LIQUID SOLUTION

CONCEPT OF VAPOUR PRESSURE

When a pure liquid is kept in closed vessel (in which no air is present) the liquid evaporates to give the vapours. After sometime a dynamic equilibrium is established between liquid and vapours. *The pressure that the vapours exert at equilibrium on the walls of the container or on the surface of the liquid is called the vapour pressure of the liquid at that temperature*, Figure (a).

Case 1:

What would happen to the vapour pressure of the liquid if we take a bigger container, Figure (b) or a wider container, Figure (c).
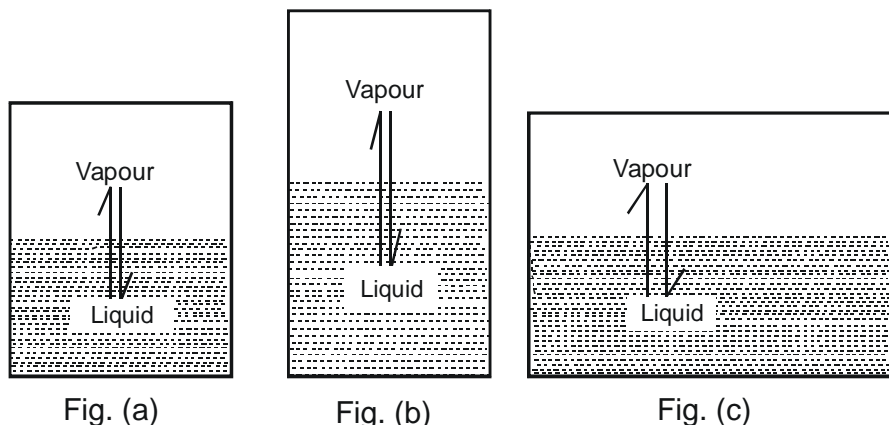

Fig. (a)   Fig. (b)   Fig. (c)

Key concept:

When the liquid is in equilibrium with vapours,   Liquid $\rightleftharpoons$ Vapours, the K_p of the system is $K_p = P_v$, where P_v is the vapour pressure. We know that Kp for a given chemical equilibrium is a constant and only depends on temperature. Therefore the vapour pressure of the liquid is a constant and does not depend on the nature of the vessel used and that it only depends on temperature.

Case 2:

Take a vessel with the same liquid as in case 1 and cover it with a glass plate (of negligible weight) having a hole in it. Would the vapour pressure be the same now?
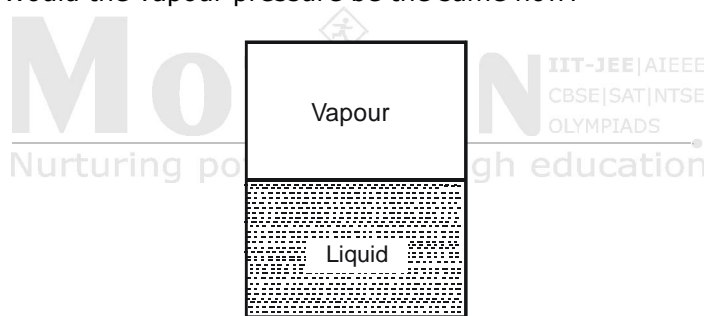
Key concept:

Well, the liquid system is the same and the temperature is also same. Therefore the vapour pressure should be same. The vapour pressure of a liquid is independent of the surface area exposed on top of the liquid surface provided the surface area exposed should not be zero.

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TYPE OF SOLUTIONS

Solutions can have continuously variable compositions, and they are homogeneous on a scale beyond the size of individual molecules. This definition can be used to cover a wide variety of systems, including ordinary solution such as alcohol in water or $HClO_4$ in benzene and even solution of large proteins in aqueous salt solutions. It is also useful sometimes to consider some colloidal suspensions undergoing Brownian motion as solutions, and there are solid solutions where one solid is uniformly dissolved in another.

SOME EXAMPLES OF SOLUTIONS			
Solute	**Solvent**	**Name of Type**	**Heat of Solution per Mole of Solute (kJ)**
$O_{2(g)}$	$N_{2(g)}$	Gaseous	0
Toluene	Benzene	Ideal	– 0.1
Acetone	Chloroform	Non ideal	5
$NaCl_{(s)}$	$H_2O_{(\ell)}$	Ionic	– 3.9
$H_2SO_{4(\ell)}$	$H_2O_{(\ell)}$	Ionic	95.3
Positive values are heat released.			

Most solutions can be described as having a majority called a *solvent* and one or more minority ingredients called *solutes*. The solvent is usually a liquid, whereas solutes can be solids, liquids, or gases. Solutions can be distinguished from compounds by the kind of interaction between ingredients. Compounds form as a result of interactions between relatively permanent partners, while the interactions in solutions involve continuously variable sets of solute and solvent molecules, and this interaction is widely distributed among a large and solvent molecules. Above table gives some examples of solutions and for each we want to be able to understand why the solute dissolves in the solvent.

$O_{2(g)}$ in $N_{2(g)}$

This first example is; of course, of one gas dissolved in another all gases dissolve in each other in all proportions. The reason for this is that solute and solvent do not interact. This is illustrated in fig. which shows that
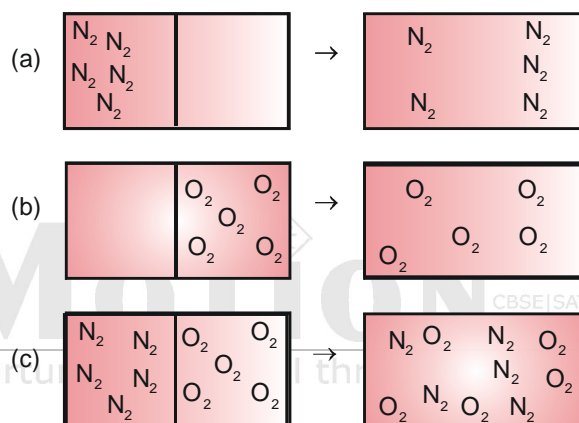

Fig. The expansion of gas as illustrated by a solution of N_2 and O_2 (diagrammatic). The expansions of (a) N_2 and of (b) O_2 are shown to be equivalent to forming (c) a solution of N_2 and O_2.

the process of two gases dissolving in each other is equivalent to the expansion of each gas into the larger volume without any interaction with the other. As we can see from this figure and as we also know from our daily experience, this mixing takes place spontaneously. In a gas, the high thermal energy that the molecules posses keeps them always on the move. This motion allows them to distribute themselves between the two bulbs in an arrangement with the greatest probability of occurring. That distribution results in equal O_2 or N_2 partial pressures in each bulb with the N_2 and O_2 completely mixed. It is important to note that the energy of the system has not changed, only the way in which the molecules are distributed; that is, the entropy, S of the system has changed.

