LIQUID SOLUTION

1. Methods of Expressing Concentration of a Solution

A solution may be defined as a homogenous mixture of a single phase containing one or more of the chemical species dispersed on a molecular scale. The characteristics of any one section of the homogenous solution will be completely identical to those of any other section of the solution. Depending upon the total constituents present in the solution, it is called binary solution (two constituents), ternary solution (three constituents), quaternary solution (four constituents) and so on. By convention, the constituent present in the largest amount is called solvent and the constituent present in relatively small amounts is called the solute. However, this classification is completely arbitrary, since it is not possible to classify the two constituents of a binary solution into solute and solvent when both of them are present in equal amounts. Any one of the two constituents may be classified as the solute or the solvent. Thus, classification is a matter of convenience only.

Various Concentration Terms

S. No	Concentration Terms	Description	Will change on changing Temperature
1.	Molarity	$\dfrac{\text{No. of mole of solute}}{\text{Volume of solution in litre}}$	Yes
2.	Normality	$\dfrac{\text{No. of gm equivalents of solute}}{\text{Volume of solution in litre}}$	Yes
3.	Molality	$\dfrac{\text{No. of mole of solute}}{\text{Mass of solvent in kilo grams}}$	No
4.	Formality	$\dfrac{\text{No. of formula units of solute}}{\text{Volume of solution in litre}}$	Yes
5.	Mole Fraction	$\dfrac{\text{No. of mole of solute}}{\text{Total mole of solution}}$	No
6.	Mass Fraction	$\dfrac{\text{Mass of solute}}{\text{Total mass of solution}}$	No
7.	Volume Fraction	$\dfrac{\text{Volume of solute}}{\text{Total Volume of solution}}$	Yes
8.	PPM (Parts per Million)	(i) Mass fraction $\times 10^6$ (ii) Mole fraction $\times 10^6$	No
9.	Strength	$\dfrac{\text{Mass of solute in gram}}{\text{Volume of solution in litre}}$	Yes

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It must be noted that the concentration terms that use volume of any component (solute, solvent or solution) are the terms that changes with the change of temperature. This is because on changing the temperature for a liquid solution, the volume expands or contracts, thereby changing the value of the physical quantity.

Concentration terms that do not depend on the volume of any component do not change with temperature. Therefore, quantities like molality, mole fraction, mass fraction etc. are independent of temperature. That is why, these concentration terms are used quite often.

Illustration 1

Calculate the mole fraction, molality and molarity of a solution containing 20 per cent acetic acid by mass in water, if the density of the solution at 20^oC is 1.026 g cm^{-3}.

Solution:

The solution has 20 g of acetic acid for every 100 g of solution.

$$\text{Volume of the solution of mass 100 g} = \frac{\text{mass}}{\text{density}} = \frac{100}{1.026}\text{cm}^3$$

$$= 97.46\text{cm}^3 = 0.09746\text{lltre}$$

$$\text{Number of mole of acetic acid} = \frac{\text{mass}}{\text{molecular weight}} = \frac{20}{60} = 0.33$$

$$\therefore \qquad \text{Molarity} = \frac{0.33}{0.09746} = \mathbf{3.38 mole/litre}$$

$$\text{Molality} = \frac{0.33}{(100-20)} \times 1000 = \mathbf{4.125 \ mol/kg}$$

$$\text{Mole fraction} = \frac{0.33}{0.33 + \frac{(100-20)}{18}} = \mathbf{0.0691}$$

Relationship between Molality and Molarity of a Solution

Let the molarity of the solution be 'M'; molality be 'm' and the density of the solution be 'd' g/c.c.

Now, molality = 'M' implies that there are 'M' moles in 1L of a solution.

If M_1 be the molecular mass of the solution then

mass of the solvent = $(d \times 1000 - MM_1)$

In 1000 g of the solvent, number of moles of solute = $M \times \dfrac{1000}{(d \times 1000 - MM_1)}$ = molality (m).

or **molality** $= \dfrac{\text{Molarity} \times 1000}{[\text{density} \times 1000 - (\text{molarity} \times \text{molecular mass of the solute})]}$.

Illustration 2

The density of 1.35 M solution of acetic acid is 1.012 g cm^{-3}. Calculate its molality.

Solution:

Let the volume of solution be 1 dm^3 and molar mass of solute be M_2. We have

Amount of solute, n_2 = 1.35 mol

Volume of solution, V = 1 dm^3 = 1L

Mass of solute, $m_2 = n_2M_2$ = (1.35 mol) (60 g mol^{-1}) = 81 g

Mass of solution = $V\rho$ = (10^3 cm^3) (1.012 g cm^{-3}) = 1012 g

Mass of solvent, m_1 = Mass of solution − Mass of solute = (1012 − 81) g

$\qquad$ = 931 g = 0.931 kg

Finally, the molality of solutions is

$$m = \frac{n_2}{m_1} = \frac{1.35\,\text{mol}}{0.931\,\text{kg}} = \textbf{1.45 mol kg}^{-1}$$

Alternatively, using the conversion formula directly, we get

$$m = \frac{M}{\rho - MM_2} = \frac{(1.35\,\text{mol dm}^{-3})}{(1.012\,\text{g cm}^{-3}) - (1.35\,\text{mol dm}^{-3})(60\,\text{g mol}^{-1})}$$

$$= \frac{1.35\,\text{mol dm}^{-3}}{\{1.012 \times (10^{-3}\text{kg}) \times (10^{-1}\text{dm})^{-3}\} - (1.35\,\text{mol dm}^{-3})\{60 \times (10^{-3}\text{kg})\text{mol}^{-1}\}}$$

$$= \frac{1.35}{1.012 - 1.35 \times 60 \times 10^{-3}}\,\text{mol kg}^{-1} = \textbf{1.45 mol kg}^{-1}.$$

Relationship between Molality and Mole Fraction

Consider a binary solution consisting of two components i.e. A (solute) and B (solvent). Let X_A be the mole fraction of A and X_B be that of B.

Then if n_A be moles of A and n_B be moles of B in the solution, then

$$X_A = \frac{n_A}{n_A + n_B} \qquad \qquad \text{...(i)}$$

$$X_B = \frac{n_B}{n_A + n_B} \qquad \qquad \text{...(ii)}$$

If molality of solution be 'm', then

$$m = \frac{n_A \times 1000}{\text{mass of the solvent in g}} = \frac{n_A \times 1000}{n_B \times M_B} \quad \text{(where } M_B \text{ is molar mass of the solvent 'B')}$$

$$= \frac{\dfrac{n_A}{n_A + n_B} \times 1000}{\dfrac{n_B}{n_A + n_B} M_B} \qquad \dots(iii)$$

or $\qquad m = \dfrac{X_A \times 1000}{X_B \times M_B}$

using equation (i), (ii) and (iii)

$\therefore$ **molality** $= \dfrac{\text{mole fraction of solute} \times 1000}{\text{mole fraction of solvent} \times \text{molecular mass of the solvent}}$

Illustration 3

The mole fraction of methanol in aqueous solution is 0.02. Determine the molality of methanol in solution.

Solution:

Let there be 1 mol of total amount of solvent and solute. Then

Amount of solute, $n_2 = 0.02$ mol

Amount of solvent, $n_1 = 0.98$ mol

Mass of solvent, $m_1 = n_1 M_1 = (0.98 \text{ mol})(18 \text{ g mol}^{-1}) = 17.64$ g

Finally, the molality of solution is

$$m = \frac{n_2}{m_1 \text{ in kg}} = \frac{0.02 \text{ mol}}{17.64 \times 10^{-3} \text{ kg}} = \textbf{1.134 mol kg}^{-1}$$

Alternatively, using the conversion expression directly, we get

$$m = \frac{x_2 \times 1000}{x_1 M_1} = \frac{0.02 \times 1000}{0.98 \times 18} = \textbf{1.134 mol kg}^{-1}.$$

Illustration 4

An aqueous solution is 1.133 molal in methanol. Determine the mole fractions of methanol and water.

Solution:

Let the mass of solvent be 1 kg. We will have

Amount of solute, $n_2 = 1.133$ mol

Amount of solvent, $m_1 = 1$ kg $= 1000$ g

Amount of solvent, $n_1 = \dfrac{m_1}{M_1} = \dfrac{1000 \text{ g}}{18 \text{ g mol}^{-1}} = 55.56$ mol

Mole fraction of solute (i.e. methanol) i.e. $x_2 = \dfrac{n_2}{n_1 + n_2} = \dfrac{1.133}{55.56 + 1.133} = 0.02$

Mole fraction of solvent (i.e. water) i.e. $x_1 = 1 - x_2 = 1 - 0.02 = \textbf{0.98}$

Alternatively, using the formula directly, we get

$$x_2 = \frac{mM_1}{1+mM_1} = \frac{(1.133 \text{ mol kg}^{-1})(18\times10^{-3}\text{kg mol}^{-1})}{1+(1.133 \text{ mol kg}^{-1})(18\times10^{-3}\text{kg mol}^{-1})} = \frac{0.020394}{1+0..020394} = 0.02$$

$x_1 = 1 - x_2 = 1 - 0.02 = \mathbf{0.98}$.

Relationship between Molarity and Mole Fraction

Let 'M' be the molarity of a solution in which 'n_A' moles of A are dissolved in 'n_B' moles of the solvent, then

$$X_A = \text{mole fraction of 'A'} = \frac{n_A}{n_A + n_B} \qquad \dots\text{(i)}$$

$$X_B = \text{mole fraction of 'B'} = \frac{n_B}{n_A + n_B} \qquad \dots\text{(ii)}$$

If M_A and M_B be the molecular masses of A and B and 'd' density, then mass of solution $= n_A M_A + n_B M_B$

$$\therefore \quad \text{Volume of the solution} = \left(\frac{n_A M_A + n_B M_B}{d}\right) \qquad \dots\text{(iii)}$$

$$\therefore \quad \text{Molarity} = \text{number of moles of solute} \times \frac{1000}{\text{Volume of the solution in mL}}$$

$$= n_A \times \left(\frac{1000}{\dfrac{n_A M_A + n_B M_B}{d}}\right) \qquad \text{[from eq. (iii)]}$$

Multiplying and dividing the numerator and denominator of equation (iv) by ($n_A + n_B$) we get

$$M = \frac{\dfrac{n_A}{n_A + n_B} \times 1000 \times d}{\left(\dfrac{n_A}{n_A + n_B}M_A + \dfrac{n_B}{n_A + n_B}M_B\right)}$$

$$\mathbf{M = \frac{X_A \times 1000 \times d}{(X_A M_A + X_B M_B)}} \qquad \text{[using eq. (i) and eq. (ii)]}$$

Illustration 5

The molarity of NH_3 in aqueous solution is 11.8 mol dm^{-3}. Calculate the mole fraction of NH_3 in solution. The density of solution is 0.916 g cm^{-3}.

Solution:

Let the volume of solution be 1 dm^3. We will have

Amount of NH_3, $n_2 = 11.8$ mol

Volume of solution, $V = 1$ dm^3

Mass of 1 dm^3 solution, $m = V\rho = (10^3 \text{ cm}^3)(0.916 \text{ g cm}^{-3}) = 916$ g

Mass of NH_3 in 1 dm^3 solution, $m_2 = n_2M_2 = (11.8 \text{ mol}) (17 \text{ g mol}^{-1}) = 200.6$ g

Mass of solvent in 1 dm^3 solution, m_1 = mass of solution − mass of solute

$$= 916 \text{ g} - 200.6 \text{ g} = 715.4 \text{ g}$$

Moles of solvent in 1 dm^3 solution, $n_1 = \dfrac{m_1}{M_1} = \dfrac{715.4 \text{ g}}{18 \text{ g mol}^{-1}} = 39.74 \text{ mol}$

Mole fraction of NH_3 in solution, $x_2 = \dfrac{n_2}{n_1 + n_2} = \dfrac{11.8}{39.74 + 11.8} = \mathbf{0.229}$.

2.   Vapour Pressure

When a liquid is placed in a closed container, it evaporates and converts to vapour. After some time, the liquid and the vapour reaches equilibrium, i.e., the rate of evaporation becomes equal to the rate of condensation. At this point of time, the pressure exerted by the vapours of the liquid on the surface of the liquid and on the walls of the container is called the vapour pressure of the liquid.

$$A(l) \rightleftharpoons A(vap)$$

Figure 2.1
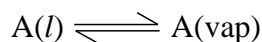
Does the vapour pressure of a liquid depend on the volume of the vessel, shape of the vessel or the amount of liquid taken in the container?

These questions can be answered by invoking the concept of equilibrium constant.

For the equilibrium, liquid $\rightleftharpoons$ vapour, the K_p for the equilibrium would be = $P_{A(vap)}$, since this is the pressure exerted by the vapours at equilibrium (by definition). We know K_p depends only on temperature and the nature of substance. This means that vapour pressure of a liquid will also be constant at a given temperature and will depend on temperature and the nature of liquid.

Therefore, it should be noted that whatever be the volume or shape of the vessel, or the amount of liquid in it (assuming it to be more than the minimum amount required to develop the equilibrium), the vapour pressure of a liquid is constant at a given temperature and changes only with the change of temperature of the liquid.

