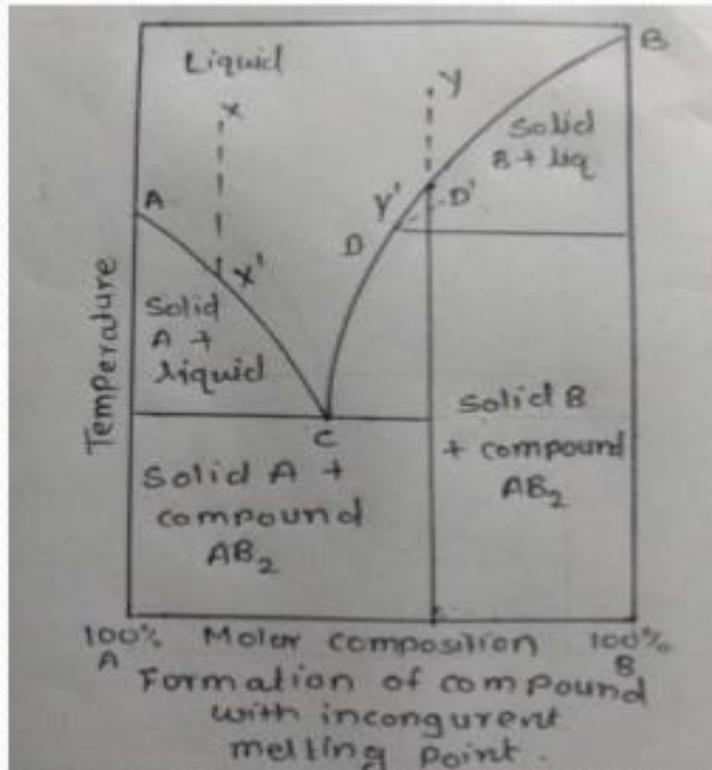
- Let A & B be the two component which combine to form a compound AB_2
- Point A & B are freezing points.
- Point C is eutectic point of the system which is non– variant as solid A, solid AB_2 & liquid phase are present in equilibrium.

- If we cool a composition X, A is the first solid to separate out at point X'
- On cooling composition Y, B is first solid to separate out at point Y'
- At point D, transition reaction occurs

  Solid AB + Solution $\longrightarrow$ Solid AB$_2$
- The compound AB$_2$ now stable. Curve CD would have proceeded upto E.
- If the curve CD is prolonged further, we get point D which would normally be the congurent M.P. of the compound this point is called a submerged maximum.

- **Examples :**
- Picric acid-benzene system
- Gold-antimony system
- Sodium sulphate- water system

REVERSIBLE AND IRREVERSIBLE CELLS

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REVERSIBLE AND IRREVERSIBLE CELLS

REVERSIBLE CELL

A cell which obey the following three conditions of thermodynamic reversibility is called reversible cell.

(i) If it is connected to an external source of e.m.f exactly equal to that of the cell and acting in the opposite direction, then no chemical reaction should occur with in the cell and hence no current is given out by the cell.

(ii) If the opposing e.m.f. Is infinitesimally smaller than that of the cell,then extremely small current should be given out by the cell and only very small amount of the reaction occurs in the cell.

(iii) If the external or opposing e.m.f is infinitesimally greater than that of the cell, an extremely small current should flow through the cell in the opposite direction and a small amount of   chemical reaction also occurs   in the reverse direction.
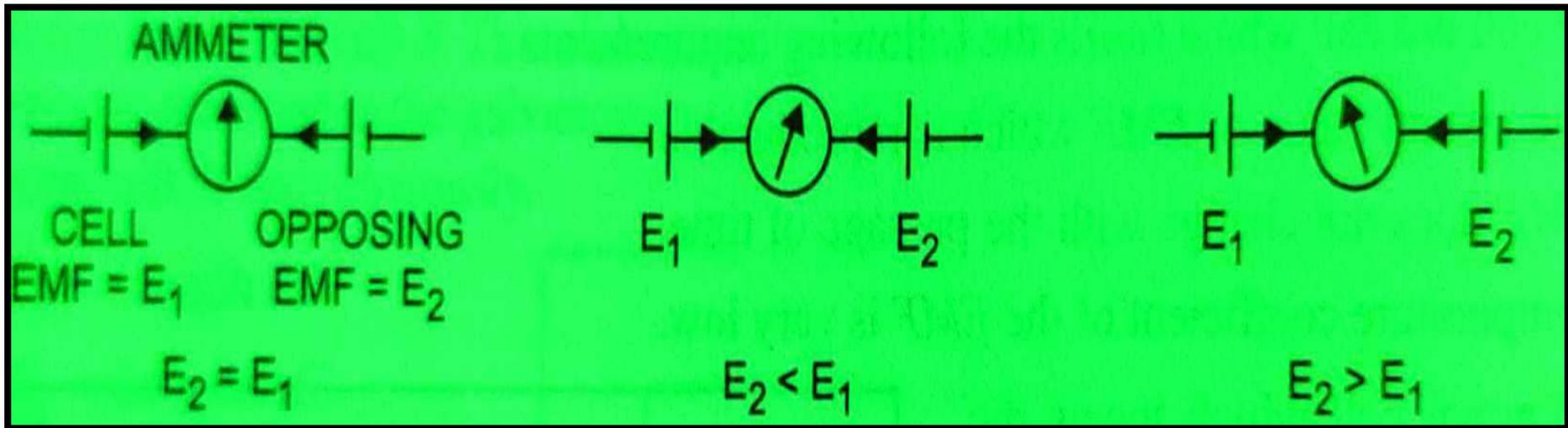
Daniel cell is a very good example for a reversible cell. In case of a Daniel cell which consists of a Zn electrode dipped in a $ZnSO_4$ solution and a copper electrode dipped in a $CuSO_4$ solution.The cell may be represented by

Zn| $ZnSO_4$ (solution) || $CuSO_4$(solution)| Cu

The e.m.f of the cell at 25^0 C is 1.1volt.

- 1.If the Daniel cell is connected to an external source of e.m.f equal to 1.1 volt ,no current flows and also no chemical reaction takes place in the cell.

- 2. If the external e.m.f is made slightly less than 1.1volt,small amount of the current flows from the cell and small chemical reaction occurs.

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

- 3 .If the external e.m.f is made slightly greater than 1.1 volt, the current will flow in the opposite direction. Copper will pass into the solution as copper ions and zinc will get deposited on the zinc electrode.

$$Cu + Zn^{2+} \longrightarrow Cu^{2+} + Zn$$

Hence both the conditions of reversibility of a cell are fulfilled so that the above cell is reversible.

IRREVERSIBLE CELLS

Cells which do not obey the conditions of thermodynamic reversibility are called irreversible cell. For example ;zinc-silver cell. It is represented as

$$Zn|H_2SO_4 (aq) |Ag$$

When the two electrodes are connected with a wire, Zn will dissolve and liberate H_2 at the Ag electrode.

$$Zn+H_2SO_4 \longrightarrow ZnSO_4+H_2.$$

However when the cell is connected to the external cell having e.m.f slightly greater than its own e.m.f, the following reaction occurs:

$$2Ag+H_2SO_4 \longrightarrow Ag_2SO_4+H_2$$

This reaction indicates that Ag dissolves with the liberation of H_2. The cell no doubt satisfy the first condition but it does not satisfy the second i.e when the cell is connected with an external source of potential slightly greater than its own, the reaction is not reversed. Thus the cell is said to behave irreversibly

THANKS

STANDARD ELECTRODE (REDUCTION) POTENTIAL AND ITS APPLICATION TO DIFFERENT KINDS OF HALF CELLS

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ELECTRODE POTENTIAL

- When a metal is placed in a solution of its ions, the metal acquires either a positive or negative charge with respect to the solution. On account of this, a definite potential difference is developed between the metal and the solution. This potential difference is called **electrode potential**. OR

- The tendency of metal to get oxidized or reduced when it is placed in a solution of its own salt is called electrode potential.

Zn in ZnSO$_4$

When Zn is placed in a solution of its own salt, zinc undergoes oxidation with the release of electrons. The electrons librated in the process, accumulate over the metal and hence, the metal is negatively charged. Now, the negatively charged metal attracts the positive ions from the solution, and hence formation of a double layer takes place near the surface of the metal.
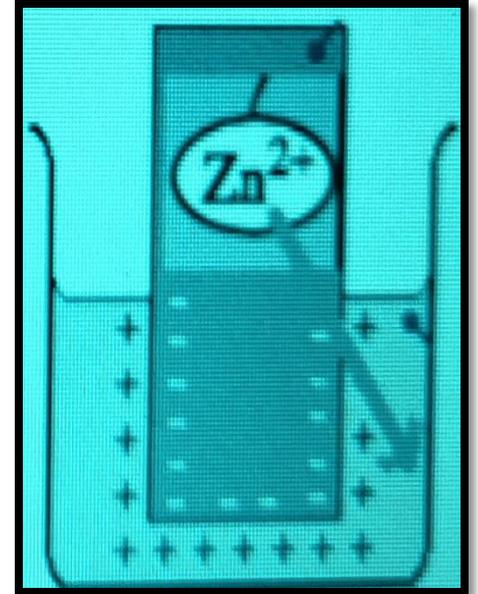
STANDARD ELECTRODE (REDUCTION) POTENTIAL

In order to compare the electrode potentials of various electrodes, it is necessary to specify the concentration of the ions present in solution in which the electrode is dipped and the temperature of the half-cell.

The potential difference developed between metal electrode and the solution of its ions of unit molarity (1M) at 25°C (298 K) is called **standard electrode potential**.

OR

It is a measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt of 1 Molar concentration at 25°C

According to the IUPAC convention, the reduction potential alone be called as the electrode potential (E^O), i.e., the given value of electrode potential be regarded as reduction potential unless it is specifically mentioned that it is oxidation potential.

Standard reduction potential of an electrode means that reduction reaction is taking place at the electrode. If the reaction is reversed and written as oxidation reaction, the numerical value of electrode potential will remain same but the sign of standard potential will have to be reversed

Standard reduction potential

   = - (Standard oxidation potential)

or

Standard oxidation potential

   = - (Standard reduction potential)

Determination of Standard Electrode Potential of Zn/Zn^{2+} Electrode

- A zinc rod is dipped in **1** M zinc sulphate solution. This half-cell is combined with a standard hydrogen electrode through a salt bridge.

- Both the electrodes are connected with a voltmeter.

- The deflection of the voltmeter indicates that current is flowing from hydrogen electrode to metal electrode or the electrons are moving from zinc rod to hydrogen electrode.

- The zinc electrode acts as an anode and the hydrogen electrode as cathode and the cell can be represented as

Cell Representation	Oxidation half reaction	Reduction half reaction
Zn|Zn^{2+} (aq)/Anode(-) || 2H(aq)| H$_2$ (g)/Cathode (+)	Zn $\rightarrow$ Zn^{2+} + 2e$^-$	2H$^+$ + 2e$^-$ $\rightarrow$ H$_2\uparrow$
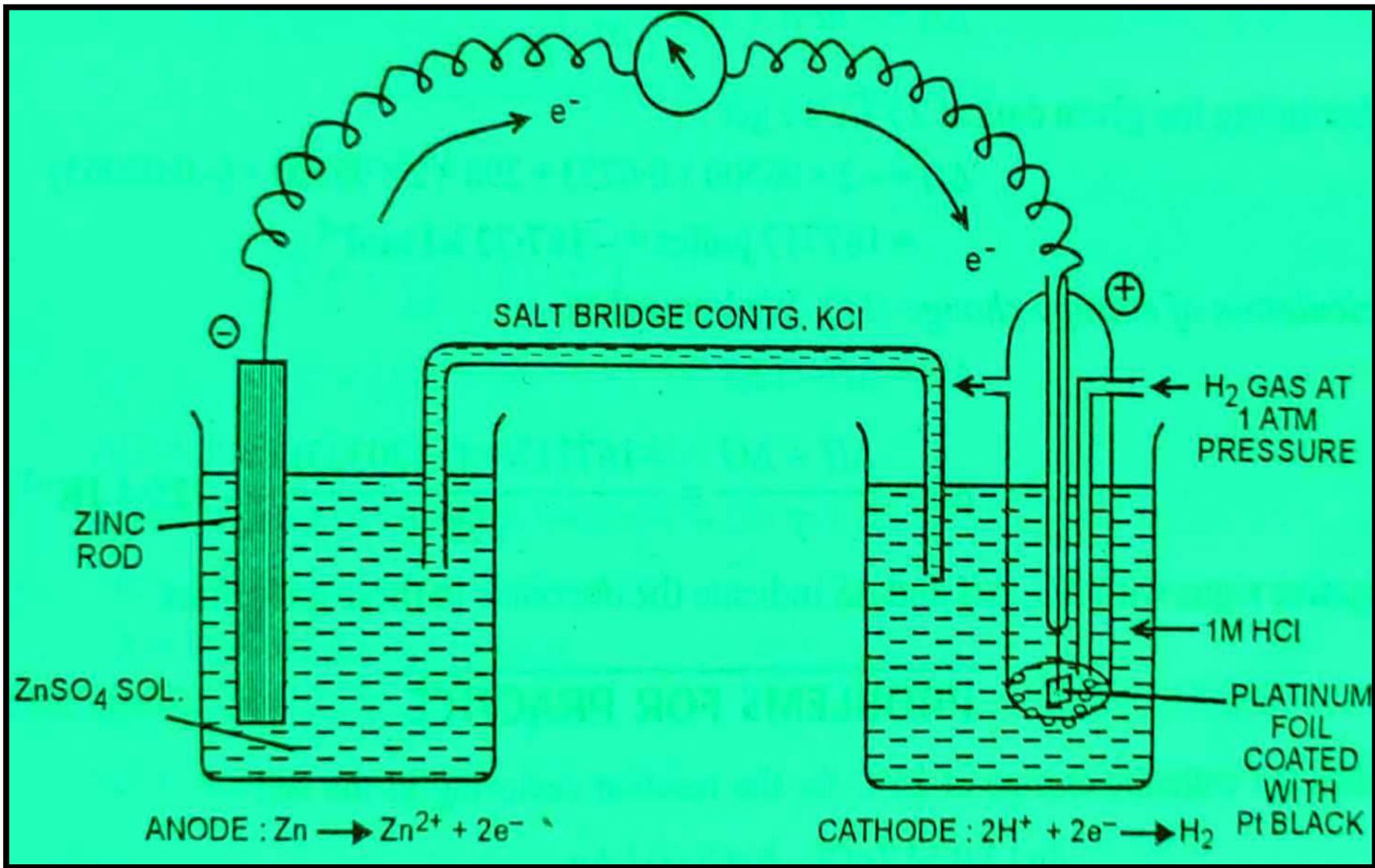
Measurement of E° using S.H.E.

The EMF of the cell is 0.76 volt

$E_{Cell} = E^o_{Anode} + E^o_{Cathode}$

$0.76 = E^o_{Anode} + 0$ or $E^o_{Anode} = +0.76$ V

As the reaction on the anode is oxidation, i.e.,

$Zn \longrightarrow Zn^{2+} + 2e^-$,

E^o_{Anode} is the standard oxidation potential of zinc. This potential is given the positive sign.

E^o_{ox} (Zn/Zn^{2+}) = +0.76 volt

So standard reduction potential of Zn, i.e., E^o (Zn/Zn^{2+})

$$= E^o = -(+0.76)$$

$$= -0.76 \text{ volt}$$

The EMF of such a cell gives the positive value of standard oxidation potential of metal M.