On the molecular level, entropy is a measure of randomness; a maximum in entropy corresponds to the

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most probable distribution on a statistical basis.

While the mixing of ideal gases is controlled by entropy, the mixing of molecules that interact with each other can surely be controlled by energy. In the mixing process the molecular interactions can either cause the energy to increases or decrease. Chemical changes that are very exothermic show a large decrease in energy and enthalpy; as a result, they are spontaneous. However, most solutes dissolve in solvents because mixing increase the system's entropy ($\Delta S > 0$); that it is more probable for the solutes to dissolve in the solvents then for them to remain separate as pure substances.

Toluene in Benzene

These two similar liquids readily dissolve in each other. At first glance we might think this solution shows the same pattern of mixing as do two ideal gases, but this cannot be correct since the molecules in a liquid interact with each other very strongly. The key to this solution is that the molecules of the two liquids have similar electronic structures and similar sizes. As a result, the benzene – benzene, benzene – toluene and toluene – toluene interactions are very similar. A toluene molecule, as an approximation, does not know if it is surrounded by other toluene molecule or by benzene molecules. As we might expect, there is a very negligible *heat of solution*. These two liquids completely dissolve one in the other and are an *ideal solution*. These two liquids completely dissolve one in what is called an *ideal solution.* The entropy gained by mixing toluene with benzene is the same as that gained by mixing two ideal gases. Solvent and solute molecules have no specific interaction with each other that do not have with molecules of their own kind. As a result the molecules distribute randomly in the solution and the change in entropy upon mixing is the same as that for two ideal gases.

Acetone in Chloroform

These two liquids are not very similar; the attraction of acetone and chloroform molecules for each other is quite different from the attraction of the like molecules for each other. When acetone and chloroform are mixed heat is given off so they do not form an ideal solution.

Even so, they are completely miscible. In some cases when the molecules in two liquids have quite different interactions, they may not be completely miscible. For example water and acetone are completely miscible, but water and chloroform are not. The property of liquids used to characterize solvent – solute interactions is called *polarity*. Polarity measures the small separation of positive and negative charges in molecules. Water is considered to be the most polar of the common solvents, as attested by the fact that it is the best solvent for ionic solutes. Acetone has an intermediate value of polarity, and chloroform is much less polar than acetone. Molecules interact very differently with molecules of widely different degrees of polarity than they do with others of their own kind. This difference in interaction leads to *immiscibility*.

NaCl(s) in H$_2$O(ℓ)

The compound NaCl has the high melting temperature characteristic of most ionic solids. It consist of Na$^+$ and Cl$^-$ ions. When NaCl dissolves in water, these ions interact with the water molecules and separate. The interaction with water is particularly large for positively charged ions, and the Na$^+$ is surrounded by six closely bound water molecules, Ions surrounded by closely bound water molecules are said to be hydrated. For salts such as CaCl$_2$ of AlCl$_3$, the water molecules interact even more strongly with their cations and they give off heat when they dissolve. For NaCl the energy required to separate the Na$^+$ and Cl$^-$ ions is nearly balanced by the energy of interaction between the water and the ions. Salts such as NaNO$_3$ or NH$_4$NO$_3$ make their solutions colder when they dissolve to produce hydrated Na$^+$,NH$_4^+$ and NO$_3^-$ ions. The entropy of solution for an ionic solid would never be expected to be as high as its entropy of vaporization; nevertheless, salts such as NaCl and NaNO$_3$ dissolve in water because there is a grater probability of finding them in the form of separated and hydrated ions than packed neatly in a solid. Again entropy is the controlling factor.

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$H_2SO_4(\ell)$ in $H_2O(\ell)$

Almost every chemist knows that H_2SO_4 gives off a large amount of heat when it dissolves in water. While pure H_2SO_4 does not contain ions, as indicted by that fact that it is a liquid at room temperature, in dilute aqueous solutions it completely ionizes into H^+ and SO_4^{2-}. Its high heat of solution arises largely from the heat of hydration of H^+. Other proton – yielding solutes like HCl(g) and $HClO_4(\ell)$ also have large, positive heats of solution so they readily dissolve in water.

RAOULT'S LAW

It states that on adding a non – volatile solute to a volatile solvent, forming an ideal solution, the vapour pressure of the solvent is lowered and it is directly proportional to the mole fraction of the solute in the solution.

Case 1:

Let us add a non – volatile solute that dissolves in the liquid and observe the effect on vapour pressure. As the non – volatile substance dissolves, some of the particles would be present on the surface of the liquid, there by decreasing the number of solvent particles present per unit area of the surface.

Key concept:

The vapour pressure of a liquid does not depend on the surface area of the solvent exposed but only depends on the no. of solvent molecules present per unit area on the surface (which decreases only on dissolving a solute).

The rate at which the solvent molecules leave the surface is proportional to the no. of solvent molecules per unit area on the surface, which in turn is proportional to the mole fraction of the solvent.

Rate of vaporization = $k\, X_{solvent}$

Where k is proportionality constant and $X_{solvent}$ is the mole fraction of the solvent in the solution. The rate with which vapour molecules condense is proportional to their concentration in the gaseous phase, which is proportional to their partial pressure.

Rate of condensation = $k'\, P_{solvent}$

Where k' is proportionality constant and $P_{solvent}$ is vapour pressure of the solvent. At equilibrium,

$$k\, X_{solvent} = k'\, P_{solvent} \qquad (\because \text{ both rates are equal})$$

or

$$P_{solvent} = \frac{k}{k'}\, X_{solvent}$$

In case of pure solvent, $X_{solvent} = 1$ and $P_{solvent} = \dfrac{k}{k'}$. If the pure vapour pressure of the solvent is $P°$, then

$$\frac{k}{k'} = P°.$$

$$\therefore \qquad P = X_{solvent}\, P°.$$

This is the mathematical expression of the Raoult's law.