Moreover, on addition of any substance to the liquid, as long as the substance does not dissolve in the liquid and covers the surface, the vapour pressure of a liquid remains constant.
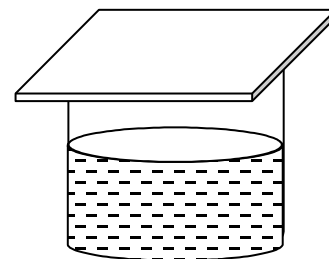
2.1   Solution of a Non-Volatile Solute in a Volatile Solvent

When a non-volatile solute is added to a liquid (solvent), it is found that the vapour pressure of the solution is less than the vapour pressure of the pure liquid. This is because of the following two reasons

1. Attraction between the solute and solvent molecules.

2. Reduction in the number of solvent molecules per unit area of the surface.

Let us understand these two reasons.

Solute-solvent attraction: When the solute is non-volatile, it is always invariably a solid. The reason a solid would dissolve in a liquid is the attraction that the solvent has for the molecules/ions of the solute. Therefore, there is a strong solute-solvent attraction present in the solution. Moreover, this attraction would be dependent on the nature of solute, as different solutes will have different extent of attraction with the same solvent. To do

away with the dependency on the nature of solute, we would like this attraction to have negligible impact on the vapour pressure of a solution.

Reduction in the number of solvent molecules: When a non-volatile solute is dissolved in a liquid, it distributes itself homogenously throughout the solution. Therefore, it occupies the surface of the liquid also. This reduces the number of solvent molecules present per unit area on the surface. This further diminishes the number of vapour molecules that are in equilibrium with the molecules of the liquid present per unit area on the surface. Thus, the vapour pressure gets reduced.

The first cause would be dependent on the nature of solute and the second cause is independent of the nature of solute. To eliminate the first cause, we propose that those solutions in which the solvent content is very high and the solute content is very low (highly dilute solutions) are the ones in which the nature of solute plays an insignificant role towards lowering the vapour pressure of a solution. This is because the solute amount being very small, the change in the vapour pressure on changing the nature of the solute would also be small. Such infinitely dilute solutions are called ideal solutions. In these solutions, the lowering of vapour pressure depends only on the amount of solute and not on its nature.

2.2   Raoult's Law

The rate of evaporation is directly proportional to the number of solvent molecules present per unit area on the surface.

Rate of evaporation $\propto$ no. of solvent molecules present per unit area on the surface

The number of solvent molecules in unit area on the surface in turn is directly proportional to the mole fraction of the solvent in the solution, represented by $X_{solvent}$.

$\therefore$ Rate of evaporation $\propto$ mole fraction of the solvent ($X_{solvent}$)

Rate of evaporation = k $X_{solvent}$, where k is the constant of proportionality.

Rate of condensation is directly proportional to the vapour pressure of the solution. This is because more the pressure on the vapours, more would be the condensation.

$\therefore$ Rate of condensation $\propto$ vapour pressure of the solution (P_S)

Rate of condensation = k′ P_S, where k′ is the constant of proportionality.

At equilibrium the two rates are equal,

Rate of evaporation = Rate of condensation

k′ P_S = k $X_{solvent}$

$P_S = \dfrac{k}{k'} X_{solvent}$

When the solvent is pure, $X_{solvent} = 1$. Under this condition, $P = \dfrac{k}{k'}$ and the vapour pressure of the pure solvent is denoted by P^o.

$\therefore$ $P_S = X_{solvent} P^o$ …..(i)

This is the mathematical representation of Raoult's Law, which states that

When a non-volatile solute is added to a solvent, the vapour pressure of the solution decreases and is equal to the product of the mole fraction of the solvent in the solution and the vapour pressure of the pure solvent.

The equation (i) can be rewritten as

$$\frac{P_S}{P^\circ} = X_{solvent} = 1 - X_{solute} \text{ (since } X_{solute} + X_{solvent} = 1)$$

$$X_{solute} = 1 - \frac{P_S}{P^\circ}$$

$$\mathbf{X_{solute}} = \frac{P^\circ - P_S}{P^\circ}$$

The relative lowering of vapour pressure of a solution is equal to the mole fraction of the solute in the solution.

2.3   Ideal Solution

A solution can be termed as ideal, if it falls into any one of the given below categories:

(i) Raoult's law

An ideal solution is that solution in which each component obeys Raoult's law under all conditions of temperature and pressure.

(ii) Thermodynamics

An ideal solution is defined as the one in which no volume change and enthalpy change takes place on mixing the solute and the solvent in any proportion i.e. $\Delta V_{mixing} = 0$ and $\Delta H_{mixing} = 0$. However, it must be kept in mind that $\Delta S_{mixing} = +ve$.

(iii) Molecular interactions

An ideal solution is defined as the solution in which the intermolecular interactions between the components are of the same magnitude as the intermolecular attractions found in the pure components. In other words, A-----B forces of attraction should have same strength as A-----A and B-----B forces of attraction.

In actual practice, no solution is ideal. However, when concentration of solute is very low the solution behaves ideally. Therefore, very dilute solutions are ideal in behaviour.

In general, substances forming similar structure and polarities form nearly ideal solution. For example,

(i) Benzene + Toluene

(ii) Hexane + Heptane

(iii) Ethyl bromide + Ethyl iodide

(iv) Ethyl bromide + Methyl bromide

(v) Chlorobenzene + Bromobenzene

2.4   Solution of a Volatile Solute in a Volatile Solvent When Both are Miscible

Generally a volatile solute is a liquid. Since the solvent is also a liquid, it is quite normal to treat either of them as a solute and the other as a solvent. Let us assume that liquid 'A' is the solvent and liquid 'B' is the solute. Since both of them are volatile, the ideal solution should be such that Raoult's Law is valid for both solvent and solute. This means

$$P_A = X_A \, P_A^o \text{ and } P_B = X_B \, P_B^o$$

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A definition of an ideal solution in this case must be different from the case of a non-volatile solute because here both solute and solvent have to satisfy Raoult's Law. If we were to follow the previous definition, the solvent would definitely obey Raoult's Law but not the solute. Therefore, here the definition must not deal with the amounts of the solute and solvent.

Consider given figure, which shows a solution of two liquids A & B. We want an ideal solution whose vapour pressure changes from that of pure A and pure B only due to the presence of each other on the surface. This means that the decrease in the vaporization of A (or B) is only due to the presence of B (or A) and should not be effected by the force of attraction or repulsion between A and B. This is only possible, if the attraction between A and B is same as that between A & A and B & B. Therefore, an ideal solution with a volatile solute has to be the one in which A-----A forces, B-----B forces and A-----B forces are equal in magnitude.
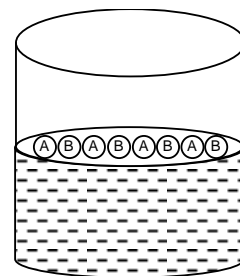
This also implies that on adding B to A, no net energy is released or absorbed and the volume of the solution is equal to the sum of the volumes of both A and B. Therefore, ΔV_{mixing} and ΔH_{mixing} is zero.

Let X_A and X_B are the mole fractions of two volatile miscible liquids A and B having vapour pressures P_A° and P_B° respectively at temperature T K. Therefore, vapour pressure of solution is given by

$$P_{Total} = P_A + P_B = X_A P_A^\circ + X_B P_B^\circ = X_A P_A^\circ + (1 - X_A) P_B^\circ = X_A (P_A^\circ - P_B^\circ) + P_B^\circ$$

A plot between P_{Total} and X_A is linear with slope equal to $(P_A^\circ - P_B^\circ)$ and intercept equal to P_B°. Thus, the total pressure increases with increase in X_A.
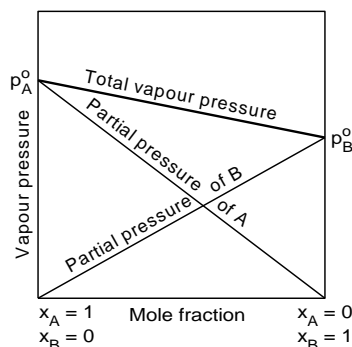
If X'_A and X'_B are the mole fractions of A and B in the vapour phase, then according to Dalton's law of partial pressure, we can write $P_A = X'_A \times P_{Total}$

$$\therefore \quad X'_A = \frac{P_A}{P_{Total}} = \frac{X_A P_A^\circ}{X_A P_A^\circ + X_B P_B^\circ}$$

and $$X'_B = \frac{X_B P_B^\circ}{X_A P_A^\circ + X_B P_B^\circ} = 1 - X'_A.$$

Now, the vapours above the solution are collected and condensed. The condensed liquid is brought to the same temperature at which original liquid mixture was kept. Then, the vapour pressure (P'_{Total}) of the resulting solution is given by

$P'_{Total} = P'_A + P'_B$ (where P'_A and P'_B are partial vapour pressures of A and B in the resulting solution).

$$P'_{Total} = P^°_A X'_A + P^°_B X'_B$$

Let X''_A and X''_B be the mole fractions of A and B in the vapours formed above the condensed liquid kept at same temperature.

$$\therefore \ X''_A = \frac{P'_A}{P'_{Total}} = \frac{P^°_A X'_A}{P^°_A X'_A + P^°_B X'_B} \ \text{and} \ \ X''_B = \frac{P'_B}{P'_{Total}} = \frac{P^°_B X'_B}{P^°_A X'_A + P^°_B X'_B}$$

Illustration 6

Calculate the mole fraction of benzene in a benzene toluene ideal solution that is in equilibrium with vapour phase that contains 60 mole % benzene. Given: $P^o_{benzene} = 600 \, mm \, Hg$ and $P^o_{toluene} = 300 \, mm \, Hg$.

Solution:

According to Raoult's Law,

$$P_{benzene} = X_{benzene} P^o_{benzene} \qquad \ldots\ldots(1)$$

$$P_{toluene} = X_{toluene} P^o_{toluene} \qquad \ldots\ldots(2)$$

where *P* is the vapour pressure of a particular component in a solution, P^o is the pure vapour pressure of that component and *X* is the mole fraction of that component.

According to Dalton's Law,

$$P_{benzene} = Y_{benzene} \, P_T \qquad\qquad \ldots\ldots(3)$$

$$P_{toluene} = Y_{toluene} \, P_T \qquad\qquad \ldots\ldots(4)$$

where *Y* is the mole fraction of a particular component in a solution.

Equating Equation (1) & (3) and (2) & (4,) we get

$$Y_{benzene} \, P_T = X_{benzene} \, P^o_{benzene} \qquad \ldots\ldots(5)$$

$$Y_{toluene} \, P_T = X_{toluene} \, P^o_{toluene} \qquad \ldots\ldots(6)$$

Dividing Equation (5) by (6),

$$\frac{Y_{benzene}}{Y_{toluene}} = \frac{X_{benzene} \times P^o_{benzene}}{X_{toluene} \times P^o_{toluene}}$$

$$\frac{Y_{benzene}}{1 - Y_{benzene}} = \frac{X_{benzene} \times P^o_{benzene}}{1 - X_{benzene} \times P^o_{toluene}} \qquad \ldots\ldots(7)$$

$$\frac{0.6}{0.4} = \frac{X_{benzene} \times 600}{1 - X_{benzene} \times 300}$$

On solving,

$$X_{benzene} = \frac{3}{4}$$

Illustration 7

A vessel labelled 1 contains 3 mole of liquid A and 1 mole of liquid B forming an ideal solution. The solution is allowed to reach equilibrium with its vapours. The vapours are then quickly taken out and condensed in vessel labelled 2. Here again, the solution is allowed to reach equilibrium with its vapours. The vapours are again quickly taken out condensed in vessel labelled 3. This process is continued several times. If the $P_A^o = 700$ mm Hg and $P_B^o = 350$ mm Hg, then calculate

(i) the composition of vapours in vessel labelled 1.

(ii) the composition of vapours in vessel labelled 2 and

(iii) the composition of vapours in vessel labelled 100.

Assume that composition of liquid mixture does not change due to formation of vapour liquid equilibrium.

Solution:

According to equation $\dfrac{Y_A}{1-Y_A} = \dfrac{X_A}{1-X_A}\left(\dfrac{P_A^o}{P_B^o}\right)$

This equation relates the mole fraction of a component of a solution in the liquid and vapour phases with each other.

(i) The composition of vapours in vessel labelled 1 is

$$\frac{Y_{A,1}}{1-Y_{A,1}} = \frac{3}{1}\times\frac{700}{350}$$

$$\therefore \qquad Y_{A,1} = \frac{6}{7}\,;\; Y_{B,1} = \frac{1}{7}$$

(ii) The Y_A of vessel 1 would become the X_A of vessel 2.

$$\therefore\; \frac{Y_{A,2}}{1-Y_{A,2}} = \frac{X_{A,2}}{1-X_{A,2}}\left(\frac{P_A^o}{P_B^o}\right) = \frac{Y_{A,1}}{1-Y_{A,1}}\left(\frac{P_A^o}{P_B^o}\right) = \frac{X_{A,1}}{1-X_{A,1}}\left(\frac{P_A^o}{P_B^o}\right)^2$$

$$\therefore Y_{A,2} = \frac{12}{13}\,;\; Y_{B,2} = \frac{1}{13}$$

(iii) Using the relation developed in (ii), we can write

$$\frac{Y_{A,n}}{1-Y_{A,n}} = \frac{X_{A,1}}{1-X_{A,1}}\left(\frac{P_A^o}{P_B^o}\right)^n \quad\text{where n is the number of the vessel}$$

$$\therefore Y_{A,100} = \frac{3}{1}\left(\frac{750}{350}\right)^{100} = 3\times 2^{100}\,;\; Y_{B,100} \approx 0.$$

One of the very important assumptions made here is that on evaporation the composition of a solution does not change much and therefore can be ignored.