The standard reduction potential (E^o) is obtained by reversing the sign of standard oxidation potential.

Determination of Standard Electrode Potential of Cu^{2+}/Cu, Electrode:

- A copper rod is dipped in 1 M solution of CuSO4. It is combined with hydrogen electrode through a salt bridge. Both the electrodes joined through a voltmeter.

- The deflection of the voltmeter indicates that current is flowing from copper electrode towards hydrogen electrode, i.e., the electrons are moving from hydrogen to copper electrode.

- The hydrogen electrode acts as an anode and the copper electrode as a cathode. The cell can be represented as:

Cell Representation	Oxidation half reaction	Reduction half reaction
H_2 (g)|$2H^+$ (aq) ||Cu^{2+} (aq) |Cu	$H_2 \rightarrow 2H^+ + 2e^-$	$Cu^{2+} + 2e^- \rightarrow Cu$
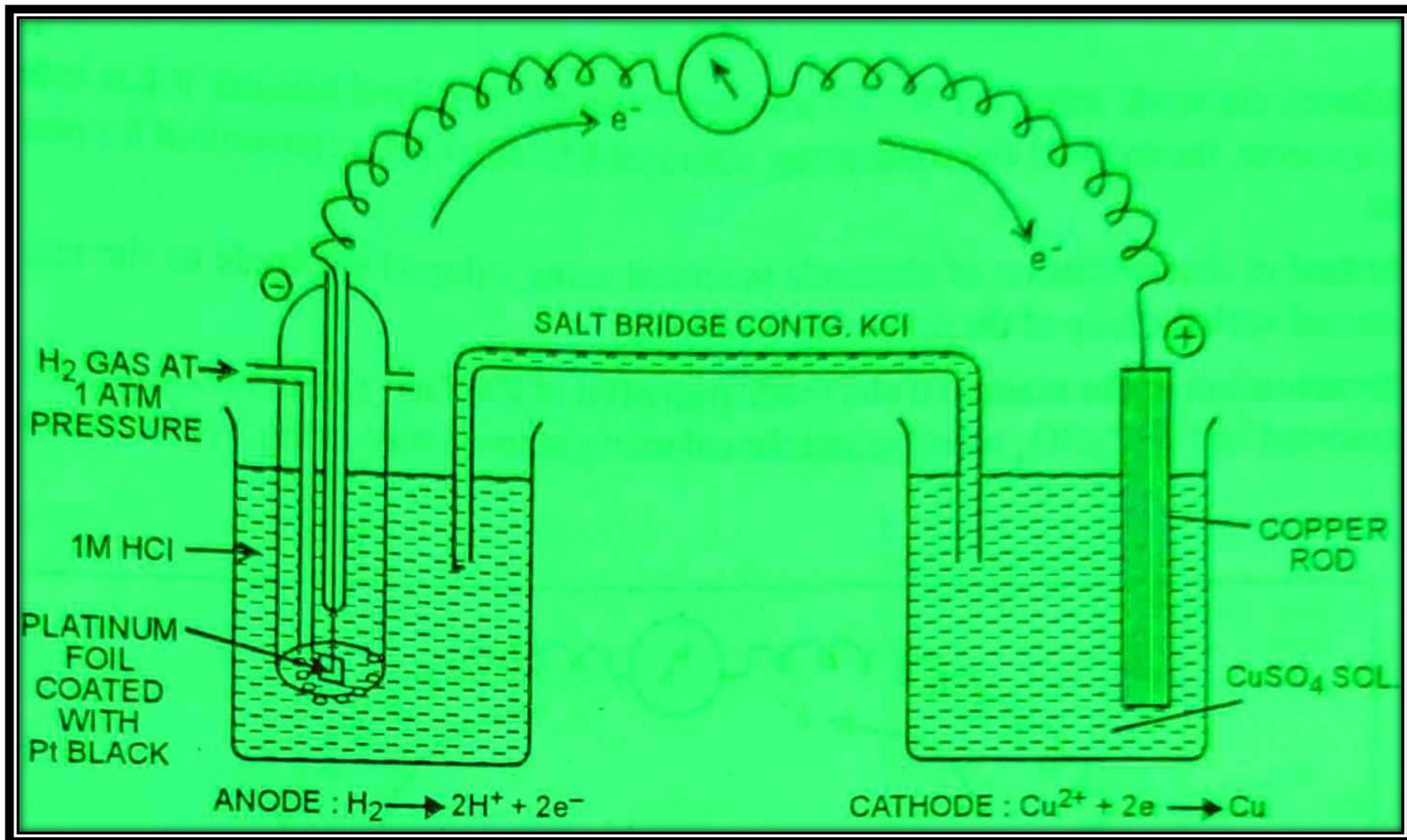
The EMF of the cell is 0.34 volt.

$E^o{}_{Cell} = E^o{}_{Anode} + E^o{}_{Cathode}$

$0.34 = 0 + E^o{}_{Cathode}$

Since the reaction on the cathode is reduction, i.e., $Cu^{2+} + 2e^- \longrightarrow Cu$,

$E^o{}_{Cathode}$ is the standard reduction potential of copper. This is given the +ve sign. E^o, i.e., standard reduction potential of $Cu^{2+}/Cu = 0.34$ volt

So $E^o{}_X$ (standard oxidation potential of copper) = -0.34 volt

The EMF of such a cell gives positive value of reduction potential of metal electrode. The standard oxidation potential of this electrode is obtained by reversing the sign of standard reduction potential.

- The EMF of such a cell gives the positive value of standard oxidation potential of metal M. The standard reduction potential (E°) is obtained by reversing the sign of standard oxidation potential.

- It is thus concluded that at the metal electrode which acts as anode with respect to hydrogen electrode (cathode), the reduction potential is given the minus sign and at the metal electrode which acts as cathode with respect to hydrogen electrode (anode), the reduction potential is given the positive sign.

The standard electrode potentials (oxidation or reduction) of various elements can be measured by combining the electrode with a standard hydrogen electrode and measuring the EMF of the cell constituted.
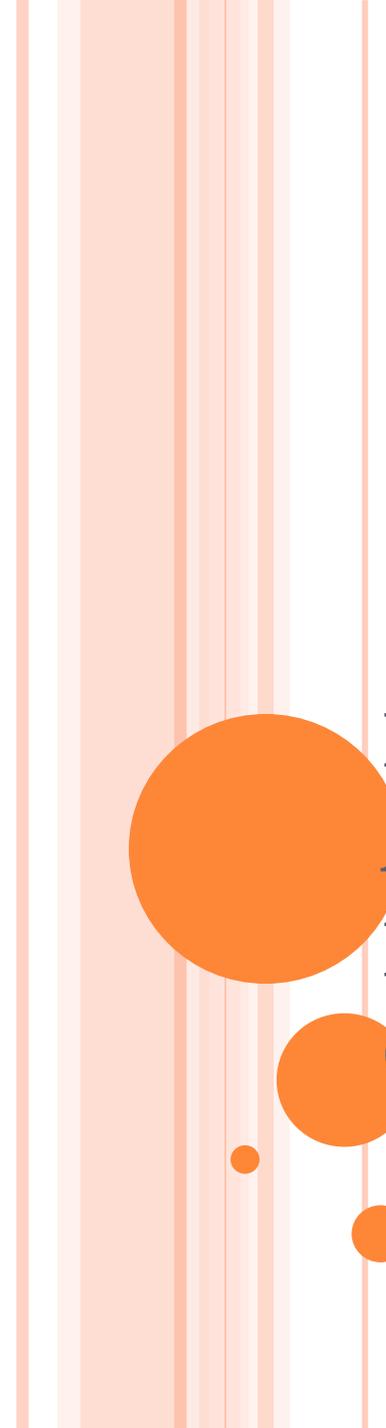
B.Sc. Semester 3

Physical Chemistry

Solutions

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SOLUTIONS

LECTURE -VII

Partially Miscible Liquids

PARTIALLY MISCIBLE LIQUIDS

We have learnt about completely miscible and completely immiscible liquids. Between these two extreme behaviours, there are liquids which are **partially miscible** with each other. Partially miscible liquids show limited solubility in each other.

For example, if a small quantity of phenol is added to water, it will at first dissolve completely. However, if the addition of phenol is continued, a stage is reached when no further dissolution takes place and two liquid layers separate out. One layer is saturated solution of phenol in water and the other layer is saturated solution of water in phenol. The two layers in equilibrium are called **conjugate solutions**.

The compositions of both the layers depend upon temperature and pressure. At constant temperature, the composition of each layer remains constant as long as the two phases are in equilibrium. As the temperature is increased the mutual solubility of two layers increases till at a particular temperature, the two layers become completely miscible and the solution has identical composition. **The temperature at which two partially miscible liquids become completely miscible in all proportions is called Critical Solution Temperature.**

Depending upon the nature of the liquids, the two liquid layers may become completely miscible at a temperature lower than the ordinary temperature ,(i.e. By cooling the system) or at a temperature higher than the ordinary temperature (i.e. By increasing the temperature of the system). **Thus, a system may have a lower critical solution temperature or an upper critical solution temperature or both.** The three types of partially miscible liquid systems are as follows:

(i) Liquid pairs, whose miscibility increases with increase in temperature i.e. the system having an upper critical solution temperature.

Eg.   Phenol-Water system.

(ii) Liquid pairs, whose miscibility decreases with increase in temperature i.e. the system having a lower critical solution temperature.

Eg. Triethyl Amine-Water system.

(iii) Liquid pairs, whose miscibility increases as well as decreases with increase in temperature i.e. the system having both upper and lower critical solution temperature.

Eg. Nicotine-Water system.

PHENOL -WATER SYSTEM

The curve is parabolic in shape. The features of the solubility curve are as follows:

- Point B represents the upper critical solution temperature at 66°C having critical composition 34% of Phenol by weight.

- Above 66°C, phenol and water are completely miscible and form single solution.

- Outside the curve, the system is homogenous and consists of single liquid phase.

- Any point within the curve represents two layers in equilibrium with each other i.e. Inside the parabola the system is heterogeneous.

- Point X represents the composition of phenol in water and point Y represents composition of water in phenol.

- The line XY is called the *tie-line*.
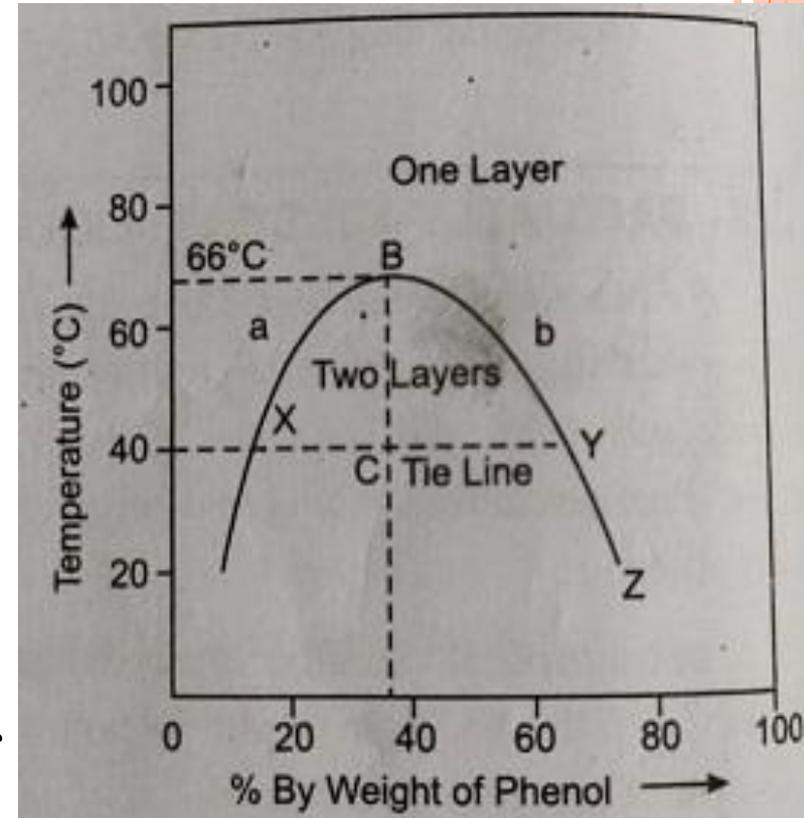
Fig. Solubility of phenol in water at different temperatures

TRIETHYL AMINE-WATER SYSTEM

- The solubility curve of this system is shown in figure. Features of this curve are:

- Point B represents the lower critical solution temperature at 18.5°C having critical composition 20% of triethyl amine by weight.

- Below 18.5°C triethyl amine and water are completely miscible.

- Outside the curve, the system is homogenous.

- At any point within the curve, there are two layers, i.e. system is heterogonous.
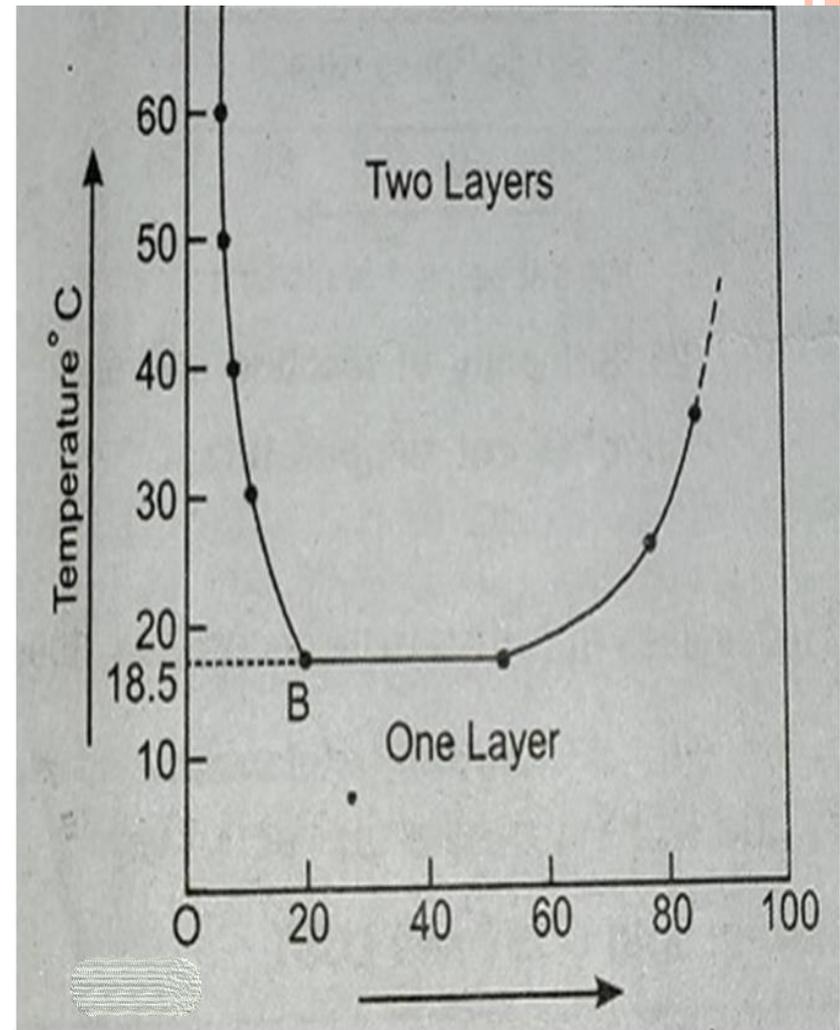
Weight per cent of Triethylamine

Fig. Solubility of triethylamine in water at different temperatures

NICOTINE-WATER SYSTEM

- In this system, solubility curve is a closed curve as shown in the figure.

