

Unit: 2PROPERTIES OF SOLUTION

Phase :

Any homogeneous part of a system having all physical and chemical properties same throughout is called a phase.

- It is that region of material that is chemically, uniformly, physically distinct and often mechanically separable.
- In a phase, particles are uniformly distributed.

A system with single phase is homogeneous mixture system whereas particles having more than one phase is heterogeneous mixture system.

- According to phase rule, a uniform part of a system in equilibrium is called a phase.

Eg: (i) All pure substance = 1 phase

(ii) Mixture of gases = 1 phase

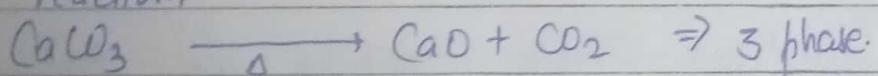
(iii) Aqueous solⁿ = 1 phase

(iv) Mixture of miscible liquid = 1 phase

(v) Mixture of non-miscible liquid = 2 phase.

(vi) Mixture of two allotropes = 2 phase.

(vii) In reaction,



Phase equilibrium

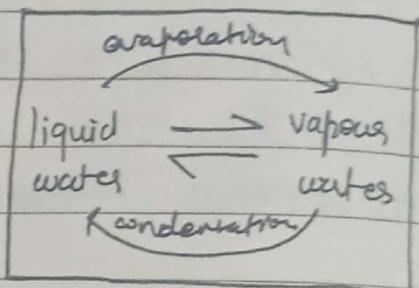
The state of equilibrium when there is no net conversion of one phase to another phase is called phase equilibrium.

Eg: Liquid water (l.p) \rightarrow Water vapour (l.p)

In this system, the liquid water converts to vapour and after vapour is collected, the vapour converts to liquid water. At one stage, these two processes reach at equilibrium, which is known as phase equilibrium.

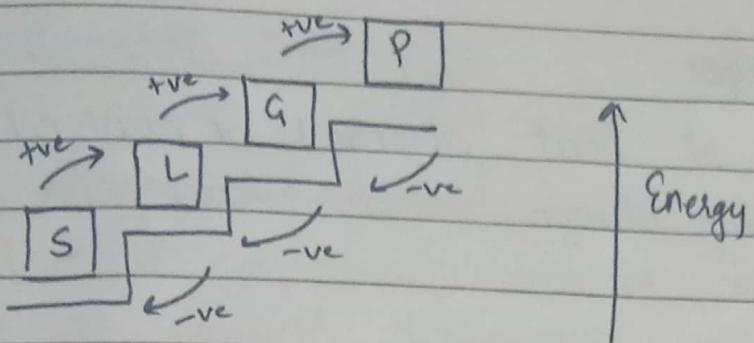
Here,

there is no net conversion of phases. ie,
phase equilibrium is obtained.



Energetics of Phase Changes

- > System: Any part of the universe which is under investigation.
- > Surrounding: External entities that may affect the behaviour of the system.
- > Boundary: Simple imaginary line that separates system from surrounding.



Whenever a system changes from one phase to another, there is change in energy during conversion known as energetics of phase change.

→ We need energy for phase transformation.

Explanation:

In solid, the molecules are strongly binded together by strong inter-molecular force. Hence, to overcome this force and to expand the substance to liquid, heat energy must be provided to overcome that force.

Again, when liquid is converted to gas, there is still inter-molecular force that has to be overcome to convert to gas. This is done by providing heat energy.

The same process is undergone to convert gas to plasma.

Thus, to convert to a state of higher energy from lower energy, heat is absorbed and to convert to state of lower energy from higher energy heat is released.

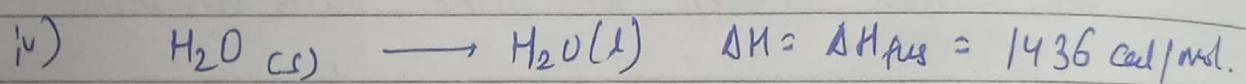
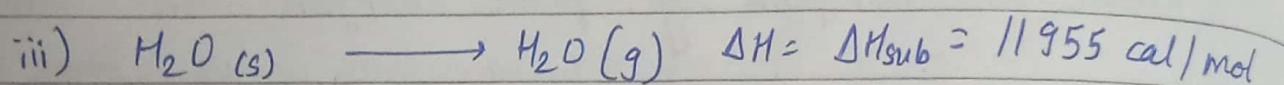
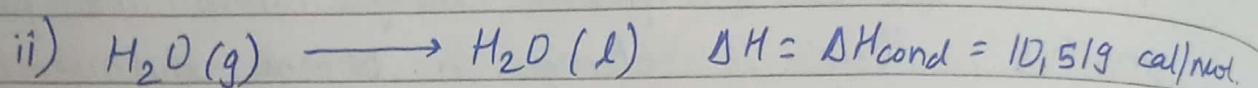
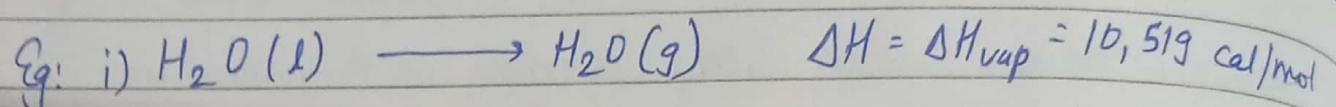
Q) Define the phase / phase equilibrium. Describe the energetic phase change in suitable examples.