Illustration 8

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

$P_{Total} = 179 \, X_B + 92$, where X_B is mole fraction of C_6H_6.

Calculate (in mmHg)

(a) Vapour pressure of pure liquids.

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

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

Solution:

(a) Given, $P_{Total} = 179X_B + 92$

For a binary volatile liquid mixture of benzene and toluene, the total pressure is given by

$$P_{Total} = P_B^° \, X_B + P_T^° \, X_T$$

where $P_B^°$ & $P_T^°$ represents vapour pressure of pure benzene & pure toluene respectively and X_B & X_T be the mole fraction of benzene & toluene respectively, in the liquid solution.

$$P_{Total} = P_B^° \, X_B + P_T^° \, (1 - X_B)$$

$$= P_B^° \, X_B + P_T^° - P_T^° X_B = (P_B^° - P_T^°)X_B + P_T^°$$

Comparing this equation with the given equation,

$$P_T^° = \textbf{92 mm of Hg}$$

$$P_B^° - P_T^° = 179$$

$\therefore \qquad P_B^° = \textbf{271 mm of Hg}$

(b) Moles of benzene $= \dfrac{936}{78} = 12$

and moles of toluene $= \dfrac{736}{92} = 8$

Now, $P_{Total} = P_B^° X_B + P_T^° X_T$

$$= 271 \times \left(\frac{12}{12+8} \right) + 92 \times \left(\frac{8}{12+8} \right) = 162.6 + 36.8 = \textbf{199.4 mm of Hg}$$

(c) Mole fraction of C_6H_6 in vapour phase of initial mixture be y_B.

$$y_B = \frac{P_B}{P_{Total}} = \frac{162.6}{199.4} = 0.815$$

and mole fraction of C_7H_8 in vapour phase of initial mixture be y_T.

$\therefore \qquad y_T = 0.185$

These vapours are collected and condensed into liquid. The liquid is again kept at 50°C to get again liquid–vapour equilibrium.

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

$\qquad$ = Mole fraction of C_6H_6 in the condensed liquid

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

$\qquad$ = Mole fraction of C_7H_8 in the condensed liquid

Therefore, $P'_{Total} = P^o_B y_B + P^o_T y_T = (271 \times 0.815) + (92 \times 0.185)$

$\qquad$ = 220.865 + 17.02 = 237.885 mm of Hg

$\therefore$ New mole fraction of C_6H_6 in vapour phase $= \dfrac{P^o_B y_B}{P'_{Total}} = \dfrac{220.865}{237.885} = \mathbf{0.928}$

New mole fraction of C_7H_8 in vapour phase = **0.072**.

2.5 Non-Ideal Solutions

In terms of Raoult's law a non-ideal solution is defined as the one which does not obeys Raoult's law. These are divided into two types as explained below:

Non–Ideal Solutions Showing Positive Deviations

These can be defined on the basis of

(a) Molecular interactions

A non–ideal solution showing positive deviation is defined as the one in which the intermolecular forces of interactions between the molecules is weaker as the interactions found in any one of the pure components or both.

(b) Thermodynamics

A non–ideal solution is defined as the one in which there is a slight increase in volume on mixing and absorption of heat takes place on mixing. ΔV_{mixing} =positive, ΔH_{mixing} = positive.

In general, the trend of molecular interactions in the molecules are hydrogen bonding > dipole–dipole interactions > van der Waal's interaction (for compounds in which there is not much difference is mass). Hence, replacement of any one of the stronger interactions by the weaker one would result in a deviation.

Positive deviations from Raoult's law

Examples:

(i) Acetone (dipole) + carbon disulphide (van der Waal's)

(ii) Acetone (dipole) + ethyl alcohol (hydrogen)

(iii) Acetone (dipole) + benzene (van der Waal's)

(iv) Carbon tetrachloride (van der Waal's) + Chloroform (dipole)

(v) Methyl alcohol + water

(vi) Ethyl alcohol + water
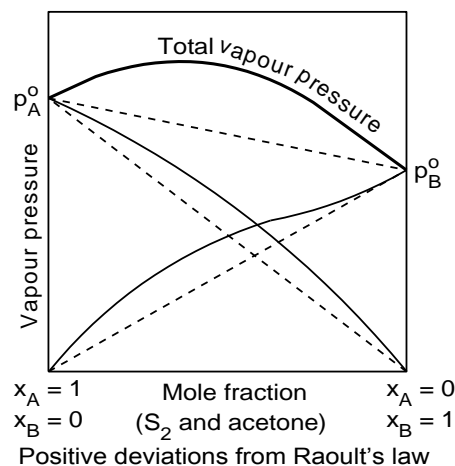
In the given examples from (i) to (vi), the molecules possessing weaker interactions get in between the molecules possessing stronger one and thereby reducing them. In examples (v) and (vi), though both the components have hydrogen bonding but the extent of hydrogen bonding in the case of water is more than that in the case of alcohols.

For one intermediate composition, the total vapour pressure of such a solution will be the highest and the boiling point will be the lowest. This solution acquires the property of boiling at a constant temperature and its composition remains unchanged. Liquid mixtures, which boil out without any change in the composition are called *azeotropes or azeotropic mixtures*. In case of positive deviations, we get minimum boiling azeotropes.

Non-Ideal Solutions Showing Negative Deviations

These can be defined on the basis of
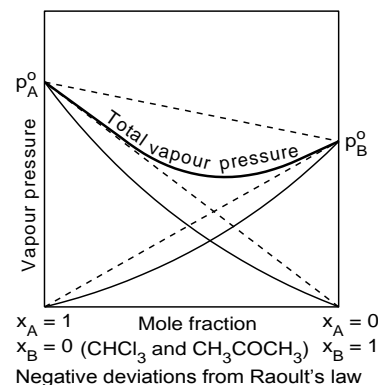
(a) Molecular interactions

Solutions in which forces of interactions between the components is more than that in between the pure components are the ones showing negative deviation from Raoult's law.

(b) Thermodynamics

In the case of such solutions, a slight decrease in volume and evolution of heat takes place on mixing i.e. ΔV_{mixing} = negative and ΔH_{mixing} = negative.

Negative deviations from Raoult's law

Examples

(i) Chloroform (dipole) + acetone (dipole)

(ii) acetone(dipole) + aniline (weak hydrogen bond)

(iii) Acetic acid (hydrogen bonding) + pyridine (van der Waal's)

(iv) HCl + water

(v) HNO_3 + water

In the above examples from (i) to (iii), the weak interactions are being replaced by strong hydrogen bonds, thus reducing the escaping tendency of the molecules. In case of (iii), one of the constituents is basic while the other is acidic. Whereas (iv) and (v) involve an aqueous solution of a strong volatile acid such as a halogen acid. In these cases, non−volatile ions are formed as a result of interaction of ions of the acid with water.

For such solutions, at one intermediate composition, the total pressure exhibited by the components is the least and hence the boiling point of the liquid mixture at that composition would be highest. The solution will thus distil without a change in composition and provide an example of maximum boiling azeotrope.

2.6   Mixture of Two Immiscible Volatile Liquids

When a volatile liquid is mixed with another volatile liquid, which are completely immiscible (at molecular level), mixture will be heterogeneous (mixing at drop level). Here each liquid will behave independent of the other and will exert its own vapour pressure. The total vapour pressure of the system will be the sum of vapour pressure of both the volatile liquids.

$\therefore$ $P_{Total} = P_A + P_B = P_A^\circ + P_B^\circ$ (as X_A and X_B = 1)

The total vapour pressure of the system remain constant as long as both the volatile liquids are present and will not depend on the relative amounts of the two liquids.

LIQUID SOLUTION

The boiling point of a liquid system is the temperature at which its vapour pressure becomes equal to the external atmospheric pressure. Since the total vapour pressure of a mixture containing immiscible volatile liquids is greater than that of either of the pure constituents, thus the mixture will boil at a temperature, which is lower than the boiling point of either of the pure constituents. The boiling point of the liquid mixture will remain constant as long as drops of both liquids are present, as the total vapour pressure is independent of the relative amounts of the two constituents.

This forms the basis of steam distillation, in which one of the volatile liquids is water.

This composition of the vapour above the liquid mixture can be calculated using Dalton's law of partial pressures. Thus,

$$P_A = P_A^{\circ} = P_{Total} X'_A \qquad \text{.......(i)}$$

$$P_B = P_B^{\circ} = P_{Total} X'_B \qquad \text{.......(ii)}$$

where X'_A and X'_B represents the mole fraction of A and B in the vapour phase. Let n_A and n_B are the moles of A and B, respectively in the vapour phase.

$$\therefore \qquad X'_A = \frac{n_A}{n_A + n_B}$$

and

$$X'_B = \frac{n_B}{n_A + n_B}$$

Dividing equation (ii) by (i),

$$\frac{P_{Total} X'_B}{P_{Total} X'_A} = \frac{P_B^{\circ}}{P_A^{\circ}}$$

$$\therefore \qquad \frac{P_B^{\circ}}{P_A^{\circ}} = \frac{X'_B}{X'_A} = \frac{\dfrac{n_B}{n_A + n_B}}{\dfrac{n_A}{n_A + n_B}} = \frac{n_B}{n_A}$$

or

$$\frac{P_B^{\circ}}{P_A^{\circ}} = \frac{w_B \times M_A}{M_B \times w_A}$$

$$\therefore \qquad \frac{w_B}{w_A} = \frac{P_B^{\circ} \times M_B}{P_A^{\circ} \times M_A}$$

Thus, the masses of the constituents in the vapour (distillate) will be proportional to their respective molar mass and vapour pressure.

Illustration 9

The steam distillation of chlorobenzene is observed to occur at a temperature of 90.6°C, when the total pressure is 1 atm. Assuming complete immiscibility of these liquids, calculate the mass of chlorobenzene in 0.1 kg of distillate. The vapour pressure of water at 90.6°C is 538.9 Torr.

Solution:

For a mixture of two immiscible liquids, the total pressure is given by

---

$P_{Total} = P_{chlorobenzene}^{\circ} + P_{water}^{\circ}$

$760 = P_{chlorobenzene}^{\circ} + 538.9$

$\therefore \quad P_{chlorobenzene}^{\circ} = 221.1 \text{ Torr}$

$P_{chlorobenzene}^{\circ} = X_{chlorobenzene(V)} \times P_{Total}$ ....(i)

and $\quad P_{water}^{\circ} = X_{water(V)} \times P_{Total}$ ....(ii)

Dividing equation (i) by (ii) gives,

$$\frac{X_{chlorobenzene(V)}}{X_{water(V)}} = \frac{P_{chlorobenzene}^{\circ}}{P_{water}^{\circ}}$$

or $\quad \dfrac{P_{chlorobenzene}^{\circ}}{P_{water}^{\circ}} = \dfrac{\dfrac{n_C}{n_C + n_w}}{\dfrac{n_w}{n_C + n_w}}$

where n_C and n_w represents the number of moles of chlorobenzene and water in the vapour phase, respectively.

$$\therefore \quad \frac{P_{chlorobenzene}^{\circ}}{P_{water}^{\circ}} = \frac{n_C}{n_w} = \frac{\dfrac{w_C}{M_C}}{\dfrac{w_{H_2O}}{M_{H_2O}}}$$

$$\therefore \quad \frac{P_{chlorobenzene}^{\circ}}{P_{water}^{\circ}} = \frac{w_C \times M_{H_2O}}{w_{H_2O} \times M_C}$$

where M_C and M_{H_2O} represents molar mass of chlorobenzene and water respectively and w_C and w_{H_2O} denotes weight of chlorobenzene and water in the vapour phase, respectively.

$$w_C = \frac{P_{chlorobenzene}^{\circ} \times w_{H_2O} \times M_C}{P_{H_2O}^{\circ} \times M_{H_2O}}$$

Total mass of the distillate = 0.1 kg = 100 g

Let the mass of chlorobenzene in the distillate be x g, then mass of H_2O would be $(100 - x)$ g.

$$x = \frac{221.1 \times (100 - x) \times 112.5}{538.9 \times 18}$$

$$x = 71.94 \text{ g}$$

3. Colligative Properties

In this section, we shall consider only those properties, which result because of the dissolution of a non−volatile solute in a volatile liquid solvent. These are, lowering of vapour pressure, elevation of boiling point depression in freezing point and osmotic pressure. These are collectively known as the "*colligative properties*" as they depend only on the number of species present (i.e., colligative properties are directly proportional to the number of mole of solute) in the solution and not on their nature. Only those solutions, which are ideal, show these properties.