- Upper critical solution temperature is 208°C while the lower critical solution temperature is 60.8^{o}C.Within the closed curve, nicotine and water are partially miscible hence two layers are present. So it is two phase region.

- Outside the curve, the two liquids are completely miscible, so it is a single phase region.

- The composition corresponding to both the critical solution temperatures is 34% by weight of nicotine.
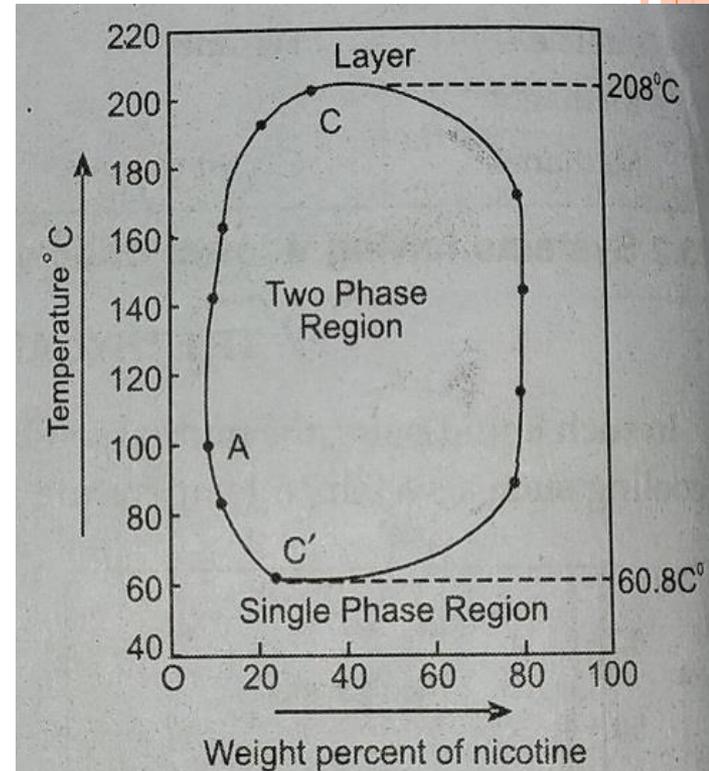
Fig. 28. Solubility of nicotine in water at different temperatures.

SOLUTIONS

LECTURE -VIII

- Effect Of Impurities On Critical Solution Temperature
- Immiscibility of liquids

EFFECT OF IMPURITIES ON CRITICAL SOLUTION TEMPERATURE:

The presence of an impurity affects the mutual solubility of the two liquids, hence it affects the critical solution temperature of the system. The effect of impurities on CST depends upon the **nature** and **amount** of added substance (impurity).

The effect of impurities on CST is studied under two headings as:

1. **When the added substance (impurity) is soluble only in one liquid.**

- If the impurity is soluble only in one liquid, it is found that the mutual solubility of the two liquids is decreased. As a result, the critical solution temperature is raised as shown by the dotted curve I in Fig.

I Substance soluble in one of the liquids
II Substance soluble in both the liquids.
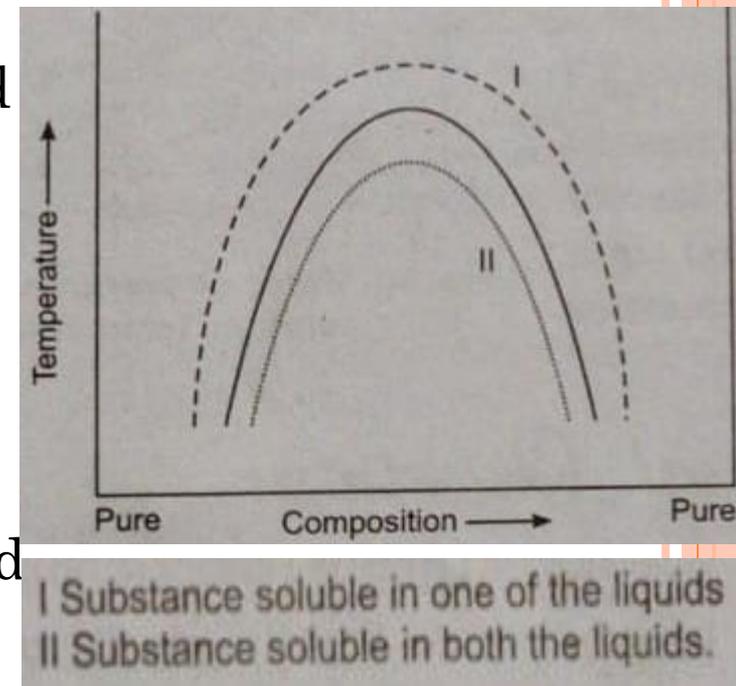
- For example, the addition of 0.1 mol of KCl per litre of water raises the CST of Phenol-Water system by about 8K whereas the addition of 0.1 mol of naphthalene per litre of phenol raises the CST of the same system by about 20K.

2. **When the impurity is soluble in both the liquids.**

- If the added substance is soluble in both the liquids, it increases the mutual solubility of both the liquids. As a result, CST is lowered as shown by curve II in Fig. This is because the added substance distributes itself between two liquids in a definite manner. The impurity is being continuously exchanged between two liquids.

- Thus, a state of dynamic equilibrium exists. The movement of molecules of added substance between the two liquids acts as a cementing force between them. This increases the mutual solubility of two liquids and hence their CST is lowered. For example:

(i) Addition of succinic acid to Phenol–Water system lowers its CST.

(ii) Addition of soap to Phenol-Water system or Cresol-Water system lowers the CST.

- It has been observed that CST varies directly with the **amount** of impurity added.

- The CST is so sensitive to the traces of impurities added that it may be used as a test for the purity of the substance.

IMMISCIBILITY OF LIQUIDS:

- Immiscible liquid pairs are those in which both the liquids are completely insoluble in each other e.g. CS_2-H_2O, CCl_4-H_2O and Water-Hg system. In such mixtures, the two liquids have vapour pressure which are independent of each other and the addition of one liquid to the other does not affect the properties of other liquid. Let us consider two immiscible liquids A and B having vapour pressures as p^o_A and p^o_B at a certain temperature. The total pressure is given as

$$p = p^o_A + p^o_B$$

- The partial pressure and the total pressure do not depend on the actual or relative amounts of the liquids present. Since the normal boiling point is the temperature at which the total vapour pressure becomes equal to the atmospheric pressure i.e.

$$p^o_A + p^o_B = \text{atmospheric pressure}$$

- Since **the total vapour pressure is higher than that of either of the components , the boiling point of mixture will be lower than that of the individual components.** Also the total vapour pressure is independent of the relative amounts of the two liquids, the liquid mixture boils at a constant temperature and the composition of distillate remains unchanged so long as two layers are present. When one of the liquid is completely boiled off, the temperature rises to the boiling point of the liquid left behind.

- At boiling point of the mixture the vapour pressure exerted by each liquid is proportional to number of moles of each component present in the vapour phase.

- Therefore, at boiling point we have

$$p^o_A / p^o_B = n_A / n_B \qquad\qquad (1)$$

- Where n_A and n_B are number of moles of components A and B in the vapour phase at the boiling point of the mixture.

- Further, $n_A = w_A / M_A$ and $n_B = w_B / M_B$

- Where w_A and w_B are the actual weights of the two components in the vapour phase and M_A and M_B are the molecular masses of A and B respectively. Substituting for n_A and n_B in eq(1) we get

$$p^o_A / p^o_B = (w_A / M_A) \times (M_B / w_B) \qquad (2)$$

$$w_A / w_B = (p^o_A \times M_A) / (p^o_B \times M_B) \qquad (3)$$

Eq(3) is the basis of steam distillation.

SOLUTIONS

LECTURE -IX

Steam distillation

STEAM DISTILLATION

Steam distillation is used to purify organic liquids which are immiscible with water. It is applied under following conditions:

(i) The organic liquid to be purified should be immiscible with water.

(ii) It should be volatile in steam.

(iii) It should possess fairly high boiling point.

(iv) The impurities present should be non-volatile.

PRINCIPLE OF STEAM DISTILLATION

Let p_w and p_l be the partial pressure of water and liquid at the distillation temperature. The liquid mixture boils when the total vapour pressure is equal to atmospheric pressure p i.e.

$$p_w + p_l = p \qquad or \qquad p_l = p - p_w$$

It is obvious that when the liquid boils in the presence of steam, the partial pressure of liquid, p_l, is less than the atmospheric pressure. Hence it boils at a temperature lower than its boiling point.

The relative amounts of liquid and water in vapour phase are given by equation (3) in which liquid A is water and liquid B is the organic liquid.

$$w_w / w_l = p_w \times M_w / p_l \times M_l = p_w \times 18 / p_l \times M_l \qquad (4)$$

Where

w_w = weight of water in vapour phase

w_l = weight of liquid in vapour phase

p_w = vapour pressure of water

p_l = vapour pressure of the liquid

M_w = molecular mass of water = 18

M_l = molecular mass of liquid

Apparatus for steam distillation is shown in the Fig.

Fig. 25. Apparatus for steam distillation
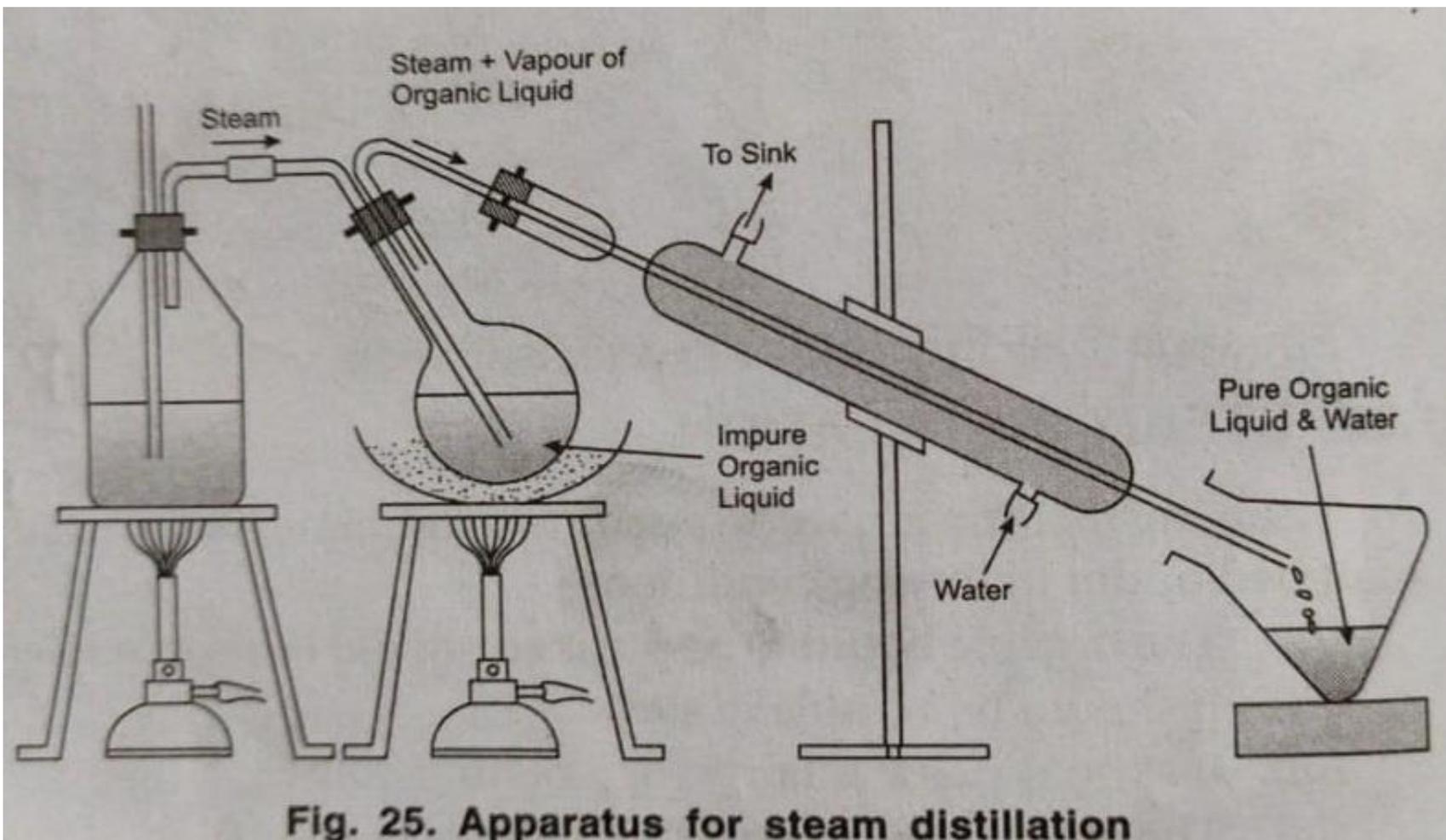
- The steam generated in the steam generator is bubbled through the liquid-water mixture in a flask placed in slanting position. The flask is heated on a sand bath to avoid excessive condensation of water into it.

- The liquid-water mixture starts boiling when the vapour pressure of the mixture becomes equal to atmospheric pressure. At this temperature, the vapours of organic liquid mixed with steam rise up and condense as they pass through water condenser. Thus the distillate collected in the receiver is a mixture of organic liquid and water. The two being immiscible are separated in a separating funnel.

- The relative amounts of liquid and water which distil over are given by equation (4).

- This equation can also be used to calculate the molecular mass of the liquid, if the ratio of weights of two components and their vapour pressures are known.

- Steam distillation can be applied for the separation of mixture of o-nitrophenol and p-nitrophenol.

- In this process, o- nitrophenol being more volatile is carried away by the steam and p- nitrophenol having higher boiling point remains in the distillation flask. The organic liquids immiscible with water and possessing fairly high boiling point e.g. aniline, benzaldehyde, nitrobenzene etc. are purified by steam distillation.

SOLUTIONS

LECTURE -X

- Nernst Distribution Law
- Validity Of The Distribution Law

NERNST DISTRIBUTION LAW:

- When a solute (solid or liquid) is added to a mixture of two immiscible liquids, in both of which it is soluble (e.g. iodine to a mixture of carbon disulphide and water or succinic acid to a mixture of ether and water), it distributes itself between the two liquids in such a way that the ratio of its concentrations in both the liquids is always constant at a constant temperature. These observations were made by Berthelot and Jungfleish in 1872.

However, it was pointed out by Nernst in 1891 that the ratio of concentrations is constant only when the solute has same molecular weight(i.e. the molecular state) in both the solvents. Hence, the generalization was put in a proper form by Nernst and is called **Nernst's Distribution Law or Partition Law**. It states :

"A solute(solid or liquid) distributes itself between two immiscible solvents in contact with each other, in such a way that the ratio of the concs. of the solute in the two solvents is constant at constant temperature, independent of the presence of any other molecular species, provided that the solute has the same molecular state in both the solvents."