Case 2:

Let us mix two volatile liquids. Assuming that both of them obey Raoult's law, $P_{total} = X_A\, P_A° + X_B\, P_B°$,

where X_A is mole fraction of component A in the solution and $P_A°$ is its pure vapour pressure and

likewise for B. This also implies that $P_A = X_A\, P_A°$ and $P_B = X_B\, P_B°$, where P_A and P_B are the partial pressures of A and B. In this case, definition of an ideal solution changes. Since both of them obey Raoult's law, one cannot assume any one of them to be in lesser amount.

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Key concept:

An ideal solution is a solution in which A – A interactions, B – B interactions and A – B interaction are same (provided that ΔH_{mix} and $\Delta V_{mix} = 0$).

Case 3:

Is the vapour pressure of a solution of a non – volatile solute in a volatile liquid also a constant?

As we know that the concentration of a solution is not a constant in this case. Therefore, this system does not have a K_p. It means that the vapour pressure of a solution is not a constant. To make the calculations involving liquid solution does not effectively change the concentration of the solution.

Key concept:

The system of solution – vapour also has a constant K_p and therefore a constant vapour pressure.

COLLIGATIVE PROPERTIES

These are the properties of solutions which depend upon the number of solute particles (molecules or ions) but not upon their nature. These are relative lowering of vapour pressure, elevation of boiling point, depression in freezing point and the osmotic pressure arising due to the presence of a non – volatile solute.

Key concept:

In dilute solutions these properties depend only on the number of solute particles present and not on their identity. For this reason they are called colligative properties (denoting depending on the collection).

We shall assume throughout the following that.

(i) The solute is non – volatile.

(ii) The solute does not dissolve in the solid solvent (the pure solid separates when the solution is frozen).

RELATIVE LOWERING OF VAPOUR PRESSURE

According to the Raoult's law, $P_{solvent} = X_{solvent} \, P^{\circ}_{solvent}$,

Where $P_{solvent}$ is the vapour pressure of the liquid solution, $X_{solvent}$ is its mole fraction in the solution

and $P^{\circ}_{solvent}$ is the pure vapour pressure.

$$\therefore \quad X_{solvent} = \frac{P_{solvent}}{P^{\circ}_{solvent}}$$

$$1 - X_{solvent} = 1 - \frac{P_{solvent}}{P^{\circ}_{solvent}} = \frac{P^{\circ}_{solvent} - P_{solvent}}{P^{\circ}_{solvent}} \quad \text{or} \quad X_{solute} = \frac{P^{\circ} - P}{P^{\circ}}$$

Above expression is called as the relative lowering of vapour pressure (fraction of the vapour pressure lowered). Thus, the relative lowering of vapour pressure of a solvent due to the dissolution of a non-volatile solute in it is equal to the molefraction of the solute in the solution. This is another form of the Raoult's law.

Key concept:

The molefraction of any substance does not change with temperature. So the molefraction of the solute (X_{solute}) does not change with temperature. Then, according to above expression the relative lowering of the vapour pressure should be independent of temperature. This is found to be so only for dilute solutions. Therefore, the Raoult's law, in this form, is applicable to the dilute solutions of non–volatile and non–electrolytic solutes only.

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OSTWALD – WALKER EXPERIMENT

When air is passed through any gas, the gas diffuses into the air due to the principle of diffusion till the pressure of the gas in the air is equal to that of the gas outside. Therefore as air is passed through the solution, it absorbs the vapours of the solvent till the pressure of the solvent vapours in the air is P (vapour pressure of solvent in the solution).

∴   Mass of vapour absorbed or loss in weight of solution $= \dfrac{PVm}{RT}$

Where, P = pressure of the solvent vapours, V = volume available for vapours in the solution bulb, T = temperature of the bulb and m = molecular weight of the solvent.

As the air passes through the solvent, the pressure difference of the vapours in the air and outside is P^0 – P. So the air absorbs this amount of vapours and gets saturated.

∴   Loss in weight of solvent bulb $= \dfrac{(P^\circ - P)Vm}{RT}$

As the sum of the losses of weight in the two containers is equal to the gain in weight of $CaCl_2$,

Gain in weight of $CaCl_2$ filled tubes $= \dfrac{P^\circ Vm}{RT}$

∴ $\dfrac{\text{Loss in wt. of solvent}}{\text{Gain in wt. of } CaCl_2} = \dfrac{P^\circ - P}{P^\circ}$.

Method

In this method a stream of dry air is passed successively through (i) a solution (ii) the pure solvent (water) and (iii) a reagent (anhydrous $CaCl_2$) which can absorb the vapours of the solvent. The complete assembly is shown in figure, given below:
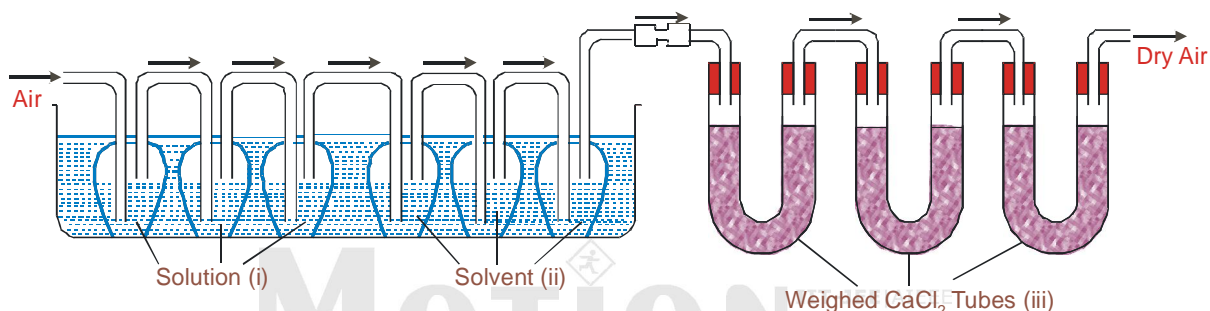
The first three bulbs contain a weighed amount of the solution under examination and the next three bulbs contain a weighed amount of the pure solvent. A weighed amount of $CaCl_2$ is taken in the set of U – tubes at the end. All the bulbs are at the same temperature and the volume available for the vapours in the solution and solvent bulbs are same temperature and the volume available for the vapours in the solution and solvent bulbs are same.

Key concept:
It is designed in order to calculate the relative lowering of vapour pressure of a solvent due to a non – volatile solute.