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•) Enthalpy change:

Amount of heat absorbed or evolved by a system in any change which takes place at constant pressure.

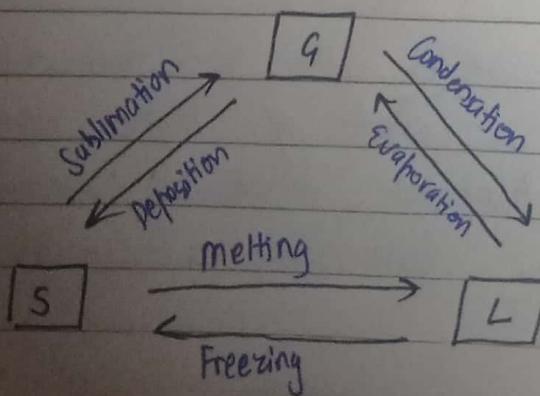


So, $\Delta H_{\text{sub}} = \Delta H_{\text{fusion}} + \Delta H_{\text{vap}}$.

$\therefore \Delta H_{\text{fus}} < \Delta H_{\text{vap}}$

Here, we can conclude,

relatively small energy is required to convert solid to liquid in comparison to the energy required to convert liquid to gas as the inter-molecular force has to be completely overcome to become gas.



Liquid-vapour Equilibrium

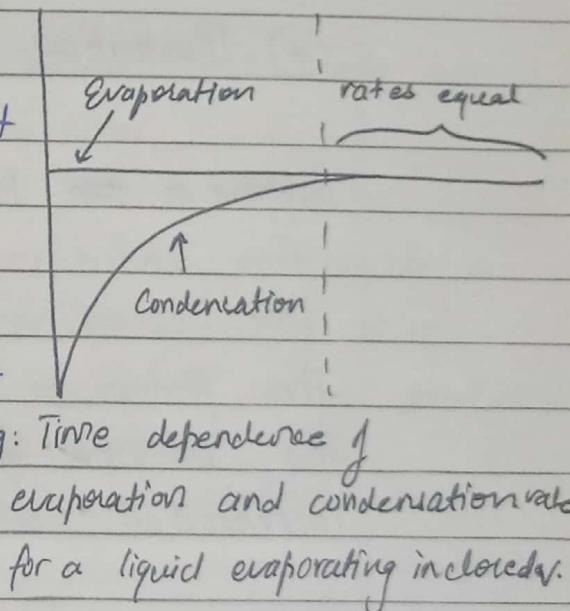
Consider liquid water and water vapour. When this is kept in a closed container. If the system is placed at constant temperature, after certain time rate of vapourization = rate of condensation

i.e., the system will be in equilibrium

i.e., the number of vapour molecules which enter into liquid per unit time = the number of liquid molecules which escape into vapour per unit time.

In the open vessel, the vapour molecules escape and equilibrium can't be achieved.

In a closed evacuated vessel, the liquid molecules on the surface start to evaporate immediately. Initially, the rate of condensation = zero.



As long as temperature remains constant, evaporation continues at constant rate and number of vapour molecules in VP increases.

When large vapour molecules be in contact with liquid, they collide to each other and come back to liquid via, condensation.

Eventually,

the rate of evaporation becomes equal to the rate of condensation.

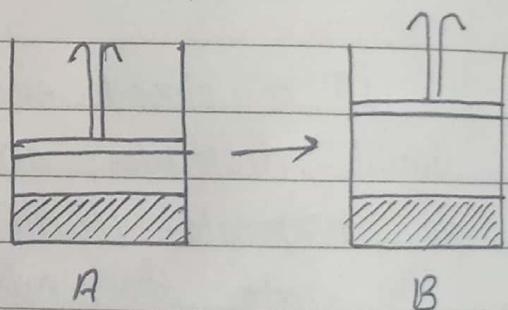
This is liquid-vapour equilibrium.

At equilibrium, evaporation and condensation processes do not stop but the vapour pressure is constant because two opposite process occurs at equal rates.

Hence, phase equilibrium is dynamic in nature.

* Illustration of l-v equilibrium by movable piston.

Suppose a ~~sq~~ liquid-vapour system is in equilibrium at A.



The piston is pulled up and the volume for vapour is increased at constant temperature.

Here,

- Vapour molecule/unit volume is lowered which lowers vapour molecule collision/unit volume
- So, rate of evaporation > rate of condensation.

After certain time, rate of evaporation = rate of condensation.
Thus, phase equilibrium is achieved.