- Thus, if a solute X distributes itself between the two immiscible solvents A and B, then if X remains in the same molecular state in both the solvents, we will have

$$\underline{\text{Concentration of X in solvent A}} = \underline{C_1} = K$$
$$\text{Concentration of X in solvent B} \quad C_2$$

X   **Solvent B**
Concentration = C_2

Solvent A
Concentration = C_1
X
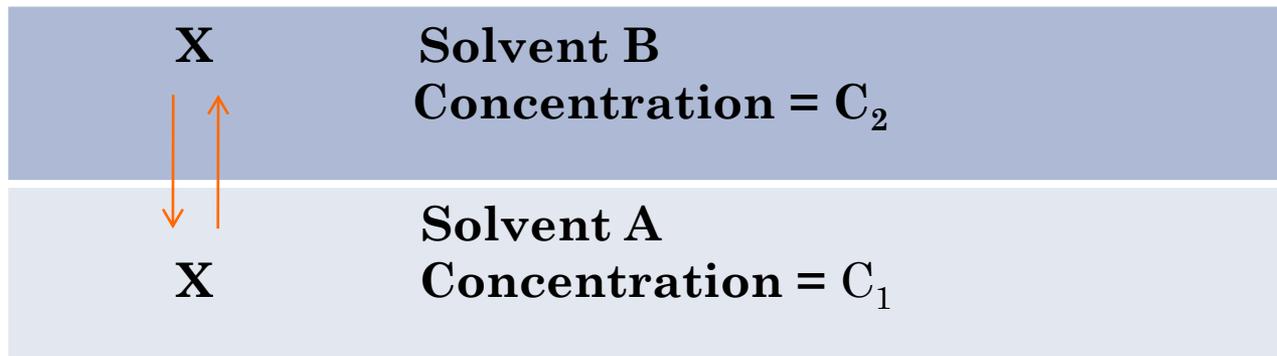
Fig.Distribution of solute X between immiscible solvents A and B

VALIDITY OF THE DISTRIBUTION LAW:

To verify the law experimentally, different amounts of a solution of iodine may be added to mixtures of carbon disulphide and water taken in different bottles . These are then shaken and allowed to stand. A known volume of each layer is pipetted out and then titrated against hypo solution to find out the conc. of iodine. Results are given in the form of a table as:

Distribution of I_2 between CS_2 & H_2O at 18^oC

Grams of I_2 in 10 ml of CS_2(C_1)	Grams of I_2 in 10 ml of H_2O(C_2)	K=C_1/C_2
1.74	0.0041	420
1.29	0.0032	400
0.66	0.0016	410
0.14	0.0010	410
0.076	0.0017	440

From these results, we observe that the ratio C_1/C_2 is constant in each case within the experimental error.

Conditions Under Which Distribution Law Is Valid:

The distribution law is valid only if the following conditions are satisfied:

(i) The temperature must remain constant throughout the experiment.

(ii) The two liquids (solvents) should be mutually immiscible.

(iii) The amount of the solute added should be small i.e. the solution should be dilute. This is essential because in certain cases, the solute added affects the mutual solubility of the two solvents.

(iv) The solute must have the same molecular state in both the solvents i.e. it should not undergo association or dissociation in any of the solvents or combination with any of the solvents. Thus, the law is not valid for the distribution of benzoic acid between water and benzene because it has been observed that in benzene, benzoic acid undergoes association to form dimers $(C_6H_5COOH)_2$ Similarly, the law is also not valid for the distribution of any electrolyte(like HCl acid) between water and a non – polar solvent like benzene, CS_2, CCl_4 etc. because the electrolytes undergo dissociation in water.

SOLUTIONS

LECTURE -XI

- Applications Of Distribution Law

Applications Of Distribution Law:

The distribution law is helpful in solving many problems of theoretical and practical nature.

1. **In calculating the solubility of a solute in a solvent.**

When the two immiscible solvents are in contact with each other and the solute is added in such a large excess that saturated solutions are formed, then the conc. of the solutions at this stage will be equal to their solubilities. Assuming that the distribution law is applicable for such concentrations, we will have

$$C_1/C_2 = S_1/S_2 = K$$

Where $C_1 = S_1$ is the solubility of the solute in the solvent 1 and $C_2 = S_2$ is the solubility of the solute in the solvent 2.

Thus, knowing the distribution coefficient K and the solubility of the solute in one of the solvents, that in the other can be calculated.

2. In studying the extent of association or dissociation of the solute in a solvent

When a solute undergoes association in one of the solvents in which its total conc. is C_2 and has the normal molecular state in the second solvent in which its conc. is C_1, then distribution law formula is modified to $C_1/nC_2 = K$, the distribution coefficient.

From this formula, the value of n can be calculated either by Hit and Trial method or by Logarithmic method.

3. **In predicting distribution indicators:**

It has been seen that iodine distributes itself between CS_2 and H_2O with a distribution coefficient equal to 400 towards CS_2. Thus if a weak solution of iodine is to be estimated, then a few drops of CS_2 may be added to this solution. As a result, a considerable amount will pass into CS_2 layer and give it a deep violet colour. Now the solution is titrated against hypo solution till the violet colour in CS_2 layer disappear. Thus, iodine acts as a distribution indicator in this case.

4. **In the study of complex ions:**

The Nernst distribution law has been successfully applied in determining the formulae of the complex ions formed between bromine and bromide ion as well as between iodine and iodide ion. The following example will illustrate the method.

On shaking a solution of iodine in carbon disulphide with water, the iodine distributes itself between the two solvents in accordance with the distribution law. Knowing the concentrations of iodine in the two layers, the partition coefficient, K, can be determined.

Now, suppose a solution of iodine in carbon disulphide containing X moles of iodine per litre is shaken with an aqueous solution of potassium iodide containing A moles of potassium iodide per litre. The total concentration of iodine in the aqueous layer will now be much higher due to formation of the soluble complex KI_3 (Fig.)
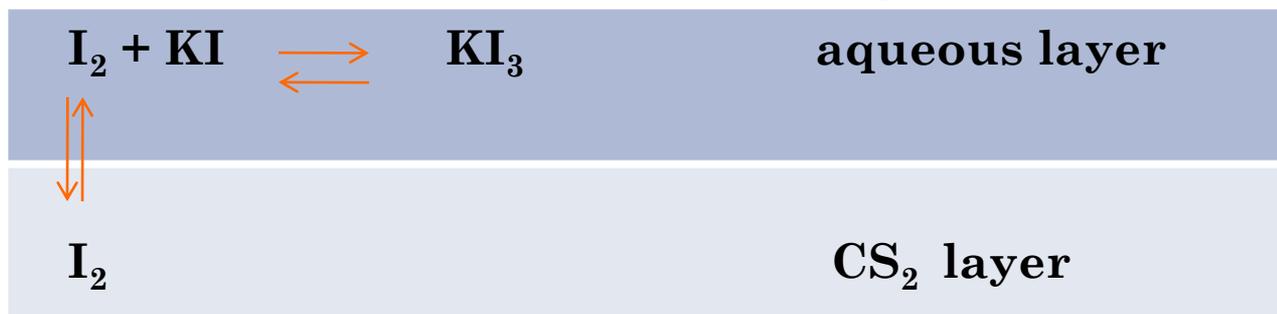
Let this conc. be B moles per litre. Evidently, the concentration of iodine in carbon disulphide layer will fall to (X-B) moles per litre. The concentration of free iodine (as I_2) in aqueous solution, according to the Nernst distribution law , should be = K (X-B) = D moles per litre

Suppose the complex ion formed is I^-_3. Then , the following equilibrium will exist in aqueous solution:

$$\bullet\ I^- + I_2 \rightleftharpoons I^-_3$$

- Evidently B-D moles of iodine must have combined with B-D moles of iodide ions (assuming that KI is completely ionised) to give B-D moles of the complex KI_3.

- Therefore , the equilibrium constant will be given by

$$K= \frac{[I^-_3]}{[I_2][I^-]}$$

- The concentrations of various species in the aqueous layer will be as follows :

$$[I^-_3] = B - D \text{ mol dm}^{-3}$$
$$[I_2] = D \text{ mol dm}^{-3}$$
$$[I^-] = A - (B - D) \text{ mol dm}^{-3}$$

- The result of determinations carried out at $30\ ^{\circ}C$ are given in the table :

A (mol dm^{-3})	B (mol dm^{-3})	D (mol dm^{-3})	K (mol dm^{-3})
0.250	0.1111	0.0261	19.72
0.125	0.0686	0.0259	20.04
0.0625	0.0625	0.0257	20.40

- The fact that K is reasonably constant, in spite of variations in A and B , shows that the formula of the complex ion is I_3^-

5. <u>Solvent Extraction</u>

- The most important application of the distribution law is in the process of extraction , in the laboratory as well as in industry. In the laboratory, for instance, it is frequently used for the removal of a dissolved organic substance from aqueous solution with solvents such as benzene, ether, chloroform, carbon tetrachloride etc. The advantage is taken of the fact that the partition co-efficient of most of the organic compounds is very largely in favour of organic solvents.

- It can be shown in a simple way that with a given volume of an extracting liquid, the extraction is more complete if it is used in a number of instalments than if the whole of it is used in a single operation.

- Suppose, one litre of an aqueous solution contains A grams of an organic solute and that one litre of ether is available as the extracting liquid. Let the partition coefficient of the solute between ether and water be 2. If all the ether is used at once , then, x, the amount that passes into ethereal layer, will be given by the equation

- $$\frac{x / 1000}{(A-x)/1000} = 2$$

  $$x = (2/3)A$$

- Thus , only 66.7 percent of the solute will be extracted, if, on the other hand , the extraction is carried out by using ether in two instalments , each of 500 ml , then x_1, the amount extracted in the first operation, will be given by the equation

$$\frac{x_1 / 500}{(A - x_1)/1000} = 2$$

$$x_1 = A/2$$

- Thus , 50 percent of the solute is taken out in the first extraction. The amount that comes out in the second extraction, x_2 ,is obtained as

$$\frac{x_2 / 500}{(A/2 - x_2) /1000} = 2$$

$$x_2 = A/4$$

- Therefore, 25 percent   of the solute comes out in the second extraction. In other words, the total amount of the solute that is extracted increase from 66.7 to 75 percent if the same one litre of ether is used in two instalments instead of one.

- Similarly , it can be shown that if the extraction is carried out in four instalments, the amount extracted will be 80.2 percent and if in ten instalments, the amount extracted will be 83.8 percent. In many cases, the partition coefficient is much more than 2 and hence , even in a few operations, practically the whole of the solute can be extracted. ***In any case, it is evident that the process of extraction is more efficient if it is carried out in parts.***
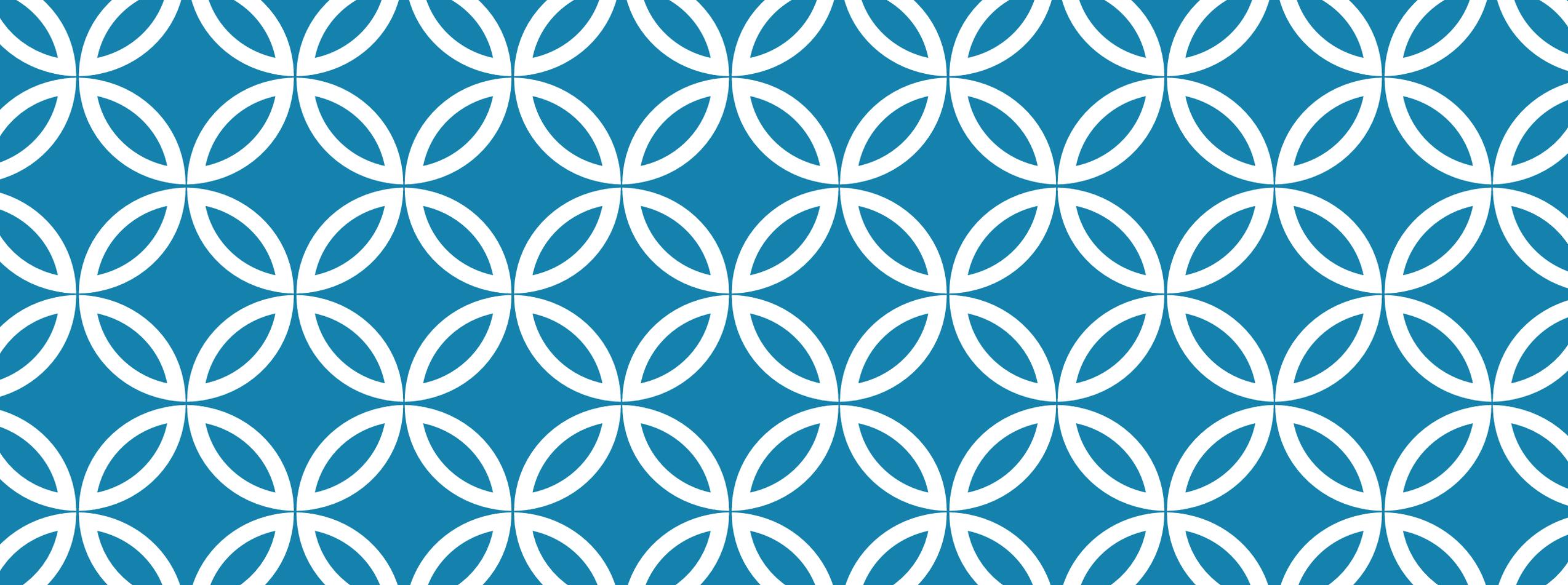
SOLUTIONS

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OBJECTIVES

- Raoult's law

- Ideal solutions

- Non ideal solutions

- Deviations from Raoult's law

RAOULT'S LAW

- Presented in 1887,

- By a French Chemist,

- Francois-Marie Raoult.

Raoult's law states that the partial pressure of any volatile component of a solution at any temperature is equal to the vapour pressure of the pure component multiplied by the mole fraction of that component in the solution.

Psolution = P^0solvent . Xsolvent
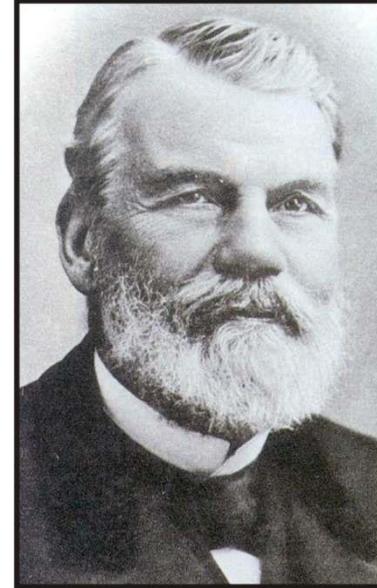
Let us consider a binary mixture of two completely miscible volatile liquids having n_A moles of a volatile liquid A and n_B moles of volatile liquid B. If P_A and P_B are the partial pressures of the two liquid components then, according to Raoult,s law

$$P_A = X_A P^0_A$$

$$P_B = X_B P^o_B$$

Where X_A is the mole fraction of the component A given by $n_A / n_A + n_B$

X_B is the mole fraction of the component B given by $n_B / n_A + n_B$

P^0_A and P^o_B are the vapour pressures of pure components A and B respectively.

If the vapour behaves like an ideal gas, then according to Dalton's law of partial pressures, the total vapour pressure P is given by

$$P = P_A + P_B$$

$$P = X_A P^0_A + X_B P^o_B$$

In general, Raoullt's law may be expressed as

$$Pi = Xi\, Pi^0$$

IDEAL SOLUTIONS

- A solution of two or more constituents is said to be ideal if it obeys Raoult's law exactly at all concentrations and at all temperatures.

- For liquid pairs which form ideal solutions implies that intermolecular or cohesive forces in such solutions are uniform, i.e., the magnitude of forces between molecules A … A , B … B and A … B are of the same magnitude.

- If two pure liquids are mixed together in any proportion to give an ideal solution, there is no change in volume i.e., ΔV mixing $= 0$

- If two pure liquids are mixed together in any proportion to give an ideal solution, there is no change in enthalpy i.e., ΔH mixing $= 0$

- Only solutions with low concentration of solute behave ideally.

- E.g. Benzene + Toluene

  Chlorobenzene + Bromobenzene

- The vapour pressure of an ideal binary solution of two components A and B having different mole fraction are shown in the figure .