Illustration

0.5 g of a non–volatile organic substance was dissolved in 100 mL of CCl_4 at 30 °C. The vapour pressure of the solution was found to be 141.9 torr. Calculate the molar mass of the substance if the vapour pressure of CCl_4 at 30 °C is 143 torr and its density is 1.58 g mL^{-1}.

Solution:
$$\frac{P^\circ - P}{P^\circ} = X_{solute} = \frac{n}{n+N}$$

Simplifying this,

$$\frac{P^\circ - P}{P^\circ} = \frac{n}{N}$$

$$\therefore \quad \frac{143 - 141.9}{141.9} = \frac{0.5 / M}{\dfrac{100 \times 1.58}{154}} \qquad \text{or} \qquad M = 62.86 \text{ g/mol}$$
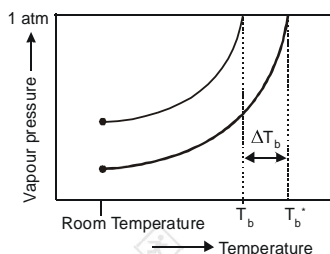
ELEVATION IN BOILING POINT

When a liquid boils, at a constant temperature the molecules of the liquid are converted into vapours, from any part of the liquid. It is different from evaporation because in evaporation the liquid converts to the vapour state only from the surface, while in boiling it does so from the bulk of the liquid also.

Consider the following figure in which a vapour of the liquid is formed in the bulk of the liquid. The vapour would exist as a vapour bubble in the liquid. This bubble experiences the atmospheric pressure on the outside while its vapour pressure is exerted inside.

Atmospheric pressure

Vapour pressure *Vapour bubble*
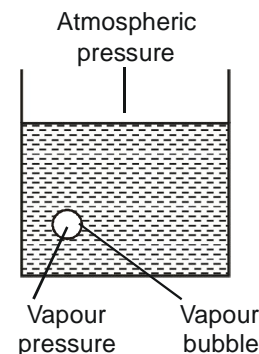
Key concept:
The bubble will be formed only when the external pressure is slightly more (or almost equal to) the internal vapour pressure. Therefore, for the bulk of the liquid to form vapour, the vapour pressure must be equal to the external atmospheric pressure. Ignore the pressure of the liquid column above the bubble because it is negligible.

Since the addition of a non volatile solute causes a decrease in the vapour pressure of a solution, the boiling point of a solution is elevated as compared to the solvent.

We can see from the figure that the solution needs to be heated to a higher temperature to make it boil. The difference between the boiling points of the solution and the solvent is known as the elevation in boiling point (ΔT_b).

Since $\Delta T_b \propto$ decrease in vapour pressure of solution $\propto$ concentration of solute in the solution $\propto$ molality of the solute in the solution,

$\therefore \quad \Delta T_b = K_b m$

Where K_b is proportionality constant and is known as the molal boiling point elevation constant or the ebullioscopic constant. It has the units of degree kg mol^{-1} or K kg mol^{-1}.

Significance of K_b

Now if, $m = 1$ then, $\Delta T_b = K_b$. Thus, the molal elevation constant is defined as the elevation of the boiling point when the molality of the solution is one i.e. when 1 mole of the solute is dissolved in 1 kg of the solvent, the elevation of boiling point is equal of K_b.

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The values of molal elevation constant (K_b) for some common solvents are given in Table.

Molal elevation and molal freezing point constants

Solvent	Boiling point (K)	K_b (K kg mol^{-1})	Freezing point (K)	K_f (K kg mol^{-1})
Water	373.0	0.51	273.0	1.86
Ethyl alcohol	351.5	1.22	155.7	1.99
Benzene	353.3	2.53	278.6	5.12
Chloroform	334.4	3.63	209.6	4.68
Carbon tetrachloride	350.0	5.02	250.5	31.8
Carbon disulphide	319.4	2.34	164.2	3.83
Ether ($C_4H_{10}O$)	307.8	2.02	156.9	1.79
Camphor ($C_{10}H_{16}O$)	480.0	5.95	452.0	37.7

K_b and K_f can be obtained from the following relationships:

$$K_b = \frac{RT_b^2\, M_{solvent}}{1000 \times \Delta_{vap}H} \quad \text{and} \quad K_f = \frac{RT_f^2\, M_{solvent}}{1000 \times \Delta_{fus}H}$$

Where, T_b = boiling point of the solvent, T_f = freezing point of the solvent, $M_{solvent}$ = molar mass of the solvent, $\Delta_{vap}H$ = enthalpy of vaporization and $\Delta_{fus}H$ = enthalpy of fusion.

Key concept:
Camphor is commonly used in determining the molecular mass of a solute because of its very high cryoscopic constant (K_f).

Illustration
A 5 percent aqueous solution by mass of a non–volatile solute boils at 100.15 °C. Calculate the molar mass of the solute. K_b =0.52 K kg mol^{-1}.

Solution:

The normal boiling point of water is 100°C.

∴ The elevation in boiling point is 0.15°C.

A 5 percent solution means that in a 100 g solution 5 g of the solute is present. This implies that the solvent is 95 g.

If the molar mass of the solute is M, then the molality of the solute in the solution is,

$$\frac{5/M}{95} \times 1000, \qquad \Delta T_b = K_b\, m$$

$$0.15 = 0.52 \times \frac{5/M}{95} \times 1000$$

∴ M = 182.4 g/mol

Illustration
Calculate the boiling point of a one molar aqueous solution (density: 1.03 g mL^{-1}) of sodium chloride. Kb for water =0.52 K kg mol^{-1}; Atomic mass: Na =23, Cl =35.5.

Solution:

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Conc. of the solution = 1 molar = 1 mol L^{-1}

Density of solution = 1.03 g mL^{-1}

Molar mass of NaCl = (23 + 35.5) g/mol = 58.5 g/mol

So, Mass of 1 litre of solution = 1000 × 1.03 = 1030 g

Therefore, Mass of water containing 1 mole of NaCl = (1030 − 58.5) g = 971.5g

Thus, Molality of the solution, $m = \dfrac{1 \times 1000}{971.5}$ mol/kg = 1.0293 mol/kg

Then, $\Delta T_b = i \times K_b \times m = (2 \times 0.52 \times 1.0293)$ K = 1.07 K

So, Boiling point of solution = (373.15 + 1.07) K = 374.22 K

Illustration

A solution of 12.5 g urea in 170 g of water gave a boiling point elevation of 0.63 K. Calculate the molar mass of urea, taking K_b =0.52 K/m.