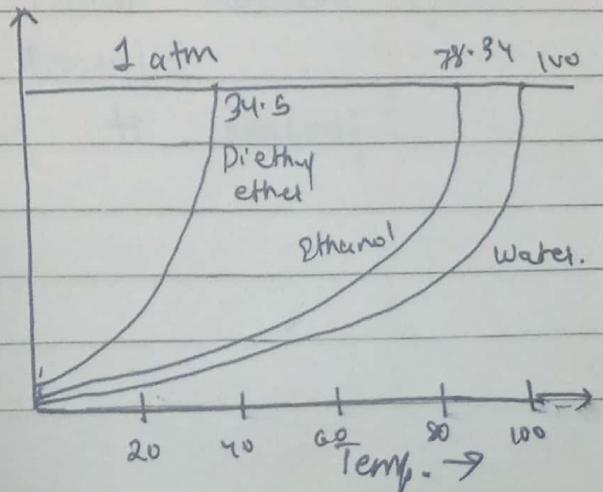
Features of Liquid-Vapour Equilibrium

- (i) Equilibrium in molecular system is dynamic and is a consequence of the equality of the rates of opposing reactions.
- (ii) A system moves spontaneously towards a state of equilibrium. If a system initially at equilibrium is perturbed by some changes in its surroundings, it reacts in a manner which restores it to equilibrium.
- (iii) The nature and properties of an equilibrium state are the same, regardless of how it is reached.
- (iv) The condition of a system at equilibrium represents a compromise between two opposing tendencies: the drive for molecules to assume the state of lowest energy and the urge to attain maximum entropy.

Temperature Dependence of Vapour Pressure

* Vapour pressure:

Vapour pressure of a liquid is defined as the pressure exerted by its vapour when it is at equilibrium with the liquid at a given temperature.



Different liquids have different vapour pressure at particular temperature.

The equilibrium vapour pressure of a liquid depends upon the temperature.

* Boiling point:

The temperature at which the equilibrium vapour pressure becomes equal to one atm. pressure is called normal boiling temperature or the boiling point.

* Volatile liquid:

A liquid that evaporates readily at normal temperature is known as volatile liquid.

i.e., The liquid that escape into vapour phase.

- They have very high vapour pressure.

* V.P. as the function of temperature

Vapour pressure & Temperature

According to the graph, as vapour pressure increases with increase in temperature.

Different liquids have different vapour pressure at particular temperature.

*) Bubble formation:

In the At boiling temperature, bubbles of vapour form throughout the bulk of the liquid. In order to form and grow bubbles, the pressure of vapour inside liquid must be equal or more than the pressure exerted on it by the liquid.

*) Bumping:

When bubble formation occurs in a superheated liquid, it produces almost explosive violence.

Here, the vapour pressure in any bubble formed greatly exceeds atmospheric pressure and bubbles tend to expand rapidly. Such violent boiling is called bumping.

It can be avoided by adding porous pieces of ceramic materials.

Q7): Define vapour pressure. Discuss the formation of bubbles during the heating of any liquid.

Q7): Vapour pressure is a function of temperature. Explain this statement.

Solution:

The homogeneous mixture of two or more substances at molecular or ionic level is called solution.

$$\text{ie, } \text{Solution} = \text{Solute} + \text{Solvent}$$

The constituent present of mixture present in a smaller amount is called solute.

The constituent present in larger amount is called solvent.

* Types of Solution:

State of solute	State of solvent	Examples
i) Gas	Gas	Air
ii) Gas	Liquid.	O_2 in H_2O , CO_2 in H_2O .
iii) Gas	Solid	Adsorption of He by palladium
iv) Liquid	Liquid	Alcohol in water.
v) Liquid	Solid	Mercury in silver.
vi) Solid	Liquid	Sugar, salt soln
vii) Solid	Solid	Metal alloys, C in iron.

Concentration of a solution

The amount of solute present in a given amount of solution.

i.e., conc. of soln = $\frac{\text{quantity of solute}}{\text{volume of soln}}$

(i) % by weight = $\frac{\text{wt. of solute} \times 100\%}{\text{wt. of soln}}$

(ii) % by mass/volume = $\frac{\text{vol. of solute} \times 100\%}{\text{vol. of soln}}$

(iii) $X_{\text{solute}} (\underline{n_1}) = \frac{\text{Moles of solute}}{\text{Moles of solute + moles of solvent}} = \frac{n_1}{n_1 + n_2}$

$X_{\text{solvent}} (\underline{n_2}) = \frac{\text{moles of solvent}}{\text{moles of solute + moles of solvent.}} = \frac{n_2}{n_1 + n_2}$

$$X_{\text{solute}} + X_{\text{solvent}} = 1$$

(iv) Molarity (M) = $\frac{\text{moles of solute}}{\text{volume of litres}} = \frac{\text{moles of solute}}{\text{volume (in ml)}} \times 1000$

(ii) Temperature dependent)

(v). Molality (m) = $\frac{\text{moles of solute}}{\text{mass of solvent in kg}} = \frac{\text{mass of solute}}{\text{mass of solvent in gm}} \times 1000$
 $(\because \text{weighing out must be done})$

(vi) Formality (F): The no. of gram formula weight of solute per litre.

(vii) Normality (N):

The number of gram equivalent weight of solute in one litre of solution.