- The graph of the partial pressure of each component against its mole fraction is a straight line.

- The total vapour pressure of the solution for any given composition is equal to the sum of partial pressures of the two constituents.

- Again emphasizing on the ideality of a solution implies

  that a molecule of a component A will have the same

  tendency to escape into the vapour phase whether it is

  surrounded by other molecules of its own type, entirely by

  the component B or partly by molecules of component A

  and partly by molecules of component B.

- Thus the intermolecular forces between A and A, B and B and

  between A and B are essentially the same.

  The escaping tendency of component A from an ideal solution is same as that from a pure liquid .
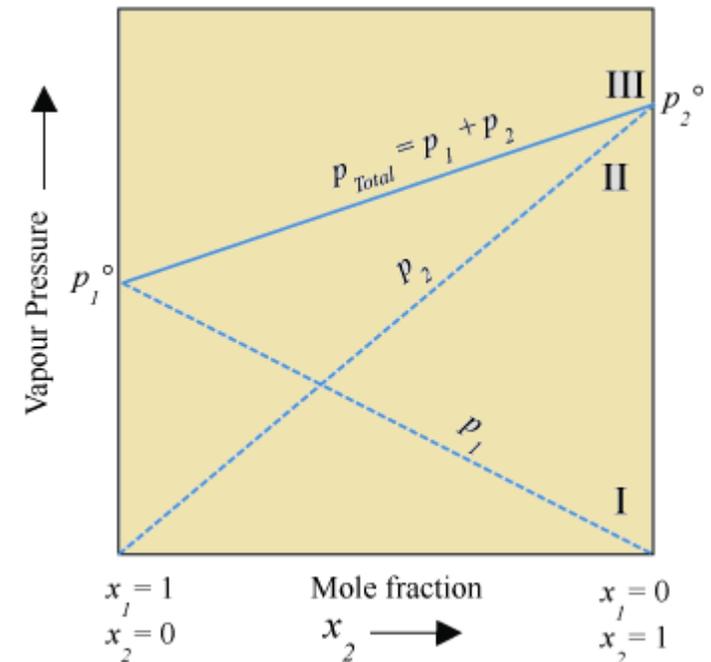
NON- IDEAL SOLUTIONS

- The solutions which do not follow Raoult's law.

- The deviations from Raoult's law arise from the non- ideality of either the vapour phase or the solution. Such solutions are called as real or non-ideal solutions.

- It is the solution in which solute and solvent molecules interact with one another with a different force than forces of interaction between the molecules of the pure component.

- $\Delta V_{mixing} \neq 0$

- $\Delta H_{mixing} \neq 0$

- E.g. Sulphuric acid(solute) and Water (solvent) the amount of heat evolved is large and the change in volume is also seen.

DEVIATIONS FROM RAOULT'S LAW

+ VE DEVIATIONS

In mixtures showing a positive deviation from Raoult's law, the vapour pressure of the mixture is always higher than that would expect from an ideal mixture.

The boiling points of such solutions are relatively lower as compared to those of pure components(because higher the vapour pressure , lower is the boiling point).

- The total vapour pressure curve rises to a maximum which is above the vapour pressure of each of the pure components.

- This behaviour is shown in the figure.

- Examples are: acetaldehyde – carbon disulphide, water – propyl alcohol and ethyl - alcohol – chloroform mixtures.
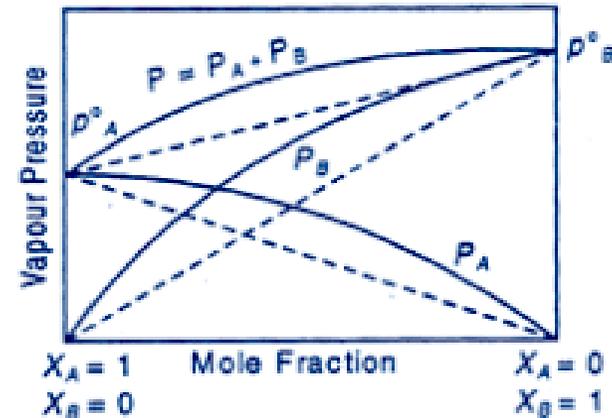
Positive deviation from Raoult's law behaviour

EXPLAINING THE DEVIATIONS

- The fact that the vapour pressure is higher than ideal in these mixtures means that molecules are breaking away more easily than they do in the pure liquids.

- That is because the intermolecular forces between molecules of A and B are weaker than they are in the pure liquids.

- Therefore the partial pressures of pure components will be higher than that predicted by Raoult's law. This leads to positive deviation from ideality.

- In such systems, when we mix the liquids. Less heat will be evolved when the new attractions are set up than was absorbed to break the original ones. Heat will therefore be absorbed when liquids mix. The enthalpy change of mixing is endothermic.

- There would also be an increase in volume on mixing.

- For an intermediate composition, the total vapour pressure of such a solution will be the highest and the boiling point will be the lowest. Such solutions boil at constant a constant temperature and its composition remains unchanged.

- Such liquid mixtures are called azeotropes.

- In case of solutions showing positive deviations, we get minimum boiling azeotropes.

⁻VE DEVIATIONS

- The vapour pressure of each component is considerably less than that predicted by Raoult's law .

- The vapour pressure curve dips to a minimum , i.e., for a certain composition, the total pressure of the mixture is below the vapour pressure of either of the pure components.

- Examples are: acetone- chloroform, water- sulphuric acid and

  water- nitric acid.

- Such solutions have higher boiling points as compared to those of

  pure components (because lower the vapour pressure , higher is

  the boiling point).

- The behaviour is shown in the figure.

- In case of a mixture of acetone and chloroform, the hydrogen

  bonding takes place between the two molecular species due to

  which the escaping tendency of either of the liquid molecules

  becomes less.

Negative deviation from
Raoult's law behaviour
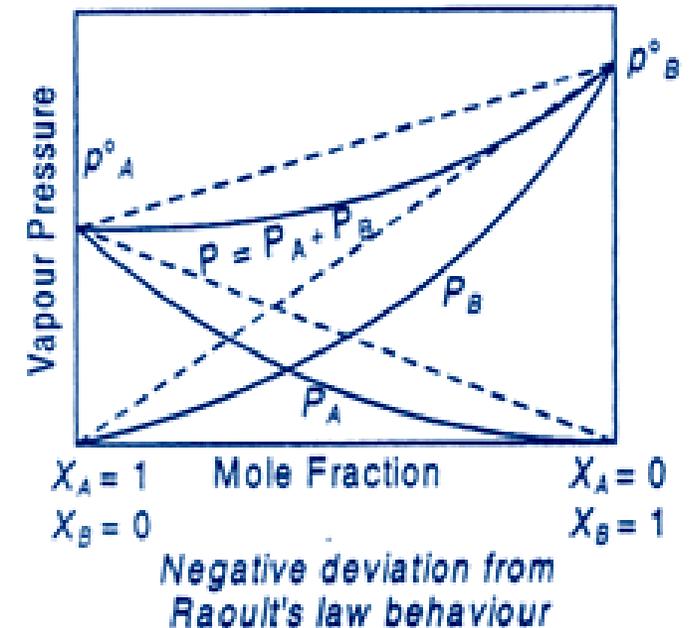
EXPLAINING THE DEVIATIONS

- These are the cases where the molecules break away from the mixture less easily than they do from the pure liquids.

- The attractive forces between the unlike molecules in solution (A…B) is stronger than those between the like molecules (A…A and B…B) in pure liquids. The escaping tendency of a component from the solution would be less than that for pure liquids.

- The heat is evolved when we mix the two liquids. More heat is evolved when the more stronger bonds are made than was used in breaking the original weaker ones.

-                              dH < 0

Example of a major negative deviation is a mixture of nitric acid and water .These two covalent molecules react to give hydroxonium ions and nitrate ions.

$$H_2O_{(l)} + HNO_{3(l)} \rightleftharpoons H_3O^+_{(aq)} + NO_3^-_{(aq)}$$
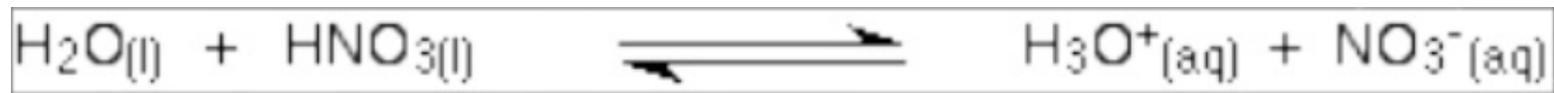
- For one intermediate composition, the total vapour pressure of the solution will be the least and the boiling point will be the highest.

- The solution will also distil without a change in composition and provides another kind of azeotropes known as maximum boiling azeotropes.
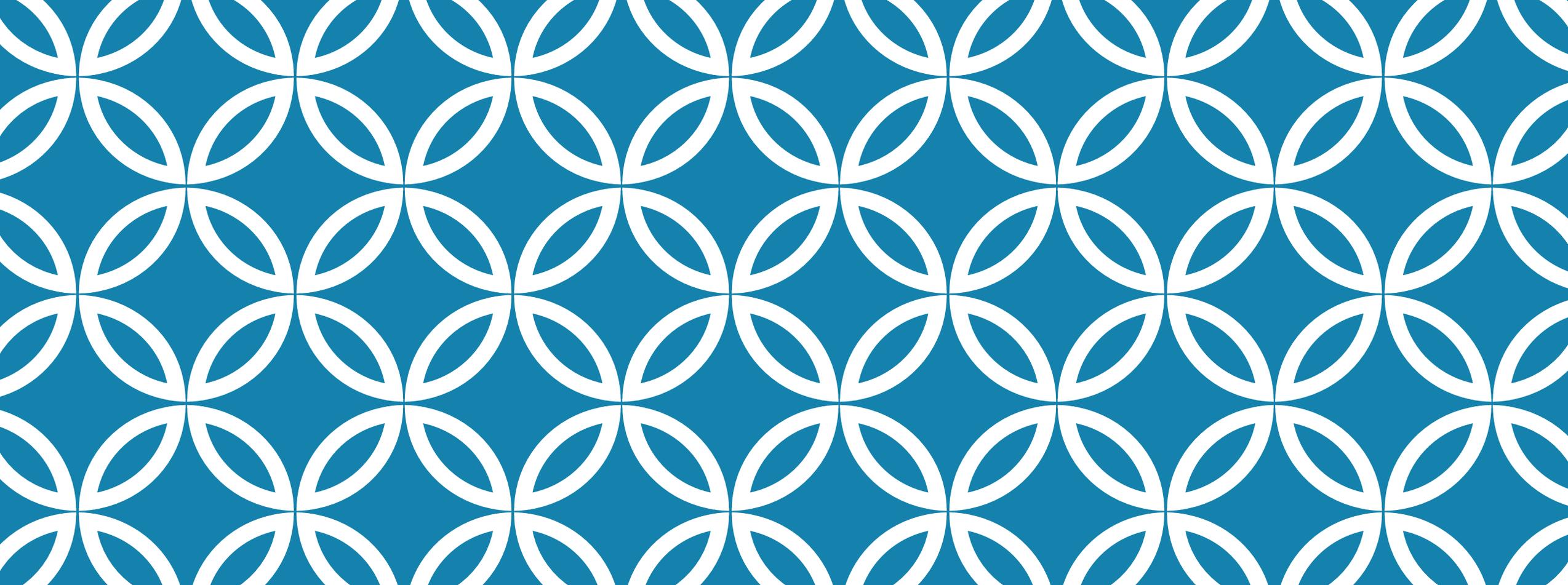
THANK YOU

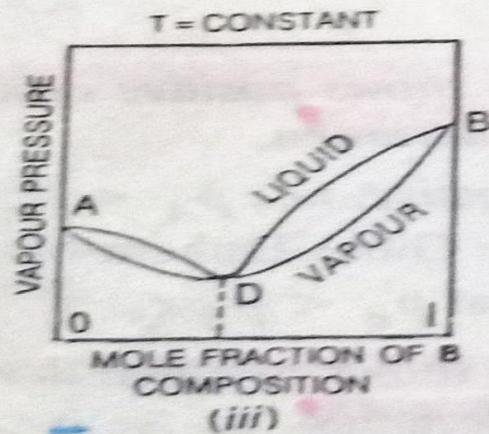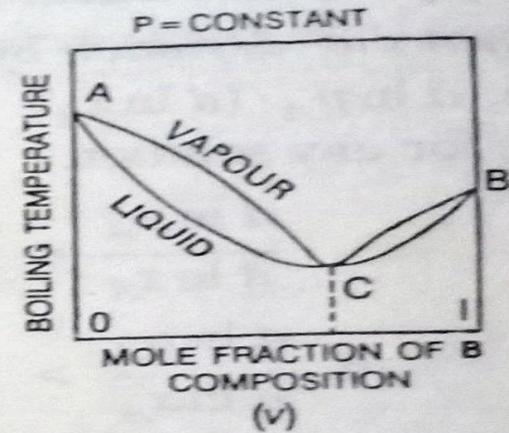# Vapour Pressure Composition Curves And Boiling Point Composition Curves

- Mixture of two liquid components A and B are completely miscible.

- On heating under constant pressure (say atmospheric pressure) mixture starts boiling at a temperature at which its total vapour pressure becomes equal to the atmospheric pressure.

- Condition for boiling is that $P = p_A + p_B$ where P represents atmospheric pressure, p_A and p_B represents partial pressures of two components A and B.

- Solutions of different compositions have different vapour pressures, thus boil at different temperatures.

- A solution of higher vapour pressure will boil at a lower temperature and vice versa.

- This makes it possible to draw boiling temperature- composition graphs from the corresponding vapour pressure – composition diagrams as.
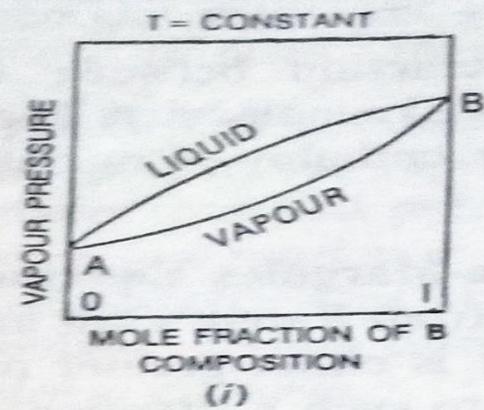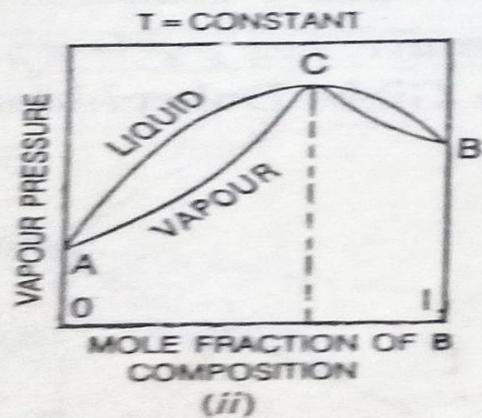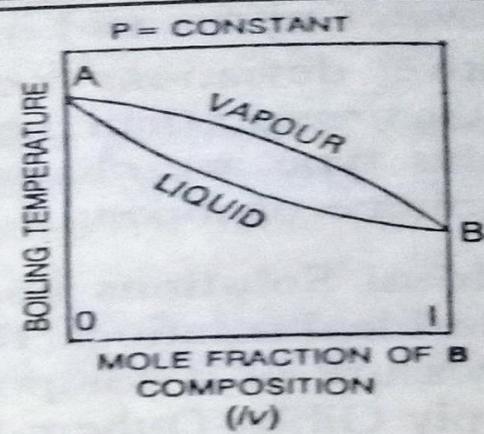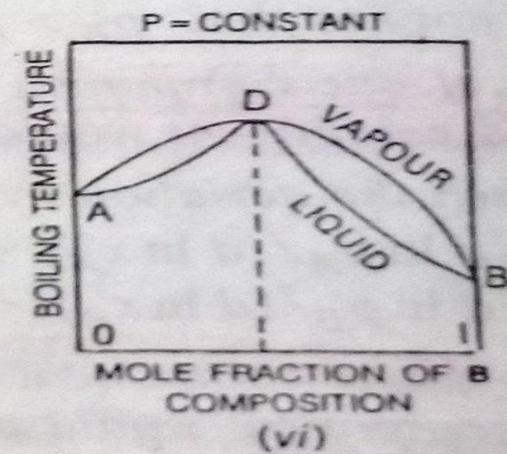
Fig. 6. Vapour pressure–Composition and Boiling point–Composition curves of completely miscible binary solutions.

