## Colligative properties:

Depends on Number of particles of the solute present in solution.

Ex: i) Lowering of vapour pressure
ii) Osmatic pressure
iii) Depression of freezing point
iv) Elevation of boiling point.

relative Lowering of vapour pressure by Raoult's law.

Law: The relative Lowering of vapour pressure of a solution is equal to the mole fraction of the solute present in the solution.

$$P_1 = X_1 P_1^0$$

## Depression of freezing point

It is Used to estimate the molecular weight of the solute as

$$M_2 = \frac{k_f W_2 \, 1000}{\Delta T_f \, W_1}$$

## Elevation of boiling point:

It is Used to determine molecular Weight of solute as

$$\Delta T_b = \frac{W_2}{M_2} \frac{1000}{W_1} \frac{R T_o^2}{1000 \times l}$$

$$\boxed{\Delta T_b = m K_b}$$

## Abnormal molar Masses :-

When the solute associates (or) dissociates in solution such abnormal results are obtained.

→ Many 'Organic' solutes undergo 'association'. two or more molecules of the solute form a bigger molecules. The molar mass of solutes will be higher than true molar masses.

Ex

| solute | solvent | ab. molar mass | cal. molar mass |
|--------|---------|---------------|-----------------|
| $CH_3 COOH$ | $C_6 H_6$ | 118 | 60 |
| $C_6 H_5 COOH$ | $C_6 H_6$ | 242 | 122 |

→ Many 'inOrganic' acids, bases & salts undergo 'dissociation' in aqueous soln. due to dissociation the molar masses of solutes in such cases will be less.

Ex

| solute | solvent | ab. molar mass | cal. molar mass |
|--------|---------|---------------|-----------------|
| $KCl$ | $H_2O$ | 38.75 | 74.5 |
| $Na_2 SO_4$ | $H_2O$ | 49.84 | 142.0 |

## Van't hoff factor :

→ The ratio b/w the experimental value of colligative property & the theoretical value is known as Van't hoff factor $i$,

$$i = \frac{\text{Experimental colligative property}}{\text{Theoretical colligative property}}$$

→ ## Degree of Dissociation of solutes

$$\alpha = \frac{\text{Number of molecules dissociated}}{\text{Number of molecules dissolved}}.$$

→ ## Degree of Association of solutes

$$i = \frac{\text{Normal Molar Mass}}{\text{Observed molar Mass}} = \frac{1 - x + \frac{x}{n}}{1}.$$

## Henry's Law

The amount of a gas that dissolves in a given amount of liquid at constant temperature is proportional to the pressure of gas in equilibrium with the liquid.
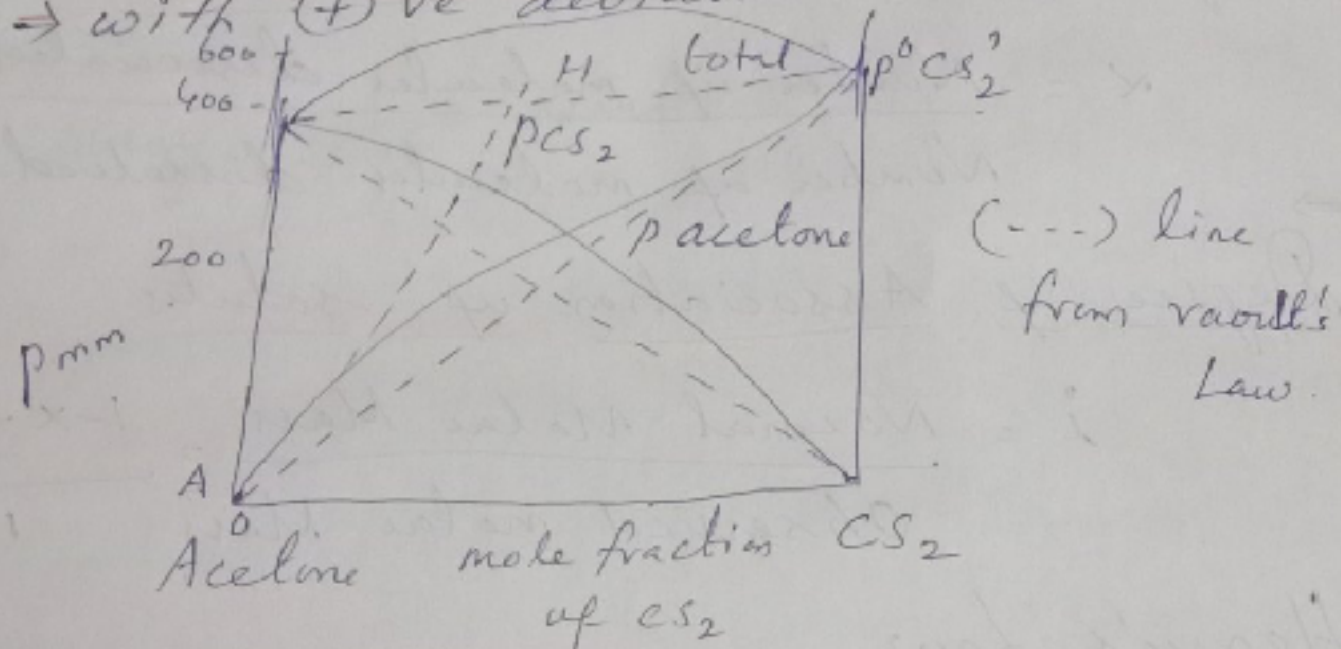
$$\boxed{W \propto P} \quad \text{or} \quad \boxed{W = kP}$$