*) Some Formulae

$$(i): \gamma. (w/v) = \frac{g/L}{10}$$

$$(ii): \gamma. (w/w) = \frac{g L^{-1}}{10 \times \text{sp.gravity}}$$

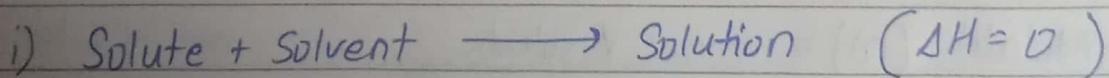
$$(iii): M = \frac{\gamma. (w/v) \times 10}{\text{Molar wt.}}$$

$$(iv): M = \frac{\gamma. (w/w) \times \text{sp.gravity} \times 10}{\text{Molar wt.}}$$

$$(v): X = \frac{M \times \text{Mol.wt} \times \text{volume in cc}}{1000}$$

Ideal Solution:

The solutions that can be formed from their components with no evolution or absorption of heat is called ideal solution.

*) Properties:

$$\text{ii) } P_{\text{solvent}} = P_1 = P_1^0 x_1 = P_1^0 \left(\frac{n_1}{n_1 + n_2} \right)$$

$$\text{iii) } P_{\text{solute}} = P_2 = P_2^0 x_2 = P_2^0 \left(\frac{n_2}{n_1 + n_2} \right)$$

(iii) Each and every component of ideal solution obeys Raoult's law.

(iv) Total volume of solution = Volume of solute + volume of solvent.

(v): Interparticle force of attraction is equal.

$$\text{ie, Solute-Solvent} = \text{Solute-Solute} = \text{Solvent-Solvent}$$

(vi): Solution tends to ideal only at low concentration.

Eg: Ethanol & Propanol, Benzene & Toluene.

Q.1: Determine the concentration of sodium chloride solution in molarity, molality. if 15 gm of NaCl is dissolved in 60 gm of water.

Soln;

Given,

$$\text{wt g NaCl} (w_1) = 15 \text{ gm}$$

$$\text{Mol wt g NaCl} (MW_1) = 58.5$$

$$\text{wt g water} (w_2) = 60 \text{ gm}$$

$$\text{Mol wt g water} (MW_2) = 18$$

$$\begin{aligned}\text{wt g soln} &= (15 + 60) \text{ gm} \\ &= 75 \text{ gm}\end{aligned}$$

Now,

$$(i) \text{ No. of moles of NaCl} = \frac{w_1}{Mw_1} = \frac{15}{58.5} = 0.256$$

$$(ii) \text{ No. of moles of water} = \frac{w_2}{Mw_2} = \frac{60}{18} = 3.33$$

$$(iii) \text{ Molality} = \frac{\text{No. of moles of NaCl}}{\text{mass of solvent in gm}} \times 1000 \\ = \frac{0.256}{60} \times 1000 \\ \therefore m = 4.267$$

$$\text{Density } (D) = 0.995$$

$$\text{So, } \frac{\text{wt. of soln}}{\text{volume}} = 0.995$$

$$\text{or, } \frac{75}{0.995} = V \quad \therefore V = 75.37 \text{ ml}$$

$$(iv) \text{ Molarity} = \frac{\text{No. of moles of solute}}{\text{Volume of soln in ml}} \times 1000 \\ = \frac{0.256}{75.37} \times 1000$$

$$\therefore M = 3.39$$

Colligative Properties

The properties of solution that depends on the number of dissolved solute particles and not the size, charge and other properties of dissolved particles is called colligative properties.

- These properties are dependent on concentration.

The four properties are as follows:

- i) Lowering of Vapour Pressure / Relative lowering of VP of Raoult's law?
- ii) Elevation of Boiling point
- iii) Depression of Freezing point
- (iv) Osmotic pressure.

(i): Lowering of Vapour Pressure / Relative lowering of vapour Pressure of Raoult's law?.

The vapour pressure of the pure solvent depends on the number of molecules evaporating from its surface.

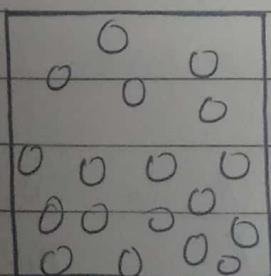


Fig: Pure solvent

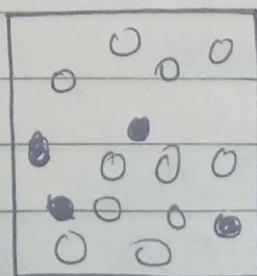


Fig: Soln Having
non-volatile solution

Let ' P_o ' be the vapour pressure of the pure solvent.

Let us consider a solution composed of non-volatile solute in a volatile solvent. This blocks a fraction of a surface for evaporation. Due to this, evaporation doesn't occur throughout the surface.

Let ' P_s ' be the vapour pressure of the solution and ' X_1 ' be the mole fraction of solvent.

We know,

$$P_s \propto X_1$$

$$\text{or } P_s = k \cdot X_1$$

$$\text{or, } P_s = k \cdot \left(\frac{n_1}{n_1 + n_2} \right) \quad \text{--- (i)}$$

For pure solvent, $n_2 = 0$

So,

$$P_s = k \cdot 1 = P_o$$

The proportionality constant 'k' is equal to the vapour pressure of the pure solvent.

Then,

Eqn (i) becomes

$$P_s = P_o \frac{n_1}{n_1 + n_2}$$

$$\text{or, } \frac{P_s}{P_o} = \frac{n_1}{n_1 + n_2} \quad \text{--- (ii)}$$

Here, $\frac{P_s}{P_o}$ is the ~~solute~~ mole fraction of solvent.