3.1 Relative Lowering of Vapour Pressure

According to Raoult's law, the lowering of vapour pressure of a solvent is given by

$$P^o - P_S = P^o - X_{solvent}P^o = P^o(1 - X_{solvent}) = P^oX_{solute}$$

Thus, $$\frac{P^o - P_S}{P^o} = X_{solute} \qquad \ldots\ldots(3.1)$$

The expression $(P^o - P_S)/P^o$ is known as the relative lowering of vapour pressure and according to Eqn (3.1), this is equal to the mole fraction of the solute in the solution.

$X_{solute} = \frac{n_{solute}}{n_{solute} + n_{solvent}}$. It can be seen that X_{solute} is not directly proportional to the number of moles of solute. So it may be seen that the relative lowering of vapour pressure would not qualify as a colligative property. But since these properties are shown by ideal solutions which happen to be infinitely dilute, it can be assumed $n_{solute} \ll n_{solvent}$, therefore in the denominator, n_{solute} can be ignored in comparison to $n_{solvent}$. Thus, $X_{solute} \approx \frac{n_{solute}}{n_{solvent}}$.

Now, X_{solute} is directly proportional to n_{solute}.

Based on Eq. (3.1) it can also be derived that, $\frac{P^o - P_S}{P_S} = \frac{n_{solute}}{n_{solvent}}$ which can be used for solving problems without making any assumption.

Ostwald−Walker Experiment
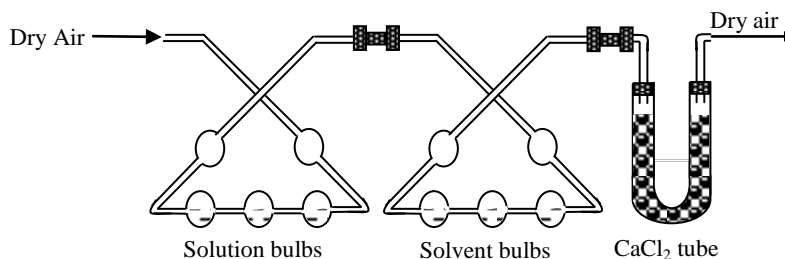
Ostwald−Walker apparatus

The Ostwald−Walker experiment is designed to calculate the relative lowering of vapour pressure of a solution. In this method, a stream of dry air is bubbled successively through (i) the solution (ii) the pure solvent and (iii) a reagent, which can absorb the vapours of the solvent. As the solvent is usually water, the reagent is generally anhydrous calcium chloride. The complete assembly is shown in figure. 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 anhydrous calcium chloride is taken in the U-tube at the end. All the bulbs are kept at the same temperature and air must be bubbled gradually to ensure that it gets saturated with the vapours in each bulb.

The principle behind this experiment is that when a gas is passed through another gas, the later diffuses into the former. This means that when dry air is bubbled through a solution, the vapours present in it diffuse into air. The diffusion takes place till the pressure of the vapours in air becomes equal to that of the vapours in the container. Therefore, there will be a loss of weight in the first container, which will be equal to

$$w = \frac{PVM}{RT}$$

where w is the weight lost by the first container (due to vapours diffusing into the air), P is the pressure exerted by the vapours in the container (equal to the vapour pressure of the solution), V is the volume in which the vapours are present, M is the molecular mass of the vapour and T is the temperature of the vapours.

When the air carrying the vapours from the solution container moves to the solvent container, vapours from the solvent container diffuse in to the partially saturated air. This is despite the fact the air already contained some vapours. This is because the pressure the vapours exerted in the air is P_S while the pressure exerted by the vapours in the solvent container is P^o. So the vapours that diffuse in to the air now have a pressure of $P^o - P_S$. Therefore, the solvent container also loses weight, which is given by

$$w' = \frac{(P^o - P_S)VM}{RT}$$

As the air passes through the third container i.e. $CaCl_2$ tube, all the vapours get absorbed by the absorbing agent, which makes the third container gain weight equal to the loss of the first two.

Thus,

$$\frac{w'}{w'+w} = \frac{P^o - P_S}{P^o} = \text{Relative lowering of vapour pressure} \quad \text{or} \quad \frac{P^o - P_S}{P_S} = \frac{w'}{w}$$

Illustration 10

Dry air was passed through a container having a solution of a non−volatile solute in water. The solute weighed 26.66 g and the solvent weighed 200 g. The air then went into a solvent container and then finally through a tube containing fused calcium chloride. The loss in weight of water container is 0.087 g and gain in weight of $CaCl_2$ tube is 2.036 g. Calculate the molecular weight of the non−volatile solute present in the solution.

Solution:

We can use the relation,

$$\frac{P^o - P_S}{P_S} = \frac{n}{N} = \frac{\text{loss in weight of solvent}}{\text{loss in weight of solution}}$$

$$\frac{0.087}{2.036 - 0.087} = \frac{\dfrac{26.66}{M}}{\dfrac{200}{18}} = \frac{26.66 \times 18}{200 \times M} \; ; \; M = \frac{26.66 \times 18 \times 1.949}{200 \times 0.087} = 53.75$$

# LIQUID SOLUTION

3.2   Elevation of Boiling Point

Boiling is the phenomenon in which a liquid converts to the vapour state from any part of the liquid. Evaporation on the other hand is the conversion of a liquid into the vapour from the surface of the liquid.

At a temperature below the boiling point of the liquid, liquid molecules from the bulk of the liquid cannot form vapour bubble and escape. This is because the pressure inside the vapour bubble is the vapour pressure of the liquid at that temperature and as long as the vapour pressure is less than the atmospheric pressure, the bubble cannot be formed. This is due to the fact that the downward pressure of the atmosphere is more than the internal outward pressure inside the vapour bubble.
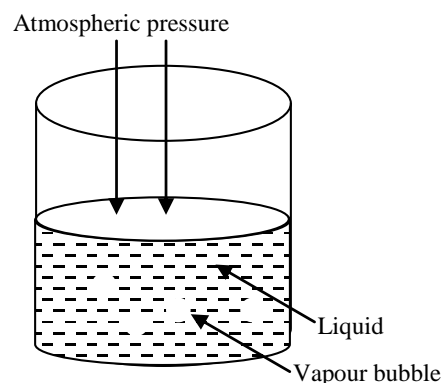
When the vapour pressure becomes slightly greater than the internal pressure, the vapours can form from any part of the liquid and escape. So, the limiting pressure is the atmospheric pressure. Therefore, a liquid boils at a temperature when its vapour pressure becomes equal to the atmospheric pressure.

Since the addition of a non−volatile solute decreases the vapour pressure of the solvent, the boiling point of the solution becomes greater than that of the pure solvent. This can be understood from the figure 3.2b.

Vapour Pressure curve
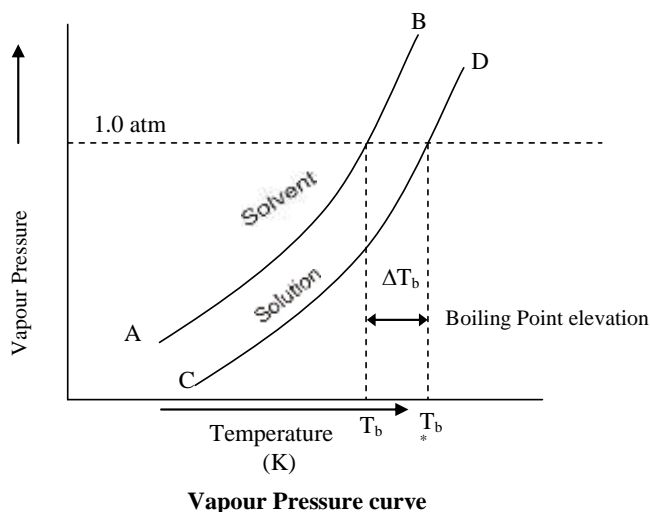
If T_b is the boiling point of pure solvent and T_b^* is the boiling point of the solution, then the elevation in boiling point is represented as ΔT_b.

Thus, $T_b^* - T_b = \Delta T_b$

Since, elevation in boiling point is proportional to the decrease in vapour pressure which in turn is proportional to concentration of solute. Thus,

$$\Delta T_b \propto m$$

where *m* is the molality of the solution.

or $\Delta T_b = K_b\, m$

where K_b is the molal boiling point elevation constant or ebullioscopic constant.

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Molal Boiling Point Elevation Constant (K_b)

It is the elevation in boiling point achieved when a solution of a non−volatile solute of concentration 1 molal is boiled. Its units are K kg mol^{-1}. K_b is related to molar enthalpy of vaporization as $K_b = \dfrac{M\ RT_b^2}{\Delta H_{vap} \times 1000}$

where M = molar mass of solvent,

   R = Universal gas constant,

   T_b = boiling point of pure solvent and

   ΔH_{vap} = enthalpy of vaporization of solvent.

Illustration 11

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

Solution:

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

   $\therefore$ P° = P_{ext} at boiling temperature, T_b.

   Now, let us dissolves a non−volatile solute in the pure liquid to form a solution. 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 point T_b', when the vapour pressure of the solution would become 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,

   $$ln\, \frac{K_{P_{T_2}}}{K_{P_{T_1}}} = \frac{\Delta H_{vap}}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

   $$\ln \frac{K_{P_{T_2}}}{K_{P_{T_1}}} = \frac{\Delta H_{vap}}{R}\left[\frac{1}{T_b} - \frac{1}{T_b'}\right] = \frac{\Delta H_{vap}}{R}\left[\frac{\Delta T_b}{T_b T_b'}\right]$$

   Assuming the solution to be very dilute, we can say T_b' would be very close to T_b.

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

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

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

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

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

where n and N are the number of moles of solute & solvent respectively.

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

(since for dilute solution, $n + N \approx N$)

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

Multiplying by 1000 on both the sides,

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

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

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

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

Illustration 12

A solution containing 0.512 g of naphthalene (molar mass 128.2 g mol^{-1}) in 50 g CCl$_4$ yields a boiling point elevation of 0.402 K, while a solution of 0.6216 g of an unknown solute in the same mass of the solvent gives a boiling point elevation of 0.647 K. Find the molar mass of the unknown solute.

Solution:

$$T^*_{b,naphthalene} - T_{b,CCl_4} = \Delta T_{b,naphthalene} = K_b \, m_{naphthalene}$$

$$T^*_{b,unknownsolute} - T_{b,CCl_4} = \Delta T_{b,unknownsolute} = K_b \, m_{unknownsolute}$$

$$\therefore \; T^*_{b,unknownsolute} - T^*_{b,naphthalene} = \Delta T_{b,unknownsolute} - \Delta T_{b,naphthalene}$$

$$= K_b \times \left(m_{unknownsolute} - m_{naphthalene}\right)$$

$$K_b = \frac{\Delta T_{b,naphthalene}}{m_{naphthalene}} = \frac{0.402 \, K}{\left(\dfrac{\dfrac{0.512 \, g}{128.2 \, g \, mol^{-1}}}{50 \, g}\right) \times 1000 g \; kg^{-1}}$$

$$K_b = \frac{0.402 \times 50 \times 128.2}{0.512 \times 1000} = 5.03 K \; kgmol^{-1}$$

$$0.647\,\text{K} - 0.402\,\text{K} = 5.03\,\text{K kg mol}^{-1} \left(\frac{0.6216\,\text{g} \times 1000\,\text{g kg}^{-1}}{\text{M g mol}^{-1} \times 50\,\text{g}} - \frac{0.512\,\text{g} \times 1000\,\text{g kg}^{-1}}{128.2\,\text{g mol}^{-1} \times 50\,\text{g}} \right)$$

Solving for M we get,

M = **96.68 g mol^{-1}**

3.3   Depression in Freezing Point

Freezing is the phenomena when a liquid is in equilibrium with its solid phase. At the freezing temperature, both the liquid as well as the solid is in equilibrium with the vapours. This implies that the vapour pressure of both the liquid and the solid are same at the freezing point. Therefore, alternatively freezing point can be defined as the temperature when the vapour pressure of the liquid and the solid are equal.

On adding a non−volatile solute, the freezing point of the solution decreases compared to that of the pure liquid because the solid that separates out from both is assumed to be pure (this means that when a solution is frozen only the liquid freezes out leaving behind the solute). This can be understood from the figure 3.3.

If T_f is the freezing point of pure solvent and T_f^* is the freezing point of the solution, then the depression in freezing point is represented as ΔT_f.

Thus, $T_f - T_f^* = \Delta T_f$

Vapour Pressure curve
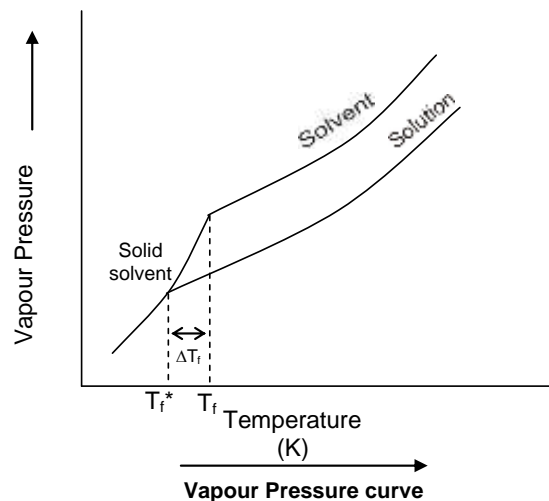
Since depression in freezing point is proportional to the decrease in vapour pressure which in turn is proportional to the concentration of solute. Thus,

$$\Delta T_f \propto m$$

where m is the molality of the solution.

or $\Delta T_f = K_f\, m$

where K_f is the molal freezing point depression constant or cryoscopic constant.