# Deviation from henry's law :-

i) difference of molecular complexity in two phases.

ii) Compound formation b/w solvent & solute
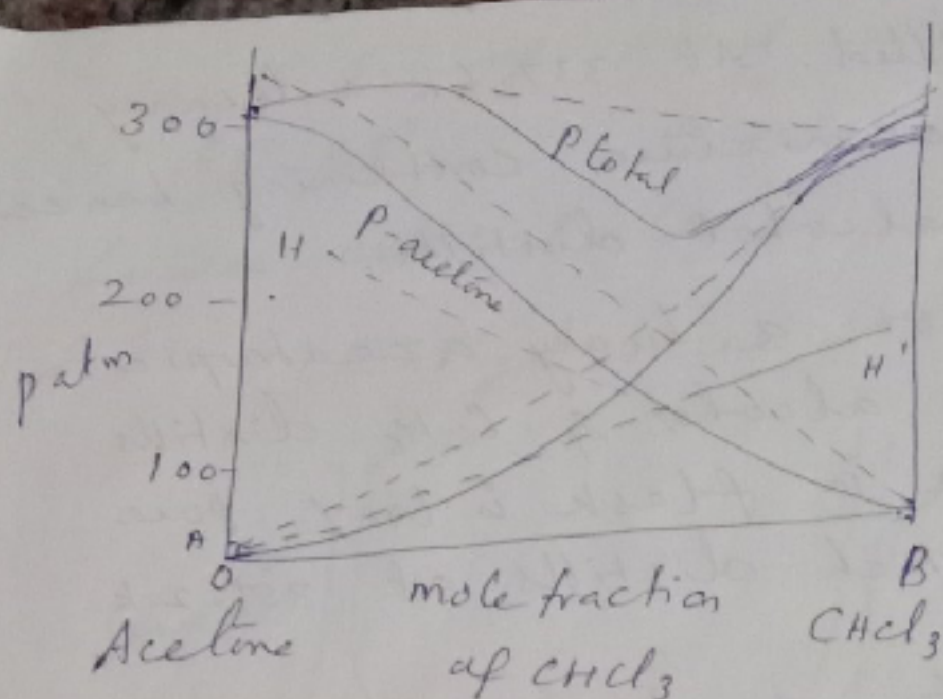
iii) ionisation

## Ex:1 Acetone – carbon disulphide

→ with (+) ve deviation.



Acetone    mole fraction of $CS_2$    $CS_2$

(---) line from raoult's Law.

→ partial 'p' are more than calculated from raoult's law. so exhibits (+) ve deviation.

→ total vapour pressure shows a maximum.

## Ex:2 Acetone – chloroform system – with (-) ve deviation from raoults law.

→ The vapour 'p' curves fall below the raoult's law predictions.

→ Total vapour 'p' has minimum value.

Reason for non ideal behaviour:

→ molecules in soln attract one another with unequal forces depending upon their individual nature.

⇒ If we have a non ideal soln of B' in A'. the inter molecular force b/w A' & A, B & B and A & B will not be equal.