This is one statement of Raoult's law. It states that, "the vapour pressure of the dilute solution is equal to the product of the ^{vapour} pressure of the pure component and mole fraction of the solvent at particular temperature.

$$\text{Mole fraction of solute } (X_2) = 1 - X,$$

$$= 1 - \frac{n_1}{n_1 + n_2}$$

$$\text{or, } 1 - X_2 = \frac{n_1}{n_1 + n_2} \quad (\text{iii})$$

So, eqⁿ (ii) can be written as,

$$\frac{P_s}{P^0} = 1 - X_2 \quad \therefore X_2 = 1 - \frac{P_s}{P^0}$$

$$\text{or, } \left(\frac{P_0 - P_s}{P_0} \right) = X_2 \quad \text{or, } \frac{\Delta P}{P_0} = X_2 \quad (\text{iv})$$

Here, $\Delta P \rightarrow (P_0 - P_s)$ is the lowering of vapour pressure and $\Delta P/P_0$ is the relative lowering of vapour pressure.

So,

eqⁿ(iv) can be written as,

$$\Delta P = P_0 \left(\frac{\frac{w_2}{Mw_2}}{\frac{w_1}{Mw_1} + \frac{w_2}{Mw_2}} \right) \quad (\text{v})$$

$$\text{Here, } P_1 = P^0 X_1$$

$$\therefore \text{Total VP} = P_1 + P_2 + \dots$$

$$P_2 = P^0 X_2$$

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Eqⁿ (iv) is Raoult's law.

Raoult's law states that, "the relative lowering of vapour pressure of a dilute solution is equal to the mole fraction of the non-volatile component present in the dilute solution."

Ideal solution strictly obeys Raoult's law.

Real solution don't obey Raoult's law.

(ii) Elevation of Boiling point:

* Boiling point: The temperature at which the vapour pressure is equal to ~~atmos~~ 1 atm pressure is called boiling point.

When non-volatile solute is mixed with volatile solvent, the vapour pressure lowers and the boiling point elevates.

* Elevation of boiling point:

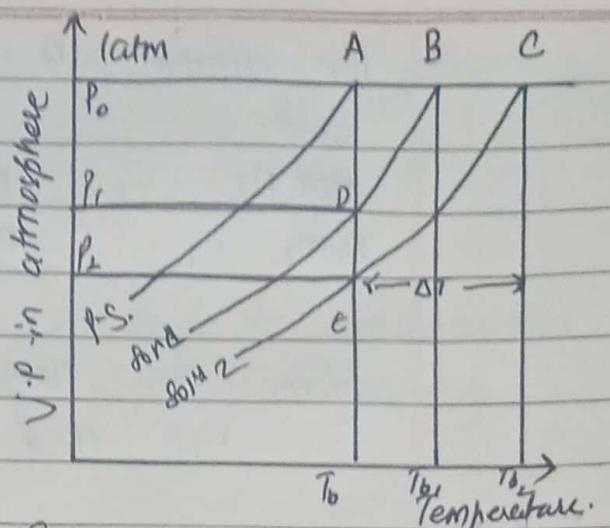
The temperature by which the boiling point of a solution rises than that of its pure solvent to make its vapour pressure equilibrium with atmospheric pressure is called elevation of boiling point.

Let ' T_b ' = boiling point of pure solvent

' T ' = boiling point of solution

' ΔT_b ' = elevation of boiling point

$$\therefore \Delta T_b = T - T_b$$



Here, the figure shows the vapour pressure curves of the pure solvent and soln (1) and soln (2) with different solute concentration.

fig: Relation between elevation of BP and lowering of VP.

If $BD \parallel CE$ and st. lines approximately, ΔACE and ΔABD are similar triangles.

So,

$$\frac{AB}{AC} = \frac{AD}{AE} \quad \text{or,} \quad \frac{T_1 - T_b}{T_2 - T_b} = \frac{P_0 - P_1}{P_0 - P_2} \quad \text{--- (i)}$$

Here, we can observe
 $\Delta T_b \propto \Delta P$ --- (ii)

According to Raoult's law, $\Delta P \propto X_2$ --- (iii)

So from eqn (ii) and (iii);

$$\Delta T_b \propto X_2 \quad \text{--- (iv)}$$

if K_b' is proportionality constant, then,

$$\Delta T_b = K_b' \cdot X_2 \quad \text{or} \quad \Delta T_b = K_b' \times \left(\frac{n_2}{n_1 + n_2} \right) \quad \text{--- (v)}$$

For dilute soln; $n_2 \ll n_1$

So,

$$\frac{n_2}{n_1+n_2} = \frac{n_2}{n_1} = \frac{w_2}{MW_2} \times \frac{MW_1}{w_1}$$

Here, n_2 = no. of moles of solute
 n_1 = no. of moles of solvent

So, eqn (v) becomes,

$$\Delta T_b = K_b \cdot \left(\frac{w_2}{MW_2} \times \frac{MW_1}{w_1} \right) \quad \text{--- (vi)}$$

We know,

$$1000 \cdot K_b = K_b' \cdot MW_1$$

\approx , So,

$$\Delta T_b = K_b \cdot \left(\frac{w_2}{MW_2 \times w_1} \right) \times 1000$$

$$\Delta T_b = K_b \times \left(\frac{w_2/MW_2}{w_1} \right) \times 1000$$

From the definition of molality, $m = \frac{(w_2/MW_2)}{w_1} \times 1000$

$$\therefore \Delta T_b = K_b \times m \quad \text{--- (vii)}$$

Here, K_b = molal boiling point constant.