Molal Freezing Point Depression Constant (K$_f$)

It is the depression in freezing point achieved when a solution of a non−volatile solute of concentration 1 molal is frozen. Its units are K kg mol^{-1}. K_f is related to the molar enthalpy of fusion as

$$K_f = \frac{M\,RT_f^2}{\Delta H_{fusion} \times 1000}$$

where   M = molar mass of solvent,

R = universal gas constant,

T_f = freezing point of pure solvent and

ΔH_{fusion} = enthalpy of fusion of solid solvent.

3.4   Osmotic Pressure

Osmosis is defined as the spontaneous flow of solvent into solution or from a more dilute to a more concentrated solution, when the two solutions are separated by a suitable membrane. The membrane allows the free passage of the solvent but not of the dissolved substances. Membranes possessing this property are said to be semipermeable.

The phenomenon of osmosis may be illustrated in a simple manner by tying an animal membrane, e.g., bladder, over the end of an inverted thistle tube, which is then partly filled with a concentrated solution of sucrose (cane sugar) and dipped into a beaker of water, as shown in the given figure. The level of the liquid will rise in the tube until the hydrostatic pressure so produced is sufficient to stop the flow of water. It is seen, therefore, that as a result of osmosis, a pressure is developed which opposes the tendency for the solvent to pass through the semipermeable membrane into the solution. This pressure is called the osmotic pressure of the solution. It is defined as "the excess pressure that must be applied to a solution to prevent the passage into of solvent when the two liquids are separated by a perfectly semipermeable membrane".
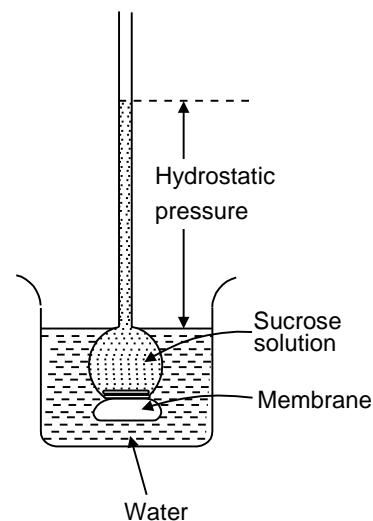
There has been some tendency to think of osmotic pressure as a pressure produced by the solution, but this point of view is misleading. The osmotic pressure is brought into existence only when the solution is separated from the solvent by a semipermeable membrane. The resulting osmosis or tendency for osmosis to occur then produces an excess pressure in the solution. When this excess pressure attains the value of the osmotic pressure, the tendency for solvent to enter the solution is exactly counterbalanced by the reverse tendency and a condition of equilibrium results.

For the accurate measurement of osmotic pressure, it is necessary to have a membrane that is perfectly semipermeable. Artificial membranes made of copper ferrocyanide, $Cu_2Fe(CN)_6$, is the best material for osmosis.

The osmotic pressure of a dilute solution of a non-volatile solute is given by

$$\pi V = nRT$$

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

$$\pi = \frac{w}{M}\frac{RT}{V}$$

where π is the osmotic pressure in atmospheres, n = number of moles of solute $\left(\dfrac{w}{M}\right)$ in V litres of solution at temperature T (Kelvin), R = 0.0821 Lit atm K^{-1} mol^{-1}. C is the molarity of the solution. Measurement of osmotic pressure provides a method of determining molecular weights of proteins, polymer and other macromolecules.

If two solutions are of equal concentrations at the same temperature, they have the same osmotic pressure and they are said to be isotonic. If two solutions have unequal osmotic pressures, the more concentrated solution is

said to be hypertonic and the more dilute solution is described as hypo tonic. To study the contents of red blood cells, which are protected by a semipermeable membrane, a technique called haemolysis is used. The red blood cells are placed in a hypo tonic solution, when water moves into the cells. The cells swell and eventually burst releasing the haemoglobin and other molecules.

When a bacterial cell is placed in a hypertonic solution (high concentration), the intracellular water tends to move out of the cell by osmosis. This causes the cell to shrink.

Illustration 13

Find the molecular weight of the polymer having the concentration of 9.6 g/l and exerting an osmotic pressure of 2.56 torr at a temperature of 298 K.

Solution:

$\pi = CRT$

$$\frac{2.56}{760} = \frac{9.6 \times 0.0821 \times 298}{M}$$

or $M = $ **67, 600 g/mol**.

4.   Van't Hoff Factor

Since colligative properties depend on the number of particles of the solute, in some cases where the solute associates or dissociates in solution, abnormal results for colligative properties are obtained.

Dissociation

Let us consider a case of acetic acid dissolved in water. Let the number of mole of acetic acid dissolved be 'n'.
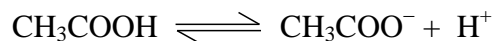
$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

Initial no. of mole   n   0   0

After dissociation $n(1-\alpha)$ $n\alpha$ $n\alpha$

Total mole of solute = $n(1 + \alpha)$

Theoretical colligative property (for example ΔT_b) (based on the no. of mole of CH_3COOH added)

$$\Delta T_b = K_b \, m = K_b \times \frac{n}{W} \times 1000, \text{ where W is the mass of solvent in gm.}$$

Experimental colligative property would be given by

$$\Delta T_b' = K_b \, m' = K_b \times \frac{n(1+\alpha)}{W} \times 1000$$

$$\frac{\text{Experimental colligative property}}{\text{Theoretical colligative property}} = \frac{n(1+\alpha)}{n} = (1+\alpha) = i, \text{ Van't Hoff factor}$$

Association

Let us consider the case of acetic acid dissolved in benzene. Let the number of mole of acetic acid dissolved be 'n' and it forms dimmer in benzene.

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

Initial no. of mole   n   0

After dissociation $n(1-\alpha)$ $n\alpha / 2$

Total mole of solute = $n(1 - \alpha / 2)$

Theoretical colligative property (for example ΔT_b) (based on the no. of mole of CH_3COOH added)

$$\Delta T_b = K_b\, m = K_b \times \frac{n}{W} \times 1000 \text{, where W is the mass of solvent in gm.}$$

Experimental colligative property would be given by

$$\Delta T_b' = K_b\, m' = K_b \times \frac{n\left(1-\dfrac{\alpha}{2}\right)}{w} \times 1000$$

$$\frac{Colligative\,property\,experimental}{Colligative\,property\,theoretical} = \frac{n\left(1-\dfrac{\alpha}{2}\right)}{n} = 1 - \frac{\alpha}{2} = i \text{, Van't Hoff factor}$$

Therefore, for dissociation $i > 1$ and for association $i < 1$. When a solute neither dissociates nor associates, the Van't Hoff factor is equal to 1.

5.   Solubilities

5.1   Solubility of a Solid in a Liquid

(i) Nature of the solute and the solvent

When a solid or liquid dissolves, the structural units (ions, molecules) and the spaces between them is occupied by the solvent molecules. Now, in this method of the dissolution, the required energy to break the bond arises from the new bond formed between the solute and the solvent particles. Now, let us see the types of bonds that are being formed between the solute and the solvent. Let us first consider the case of ionic solutes.

A great deal of energy is necessary to overcome the powerful electrostatic forces holding together an ionic lattice. Only water or other highly polar solvents are able to dissolve ionic compounds appreciably. This is because the molecule of a polar solvent has a positive or negative end. Consequently, there is electrostatic attraction between a positive ion and a negative end of the solvent molecule and between a negative ion and positive end of the solvent molecule. These attractions are called *ion–dipole interactions*. Each ion–dipole bond is relatively weak, but in the aggregate they supply enough energy to overcome the interionic forces in the crystal. In solution, each ion is surrounded by a cluster of solvent molecules and is said to be solvated. If the solvent happens to be water, the ion is said to be hydrated and the energy released in this process is called as the hydration energy or solvation energy (in general).

Or   solute + solvent $\rightleftharpoons$ (solute – solvent) + energy

A solute is said to be soluble if lattice energy is less than the hydration energy.

The high dielectric constant of the solvent also contributes a lot to the solubility of the solute. Higher dielectric constant implies high insulating properties which lower the attraction between oppositely charged ions once they are solvated.

Dissolution of non–ionic solutes is chiefly determined by their polarity. Non–polar or weakly polar compounds dissolve in non–polar or weakly polar solvents, highly polar solvents, highly polar compounds dissolve in highly polar solvents. "*Like dissolves like*" is an extremely useful rule of thumb. Methane dissolves in carbon tetrachloride because the forces holding methane molecules to each other and carbon tetrachloride molecules to each other are Van der Waals interactions and are replaced by very similar forces holding methane molecules to carbon tetrachloride molecules. Neither methane nor carbon tetrachloride is readily soluble in water. In contrast, the highly polar organic molecules/ compounds like CH_3OH is quite soluble in water. Hydrogen bonds between water and methanol molecules readily replace the very similar hydrogen bonds between different methanol molecules and different water molecules.

(ii) Temperature:

On the basis of the effect of temperature on solubility in water, the various ionic substances are divided into three categories.

(a) Solutes whose solubility increases continuously with increase of temperature. Most of the substances like $NaNO_3$, KNO_3, $NaCl$, KCl etc fall into this category. The reason for this behaviour is that for such substances, the process of dissolution is endothermic i.e.

$$Solute + Solvent + Heat \rightleftharpoons Solution$$
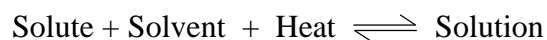
Applying Le Chatelier's principle, as the temperature is increased, equilibrium will shift in a direction in which heat is being absorbed i.e. in the forward direction. Consequently more of the solute passes into the solution.

(b) Solutes whose solubility decreases continuously with increase of temperature. There are a few substances like cerium sulphate, lithium carbonate, sodium carbonate monohydrate ($NaCO_3.H_2O$) etc. whose solubility

decreases with increase of temperature. This is due to the fact that the process of dissolution of these substances is exothermic and accompanied by evolution of heat.

(c) Solutes substances whose solubility does not increase or decrease continuously. There are some substances which on heating change at a particular temperature from one polymorphic form to another (like α to $\beta-$form as in the case of ammonium nitrate) to form one hydrated form to another

$$CaCl_2.6H_2O \longrightarrow CaCl_2.4H_2O \longrightarrow CaCl_2.2H_2O$$
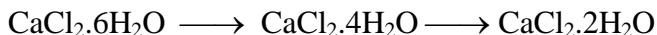
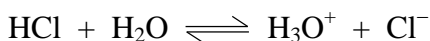or from hydrated to anhydrous form

$$e.g.\ Na_2SO_4.10H_2O \longrightarrow Na_2SO_4)$$

Such substances donot show a continuous increase or decrease of solubility. For example, in case of Na_2SO_4, the solubility first increases up to 32.4°C and then begins to decrease. The temperature at which one form of the substance changes into another is called transition temperature.

$$Na_2SO_4.10H_2O \underset{\text{below 32.4°C}}{\overset{\text{above 32.4°C}}{\rightleftharpoons}} Na_2SO_4$$
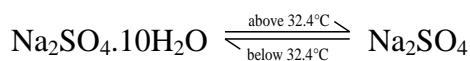
5.2 Solubility of a Gas in a Liquid

(i) Nature of the Solute and the Solvent

Like solid solutes, the gases too follow the thumb rule, "*like dissolves like*" For example, gases like, ammonia, sulphur dioxide and hydrogen chloride is highly soluble in water.

$$NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$SO_2 + H_2O \rightleftharpoons H_2SO_3 \rightleftharpoons HCO_3^- + H^+$$

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

(ii) Effect of Pressure

The solubility of a gas in a liquid increases with the increase in the pressure of the gas. The quantitative relation connecting the solubility with pressure was stated by W. Henry and is known as *Henry's law*. The law states, "*At a given temperature the mass of dissolved gas in a given volume of solvent is proportional to the pressure of the gas with which it is in equilibrium*". If 'm' is the mass of the gas dissolved by unit volume of solvent at equilibrium pressure 'p', then according to Henry's law, we have

$$m \propto p$$

or $\qquad m = kp$

where k is the constant of proportionality. Thus, if a graph of the solubility and the external equilibrium pressure is plotted, a straight line would be observed.
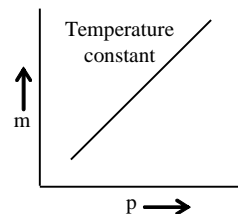

(iii) Effect of Temperature

In general, the solubility of a gas decreases with increase in temperature. This is expected because on heating the solution of a gas, some gas is usually expelled out of the solution.