## Azeotropic Distillation :

→ Azeotropic mixtures of suitable Components are mixed & distilled 100%. pure components, such distillation are called azeotropic distillation
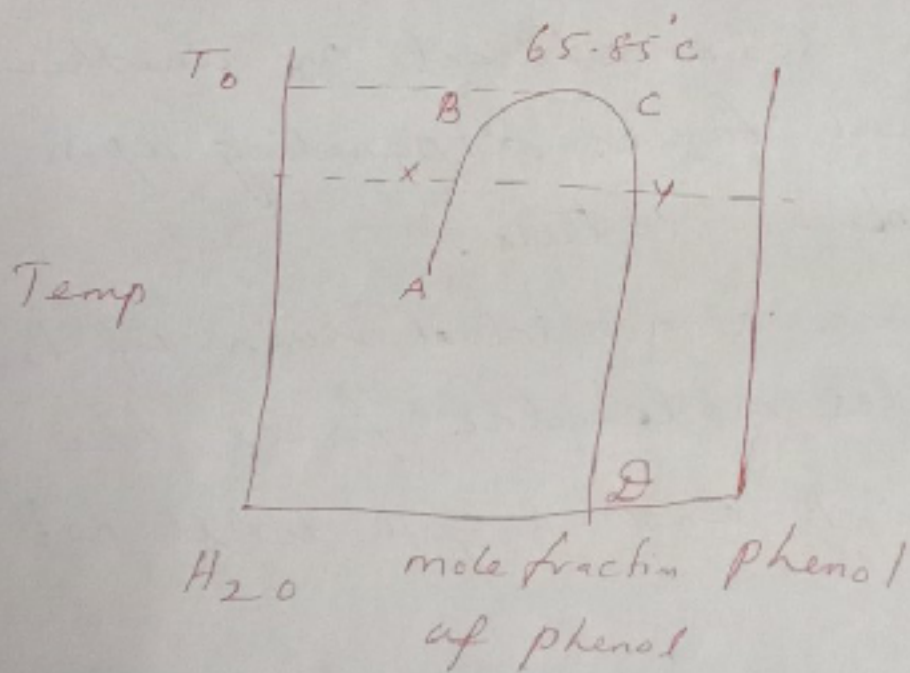
⇒ Ethyl alcohol & water form azeotropic mixture Containing 95.6% alcohol with boils at 351.2k. This is called rectified spirit. This is mixed with $C_2H_6$

⟹ And distilled. At 337.6K a ternary
azeotropic mixture containing benzene
water & alcohol distills.

⟹ At 340.8k a binary azeotropic
mixture of alcohol & $C_6H_6$ distills.

⟶ The residue in flask is 100% pure
ethanol which distills at 351.2k.

## Phenol – water system :-



To

65.85°C

B    C

--x--    --Y--

Temp        A

D

$H_2O$     mole fraction phenol
of phenol

⟶ The Area ABCD – system with two
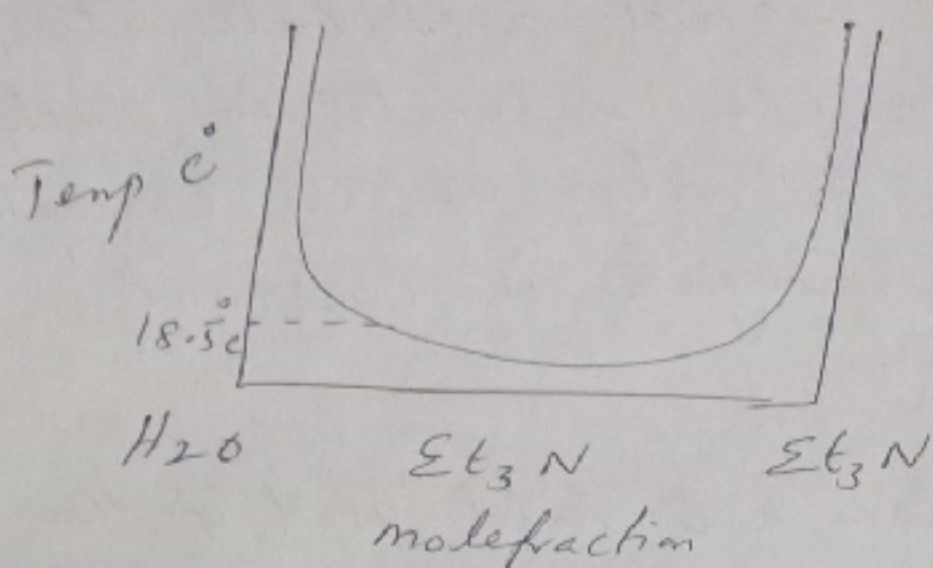layers.        (inside)