Molar boiling point constant is defined as the boiling point elevation produced when one mole of solute is dissolved in one kg solvent.

Here, eqn(vi) shows ΔT_b is related to concentration.
Hence, elevation of boiling point is colligative property.

$$\therefore K_b \text{ of water} = 0.51.$$

(iii) Depression of freezing point:

* Freezing point: The temperature at which the first crystals of the solvent appear when the solution is cooled is called freezing point.

When non-volatile solute is mixed into volatile pure solvent, the free vapour pressure of solution is lowered and the freezing point is also lowered.

* Depression of Freezing point:

The temperature by which the freezing point of a solution drops than that of its pure solvent is called depression of freezing point.

Let T_f = freezing point of pure solvent

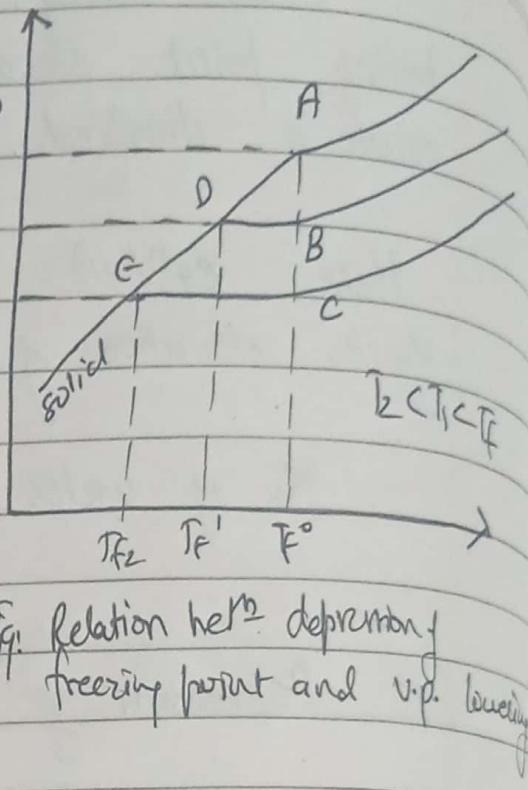
\bar{T} = freezing point of solution

ΔT_f = Depression of freezing point

$$\therefore \Delta T_f = T_f - \bar{T}$$

Here, the figure shows the vapour pressure curves of the

pure solvent and solution (1) & (2) with different concentration of solute.



for dilute soln, $BD \parallel CE$ & $g\cdot l$ lines approximately. Hence.

$\triangle ACE$ and $\triangle ABD$ are similar triangles.

So,

$$\frac{BD}{CE} = \frac{AB}{AC}$$

$$\text{or } \frac{\bar{T}_f - T_f^1}{T_f - T_f^2} = \frac{P^0 - P_1}{P^0 - P_2} \quad -(i)$$

Here, we can observe,

$$\Delta T_f \propto \Delta P \quad -(ii)$$

According to Raoult's law,

$$\Delta T_f \propto \Delta P \propto X_2 \quad -(iii)$$

So, from eqn (ii) and (iii),

$$\Delta T_f \propto X_2 \quad -(iv)$$

if ' K_f' ' is proportionality constant then,

$$\Delta T_f = K_f' \cdot X_2$$

$$\text{or, } \Delta T_f = K_f' \cdot \left(\frac{n_2}{n_1 + n_2} \right) - (v)$$

Since, for dilute soln $n_2 \ll n_1$,

so,

$$\frac{n_2}{n_1 + n_2} = \frac{n_2}{n_1} = \frac{w_2}{MW_2} \times \frac{MW_1}{w_1}$$

So, eqn (v) becomes,

$$\Delta T_f = K_f' \cdot \frac{w_2}{MW_2} \times \frac{MW_1}{w_1} - (vi)$$

We know,

$$1000 \times K_f = K_f' \times MW_1$$

so,

$$\Delta T_f = 1000 \times K_f \times \left(\frac{w_2}{MW_2 \times w_1} \right)$$

$$\text{or } \Delta T_f = K_f \times \left(\frac{w_2/MW_2 \times 1000}{w_1} \right)$$

From the definition of molality, $m = \frac{w_2/MW_2}{w_1} \times 1000$

so,

$$\Delta T_f = K_f \times m - (vii)$$

Here

ΔK_f = molal freezing point constant.

Molal freezing point constant is defined as the freezing point depression produced when 1-mol of solute is dissolved in 1 kg of solvent.