6.   Viscosity

We all know that different liquids flow with different speeds. For example, water flows with greater speed than glycerol. This means that some sort of an internal friction is operating which checks the flow of liquids and which varies from liquid to liquid. This internal friction in liquids is primarily due to forces of attraction between the molecules. If we have a laminar flow of a liquid in a cylindrical tube, then the velocity of the layer just in contact with the surface of the tube is zero and it increases as we proceed towards the centre of the tube. Thus, there exists a velocity gradient between different layers of the liquid.
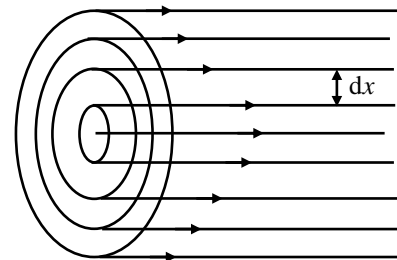
Due to greater intermolecular attractions between molecules of a liquid, the molecules moving in any one layer will tend to reduce the movement of the molecules in the adjacent faster moving layer. As a result, the velocity of molecules in the faster layer decreases. This decrease in velocity is due to frictional force acting along the layer in the forward direction.

This internal frictional force, which resists the flow of a liquid, is directly proportional to A (the area of contact of two adjacent layers) and du (the velocity difference between two adjacent layers), and is inversely proportional to dx, (the distance between the two adjacent layers).

Taking all these factors into account, we express frictional force, F as

$$F \propto A \times \frac{du}{dx}$$

where $\frac{du}{dx}$ is called velocity gradient.

Removing the proportionality sign, we get

$$F = \eta \times A \times \frac{du}{dx}$$

or $$\eta = \frac{F}{A(du/dx)}$$

The constant η is known as the coefficient of viscosity of a liquid or simply viscosity of a liquid.

Viscosity is defined as the internal resistance to the flow of liquids, which is calculated as the force per unit area required to maintain a velocity difference of unity between two parallel layers of liquid unit distance apart.

The unit of viscosity in CGS units is dyn cm^{-2} s is known as *poise*. The unit of viscosity in SI units is N m^{-2} s. The viscosities of most of the liquids are small in magnitude. Therefore, these are usually expressed in the units of centipoise (10^{-2}) and millipoise (10^{-3} poise). The SI equivalent of the poise unit may be derived as follows

$$1 \text{ poise} = 1 \text{ dyn cm}^{-2} \text{ s} = 1 \, (10^{-5} \text{ N}) \, (10^{-2} \text{ m})^{-2} \text{ s} = 10^{-1} \text{ N m}^{-2} \text{ s}$$

The viscosity of a liquid is determined using Ostwald's viscometer method. This method is based on the Poiseuille's equation. If the volume 'v' of a liquid requires time 't' to flow through a capillary tube of radius 'r' and length '*l*' under pressure 'P', then the coefficient of viscosity given by Poiseuille's equation is

$$\eta = \frac{\pi P r^4 t}{8vl} \qquad \text{.....(i)}$$

The apparatus used, known as Ostwald's viscometer, is shown in figure. It consists of two bulbs A and B connected through a fine capillary tube. The bulb A is of bigger size whereas the bulb B is of smaller size. A known volume of liquid is taken in the bulb A and the liquid is sucked into the bulb B. The time taken in seconds for the liquid to flow from the mark X to mark Y is noted down.

In order to avoid measurements of l, v and other factors in equation (i), we use the relative method. Using the same viscometer, the experiment is repeated by taking same volume of a liquid whose viscosity is known. Water is usually employed for this purpose. If t_l and t_w are the times taken by the liquid and water to flow from mark X to mark Y, respectively, we have

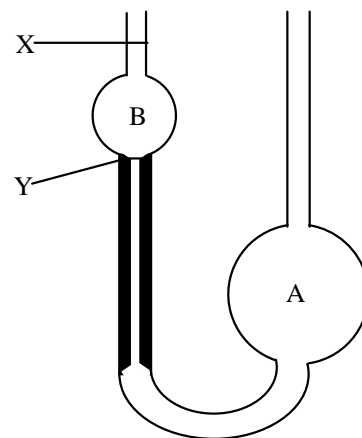$$\eta_l = \frac{\pi P_l\, r^4 t_l}{8vl} \quad \text{and} \quad \eta_w = \frac{\pi P_w r^4 t_w}{8\,vl}$$

Dividing, we get

$$\frac{\eta_l}{\eta_w} = \frac{P_l\, t_l}{P_w t_w}$$

Since, P = hd g

$$\therefore \qquad \frac{\eta_l}{\eta_w} = \frac{d_l\, t_l}{d_w t_w}$$

$$\eta_l = \left(\frac{d_l\, t_l}{d_w t_w}\right) \eta_w \qquad \text{......(ii)}$$

Thus, if the factors on the right side of equation (ii) are known, the value of η_l can be calculated.

The viscosity of a liquid decreases with increase in temperature and this decrease is roughly of the order of 2 percent per degree Celsius. This is due to the fact that on raising the temperature of a liquid, the average thermal energy of its molecules is increased and thus the effect of intermolecular attractions is decreased. Hence, viscosity of a liquid decreases. The relation governing dependence of viscosity on temperature is given by

$$\eta = A\; e^{E/RT}$$

where A is a constant and E is the activation energy for viscous flow. Both A and E are characteristic of a liquid.

Illustration 14

At 20°C, pure water with an absolute viscosity of 1.002×10^{-3} N m^{-2} s requires 102.2 s to flow through the capillary of an Ostwald viscometer. At 20°C, toluene requires 68.9 s. If the densities of water and toluene be 0.998 and 0.866 g/cm^3 respectively, calculate the viscosity of toluene.

Solution:

The viscosity of a liquid by Ostwald's viscometer method is given by $\eta = \frac{\pi P r^4 t}{8vl}$

Comparing viscosities of 2 liquids give

$$\frac{\eta_{water}}{\eta_{toluene}} = \frac{d_{water} \times t_{water}}{d_{toluene} \times t_{toluene}}$$

$$\eta_{toluene} = \frac{0.866 \times 68.9}{0.998 \times 102.2} \times 1.002 \times 10^{-3}$$

$$= \mathbf{5.86 \times 10^{-4} \, N \, m^{-2} \, s}$$
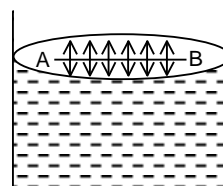
7.   Surface Tension

It was seen during the study of vapour pressure that the molecules at the surface of a liquid experience a net inward pull because of the larger number of molecules towards the liquid side than towards the vapour side. Thus, there is a tendency of surface molecules to go in the bulk of the liquid. Therefore, the surface of liquid is in some sort of tension and it tends to contract to the smallest possible area in order to have the minimum number of molecules at the surface. It is for this reason that the surface of a liquid is spherically curbed, since the surface area is minimum for a given volume in the case of a sphere. Surface tension is the characteristic property of liquids.

To understand it, let us consider a molecule inside the bulk of the liquid. This molecule is surrounded by other molecules in all directions and the net force acting on the molecule is zero. While a molecule lying at the surface experiences a net inward attraction. Due to this inward pull on molecules at the surface, the liquid surface tends to contract to minimum possible area and thus surface behaves as if it were under tension. Hence, the property is called surface tension.
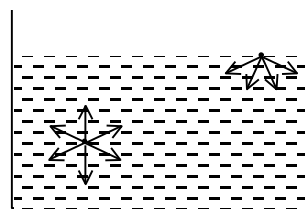
Thus, surface tension is the property by virtue of which the free surface of a liquid at rest behaves like a stretched elastic membrane tending to contract to possess minimum surface area.

Let us imagine a line AB on the free surface of a liquid at rest. The force of surface tension is measured as the force acting per unit length on either side of the imaginary line AB. The direction of this force is perpendicular to the line and tangential to the liquid. Let F be the force acting and l be the length of the imaginary line, then surface tension (denoted by γ) is given by

$$\gamma = \frac{F}{l}$$

The unit of surface tension in CGS system is dyn cm^{-1} and in SI system, the unit is N m^{-1}.

Thus, the free surface of a liquid at rest is always under tension and the force of surface tension tends to decrease the surface area to minimum. If the surface area of liquid is to be increased, work shall have to be done against the force of surface tension. This work done is stored in the liquid surface film as its potential energy.

Thus, the amount of work done in increasing the surface area of the film through unit length, keeping temperature constant is called surface energy.

For example, consider a U–shaped wire having a movable wire section AB at the open end.
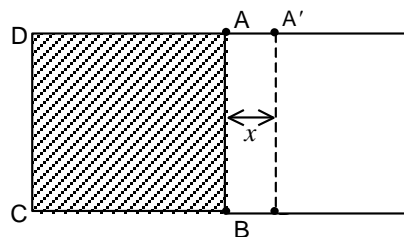
A soap film is formed in the wire frame ABCD by dipping it in soap solution. The surface tension pull the movable wire section AB and keep it in fixed position. If the movable wire section AB is stretched by a small distance, x to the position $A' B'$ at constant temperature, then work shall be done to do so. This amount of work done in increasing the surface area of the film by unity is called surface energy.

$$\text{Surface energy} = \frac{\text{Amount of work done}}{\text{Amount of area extended}} = \frac{\text{Force} \times \text{distance}}{\text{Area}}$$

Hence in CGS units, we have

$$\text{Surface energy} = \frac{\text{dyn} \times \text{cm}}{\text{cm}^2} = \text{dyn cm}^{-1}$$

and in SI units, we have

$$\text{Surface energy} = \frac{\text{N} \times \text{m}}{\text{m}^2} = \text{N m}^{-1}$$

Thus, surface tension and surface energy have same units.

Obviously, 1 dyn cm^{-1} = $(10^{-5} \text{ N}) (10^{-2} \text{ m})^{-1} = 10^{-3} \text{ N m}^{-1}$

The formation of a bubble is basically due to surface tension. It is obvious that the total pressure acting on a concave side must be larger than the pressure acting on the convex side. Therefore, the pressure inside a bubble must be larger than the external pressure. If this excess of pressure is not balanced by any other force, then the bubble will not be stable and will collapse immediately. Since we get stable bubbles, therefore, this excessive pressure must be balanced by forces due to surface tension and are called the cementing forces.

When a capillary tube is dipped in a liquid, there occurs either a rise or a fall of liquid in the tube. This phenomenon is known as capillary action and is basically due to surface tension of the liquid. If the forces of attraction between the molecules of a liquid and those of the solid surface of the tube are greater than those existing amongst the molecules of the liquid, then the liquid has a tendency to spread on the solid surface and its meniscus in the tube is concave upwards. Such types of liquids are known as wetting liquids and they rise in the capillary tube. The angle of contact, which is measured within the liquid from the side of the tube to the tangent drawn at the meniscus touching the surface of the tube, in this case is less than 90°. This is shown in Fig. 6d(i. If the cohesive forces in the liquid are greater than the solid–liquid attraction forces, or if there occurs repulsion between the molecules of the liquid and those of the solid surface, the liquid detaches from the surface of the solid. The meniscus of such a liquid in the tube is convex upwards and its level falls within the tube. The angle of contact, in this case, is greater than 90° as shown in Fig. 6d(ii).

(i)   (ii)
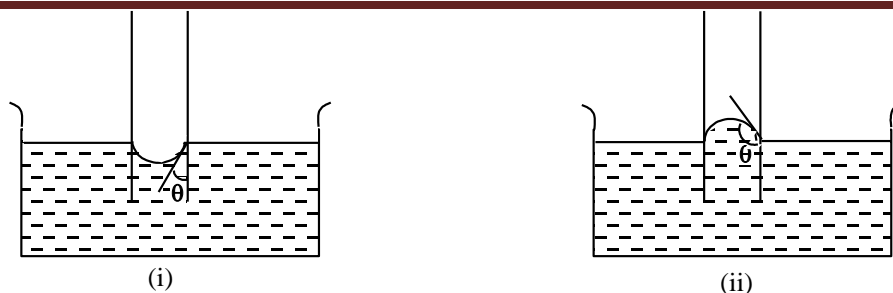
Figure 6d: The angle of contact of the meniscus (a) wetting liquid, < 90° and (b) non−wetting liquid, > 90°

As mentioned above, the rise and fall of a liquid in a capillary tube is due to surface tension. Let us take the case of a wetting liquid. The surface tension forces act all around the capillary tube in the direction shown in Fig 6e. The liquid rises in the tube because of these upward forces. It continues to rise till the vertical component of the lifting force becomes equal to the weight of the liquid in the capillary tube. Thus,

Lifting force = $(\gamma \cos \theta)(2\pi\, r_c)$

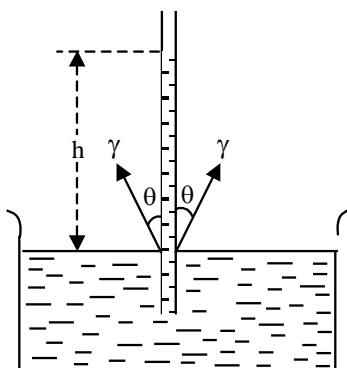Weight of the liquid in the capillary tube = $\pi r_c^2 hdg$

FIGURE 6E

At equilibrium, lifting force is equal to the downward force due to weight of the liquid in the capillary tube. Therefore,

$$(\gamma \cos \theta)(2\pi\, r_c) = \pi r_c^2\, hdg$$

or $\gamma = \frac{1}{2}\, hdg\, \dfrac{r_c}{\cos\theta}$ .....(i)

For most of the wetting liquids, θ is very very small and thus $\cos \theta \simeq 1$. Therefore, the value of γ for such liquids is

$$\gamma = \frac{hdgr_c}{2}$$

where h is the height of liquid rise in capillary, d is the density of liquid and g is the acceleration due to gravity.