Solution:

Given: Mass of urea, w_2 = 12.5 g

Mass of water, w_1 = 170 g = 0.17 kg

Evaluation of boiling point, ΔT_b = 0.63 K

Molar mass of urea, M = ?

K_b = 0.52 K m^{-1}

Molar mass of the solute (urea) is given by:

$$M = \dfrac{K_b \times w_2}{w_1 \times \Delta T_b} = \dfrac{0.52 \times 12.5}{0.17 \times 0.63} \text{ g/mol} = 60.7 \text{ g mol}^{-1}$$

Illustration

Calculate the molecular mass of a substance 1.0 g of which on being dissolved in 100 g of solvent gave an elevation of 0.307 K in the boiling point. (Molal elevation constant (K_b) =1.84 K/m).

Solution:

We know that, $\Delta T_b = \dfrac{K_b \times n_2}{w_1}$, where n_2 is the no. of moles of solute; w_1 is the mass of the solvent in kg.

$n_2 = \dfrac{\text{Mass of solute}}{\text{Molar mass of the solute}} = \dfrac{1.0 \text{ g}}{M}$ and w_1 = 100 g = 0.1 kg

Substituting these values, we get,

$$0.307 \text{ K} = \dfrac{1.84 \text{ K kg mol}^{-1}}{0.1 \text{ kg}} \times \dfrac{1.0 \text{ g}}{M}$$

So, $M = \dfrac{1.84 \text{ K kg mol}^{-1} \times 1.0 \text{ g}}{0.1 \text{ kg} \times 0.307 \text{ K}} = \dfrac{1.84 \times 1.0}{0.1 \times 0.307} \text{ g/mol} = 59.9 \text{ g/mol}$

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DEPRESSION IN FREEZING POINT

Freezing point of a substance is the temperature at which it's liquid and the solid phases have the same vapour pressure.

Key concept:

As we already know from the definition of colligative properties that when a solution freezes, it is only the pure solvent which separated out in the solid form. It is this that causes a depression in the freezing point.
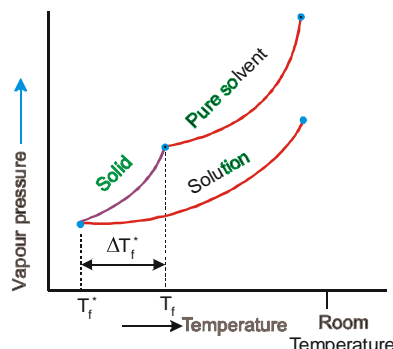
If the difference between the freezing point of the solvent and the solution is represented as ΔT_f, then $\Delta T_f = K_f m$, where, m = molality of the solution and K_f = molal freezing point depression constant or the cryoscopic constant. It has the units of degree kg mol^{-1} or K kg mol^{-1}.

Significance of K_f

$\Delta T_f = K_f m$. So, if m = 1 i.e. one mole of solute is dissolved in one kg of the solvent, then, $\Delta T_f = K_f$. Thus, the molal freezing point depression constant is equal to the depression in the freezing point produced when one mole of solute is dissolved in 1 kg of the solvent.

Illustration

An aqueous solution of a non–volatile solute boils at 100.17°C. At what temperature would it freeze? ($K_b = 0.52$ K kg mol $^{-1}$ and $K_f = 1.88$ K kg mol $^{-1}$).

Solution:

$\Delta T_b = 0.17°C$

$\therefore \quad m = \dfrac{\Delta T_b}{K_b} = \dfrac{0.17}{0.52} = 0.327$ molal, $\Delta T_f = K_f m$

$\Delta T_f = 1.86 \times 0.327 = 0.608$

$\therefore \quad$ Freezing point of the solution is $- \quad 0.608°C$.

Illustration

Calculate the freezing point of a one–molar aqueous solution (density 1.06 g mL^{-1}) of KBr. K_f for water = 1.86 K kg mol^{-1}. Atomic mass: K = 39, Br = 80.

Solution:

Mass of 1 litre of solution = 1000 mL $\times$ 1.06 g mL^{-1} = 1060 g

Molarity of solution = 1 mol L^{-1}

Mass of KBr in 1 litre of solution = (39 + 80) g = 119 g

So, Mass of water containing 1 mole of KBr = (1060 − 119) g = 941 g

Molality of KBr solution = $\dfrac{1\,mol}{941\,g} \times 1000$ g = 1.0627 mol/kg

Then, depression of freezing point (ΔT_f) is given by:

$\Delta T_f = i\, K_f m = 2 \times 1.86 \times 1.0627$ K $= 3.95$ K

So, Freezing point of the solution = (273.15 − 3.95) K $= 269.2$ K

Illustration

Ethylene glycol (HOH$_2$C − CH$_2$OH) is used as an antifreeze for water to be used in car radiators in cold places. How much ethylene glycol should be added to 1 kg of water to prevent it from freezing at −10 ℃? Molal depression constant of water is 1.86 K kg mol⁻¹.

Solution:

Mass of water (solvent), w_1 = 1 kg

$$\Delta T_f = 10°C$$

$$K_f = 1.86 \text{ K kg mol}^{-1}$$

Mass of ethylene glycol required, w_2 = ?

Molar mass of ethylene glycol   = (12 + 3 + 16) × 2 g/mol = 62 g/mol

We know, $\Delta T_f = \dfrac{K_f(w_2 / 62)}{w_1}$ or $10 = \dfrac{1.86 \times w_2}{62 \times 1}$

This gives, $w_2 = \dfrac{10 \times 62 \times 1}{1.86}$ g = 333.3 g

Illustration

Normal freezing point of a solvent is 150 ℃. A 0.5 molal solution of urea in the above solvent causes a freezing point depression of two degrees. Calculate the molal depression constant

Solution:

We know, $\Delta T_f = K_f m$

So, $K_f = \dfrac{\Delta T_f}{m} = \dfrac{2 \text{ deg}}{0.5 \text{ mol kg}^{-1}} = 4 \text{ deg. kg mol}^{-1}$

Illustration : A solution of urea in water freezes at 0.400 ℃. What will be the boiling point of the same solution if the depression and elevation constants for water are 1.86 deg kg mol⁻¹ and 0.512 deg kg mol⁻¹ respectively?