⟶ inside ABCD – One layer

⟹ outside of ABCD – One layer

⟹ The C.S.T; The temp at which
two partially miscible liquids become
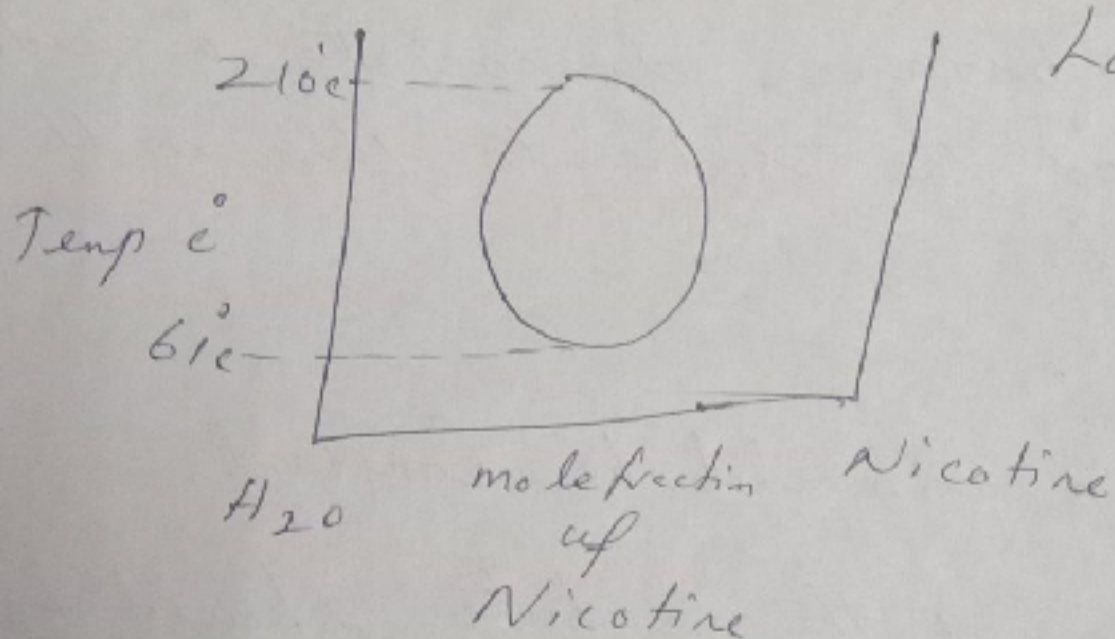Completely miscible is called CST –
critical solution temperature.

$\Rightarrow$ The C.S.T of phenol-water system
is 65.85°C.

$\rightarrow$ Lower critical temp

$Ex$ : Triethylamine — water system.

Temp °C

18.5°C

$H_2O$      $Et_3N$        $Et_3N$
molefraction

$\Rightarrow$ Nicotine — water system: it appear
Lower & upper
C.S.T.

210°C

Temp °C

61°C

$H_2O$     molefraction    Nicotine
              of
             Nicotine

## Immiscible liquids

A & B — two immiscible liquids

$P_A$ & $P_B$ — Vapour pressure

$P = P_A + P_B$ — Total vapour pressure.

$P_A V = n_A RT$

$P_B V = n_B RT$

# SOLUTIONS

A solution is a homogeneous mixture of two or more chemical substances. Therefore a solution forms a single phase. A solution may be gaseous, liquid or solid. A binary solution consists of two constituents. A ternary solution consists of three constituents. A quarternary solution consists of four constituents. The constituents of a solution are classified as solvent and solute. A solvent is that constituent which is present to a larger extent in the solution. A solute is that constituent which is present to a smaller extent in the solution. The following are some examples for the kinds of solutions.

## Gaseous solutions :

Gas mixtures. Eg. : $CO_2 + N_2$.

## Liquid solutions:

i. A gas dissolved in a liquid. E.g. $CO_2$ in water.
ii. A liquid dissolved in a liquid. E.g., Alcohol in water.
iii. A solid dissolved in a liquid Eg., NaCl in water.

## Solid solutions:

i) A gas dissolved in a solid, Eg., $H_2$ in palladium; $N_2$ in titanium.
ii) A liquid dissolved in a solid. Eg., Mercury in gold.
iii) A solid dissolved in a solid. Eg., Copper in gold, zinc in copper and many alloys.

## DEFINITION OF IDEAL SOLUTION

Just as we have the concept of ideal gas, we have the concepts of ideal solution also. Ideal gas has no inter molecular forces of attraction. So when there is a change in volume, there is no change in the internal energy. This postulate cannot hold good for the condensed phases namely liquids and solids.

What is it / Definition: In an ideal solution, the molecules in the solution attract one another with equal force irrespective of their nature. If we have an ideal solution of B in A, the forces between A and A, B and B, and A and B should be the same.

The total volume of an ideal solution will be the sum of the volumes of its constitutents. That is total volume of an ideal solution=Volume of A + volume of B. No heat is evolved or absorbed on mixing the constituents of an ideal solution.

## DEFINITION OF NON IDEAL SOLUTIONS

In a non ideal solution, the molecules in the solutions attract one another with unequal forces depending upon their individual nature. If we have a non-ideal solution of B in A, the forces between A and A, B and B, and A and B will not be the same. The total volume of the solution will not be the sum of the volumes of the constituents. That is, the total volume of the solution ≠ volume of A+volume of B. Heat will be either absorbed or evolved on mixing the constituents. E.g., $H_2SO_4+H_2O$.

### Reason for deviation form ideal behaviour :

The reason for deviation from ideal behaviour is the fact that the molecules in the solution attract one another with unequal forces depending upon their individual nature. If we have a non ideal solution of B in A, the inter molecular forces between A and A, B and B and A and B will not be equal.