For non−wetting liquids, equation (i) is still applicable, where h denotes depression or fall of the liquid level.

The relative surface tension (of liquid which wets the surface) can be measured using the relation,

$\dfrac{\gamma_1}{\gamma_2} = \dfrac{h_1 d_1}{h_2 d_2}$ (Capillary tube of similar radius is used for measuring their surface tensions)

where γ_1 and γ_2 represents the surface tension of liquid 1 and 2 respectively, h_1, h_2 represents height of liquid rise in capillary and d_1, d_2 represents the density of liquid 1 and 2 respectively.

As the forces of attraction between the molecules of a liquid decreases with increase in temperature, the surface tension will decrease when the temperature is increased. The relation between surface tension and temperature is given by

$$\gamma\left(\frac{M}{d}\right)^{2/3} = k\,(t_c - t)$$

where M is the molar mass of liquid, d is the density of liquid, k is a constant, t_c is the critical temperature and t is the temperature of the system (t is always $< t_c$).

Illustration 15

The surface tension of liquid mercury is 0.49 N m^{-1} and its density is 13.6×10^3 Kg / m^3. How far will the mercury level be depressed when a glass capillary with 0.40 mm radius is placed in a dish of mercury?

Solution:

The surface tension of a liquid is given by

$$\gamma = \frac{r_c h d g}{2}$$

$$h = \frac{2\gamma}{dgr_c} = \frac{2 \times 0.49}{0.40 \times 10^{-3} \times 13.6 \times 10^3 \times 9.8}$$

$$= 0.0183 \text{ m} = \textbf{18.3 mm}$$

Solved Fundamental Examples

Example 1

Calculate the mole fraction of benzene in a benzene – toluene ideal solution that contains 60 mole percent benzene in the vapour phase.

Given: $P^{\circ}_{benzene} = 90$ mm Hg ; $P^{\circ}_{toluene} = 40$ mm Hg.

Solution:

According to the Raoult's law,

$$P_{benzene} = P^{\circ}_{benzene} \times x_{benzene}$$

where $x_{benzene}$ is the mole fraction of benzene in the liquid solution and according to the Dalton's law of partial pressures,

$$P_{benzene} = P_{Total} \times y_{benzene}$$

where $y_{benzene}$ is the mole fraction of benzene in the vapour phase and P_{Total} is the total pressure of the binary liquid system.

$$y_{benzene} \times P_{Total} = x_{benzene} \times P^{\circ}_{benzene}$$

$$y_{toluene} \times P_{Total} = x_{toulene} \times P^{o}_{toulene}$$

Since, $x_{benzene} + x_{toluene} = 1$

and $y_{benzene} + y_{toluene} = 1$

$$y_{benzene} \times P_{Total} = x_{benzene} \times P^{o}_{benzene} \qquad \text{...(i)}$$

$$(1 - y_{benzene}) P_{Total} = (1 - x_{benzene}) P^{o}_{toluene} \qquad \text{...(ii)}$$

Dividing equation (i) and (ii), we get

$$\frac{y_{benzene}}{(1-y_{benzene})} = \frac{x_{benzene} P^{o}_{benzene}}{(1-x_{benzene}) P^{o}_{toluene}}$$

$$\therefore \quad \frac{0.6}{0.4} = \frac{x_{benzene}}{(1-x_{benzene})} \times \frac{90}{40}$$

$$\therefore \quad x_{benzene} = 0.4.$$

Example 2

At 300 K, the vapour pressure of an ideal solution containing one mole of A and 3 moles of B is 550 mm of Hg. At the same temperature, if one mole of B is further added to this solution, the vapour pressure of the solution increases by 10 mm of Hg. Calculate the vapour pressures of A and B in their pure state.

Solution:

In the beginning,

$$P_{Total} = P^{o}_{A} X_{A} + P^{o}_{B} X_{B}$$

$$550 = P^{o}_{A} \times \left(\frac{1}{1+3}\right) + P^{o}_{B} \times \left(\frac{3}{1+3}\right) = \frac{1}{4}(P^{o}_{A} + 3P^{o}_{B})$$

or $P^{o}_{A} + 3P^{o}_{B} = 2200 \qquad \text{...(i)}$

When one mole of B is further added to the solution, $P'_{Total} = P^{o}_{A} X'_{A} + P^{o}_{B} X'_{B}$

$$560 = P^{o}_{A} \times \left(\frac{1}{1+4}\right) + P^{o}_{B} \times \left(\frac{4}{1+4}\right) = \frac{1}{5}(P^{o}_{A} + 4P^{o}_{B})$$

$$\therefore \quad P^{o}_{A} + 4P^{o}_{B} = 2800 \qquad \text{...(ii)}$$

Solving eqs. (i) and (ii), we get

$P^{o}_{A} = 400$ mm of Hg $P^{o}_{B} = 600$ mm of Hg

Example 3

The molar volume of liquid benzene (density = 0.877 g ml^{-1}) increases by a factor of 2750 as it vapourizes at 20°C and that of liquid toluene (density 0.867 g ml^{-1}) increases by a factor of 7720 at 20°C. A solution of benzene and toluene at 20°C has a vapour pressure of 46.0 Torr. Find the mole fraction of benzene in the vapours above the solution.

Solution:

Let x mole of benzene goes in the vapour to exert vapour pressure at 20°C.

Volume of 1 mole of liquid benzene $= \dfrac{78}{0.877}$

Volume of x mole of benzene vapour $= \dfrac{78x}{0.877} \times 2750$

$\therefore$ Vapour pressure of benzene at 20°C $= \dfrac{x \times 0.0821 \times 293 \times 0.877}{78x \times 2750 \times 10^{-3}}$

$$= 0.098 \text{ atm} = 74.48 \text{ Torr}$$

Let the mole of toluene that goes in vapour phase to exert vapour pressure be y at 20°C.

Volume of 1 mole of liquid toluene $= \dfrac{92}{0.867}$

Volume of y mole of toluene vapour $= \dfrac{92y}{0.867} \times 7720$

$\therefore$ Vapour pressure of toluene at 20°C $= \dfrac{y \times 0.0821 \times 293 \times 0.867}{92y \times 7720 \times 10^{-3}}$

$$= 0.029 \text{ atm} = 22.04 \text{ Torr}$$

Let x_B and x_T represents the mole fraction of benzene & toluene respectively in the liquid solution & their respective mole fractions in the vapour phase are x'_B & x'_T.

$P_{\text{Total}} = P_B^{\circ} x_B + P_T^{\circ} x_T$

$46 = (74.48 \times x_B) + 22.04(1 - x_B)$

$\therefore x_B = 0.45$

$\& \quad x_T = 0.55$

Also,

$$P_B^{\circ} x_B = P_{Total} x'_B$$

$$\therefore x'_B = \frac{P_B^{\circ} x_B}{P_{Total}} = \frac{74.48 \times 0.45}{46}$$

$$x'_B = \mathbf{0.728}$$

Example 4

A very small amount of a non−volatile solute (that does not dissociate) is dissolved in 56.8 cm^3 of benzene (density 0.889 g cm^{-3}). At room temperature, vapour pressure of this solution is 98.88 mm Hg while that of pure benzene is 100 mm Hg. Find the molality of this solution. If the freezing temperature of this solution is 0.73 degree lower than that of benzene, what is the value of molal freezing point depression constant of benzene?

Solution:

$\dfrac{P^o - P_s}{P_s} = \dfrac{w}{m} \times \dfrac{M}{W}$, where w & W represents the weight of solute and solvent respectively and m & M

represents molar mass of solute and solvent respectively.

$\therefore \quad \left(\dfrac{100 - 98.88}{98.88}\right)1000 = \dfrac{w \times 78 \times 1000}{m \times W}$

$\dfrac{1.12 \times 1000}{98.88} \times \dfrac{1}{78} = \dfrac{w}{m} \times \dfrac{1000}{W} = \text{molality}$

$\therefore \qquad \text{molality} = 0.145$

Also, $\quad \Delta T_f = K_f \times \text{molality}$

$\qquad\qquad 0.73 = K_f \times 0.145$

$\therefore \qquad K_f = 5.034 \text{ K molality}^{-1}$

Example 5

A motor vehicle radiator was filled with 8 liter of water in which 2 liter of methyl alcohol (density 0.8 g/ml) were added. What is the lowest temperature at which the vehicle can be parked out doors without a danger that the water in radiator will freeze? K_f for $H_2O = 1.86° \text{ mol}^{-1}$ kg.

Solution:

$$\Delta T_f = K_f \times \dfrac{w \times 1000}{m \times W}$$

$\therefore \qquad \Delta T_f = \dfrac{1.86 \times 2000 \times 0.8 \times 1000}{32 \times 8000} = 11.625$

$\therefore$ Freezing point of solution

$$= 0 - 11.625 = -11.625$$

$\therefore$ Vehicle cannot be kept out door below $-11.625°C$.

Example 6

The freezing point of a solution of acetic acid (mole fraction = 0.02) in benzene is 277.4 K. Acetic acid exists partly as a dimer. Calculate the equilibrium constant for the dimerization reaction. The melting point of pure benzene is 278.4 K and its molar enthalpy of fusion is 10.042 kJ mol^{-1}.
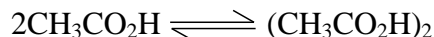
Solution:

The depression in freezing point for acetic acid solution in benzene is given by $\Delta T_f = K_f (\text{molality})_{obs}$.

$$K_f = \dfrac{RT_f^2 \times M}{\Delta H_f} = \dfrac{8.314 \times (278.4)^2 \times 78 \times 10^{-3}}{10.042 \times 10^3} = 5 \text{ K kg mol}^{-1}$$

$\therefore \qquad (\text{molality})_{obs} = \dfrac{\Delta T_f}{K_f} = \dfrac{(278.4 - 277.4)}{5} = 0.2 \text{ mol kg}^{-1}$

The equilibrium expression is represented as

$$2CH_3CO_2H \rightleftharpoons (CH_3CO_2H)_2$$

Initial molality $\quad\quad\quad\quad\quad$ m $\quad\quad\quad\quad\quad\quad$ 0

Molality at equilibrium $\;$ m $(1 - \alpha)$ $\quad\quad\quad\quad$ mα/2

Initial molality = $\dfrac{\text{Number of moles of CH}_3\text{CO}_2\text{H}}{\text{Weight of benzene in kg}}$

As the mole fraction of CH_3CO_2H is 0.02, thus mole fraction of benzene would be $(1 - 0.02) = 0.98$.

Initial molality = $m = \dfrac{0.02}{0.98 \times 78 \times 10^{-3}} = 0.26$ mol kg^{-1}

$(m)_{obs} = m \times i = m \times \left(1 - \dfrac{\alpha}{2}\right)$

$0.2 = 0.26 \left(1 - \dfrac{\alpha}{2}\right); \quad\quad \alpha = 0.46$

In order to calculate equilibrium constant for the equilibrium reaction, we always assume that the molality and molarity of solution is same.

$$\therefore \; K_C = \frac{[(CH_3CO_2H)_2]}{[CH_3CO_2H]^2} = \frac{\dfrac{m\alpha}{2}}{[m(1-\alpha)]^2} = \frac{0.26 \times 0.46}{2[0.26(1-0.46)]^2}$$
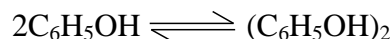
$\quad \therefore K_C = 3.03$

Example 7

When phenol is dissolved in a particular solvent, it is partially dimerized. If 2.58 g of phenol is dissolved in 100 g of the solvent, the freezing point of solvent ($K_f = 14.1$ K mol^{-1} kg) is depressed by 2. 37 K. Find how much of phenol is dimerized in the solution.

Solution:

The equilibrium reaction of dimerization of phenol is represented as

$$2C_6H_5OH \rightleftharpoons (C_6H_5OH)_2$$

Initially $\quad\quad\quad\quad\quad$ 1 $\quad\quad\quad\quad\quad$ 0

At equilibrium $\quad\quad\quad$ $(1 - \alpha)$ $\quad\quad\quad\quad$ α/2

$\Delta T_f = K_f \times (m)_{obs} = K_f \times m \times i$

$\Delta T_f = K_f \times m \times \left(1 - \dfrac{\alpha}{2}\right)$

$2.37 = 14.1 \times \dfrac{2.58}{94} \times \dfrac{1000}{100} \times \left(1 - \dfrac{\alpha}{2}\right)$

$\therefore \quad\quad \alpha = 0.78$

The fraction of phenol dimerised is 0.78 or 1.996 g (≈ 2.0 g) of phenol is dimerized in solution.

Example 8

At 303 K, the vapour pressure of pure toluene and pure benzene are 36.7 and 118.2 Torr, respectively and the two liquids form a nearly ideal solution.

(a) For a solution containing 50 mass % of toluene, calculate the total vapour pressure and the mole fraction of each component in the vapour phase.