Solution: We have the relationships:

$$\Delta T_b = \dfrac{K_b n_2}{w_1} \qquad \text{...(i)}$$

And $\Delta T_f = \dfrac{K_f n_2}{w_1}$ ...(ii)

Where, n_2 is the number of moles of the solute, and w_1 is the mass of solvent in kg.

Dividing equation (i) by equation (ii),

$$\dfrac{\Delta T_b}{\Delta T_f} = \dfrac{K_b}{K_f}$$

or, $\Delta T_b = \dfrac{\Delta T_f \times K_b}{K_f} = \dfrac{0.4 \times 0.512}{1.86}$ °C = 0.11°C

Then, Boiling point of the urea solution = 100°C + 0.11°C = 100.11°C

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CONCEPT OF OSMOTIC PRESSURE

In the process of Osmosis, solvent moves from a region of its higher concentration to a region of its lower concentration through a semi−permeable membrane, which allows the free passage of only solvent molecules. The extra pressure developed on the solution side as a result of the solvent flow is called osmotic pressure (π). It can also be defined as: *the minimum pressure which should be applied on the solution, so as to prevent the migration of solvent molecules into the solution through a semi−permeable membrane*. Some typical examples of osmosis and osmotic pressure are:

(i) The climbing of water up a tall tree from the soil.

(ii) Bursting of red−blood cells when placed in water.

(ii) Swelling of dry raisings when placed in water.

Key concept: ***The semipermeable membranes allow a selective passage to only the solvent molecules. Cellophane, parchment paper and animal protein membranes are typical semipermeable membranes.***
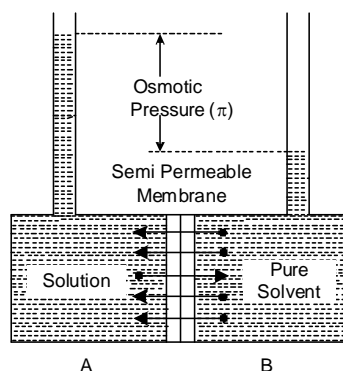
The Van't Hoff equation describes the relationship between the osmotic pressure and concentration of solute in the solution. $\pi = \dfrac{n}{V}RT = cRT$, where n is the no. of moles of solute in the solution and V is the volume of the solution.

Difference between Osmotic Pressure and Vapour Pressure

Osmotic pressure	Vapour pressure
It is the minimum pressure which should be applied on the solution so as to prevent the migration of solvent molecules into the solution through a semi−permeable membrane.	It is the maximum pressure exerted by the vapour above the surface of solution in a closed container.

Illustration

Calculate the osmotic pressure and vapour pressure of 0.6% aqueous solution of a non−volatile, non−electrolyte solute, urea (NH_2CONH_2) at 25°C. The vapour pressure of pure water at 25°C is 24 mm Hg. Take densities to be 1 g mL^{-1} and assume ideal behaviour of the solution. Gas constant, R = 0.082 L atm. mol^{-1} K^{-1}.

Key concept:

Please refer to difference between osmotic pressure and vapour pressure while solving this illustration.

Solution:

Concentration of urea solution = 0.6%

This means, solution contains 0.6 g of urea per 100 g, and hence 100 mL of the solution,

So,

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Mass of urea per litre of solution $= \dfrac{0.6}{100} \times 100 = 6$ g

Molar mass of urea, M = 60 g/mol

Concentration of urea in solution $= \dfrac{6}{60}$ mol/L = 0.1 mol/L

Illustration

At 25°C, the osmotic pressure of human blood due to the pressure of various solutes in the blood is 7.65 atm. Assuming that molarity and molality are almost same, calculate the freezing point of blood. $K_f = 1.86$ K kg/mol.

Solution:

According to the Van't Hoff equation,

$\pi = cRT$

$c = \dfrac{7.65}{(0.082)(298)} = 0.313$ mol/I

Since molarity and molality are same,

$\Delta T_f = K_f m$

$\Delta T_f = 1.86 \times 0.313 = 0.582$

∴ Freezing point of blood is – 0.582°C.

VAN'T HOFF FACTOR

Several solutes have a tendency to dissociate or associate when dissolved in a solvent. Since the colligative properties are directly proportional to the no. of mole of the solute, dissociation or association may cause some abnormal increase or decrease in the measured values of colligative properties. Van't Hoff factor is a factor that takes into account this abnormal behaviour and can be defined as,

$i = \dfrac{\text{Observed magnitude of any colligative property}}{\text{Normal magnitude of the same colligative property}}$

Since, colligative properties are inversely related to the molar mass of the solute, hence, one can write,

$i = \dfrac{\text{Normal molar mass}}{\text{Observed molar mass (obtained from a colligative property)}}$

Thus, the value of i depends upon the state of solute in the solution. Following cases become possible.

1. When, i = 1, then the solute remains unaffected (i.e., normal) in solution.
2. When, i > 1, then the solute undergo dissociation in solution.
3. When, i < 1, then the solute undergo association in solution.

Thus, for   Potassium chloride (KCl)   in aqueous solution, i is nearly equal to 2.

Barium chloride ($BaCl_2$)   in aqueous solution, i is nearly equal to 3.

Benzoic acid (C_6H_5COOH)   in benzene, i is nearly equal to 0.5.

Acetic acid (CH_3COOH)   in benzene, i is nearly equal to 0.5.

Let us take for example the dissolution of acetic acid in water. When dissolved, acetic acid would dissociate as:

	CH_3COOH	$\rightleftharpoons$ CH_3COO^-	+	H^+
Initial moles	n	0		0
At equilibrium	$n(1 - \alpha)$	$n\alpha$		$n\alpha$
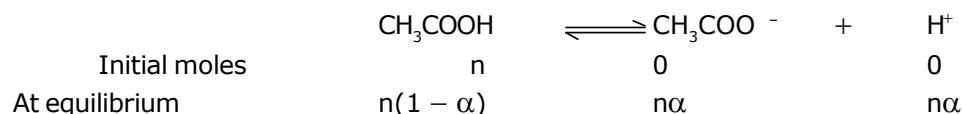
Total number of moles at equilibrium = n – $n\alpha + n\alpha + n\alpha = n(1 + \alpha)$

Van't Hoff factor is defined as the ratio of the no. of moles after dissolution to the no. of moles before dissolution.