## CONCENTRATION UNITS

The amount of solute dissolved in a unit volume, say $1m^3$ of solvent is called concentration. There are several ways of expressing the concentration of a solution. The different terms usually used are molality, molarity, activity and activity co-efficients. These are the various concentration units that we use in connection with solutions.

### Molality

The molality of solution is defined as the number of moles of solute dissolved in one kilogram of a solvent. It is denoted by $m$.

$$m = \frac{1000W_B}{M_B W_A}$$

Here, $m$=molality, $W_A$ = Weight of solvent; $W_B$=Weight of solute and $M_B$=Molecular weight of the solute.

### Molarity

The molarity of a solution is defined as the number of moles of solute dissolved in $1dm^3$ of solution (one litre of solution). It is denoted by M.

$$M = \frac{\text{Total number of moles}}{\text{Volume } (dm^3)}$$

$$= \frac{W_B}{M_B} \times \frac{1}{V(dm^3)}$$

where, M=Molarity; $W_B$=weight of solute $M_B$= Molecular weight of solute and V is the volume of the solution in $dm^3$ (in litres).

## Formality (F)

Formality or formal strength of a solution signifies the number of gram-formula weights of the solute present per litre of solution.

A symbol F is used to denote formality. Since, on increasing the temperapture of a solution its volume increases while the quantity of the solute remains unchanged, the formality of a solution decreases as its temperature rises.

In volumetric estimations the concentrations are expressed in normality. Normality of a solution is the number of gram equivalents of the solute present per litre of the solution. It is denoted by the symbol N.

## Mole Fraction

The mole fraction of a solute in a solution is the ratio of number of moles of the solute present in the solution to the total number of moles of the solute and the solvent present in the solution. It $n_2$ moles of a solute are dissolved in $n_1$ moles of a solvent then the mole fraction of the solute in the solution is given by

$$x_2 = \frac{n_2}{n_1 + n_2}$$

## ACTIVITY AND ACTIVITY CO - EFFICIENTS

Many of the gaseous or liquid systems are found to be non-ideal. How to deal with these non-ideal systems? These systems are handled conveniently using the concept of fugacity and activity, first introduced by G.N. Lewis.

## Activity (a)

The activity of any substance taking part in chemical equilibrium is a measure of its effective concentration in the equilibrium system.

The effective concentration or activity 'a' is defined differently in different cases.

In the case of gases the activity is a mere number and equal to its partial pressure in atmospheres.

In the case of an ideal solution, the activity is a mere number and is equal to the concentration of the solute expressed in moles per litre.

In the case of any solid the activity remains constant.

The standard state of a substance is defined as the state at which its activity is equal to one. The above definitions of activity are true for ideal systems only. For non-ideal systems the term activity co-efficient is introduced. *The activity co-efficient γ is a measure of the extent of deviation from ideality.*

For an ideal gas the activity is equal to its pressure that is a = P. For real gases, activity is only proportional to its pressure.

$$a \,\alpha\, P ; \qquad i.e., \quad a = \gamma P$$

where γ is the activity co-efficient. [The activity is also defined as the ratio of fugacity to pressure. i.e.,

$$\gamma = f / P$$

Thus when P = 1 then γ = f.

Fugacity is the true measure of the escaping tendency of a component in solution.

Similarly for ideal dilute solutions the activity is equal to its concentration.
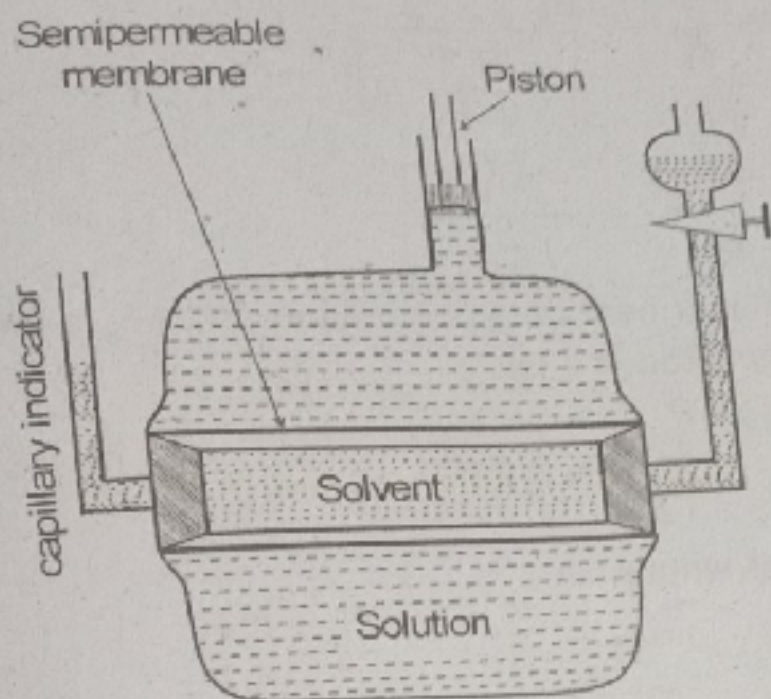
$$a = C$$

For non-ideal solutions, the activity is only proportional to concentration.

$$a \,\alpha\, C ; \quad i.e., \quad a = \gamma C$$

where γ is the activity co-efficient.