- There are three types of mixtures:

- Type I.   Here the vapour pressure changes continuously with composition of the mixture.

- Type II. Here the vapour pressure shows a maximum in its vapour pressure- composition curve.

- Type III. Here the vapour pressure shows a minimum in its vapour pressure – composition curve.

- In type I, the vapour pressure of pure A is the lowest and that of pure B is the highest, which indicates that the boiling point of A will be the highest and that of B will be the lowest. At a given temperature, the vapour phase will be richer in the more volatile component B, the composition of the vapour phase will be always richer in B than that of the liquid phase .   Therefore, the vapour – composition curve will lie above the liquid- composition curve.

- In type II, the vapour pressure curve shows a maximum for a certain composition, say, C as in the figure, the solution of that composition will boil at the lowest temperature. It will give minimum in the boiling point curve.

- In type III, the vapour pressure curve shows a minimum for a certain composition, say, D, the the solution of that composition will boil at the highest temperature. It will give a maximum in the boiling point curve.
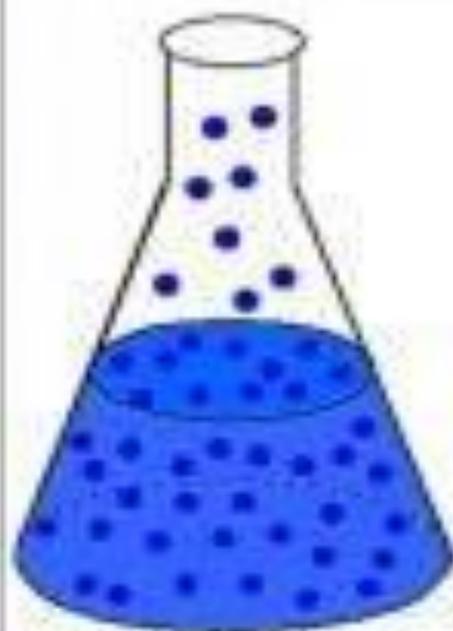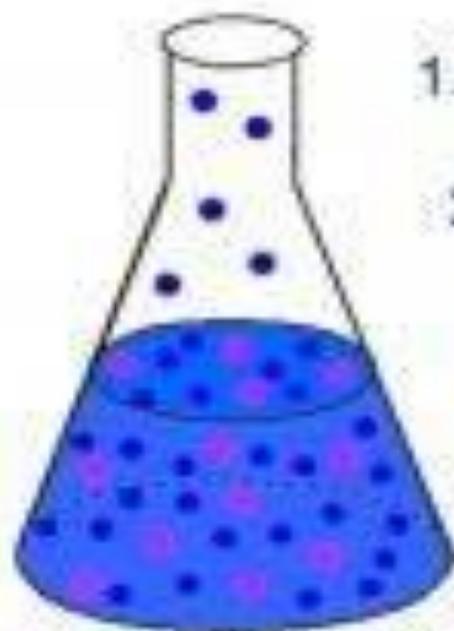
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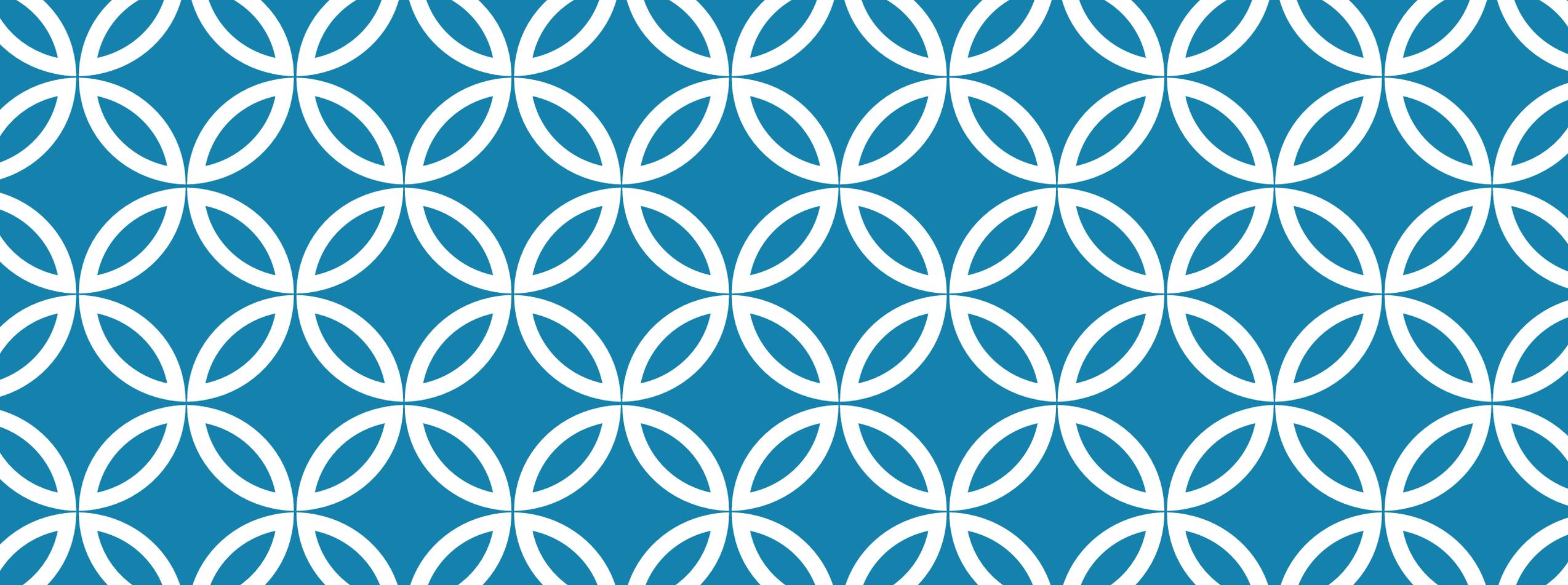
SOLUTIONS III

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Colligative Properties

- Properties that depend only on the *number* of solute particles present, not on the *identity* of the solute particles.

Pure solvent

Solvent + Solute

1. Vapor pressure lowering
$$P_A = X_A \cdot P^\circ_A$$
2. Boiling point elevation
$$\Delta T_b = K_b \cdot m$$
3. Freezing point depression
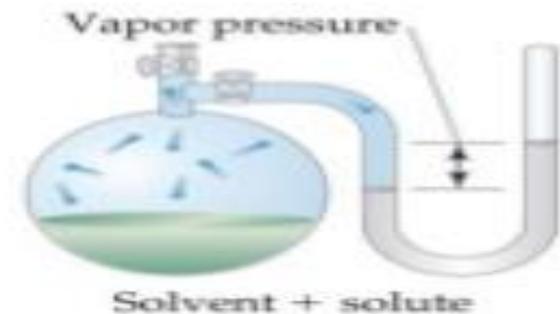$$\Delta T_f = K_f \cdot m$$
4. Osmotic pressure
$$\pi = MRT$$

LOWERING OF VAPOUR PRESSURE

Because of solute solvent intermolecular attractions, higher concentrations of non volatile solutes make it harder for solvent to escape to the vapour phase.

Therefore, the vapour pressure of a solution is lower than that of the pure solvent.

Vapor pressure

Solvent alone
(a)

Vapor pressure

Solvent + solute
(b)

- When non volatile solute is dissolved in solvent, the vapour pressure of solvent is lowered.

- Solvent molecules on the surface which can escape into vapour is replaced by solute molecules have little vapour pressure.

- For ideal solutions of non - electrolytes, vapour pressure of solution follows Raoult,s law.

- The vapour pressure of a solution, P_1, equals the mole fraction of the solvent, X_1, multiplied by the vapour pressure of the pure solvent, P^0_1.

- $P_1 = X_1 P_1^{\;0}$ $\qquad\qquad\qquad\qquad\qquad$ P_1 = v.p of solution

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ $P_1^{\;0}$ = v.p of pure solvent

- $\dfrac{P_1^{\;0} - P_1}{P_1^{\;0}} = (1 - X_A)$ $\qquad\qquad$ X_1 = mole fraction of solvent

or $\dfrac{P_1^{\;0} - P_1}{P_1^{\;0}} = X_B$ $\qquad\qquad\qquad$ X_2 = mole fraction of solute

i.e. Relative lowering of vapour pressure $\dfrac{P_1^{\;0} - P_1}{P_1^{\;0}}$ is equal to the mole fraction of the solute X_2
.

The mole fraction X_2 is given by $X_2 = n_2 / (n_1 + n_2)$

For a dilute solution, the number of moles of the solute (n_2) can be neglected as compared to the number of moles of the solvent(n_1).

$$\text{Hence, } X_2 = n_2 / n_1 = \frac{w2/M2}{w1/M1} = \frac{w2\,M1}{w1\,M2}$$

Where $w2$ is the amount of the solute dissolved in $w1$ amount of the solvent , $M1$ is the molecular mass of the solvent and $M2$ is the molecular mass of the solute .

Thus relative lowering of vapour pressure is also written

$$\frac{P_1^0 - P_1}{P_1^0} = X_2 = \frac{w2\,M1}{w1\,M2}$$

If m moles of the solute are dissolved in 1000 grams of the solvent, i.e., $\frac{w2}{M2} = m$ and $w1 = $ 1000gm, then the above equation takes the form

$$\frac{P_1^0 - P_1}{P_1^0} = X_2 = \frac{m\,M1}{1000}$$

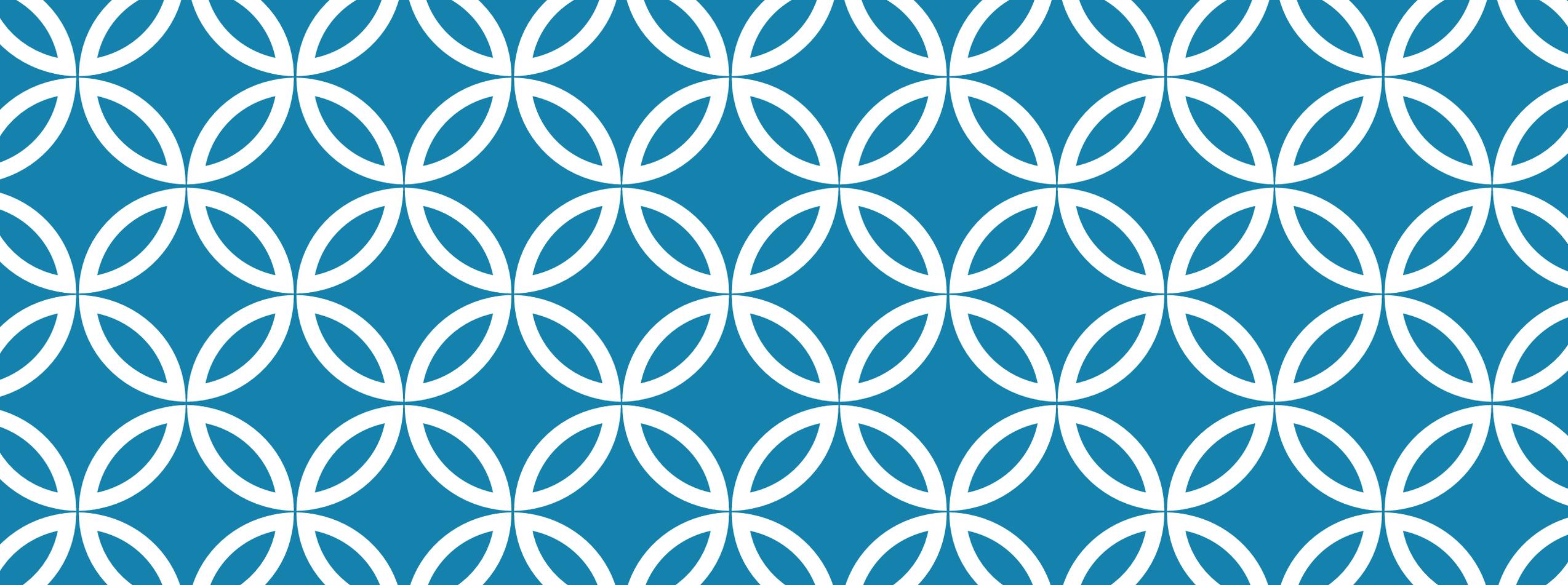where m is the molality of the solution.

The absolute lowering of vapour pressure ($P_1^0 - P_1$) or ΔP of the solution is given by

$$P_1^0 - P_1 = X_2 P_1^0$$

$$\Delta P \, \alpha \, X_2$$

Lowering of vapour pressure is proportional to mole fraction of solute.
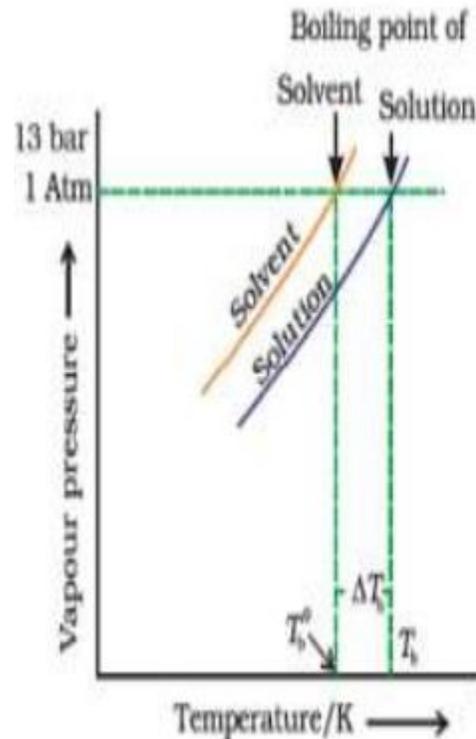
Elevation In BOILING Point:

The boiling point of a liquid is defined as the temperature at which the vapour pressure of that liquid equals the atmospheric pressure(760 mm Hg)

For a solution :

The vapour pressure of the solvent is lower at any given temperature.

Therefore, a higher temperature is required to boil the solution than the pure solvent.

In the graph shown above, we can see the change in vapour pressure of a pure solvent and a solution with the increase in temperature. Here, we can see that the two samples, the solvent and the solution, will attain the condition of boiling when their vapour pressure becomes equal to the atmospheric pressure. We can see here, the pure solvent attains this condition at a temperature equal to $T_b^°$ whereas, for the solution to attain this pressure, the temperature of the sample needs to be increased by a small amount equal to ΔT_b, such that,

$$T_b = T_b^° + \Delta T_b$$

$$\Delta T_b = T_b - T_b^°$$

If we represent the difference in boiling point between the pure solvent and a solution as ΔT_b,

We can calculate that change in boiling point from the formula:

$$\Delta T_b = i\ K_b\ m$$

Where   m : molality (because molality is temperature independent)

   K_b : boiling point elevation constant that depends on the particular solvent being used.(K_b water=0.51)

   i: Van't hoff factor and represents the number of dissociated moles of particles per mole of solute.