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$\therefore \quad \dfrac{n(1+\alpha)}{n} = i = $ Van't Hoff factor

$\therefore \quad i = 1 + \alpha$

When acetic acid is dissolved in benzene, it associates as:

$$CH_3COOH \rightleftharpoons (CH_3COOH)_2$$
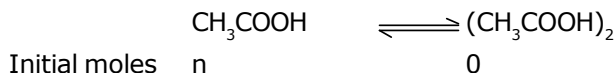
Initial moles	n	0
At equilibrium	$n(1-\alpha)$	$\dfrac{n\alpha}{2}$

$\therefore \quad i = \dfrac{n\left(1 - \dfrac{\alpha}{2}\right)}{n} = 1 - \dfrac{\alpha}{2}$

Therefore when a solute dissociates, i will be more than 1 and when it associates, i will be less than 1, when it does neither, i is equal 1.

A colligative property is a property which is such that,

$$\dfrac{\text{Actual colligatve property}}{\text{Theoretical colligative property}} = i$$

Where actual colligatvie property is the value that is calculated experimentally and the theoretical colligative property is the value that is calculated based on the no. of moles of solute added.

Key concept:

Among all the colligative properties that we have studied so far, relative lowering of vapour pressure does not satisfy the equation given above. It would do so if the solution were very dilute so that we ignore n in the denominator.

$\therefore \quad \dfrac{P^o - P}{P^o} = \dfrac{n}{n+N} \approx \dfrac{n}{N}$. *In fact it would be convenient to use the expression* $\dfrac{P^o - P}{P^o}$ *in numerical*

*problems which is equal to* $\dfrac{n}{N}$ *rather than* $\dfrac{P^o - P}{P^o}$.

Modified Equations for Colligative Properties

For solutes which undergo dissociation or association in solutions, the equations for the colligative properties are modified by inserting the van't–Hoff's factor in them as follows:

	Colligative property	equation for colligative property	
		when solute remains normal	when the solute undergoes association/dissociation
1.	Relative lowering of vapour pressure	$\dfrac{p_s^o - p_s}{p_s^o} = X_{solute}$	$\dfrac{p_s^o - p_s}{p_s^o} = i\, X_{solute}$
2.	Elevation of the boiling point	$\Delta T_b = K_b \times m$	$\Delta T_b = i\, K_b \times m$
3.	Depression of the freezing point	$\Delta T_f = K_f \times m$	$\Delta T_f = i\, K_f \times m$
4.	Osmotic pressure	$\pi = CRT$	$\pi = i\, CRT$

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Illustration

Acetic acid (CH₃COOH) associates in benzene to form double molecules. 1.65 g of acetic acid when dissolved in 100 g of benzene raised the boiling point by 0.36 °C. Calculate the Van't Hoff factor and the degree of association of acetic acid in benzene. ($K_b = 2.57$ K kg mol⁻¹).

Solution:

$$2CH_3COOH \rightleftharpoons (CH_3COOH)_2$$

Initial moles $1.65/60$ 0
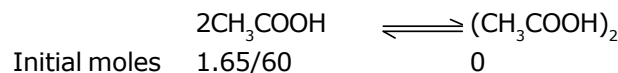
At equilibrium $\dfrac{1.65}{60}(1-\alpha)$ $\dfrac{1.65}{60}\dfrac{\alpha}{2}$

Total moles at equilibrium $= \dfrac{1.65}{60}\left(1-\dfrac{\alpha}{2}\right)$

$\Delta T_b = K_b \times m$, $0.36 = 2.57 \times \dfrac{1.65}{60}\left(1-\dfrac{\alpha}{2}\right)$

$\alpha = 0.981$

Van't Hoff factor $= \dfrac{\text{no. of moles at equilibrium}}{\text{Initial no. of moles}} = i$

$i = 1-\dfrac{\alpha}{2} = 0.5$

Illustration : Derive a relationship between K_b, T_b and ΔH_{vap} for a liquid.

Solution:

Let us consider a pure liquid. At its boiling point, T_b, its vapour pressure $P°$ would be equal to the external pressure.

∴ $P° = P_{ext}$ at temperature T_b.

Now let us consider a non−volatile solute dissolved in the liquid. When the solution reaches temperature T_b, the vapour pressure of the system, would be less than the external pressure. When the solution is heated further and it reaches its boiling T_b^*, the vapour pressure of the solution would be equal to P_{ext} which is equal to the $P°$ of the pure liquid at its boiling point. Since vapour pressure of a system are the K_p's for the respective equilibrium,

$$\ln\frac{K_{PT_2}}{K_{PT_1}} = \frac{\Delta H}{R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

$$\ln\frac{P°}{P} = \frac{\Delta H_{vap}}{R}\left[\frac{1}{T_b}-\frac{1}{T_b^*}\right] = \frac{\Delta H_{vap}}{R}\left[\frac{\Delta T_b}{T_b T_b^*}\right]$$

Assuming the solution to be highly dilute, T_b^* would be very close to T_b.

∴ $$\ln\frac{P°}{P} = \frac{\Delta H_{vap}}{R}\left[\frac{\Delta T_b}{T_b^2}\right]$$

$$-\ln\frac{P}{P°} = \frac{\Delta H_{vap}}{R}\left[\frac{\Delta T_b}{T_b^2}\right]$$

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$$-\ln\left[1-\left(\frac{P^\circ - P}{P^\circ}\right)\right] = \frac{\Delta H_{vap}}{R}\left[\frac{\Delta T_b}{T_b^2}\right]$$

$$-\ln\left[1 - X_{solute}\right] = \frac{\Delta H_{vap}}{R}\left[\frac{\Delta T_b}{T_b^2}\right]$$

Since X_{solute} is very small, we can make the approximation that in $(1 - x) = -x$ (when x is very small).

$$\therefore \quad X_{solute} = \frac{\Delta H_{vap}}{R}\left[\frac{\Delta T_b}{T_b^2}\right] \quad \text{or} \quad \frac{n}{n+N} = \frac{\Delta H_{vap}}{R}\left[\frac{\Delta T_b}{T_b^2}\right]$$

Ignoring n in comparison to N in the denominator

$$\frac{n}{N} = \frac{\Delta H_{vap}}{R}\left[\frac{\Delta T_b}{T_b^2}\right]$$

$$\frac{n}{\dfrac{W_{solvent}}{M_{solvent}}} = \frac{\Delta H_{vap}}{R}\left[\frac{\Delta T_b}{T_b^2}\right] \quad \text{or} \quad \frac{n}{W_{solvent}} = \frac{\Delta H_{vap}}{M_{solvent}R}\left[\frac{\Delta T_b}{T_b^2}\right]$$