Here, eqn(vii) shows that ΔT_f is related to concentration. So, the depression in freezing point is a colligative property.

$$1 \text{ Kf of water} = 1.86$$

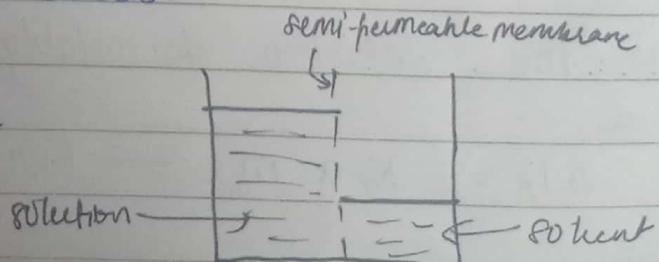
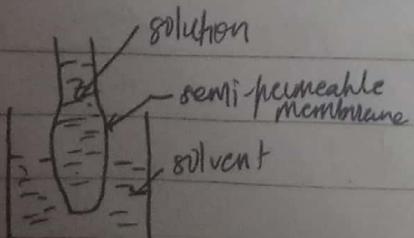
(iv) Osmotic pressure:

* Semi-permeable membrane:

The membrane that has pores large enough to allow passage of small solvent molecules but small enough to prevent the flow of high solute from passing through it is called semi-permeable membrane.

* Osmosis:

The spontaneous flow of solvent molecules from pure solvent to the solution, or from dilute solution to concentrated solution is called through semi-permeable membrane is called osmosis.



Osmotic pressure continues until osmotic pressure becomes equal to the hydrostatic pressure. i.e., the flow of solvent molecule stops and system reaches equilibrium after the solution rises to certain height.

* Osmotic pressure (Π)

The hydrostatic pressure built upon the solution or external pressure applied to the solution in order to just stop the pure solvent into solution through semi-permeable membrane is called osmotic pressure.

Vant Hoff equations for solution:

→ Boyle's Vant Hoff law:

It states that osmotic pressure is directly proportional to molar concentration of solution at constant temperature.

$$\text{or, } \Pi \propto \frac{n}{V} \quad \text{--- (i)}$$

→ Charles Vant Hoff law:

It states that osmotic pressure is directly proportional to the absolute temperature of solution at constant pressure.

$$\text{or, } \Pi \propto T \quad \text{--- (ii)}$$

Combining (i) & (ii); we get

$$\Pi \propto \frac{n}{V} T$$

$$\text{or, } \Pi V = nRT \quad \text{--- (iii)}$$

Here,

$$R = \text{universal gas constant} = 0.082 \text{ lit.atm / mol}$$

from eqn (iii),

$$\pi V = nRT$$

$$\text{or } \pi V = \frac{MW_2}{MW_1} RT \quad (\text{iv}).$$

\therefore

Now, at Also,

$$\pi L = \frac{n}{V} RT$$

$$\text{or, } \pi L = C RT$$

i.e., $\pi \propto C$ at constant temperature.

Hence, at constant temperature, the osmotic pressure is directly proportional to the concentration of the solution.

So, osmotic pressure is also a colligative property.

Solution of Two Volatile Compounds.

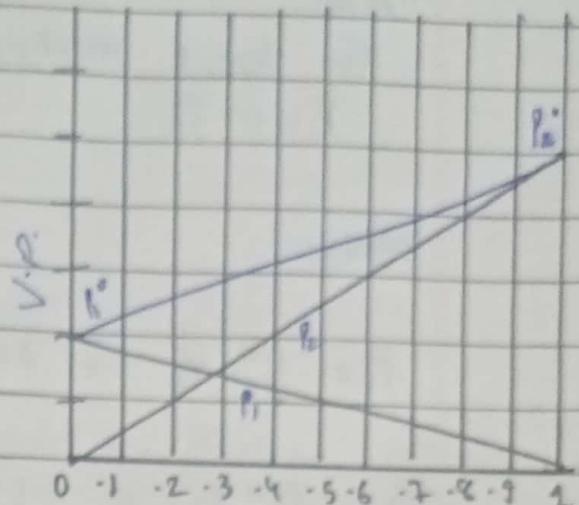
Let us consider an ideal solution of two volatile compounds.

Then, according to Raoult's law,

$$P_1 = P_1^{\circ} x_1 \quad \text{--- (i)}$$

and

$$P_2 = P_2^{\circ} x_2 \quad \text{--- (ii)}$$



So, the total pressure of the solution is $P_T = P_1^{\circ} x_1 + P_2^{\circ} x_2$

At a certain temperature, the system attains the state of equilibrium. i.e., $\nabla P = \text{constant}$.

$$\text{So, mole fraction of 1} = \frac{P_1}{P_T}$$

$$\text{mole fraction of 2} = \frac{P_2}{P_T}$$

(Q.2): Calculate the composition of two components in vapour. from the given data on liquid.