Derivation of Expression for Elevation in Boiling Point

It is evident that greater the lowering in vapour pressure (Δp), higher is the elevation in boiling point (ΔT_b), i.e., ΔT_b α Δp

But according to Raoult;s law

Δp α x_2, the mole fraction of the solute in the solution.

Hence,

$$\Delta T_b \text{ α } x_2$$

or $$\Delta T_b = k\,x_2 \text{ where k is the constant of proportionality.}$$

Therefore, $$\Delta T_b = k\,M_1 \frac{n_2}{w1}$$

If the mass of the solvent ,w_1 =1 kg, then evidently $\frac{n_2}{w1}$ =m, molality of the solution. Also for a given solvent, its molecular mass M_1 is constant so that k M_1 =K_b, another constant. Hence, the above result reduces to $\Delta T_b = K_b\,m$

It is clear that the elevation in boiling point depends on molality, i.e., the no. of moles of the solute dissolved in 1000 gm. of the solvent and not upon the nature of the solute. Hence it is a colligative property.

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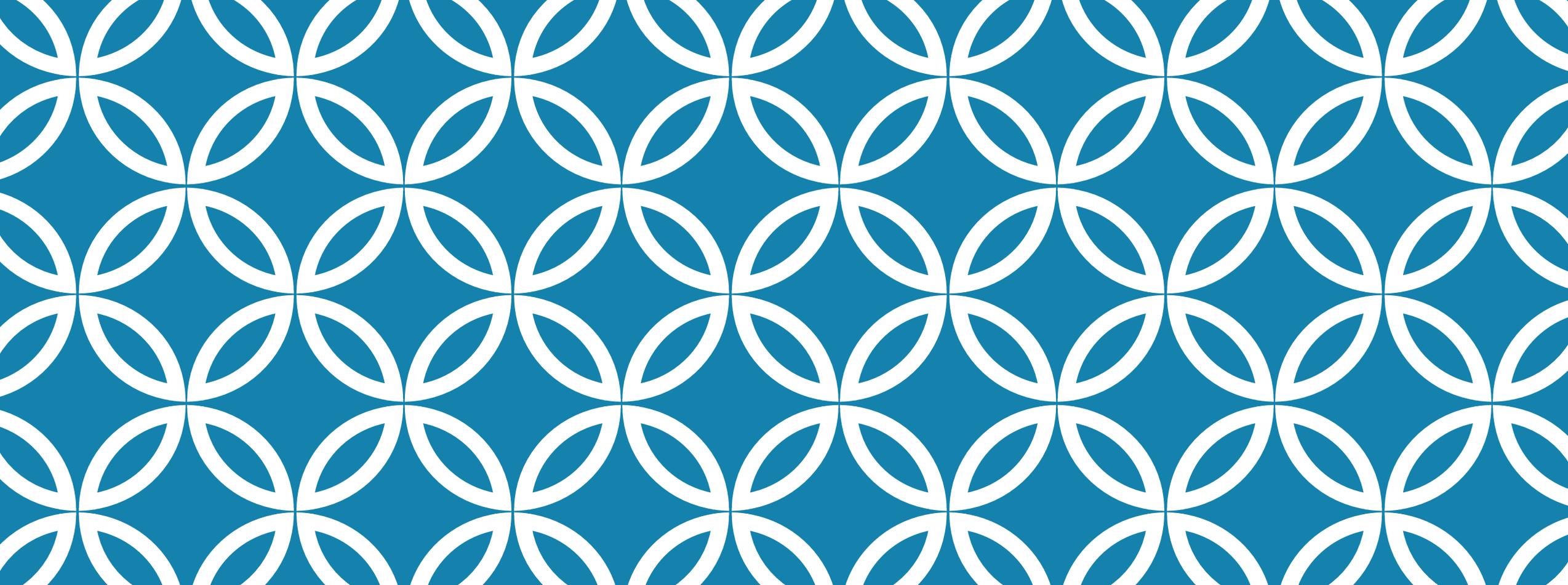
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Depression In Freezing Point

Normal freezing or melting point:

- It is the temperature at which the vapour pressure of solid is equal to the vapour pressure of   liquid.

- Addition of solute will decrease the vapour pressure and so will decrease the freezing point.

- Freezing point depression is a colligative property observed in solutions that result from the introduction of solute molecules to a solvent.

- $\Delta T_{f} = T^{0}{}_{f} - T_{f}$

  ΔT_{f} is the depression in freezing point.

  $T^{0}{}_{f}$ is the freezing point of pure solvent.

  T_{f} is the freezing point of the solution.

- The freezing point of solution $\Delta T_{f} = T^{0}{}_{f\,(solvent)}) - T_{f}(\,solution)$
  $T_{f} = T^{0}{}_{f} - \Delta T_{f}$

- In the given figure, in the curve AB for a pure solvent, at point B, there exists an equilibrium between the solid and liquid so that the vapour pressures of the solid phase and the liquid phase are equal and so are there chemical potentials and escaping tendencies. The vapour pressure decreases steeply along the path BC.

- Thus B represents the freezing point T_{t} of the pure solvent.

- On the addition of a non- volatile solute to the solvent which is solution 1, the escaping tendency of solvent molecules from liquid to solid phase diminishes .

- As at any temperature, the vapour pressure of solution is less than that of the solvent, the curve for the solution is less than that of the solvent.
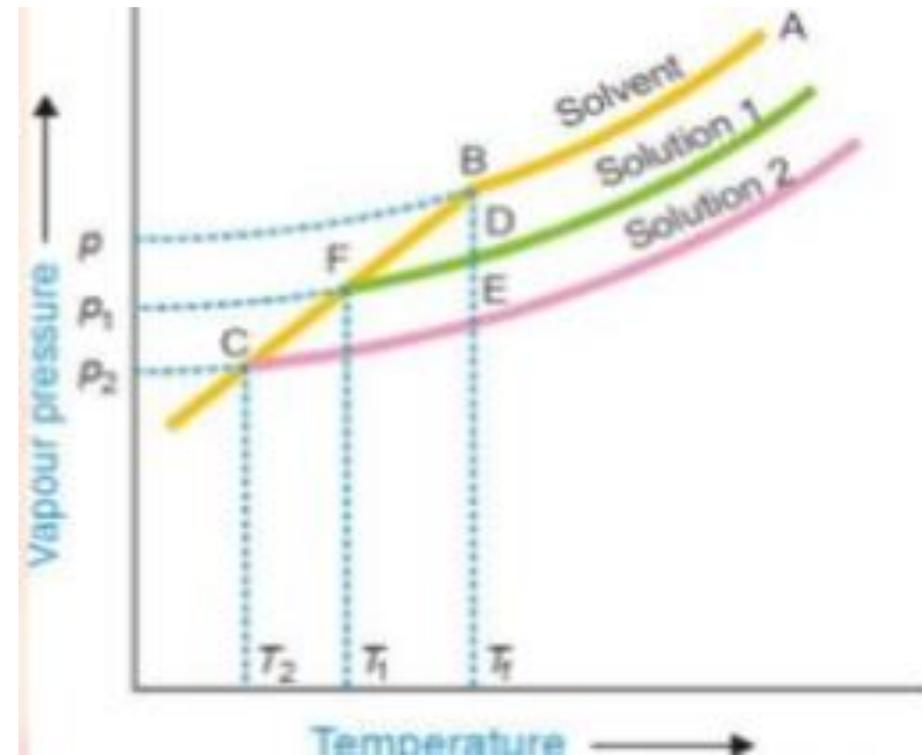
- On cooling it will follow the path DF. At F, the solid appears.

- Hence, F represents the freezing point , T_1, of the solution. Obviously, T_1 is less than T_t. The difference, called the depression in freezing point, ΔT_f is given by

- $$\Delta T_f = T_{t.} - T_1$$

- The depression in freezing point depends on the concentration of the solute in a solution and has been found to be related to molality, m as given :

- $\Delta T_f = K_f$ m where K_f is known as molal depression constant or cryoscopic constant of the solvent and m is the molality of the solution, i.e., the no. of moles of the solute dissolved in 1000 gm. of the solvent.

- If m = 1, $\Delta T_f = K_f$. Hence molal depression constant may be defined as the depression in freezing point when the molality of the solute is unity, i.e., one mole of the solute is dissolved in 1000 gm (1 Kg) of the solvent.

- The units are therefore degrees / molality, i.e., K/ m or K kg /mol.

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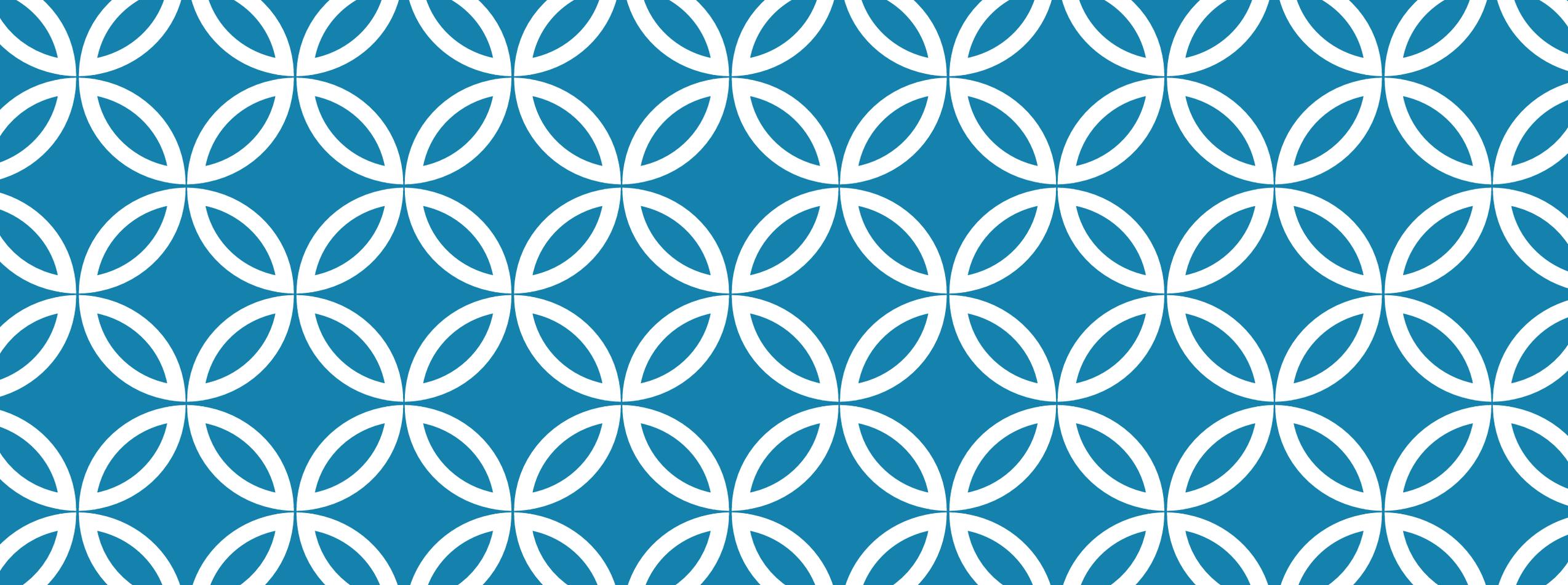
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AZEOTROPES

INTRODUCTION

- Such solution cannot be separated into components by fractional distillation as in contrast to ideal solutions with one component typically more volatile than others. If the mixture forms an azeotrope then vapour and liquid concentrations will be same that prevents the separation through simple approach.

- Azeotropes are mixtures of two or more different liquids which can either have a higher boiling point than either of the component or they can have a lower boiling point.

- Unlike azeotropes, ideal solutions have uniform mixtures of components. Ideal solutions always follow Raoult's law.

- Mixtures of benzene and toluene is good example of ideal solution.

- Azeotropes do not follow Raoult's law because during boiling, the ratio of components in solution and vapour is same.

- A binary mixture which boils at constant temperature have the same composition in vapour and liquid phase and distils over completely at the same temperature without any change in composition are called azeotropes.

Types of Azeotropes

1. Minimum boiling azeotropes
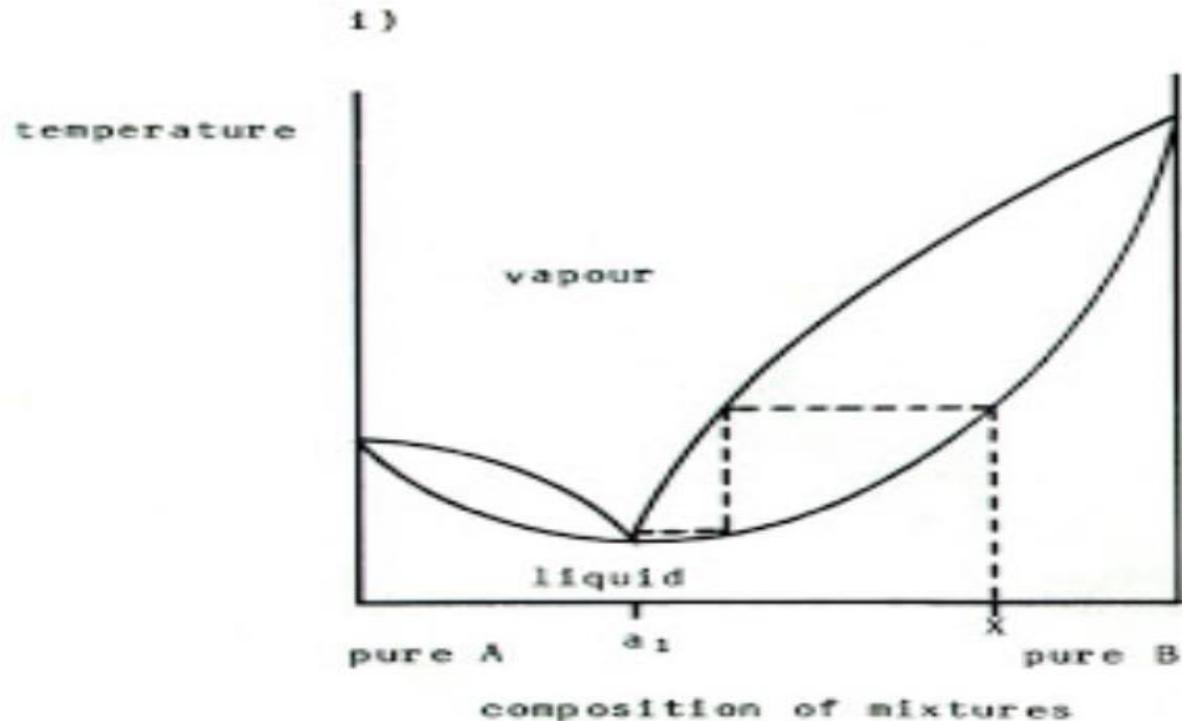
2. Maximum boiling azeotropes

Minimum boiling azeotropes

A solution that shows greater positive deviation from Raoult' s law forms a minimum boiling azeotrope at a specific composition.

For example, an ethanol – water mixture obtained by fermentation on fractional distillation yields 95% ethanol by volume.