**3.  Berkeley and Hartley's method :**

The apparatus consists of a porous pot containing copper ferrocyanide deposited on its walls. The porous pot is surrounded by a bronze cylinder fitted with a piston. Solvent is taken in the porous pot and the solution is taken in the jacket. Water placed in the porous pot tends to pass into the solution through the semipermeable membrane. Due to this the water level in the capillary indicator tends to fall. Now sufficient pressure is applied on the piston so that the level of water in the capillary is maintained at the original level. The maximum pressure applied is the osmotic pressure of the Solution.



Figure

## ELEVATION OF BOILING POINT

The boiling point of a solution is more than the boiling point of the pure solvent. This is a consequence of the lowering of the vapour pressure. We can derive an expression for the relationship between the elevation of boiling point ($\Delta T_b$) and the mole fraction of the solute ($x_2$).

## THERMODYNAMIC DERIVATION

The Clapeyron-Clausius equation is

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_v}{R} \left[ \frac{T_2 - T_1}{T_2 T_1} \right]$$

In this equation $T_1$ and $T_2$ may be replaced by $T_0$ and $T$ the boiling points of the solvent and solution respectively. $P_2$ and $P_1$ may be replaced by $P_0$ and $P$, the vapour pressures of the solvent and the solution respectively.

$$\ln \frac{P_0}{P} = \frac{\Delta H_v}{R} \left[ \frac{T - T_0}{TT_0} \right]$$

when the solution is dilute $T$ will be nearly equal to $T_0$ then $TT_0 = T_0^2$

So

$$\ln \frac{P_0}{P} = \frac{\Delta H_v}{R} \left[ \frac{T - T_0}{T_0^2} \right]$$

i.e., 

$$\ln \frac{P_0}{P} = \frac{\Delta H_v}{R} \frac{\Delta T_b}{T_0^2} \qquad (7)$$

where $\Delta H_v$ is the molar heat of vapourisation and $\Delta T_b$ is the elevation of boiling point. From Raoult's law

$$\frac{P}{P_0} = x_1 = 1 - x_2 \qquad (8)$$

Equation (7) can be written as

$$-\ln \frac{P}{P_0} = \frac{\Delta H_v}{R} \cdot \frac{\Delta T_b}{T_0^2}$$

Substituting the value of $\dfrac{P}{P_0}$ from eqn. (8)

$$-\ln (1-x_2) = \frac{\Delta H_v}{R} \cdot \frac{\Delta T_b}{T_0^2} \qquad (9)$$

Expansion of $-\ln(1-x_2)$ in this series

$$-\ln (1-x_2) = x_2 + \frac{x_2^2}{2} + \frac{x_2^3}{3} + \ldots\ldots$$

Neglecting the higher powers in the series

$$-\ln (1-x_2) \approx x_2 \qquad (10)$$

Substituting (10) in (9)

$$x_2 = \frac{\Delta H_v}{R} \cdot \frac{\Delta T_b}{T_0^2} \quad \text{or} \quad \Delta T_b = \frac{x_2 R T_0^2}{\Delta H_v} \qquad (11)$$

We know that $x_2 = \dfrac{n_2}{n_1 + n_2} = \dfrac{n_2}{n_1} = \dfrac{W_2 M_1}{M_2 W_1}$

Substituting in equation (11)

$$\Delta T_b = \frac{W_2}{M_2} \cdot \frac{M_1}{W_1} \cdot \frac{R T_0^2}{\Delta H_v} \qquad (12)$$

$\dfrac{\Delta H_v}{M_1} = 1$, the latent heat of vapourisation of one gram of the solvent. Then (12) becomes