1 is benzene

$$P_1^{\circ} = 75 \text{ mm}$$

$$X_1 = 0.33$$

2 is toluene.

$$P_2^{\circ} = 22 \text{ mm}$$

$$X_2 = 0.67$$

Sol:

Given,

For liquid mixture.

$$X_1 = 0.33$$

$$X_2 = 0.67$$

Now,

$$P_1 = P_1^{\circ} \cdot X_1 = 75 \times 0.33 = 24.75 \text{ mm}$$

$$P_2 = P_2^{\circ} X_2 = 0.67 \times 22 = 14.74 \text{ mm}$$

So,

$$\begin{aligned} P_T &= P_1 + P_2 = 24.75 + 14.74 \\ &= 39.49 \text{ mm} \end{aligned}$$

Now,

composition of vapour:

$$X'_1 = \frac{P_1}{P_T} = \frac{24.75}{39.49} = 0.63$$

$$X'_2 = \frac{P_2}{P_T} = \frac{14.74}{39.49} = 0.37$$

Again,

$$P_1'' = P_1^{\circ} \cdot X'_1 = 75 \times 0.63 = 47.25 \text{ mm}$$

$$P_2'' = P_2^{\circ} \cdot X'_2 = 22 \times 0.37 = 8.1 \text{ mm}$$

$$\therefore P_T'' = 47.25 + 8.1 = 55.35 \text{ mm}$$

So, mole fraction ie, composition of new vapour.

$$X_1'' = \frac{P_1''}{P_T''} = \frac{47.25}{55.35} = 0.854$$

$$X_2'' = \frac{P_2''}{P_T''} = \frac{8.1}{55.35} = 0.146.$$

The repetition of this ^{two} process tends to produce vapour nearly pure benzene and a liquid that is very nearly pure toluene.

Non-ideal solutions

The solution accompanied by evolution or absorption of heat during its formation and that which don't obey Raoult's law are called non-ideal solutions.

*) Types of Non-ideal solutions:

(i): Non-ideal solution showing negative deviation from Raoult's law

- The components in the solution are found to have lower energy than in their pure states.
- Accompanied by evolution of heat
- Occurs when there is strong attractive force between unlike molecules than like molecules of the same kind.
- VP is less than ideal solution of the same components.

Eg: Evolution of acetone and chloroform.

Let us consider a mixture of the components acetone and chloroform. The dissolution is accompanied by the evolution of heat.

So, each component is in lower energy than the ideal level. due to strong opposite attraction between the opposing molecules than the molecules of the same kind.

Here, the oxygen of acetone forms hydrogen bond with the hydrogen of chloroform. This is because acetone lacks pure hydrogen and chloroform lacks pure hydrogen to form bond with its themselves.

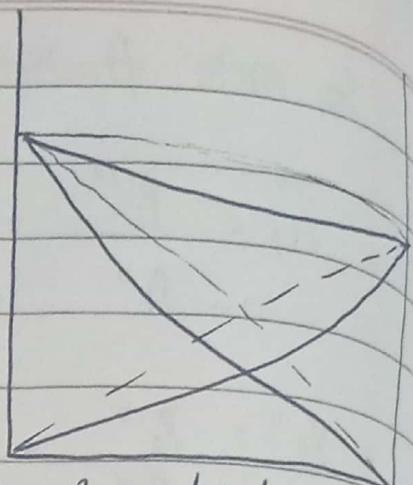
At this condition, the component of the mixture is at lower energy state and they have vapour pressure of the evolution is less than that of an ideal solution of the same component.

So, they show lesser tendency to escape into the vapour. since the components are polar and have higher force of attraction.

(iii) Non-ideal solution showing positive deviation from Raoult's law:

- The components in the solution are found to have higher energy than in their pure states.
- accompanied by absorption of heat

Fig: VP as a function of composition of acetone-chloroform solution



- Occurs between when there is weaker attractive forces between unlike molecules than the molecular of the same kind.
- Vapour pressure of solution is greater than that of the predicted from Raoult's law.

Eg: Soln of acetone and carbon-disulphide.

Let us consider a mixture of the components of acetone and carbon disulphide. This dissolution is accompanied by the absorption of heat.

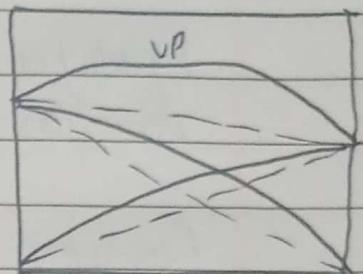


Fig: VP as a function of composition of acetone - carbon disulphide solution

So, each component is in higher energy state than the ideal level due to lack of attraction between the opposing molecules.

Here, although acetone has the polar O-atom, CS_2 lacks polar hydrogen atom to form polar bond between the molecules.

Since the mixture is non-polar, they show greater tendency to escape into vapour as the components are in higher energy state and their vapour pressure is higher than that predicted by Raoult's law.

Azeotropic mixture

The mixture that boils at constant composition and that cannot be separated from each other is called azeotropic mixture.

Azeotropes having minimum boiling points show positive deviation from Raoult's law.

Azeotropes having maximum boiling points show negative deviation from Raoult's law.

Solubility

The solubility of a substance in a particular solvent at a given temperature is the concentration of solute in saturated solution at that temperature.

i) Factors affecting solubility:

- i) Nature of solute and solvent
- ii) Condition of temperature and pressure.

ii) Effect of temperature on solubility:

Change in temperature affects solubility.

i) If $\Delta H_{\text{solution}} = +\text{ve}$ i.e., endothermic, solubility increases with increase in temperature.

ii) If $\Delta H_{\text{solution}} = -\text{ve}$, i.e., exothermic, solubility of solute decreases with increase in temperature.