Once this composition has been achieved, the liquid and vapour have the same composition , and no further separation occurs.

Boiling point of such solutions will be less than the two components due to weakening of inter molecular forces therefore such solutions are known as minimum boiling azeotropes.

i)

temperature

vapour

liquid

pure A   a₁   x   pure B

composition of mixtures

Maximum Boiling Azeotropes

 A solution that shows large negative deviation from Raoult's law form maximum boiling azeotrope at specific composition .

• It is due to strong attractive interaction between solute and solvent, less molecule will be vaporised and thus vapour pressure will be less and boiling temperature will be more.

• For example, HNO_3 (68%) and water 32(%) by mass form such type of azeotropes with boiling point 393.5 K

- On boiling a mixture of HNO_3 and water, vapour will be rich with any one of the component present in large amount in original solution but the remaining liquid will become an azeotrope.

- In general, a negative azeotrope boils at a higher temperature than any other ratio of its constituents.
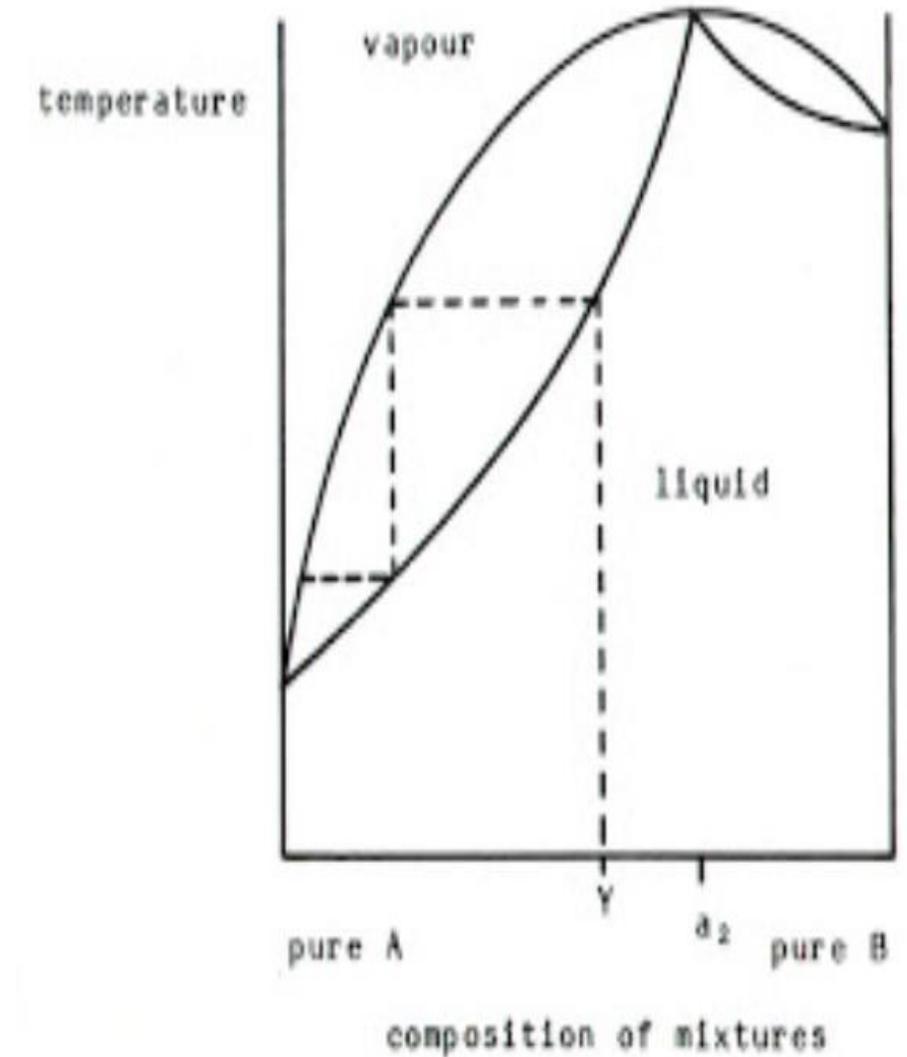
Methods of Separation of Azeotrope

1. Methods with no entrainer
- Pressure swing distillation

2. Methods with entrainer
- Homogenous azeotropic distillation
- Heterogenous azeotropic distillation
- Extractive distillation

Entrainer : substance / chemical that enhance the separation of azeotrope.

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TYPES OF ELECTRODE
PRIMARY AND SECONDARY ELECTRODES
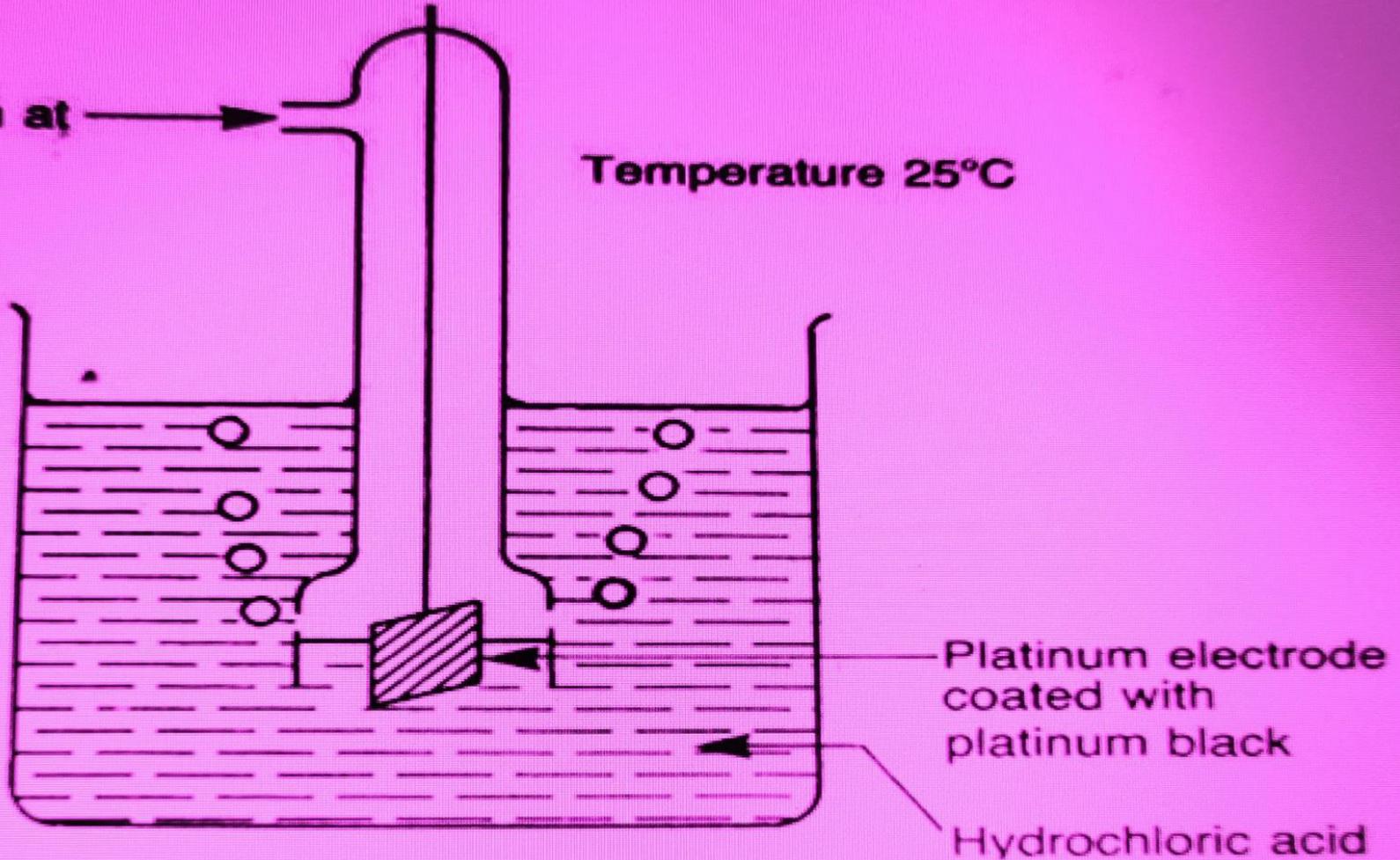
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GDC UDHAMPUR

PRIMARY REFERENCE ELECTRODE

- It is a electrode whose potential under standard conditions is to be defined exactly equal to zero.

- A standard Hydrogen Electrode(SHE) is referred to as primary standard electrode.

- It consist of Pt electrode, H_2 gas and H^+ ions in aqueous medium.

$$2H^+ + 2e^- \longrightarrow H_2$$

Hydrogen at 1 atm pressure

Temperature 25°C

Platinum electrode coated with platinum black

Hydrochloric acid

A standard hydrogen electrode (S.H.E.)

- Hydrogen electrode is the primary standard electrode.

- It consists of a small platinum strip coated with platinum black as to adsorb hydrogen gas.

- A platinum wire is welded to the platinum strip and sealed in a glass tube as to make contact with the outer circuit through mercury.

- The platinum strip and glass tube is surrounded by an outer glass tube which has an inlet for hydrogen gas at the top and a number of holes at the base for the escape of excess of hydrogen gas.

- The platinum strip is placed in an acid solution which has H^+ ion concentration 1 M.

- Pure hydrogen gas is circulated at one atmospheric pressure.

- A part of the gas is adsorbed and the rest escapes through holes. This gives an equilibrium between the adsorbed hydrogen and hydrogen ions in the solution.

The cell is represented as;

$$Pt_{(s)} H_{2(g)} \ 1\,atm / H^+_{(aq)} \ 1M$$

- In a cell when the standard hydrogen electrode acts as the anode, i.e oxidation takes place, the electrode reaction can be written as

$$H_2 \longrightarrow 2\,H^+ + 2e^-$$

- When the standard hydrogen electrode acts as cathode, i.e reduction takes place, the electrode reaction can be written as

$$2\,H^+ + 2e^- \longrightarrow H_2$$

- Based on the electrode potential obtained with reference to hydrogen, electrochemical series is obtained.

- The temperature of the cell is maintained at 25^0C. By international agreement the standard hydrogen electrode is arbitrarily assigned a potential of exactly $\pm\, 0.000$ . .. volt.

- The hydrogen electrode thus obtained forms one of two half-cells of a voltaic cell. When this half-cell is connected with any other half-cell, a voltaic cell is constituted. The hydrogen electrode can act as cathode or anode with respect to other electrode.

SHE half reaction	Electrode potential
$H_2 \rightarrow\ 2H^+ + 2e^-$	0.0 V (Anode)
$2H^+ + 2e^- \rightarrow\ H_2$	0.0 V (Cathode)

Limitations

- The standard Hydrogen electrode is difficult to set up.

- It is also difficult to handle.

- It cannot be used in the solution containing oxidising and reducing agent.

- It cannot be used also with unsaturated organic compounds and compounds containing sulphur and arsenic.

Need for Secondary Reference Electrode

The use of SHE is difficult, because it is difficult to maintain 1M H^+ion concentration and the pressure of the gas at one atmosphere. Also, the electrode will easily get poisoned in case of traces of impurities in the gas and hence, other reference electrodes are used.

SECONDARY REFERENCE ELECTRODE:

- It is a electrode whose potential is measured against standard hydrogen electrode and can be used to measure potential of other electrodes.

- e.g calomel electrode, silver – silver chloride and mercury- mercurous sulphate electrode.

- The calomel electrode is easy to work with and can be used in any solution.

- The saturated calomel Electrode (SCE)is represented as :

$$Hg\text{-}Hg_2Cl_{2(s)} \mid kCl_{\text{ sat.}}$$

Calomel Electrode

- It consists of a thin platinum wire sealed through a glass tube which is in contact with mercury and mercurous chloride paste(calomel).

- This tube is enclosed in a wider glass tube filled with KCI solution and provided with a porous plug at the base.

- The concentration of the KCl solution may be 1M, O.1M or saturated.

- The potential of the calomel electrode is varies with the concentration of KCl solution.
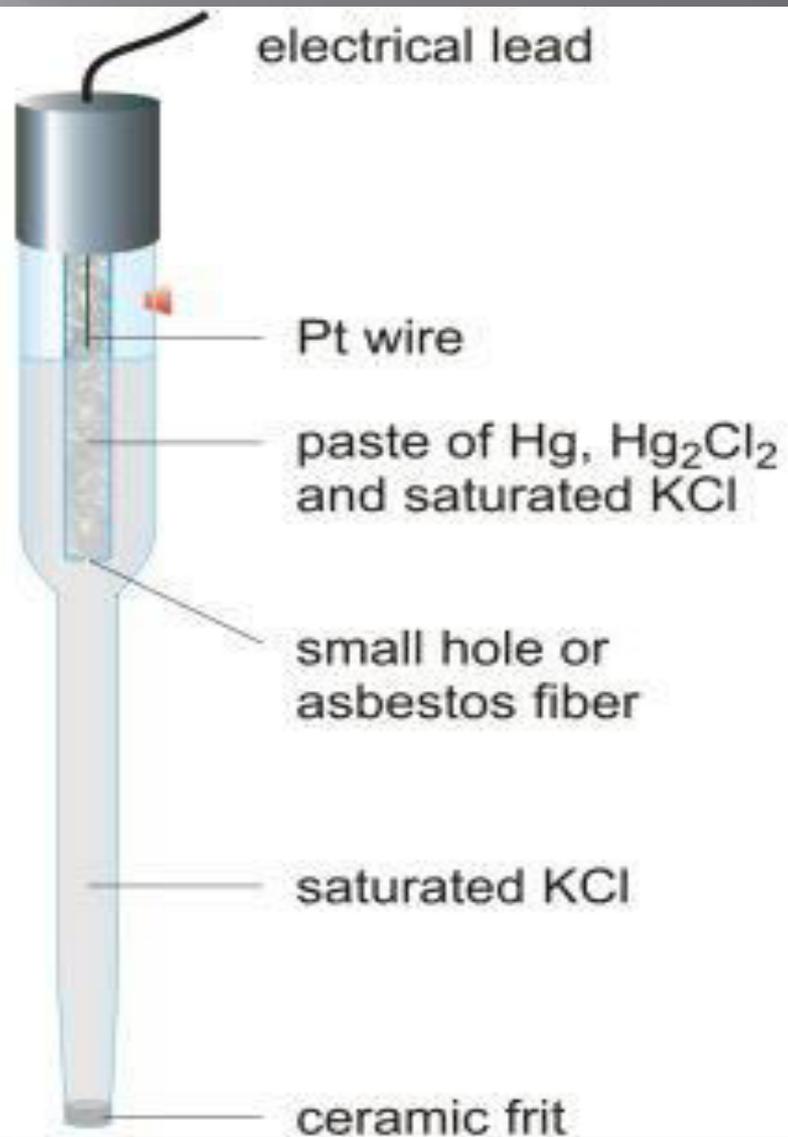
Calomel Electrode

- If potassium chloride solution is saturated, the electrode is known as saturated calomel electrode (SCE) and if the potassium chloride solution is 1 N, the electrode is known as normal **calomel electrode** (NCE) while for 0.1 N potassium chloride solution, the electrode is referred to as decinormal calomel electrode (DNCE).

The electrode reaction when the electrode acts as cathode is:

$$1/2\ Hg_2Cl_2 + e^- \rightleftharpoons Hg + Cl^-$$

The reduction potentials of the calomel electrodes on hydrogen scale at 298K are as follows:

Concentration of KCl	Reduction Potential
Saturated KCl	0.2415 V
1.0NKCl	0.2800 V
0.1NKCl	0.3338 V