$$\Delta T_b = \frac{W_2 R T_0^2}{M_2 W_1 1} \qquad (13)$$

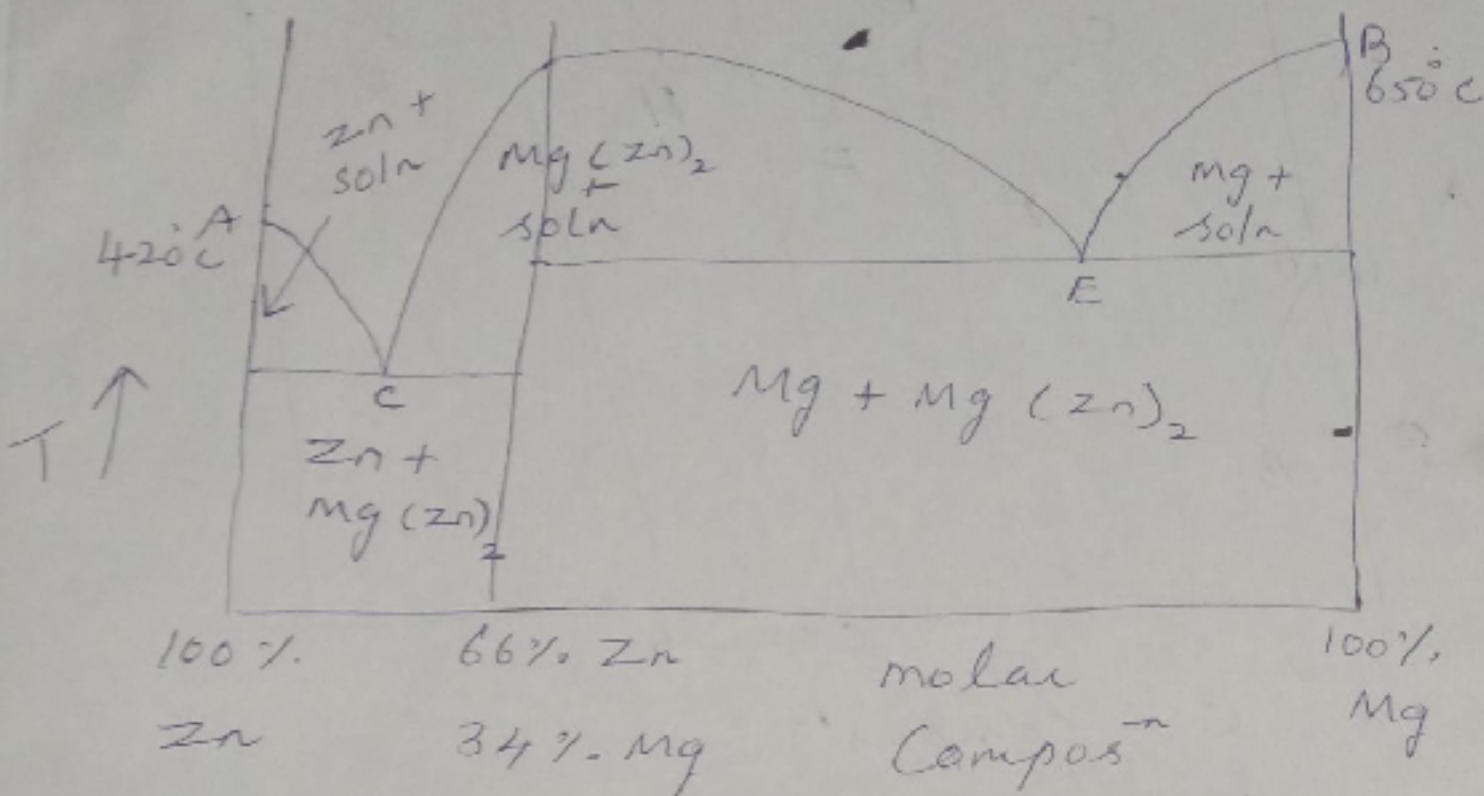Multiplying and dividing the equation (11) by 1000

$$\Delta T_b = \frac{W_2}{M_2} \cdot \frac{1000}{W_1} \cdot \frac{R T_0^2}{1000 \times 1} \qquad (14)$$

$$\Delta T_b = m K_b \qquad (15)$$

'm' is the molality of the solution. $K_b$ is the molal elevation constant or ebulioscopic constant. From equation (16) the molecular weight of the dissolved solute can be determined as

## Mg - Zn System



Diagram labels:
- B 650°C
- A 420°C
- Zn + soln
- Mg (Zn)₂ + soln → $Mg(Zn)_2 + soln$
- Mg + soln
- E
- C
- Zn + Mg(Zn)₂ → $Zn + Mg(Zn)_2$
- Mg + Mg(Zn)₂ → $Mg + Mg(Zn)_2$
- T ↑

Bottom axis:
- 100% Zn
- 66% Zn, 34% Mg
- molar Compositⁿ
- 100% Mg

⟹ 'A' represent melting point of A (Zn)

B' " " " B (Mg)