Multiplying by 1000 on both the sides, we get,

$$\frac{n}{W_{solvent}} \times 1000 = \frac{\Delta H_{vap}}{M_{solvent}R}\left[\frac{\Delta T_b}{T_b^2}\right] \times 1000$$

$$m = \frac{\Delta H_{vap}}{M_{solvent}R}\left[\frac{K_b m}{T_b^2}\right] \times 1000$$

$$\therefore \quad K_b = \frac{RT_b^2 M_{solvent}}{1000\,\Delta H_{vap}}$$

Similarly, $K_f = \dfrac{RT_b^2 M_{solvent}}{1000\,\Delta H_{fus}}$

Illustration : To 500 cm³ of water, 3.0 × 10⁻³ kg of acetic acid is added. If 23% of acetic acid is dissociated, what will be the depression in freezing point? K_f and density of water are 1.86 K kg⁻¹ mol⁻¹ and 0.997 g cm⁻³ respectively.

Solution: Molality of acetic acid $= \dfrac{3\times10^{-3}\times10^3\times1000}{60\times0.997\times500} = 0.1003$

Total number of moles per kg of solvent $= 0.1003\,(1 + 0.23)$

$\Delta T_f = K_f m = 1.86 \times 0.1003 \times 1.23 = 0.23°C$

Illustration : At 300 K, the vapour pressure of an ideal solution containing one mole of A and 3 moles of B is 500 mm of Hg. At the same temperature, if one mole of B is added to this solution, the vapour pressure of the solution increases by 10 mm of Hg. Calculate the V.P. of A and B in their pure state.

Solution: Initially, $P_M = P_A^\circ X_A + P_B^\circ X_B$

$$550 = P_A^\circ \frac{1}{1+3} + P_B^\circ \frac{3}{1+3} \quad \text{or} \quad P_A^\circ + 3P_B^\circ = 2200 \quad \text{...(i)}$$

When, one mole of B is further added to it, $P_M = P_A^\circ X_A + P_B^\circ X_B$

$$56. = P_A^\circ \frac{1}{1+4} + P_B^\circ \frac{4}{1+4} \quad \therefore \quad P_A^\circ + 4P_B^\circ = 2800 \quad \text{...(ii)}$$

Solving equations (i) and (ii), we get

$$P_A^\circ = 440 \text{ mm}, \ P_B^\circ = 600 \text{ mm}$$

Illustration : A decinormal solution of NaCl exerts an osmotic pressure of 4.6 atm. at 300 K. Calculate its degree of dissociation. (R *=0.082 L atm. K⁻¹ mol⁻¹).*

Solution: No. of moles of NaCl per litre of solution = 0.1

Osmotic pressure (π) = 4.6 atm., Temperature (T) = 300 K

Had NaCl not dissociated, then

$$\pi_{normal} = CRT = 0.1 \times 0.082 \times 300 \text{ atm.} = 2.46 \text{ atm.}$$

But, π_{obs} = 4.6 atm.

As per definition,

$$i = \frac{\text{Observed magnitude of a colligative property}}{\text{Normal magnitude of a colligative property}} = \frac{\pi_{obs}}{\pi_{normal}} = \frac{4.6 \text{ atm.}}{2.46 \text{ atm.}} = 1.87$$

For the dissociation of an electrolyte producing n ions,

$$\alpha = \frac{i-1}{n-1} = \frac{1.87-1}{2-1} = \frac{0.87}{1} = 0.87$$

So, Percentage dissociation = $100 \times \alpha = 100 \times 0.87 = 87\%$

Illustration : Vapour pressure of C_6H_6 ***and*** C_7H_8 ***mixture at 50°C are given by:***

P =179 X_B ***×92, where*** X_B ***is mole fraction of*** C_6H_6***. Calculate (in mm):***

(A) ***Vapour pressure of pure liquids.***

(B) ***Vapour pressure of liquid mixture obtained by mixing 936 g*** C_6H_6 ***and 736 g toluene.***

(C) ***If the vapours are removed and condensed into liquid and again brought to the temperature of 50°C, what would be mole fraction of*** C_6H_6 ***in vapour state?***

Solution: (A) Given, P = $179X_B + 92$

For pure, C_6H_6, $X_B = 1$

$$\therefore \ P_B^\circ = 179 + 92 = 271 \text{ mm}$$

For pure C_7H_8, $X_B = 0$

$$\therefore \ P_T^\circ = 179 \times 0 + 92 = 92 \text{ mm}$$

(B)   Now $PM = P_B^° X_B + P_T^° X_T$

$$= 271 \times \frac{12}{12+8} + 92 \times \frac{8}{12+8} = 162.6 + 36.8 = 199.4 \text{ mm}$$

Moles of $C_6H_6 = \dfrac{936}{78} = 12$

Moles of $C_7H_8 = \dfrac{736}{92} = 8$

(C)   Now mole fraction of C_6H_6 in vapour phase of initial mixture $\left(X_T^/\right)$

$$X_T^/ = \frac{P_B^/}{P_M} = \frac{162.6}{199.4} = 0.815$$

Moles fraction of C_7H_8 in vapour phase of initial mixture $\left(X_T^/\right)$

$$X_T^/ = \frac{P_T^/}{P_M} = \frac{36.8}{199.4} = 0.185$$

These vapours are taken out and condensed into liquid. The liquid is again brought to 50°C to get again vapour–liquid equilibrium.

Thus, mole fraction of C_6H_6 in vapour phase of initial mixture

= Mole fraction of C_6H_6 in liquid phase on II mixture $X_B^/$

Similarly, mole fraction of C_7H_8 in vapour phase of initial mixture

= Mole fraction of C_7H_8 in liquid phase on II mixture $X_T^/$

New $P_M = P_B^/ + P_T^/$

Therefore, new $P_M = P_B^° X_B^/ + P_T^° X_T^/$

$= 271 \times 0.815 + 92 \times 0.185 \text{ mm}$

$= 220.865 + 17.02 = 237.885 \text{ mm}$

∴   New mole fraction of C_6H_6 in vapour phase $= \dfrac{\text{New } P_B^/}{\text{New } P_M} = \dfrac{220.865}{237.885}$

$$= 0.928$$

∴   New mole fraction of C_7H_8 in vapour phase $= 0.072$