⟹ D — m.p of AB $(Mg(Zn)_2)$

⟹ AC — variation of m.p. of A' on addⁿ of B'
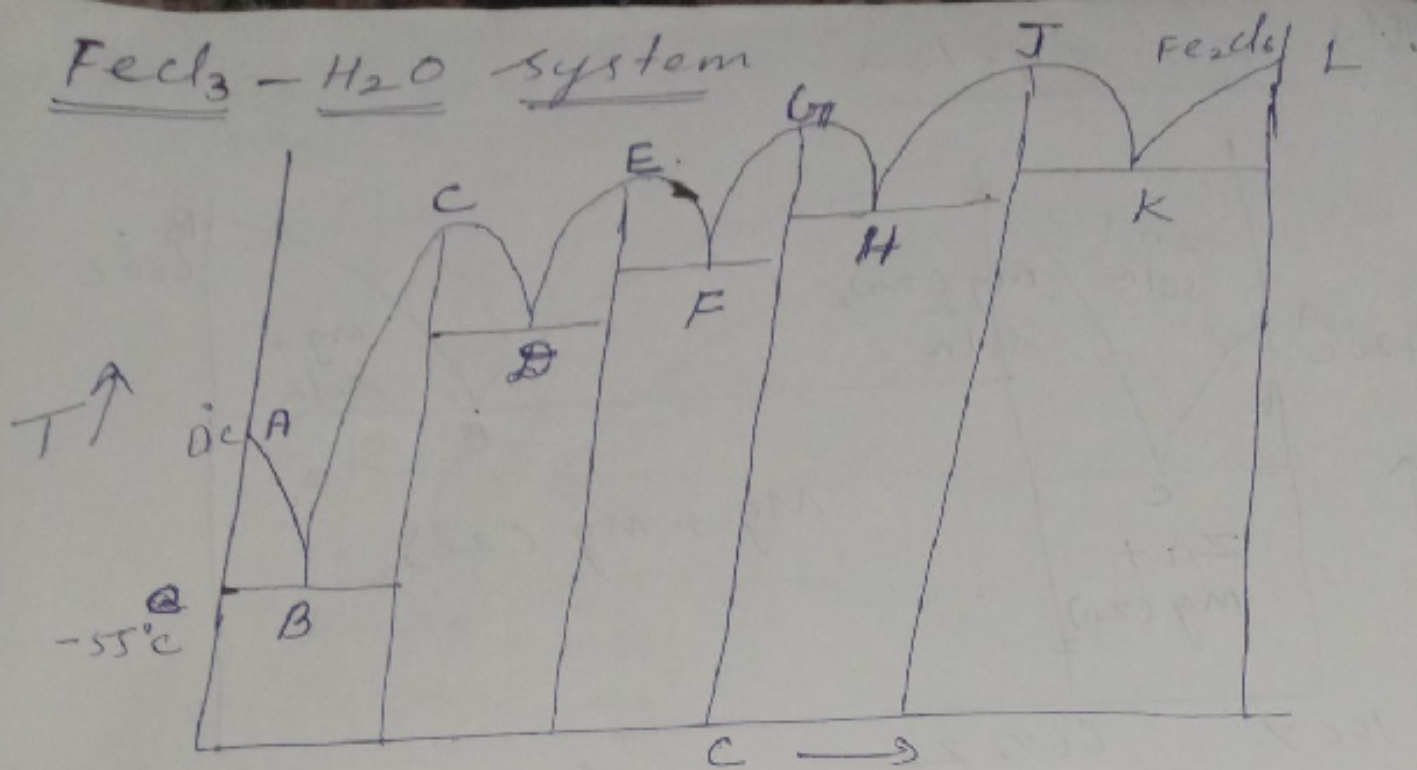
BE — " " B on addⁿ of A'

⟹ Eutectic point : C

Solid A, AB & liquid are equilibrium

⟹ degree of freedom
$$F = C - P + 1 = 2 - 3 + 1 = 0$$

no variant.

# $FeCl_3 - H_2O$ system



$$C - compos^n$$
$$T - Temperature$$

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

point $D \Rightarrow Fe_2Cl_6 \cdot 7H_2O$ seperate out.

$DEF \Rightarrow$ Solubility curve of $Fe_2Cl_6 \cdot 7H_2O$

$E \Rightarrow$ Congruent melting point of $Fe_2Cl_2 \cdot 7H_2O$

$F \Rightarrow Fe_2Cl_6 \cdot 5H_2O$ separates out.

$FGH \Rightarrow$ solubility curve of $Fe_2Cl_6 \cdot 4H_2O$

$G \Rightarrow$ Congruent m.p of $Fe_2Cl_6 \cdot 4H_2O$.

$H \Rightarrow Fe_2Cl_2 \cdot 4H_2O$ separates out

$HJK \Rightarrow$ solubility curve of $Fe_2Cl_6 \cdot 4H_2O$

$J \Rightarrow$ Congruent melting m.p of $FeCl_2 \cdot Cl_6 \cdot H_2$

$K \Rightarrow$ Anhydrous ferric chloride separates out.

$KL \Rightarrow$ Solubility curve of the anhydrous $FeCl_3$