(b) Determine the composition of a solution of benzene and toluene that will boil at 303 K at a pressure of 50 Torr.

Solution:

(a) In the problem, we are given the mass % of toluene while we need the mole % of toluene. The mol % of toluene will not be same as the mass % of toluene since the molar mass of benzene and toluene are not same.

Let x_B and x_T represents the mole fraction of benzene and toluene respectively.

$$\therefore \quad x_T = \frac{50/92}{\left(\dfrac{50}{92}+\dfrac{50}{78}\right)} = 0.46$$

The total pressure of benzene–toluene liquid mixture would be given as

$$P_{Total} = P_B + P_T$$

where P_B and P_T represents the partial pressures of benzene and toluene at 303 K.

$$P_{Total} = P_B^o x_B + P_T^o x_T$$

$P_{Total} = (118.2 \times 0.54) + (36.7 \times 0.46) = 63.82 + 16.88 = 80.7$ Torr.

Let the mole fraction of benzene and toluene in the vapour phase be y_B and y_T respectively.

$$y_T = \frac{P_T^o x_T}{P_{Total}} = \frac{36.7 \times 0.46}{80.7} = 0.21$$

$$\text{and} \quad y_B = \frac{P_B^o x_B}{P_{Total}} = \frac{118.2 \times 0.54}{80.7} = 0.79$$

(b) Let the mole fractions of benzene and toluene in the mixture that will boil at 303 K at a pressure of 50 Torr be x_B' and x_T' respectively.

The total pressure of benzene – toluene binary solution would be given as

$$P_{Total}' = P_B^o \, x_B' + P_T^o x_T'$$

$$= P_B^o \, x_B' + P_T^o (1 - x_B') = P_T^o + x_B' (P_B^o - P_T^o)$$

$$\therefore \quad x_B' = \frac{(P_{Total}' - P_T^o)}{(P_B^o - P_T^o)} = \frac{(50 - 36.7)}{(118.2 - 36.7)}$$

$$x_B' = 0.16 \quad \text{and} \quad \text{thus } x_T' = \mathbf{0.84}$$

Example 9

The vapour pressure of two pure liquids, A and B that form an ideal solution are 300 and 800 Torr respectively, at temperature T. A mixture of the vapours of A and B for which the mole fraction of A is 0.25 is slowly compressed at temperature T. Calculate

(a) the composition of the first drop of the condensate,

(b) the total pressure when this drop is formed,

(c) the composition of the solution whose normal boiling point is T,

(d) the pressure when only the last bubble of vapour remains, and

(e) the composition of the last bubble.

Solution:

(a) Let y_A and y_B be the mole fraction of A and B in the vapour phase, respectively.

$$y_A = \frac{P_A}{P_{Total}} = \frac{P_A^\circ x_A}{P_A^\circ x_A + P_B^\circ x_B} = \frac{P_A^\circ x_A}{P_B^\circ + (P_A^\circ - P_B^\circ) x_A}$$

where x_A is the mole fraction of A in the first drop of the condensate.

$$\therefore \qquad x_A = \frac{y_A P_B^\circ}{P_A^\circ - (P_A^\circ - P_B^\circ) y_A}$$

Substituting the given values,

$$x_A = \frac{0.25 \times 800}{300 - [(300 - 800) \times 0.25]} = 0.47$$

(b) The total pressure when this drop is formed is given by

$$P_{Total} = P_A + P_B = P_A^\circ x_A + P_B^\circ x_B$$

$P_{Total} = (300 \times 0.47) + (800 \times 0.53)$

$\qquad = 141 + 424 = 565$ Torr

(c) Normal boiling point implies that the solution boil at a temperature when vapour pressure of the solution becomes equal to the atmospheric pressure (1 atm or 760 Torr).

Thus, $\quad P_{Total} = 760 = P_A^\circ x_A + P_B^\circ (1 - x_A)$

$$x_A = \frac{760 - P_B^0}{P_A^\circ - P_B^\circ} = \frac{760 - 800}{300 - 800} = 0.08 \quad \text{and} \qquad x_B = 0.92$$

(d) Now when the entire vapours are condensed and only last bubble of vapour remains, then we can assume that the mole fraction of A, which was in the vapour phase originally, will now be in the liquid phase and the mole fraction of A remaining in the vapour phase be x_A' and P_T' be the total pressure when last bubble of vapour remains.

$$P_T' = P_A^\circ y_A + P_B^\circ y_B = (300 \times 0.25) + (800 \times 0.75)$$

$$P_T' = 75 + 600 = 675 \text{ Torr}$$

(e) According to Raoult's law and Dalton's law of partial pressures,

$$P_T' \, x_A' = P_A^o y_A$$

$$\therefore \quad x_A' = \frac{P_A^o y_A}{P_T'} = \frac{300 \times 0.25}{675} = 0.11$$

and $x_B' = 0.89$

Example 10

The vapour pressure of two pure liquids, A and B, which form an ideal solution are 300 and 800 Torr respectively, at temperature T. A liquid solution of A and B for which the mole fraction of A is 0.60 is contained in a cylinder closed by a piston on which the pressure can be varied. The solution is slowly vaporized at temperature T by decreasing the applied pressure, starting with a pressure of about 1 atm. Calculate

(a) the pressure at which the first bubble of vapour is formed,

(b) the composition of the vapour in this bubble,

(c) the composition of the last droplet, and

(d) the pressure when only this last droplet of liquid remains.

Solution:

(a) When the first bubble of vapour is formed, we can assume that the composition of the remaining solution do not change. Thus, total pressure of the system at the stage when first bubble of vapour is formed would be

$$P_{Total} = P_A^o x_A + P_B^o x_B = (300 \times 0.6) + (800 \times 0.4)$$

$$= 180 + 320 = 500 \text{ Torr}$$

(b) Let the mole fraction of A and B in the first bubble of vapour be y_A and y_B respectively. Thus

$$y_A = \frac{P_A}{P_{Total}} = \frac{P_A^o x_A}{P_{Total}} = \frac{300 \times 0.6}{500} = 0.36$$

and $y_B = 1 - 0.36 = 0.64$

(c) When most of the liquid has vaporized and last droplet remains, then we can assume that the mole fractions, which were originally in the liquid phase will now be in the vapour phase and the mole fraction of A remaining in the liquid phase be x_A' and P_T' be the total pressure when last droplet remains.

$$\therefore \quad y_A = \frac{P_A}{P_T'} = \frac{P_A^o x_A'}{P_A^o x_A' + P_B^o x_B'} = \frac{P_A^o x_A'}{P_B^o + (P_A^o - P_B^o) x_A'}$$

Substituting the given data, we get

$$0.60 = \frac{x_A'(300)}{800 + (300 - 800) x_A'}$$

$\therefore \qquad x_A^{'} = 0.80$

and $\qquad x_B^{'} = 1 - 0.80 = 0.20$

(d) $\qquad$ The total pressure when the last droplet of liquid remains would be calculated as

$$P_{Total} = P_A^o x_A^{'} + P_B^o x_B^{'} = (300 \times 0.80) + (800 \times 0.20)$$

$$P_{Total} = 240 + 160 = 400 \text{ Torr}.$$

Example 11

A solution containing 0.122 kg of benzoic acid in 1 kg of benzene (boiling point 353 K) boils at 354.5 K. Determine the apparent molar mass of benzoic acid (which dimerizes) in the solution and the degree of dimerization. Given: ΔH_{vap} (benzene) = 394.57 J g^{-1}.

Solution: Initial moles of $C_6H_5CO_2H = \dfrac{0.122 \times 10^3}{122} = 1$

The dimerization equilibrium of benzoic acid is represented as

$$2C_6H_5CO_2H \rightleftharpoons (C_6H_5CO_2H)_2$$
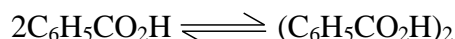
Initial moles $\qquad\qquad$ 1 $\qquad\qquad\qquad\qquad$ 0

Moles at equilibrium $\qquad$ 1 − α $\qquad\qquad\qquad$ α/2

Total moles of solute at equilibrium $= 1 - \alpha + \dfrac{\alpha}{2} = \left(1 - \dfrac{\alpha}{2}\right)$

The solution of benzoic acid in benzene produces elevation in boiling point.

Elevation in boiling point, $\Delta T_b = K_b \times (\text{molality})_{obs}$

$$(354.5 - 353) = K_b \times \dfrac{0.122 \times 10^3 \times 1}{122} \times \left(1 - \dfrac{\alpha}{2}\right)$$

The boiling point elevation constant (K_b) is calculated using the relation,

$$K_b = \dfrac{RT_b^2 \times M}{\Delta H_{vap}}$$

$\therefore \qquad K_b = \dfrac{8.314 \times (353)^2}{394.57 \times 78} \times 78 \times 10^{-3} = 2.626 \text{ K kg mol}^{-1}.$

$\therefore \qquad (354.5 - 353) = 2.626 \times \left(1 - \dfrac{\alpha}{2}\right)$

$\qquad\qquad \alpha = 0.86$

Observed molarity of solution $= \dfrac{\Delta T_b}{K_b} = \dfrac{(354.5 - 353)}{2.626} = 0.57 \text{ mol kg}^{-1}$

$\therefore \qquad (\text{molality})_{obs} = \dfrac{0.122 \times 10^3 \times 1}{M_{app} \times 1}$

$$\therefore \quad M_{app} = \frac{122}{0.57} = 214 \text{ g mol}^{-1}$$

Example 12

When a liquid that is immiscible with water was steam distilled at 95.2°C at a total pressure of 747.3 Torr, the distillate contained 1.27 g of the liquid per gram of water. Calculate the molar mass of the liquid. The vapour pressure of water is 638.6 Torr at 95.2°C.

Solution:

For a mixture of two immiscible liquids, the total pressure is given by

$$P_{Total} = P_{liquid}^{o} + P_{water}^{o}$$

$$747.3 = P_{liquid}^{o} + 638.6$$

$$\therefore \quad P_{liquid}^{o} = 108.7 \text{ Torr}$$

$$P_{liquid}^{o} = Y_{liquid(Vap)} \times P_{Total} \qquad \qquad \text{...(i)}$$

$$\text{and } P_{water}^{o} = Y_{water(Vap)} \times P_{Total} \qquad \qquad \text{...(ii)}$$

Dividing equation (i) by (ii) gives,

$$\frac{Y_{liquid(V)}}{Y_{water(V)}} = \frac{P_{liquid}^{o}}{P_{water}^{o}}$$

$$\text{or} \quad \frac{P_{liquid}^{o}}{P_{water}^{o}} = \frac{\dfrac{n_l}{n_l + n_w}}{\dfrac{n_w}{n_l + n_w}}$$

where n_l and n_w represents the number of moles of liquid and water in vapour phase, respectively.

$$\therefore \quad \frac{P_{liquid}^{o}}{P_{water}^{o}} = \frac{n_l}{n_w} = \frac{\dfrac{w_l}{M_l}}{\dfrac{w_{H_2O}}{M_{H_2O}}}$$

$$\therefore \quad \frac{P_{liquid}^{o}}{P_{water}^{o}} = \frac{w_l \times M_{H_2O}}{w_{H_2O} \times M_l}$$

where M_l and M_{H_2O} represents molar mass of liquid and water respectively and w_l and w_{H_2O} denotes weight of liquid and water in vapour phase, respectively.

$$\therefore \quad M_l = \frac{P_{water}^{o} \times w_l \times M_{H_2O}}{P_{liquid}^{o} \times w_{H_2O}}$$

$$M_l = \frac{638.6 \times 1.27 \times 18}{108.7 \times 1} = 134.3 \text{ g mol}^{-1}$$

Example 13

1.22 g of benzoic acid is dissolved in acetone and benzene separately. Boiling point of mixture with acetone increases by 0.17°C and boiling point of mixture with benzene increases by 0.13°C.

K_b(acetone) = 1.7 K kg mol^{-1} , Mass of acetone = 100 g. ; K_b(benzene) = 2.6 K kg mol^{-1} ; Mass of benzene = 100 g.

Find molecular weight of benzoic acid in acetone and in benzene solution. Justify your answer with structure.

Solution:

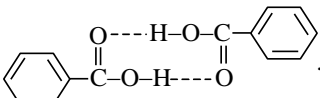m, molality of a solution of benzoic acid in acetone = 0.1 ;

Van't Hoff factor, $i = \dfrac{\Delta T_b}{mK_b} = \dfrac{0.17}{0.1 \times 1.7} = 1.0$

$\therefore$ Observed molecular wt. = actual molecular wt. = 122

Similarly, Van't Hoff factor, i for solution in benzene $= \dfrac{\Delta T_b}{mK_b} = \dfrac{0.13}{0.1 \times 2.6} = 0.5$

Observed molecular weight = 2 × actual molecular weight = 2 × 122 = 244

Benzoic acid neither associates nor dissociates in acetone and dimerizes completely in benzene. The

structure of dimer is given as .

Example 14

The composition of vapour over a binary ideal solution is determined by the composition of the liquid. If x_A and y_A are mole fractions of A in liquid & vapour, respectively, find the value of x_A for which $y_A - x_A$ is maximum. What is the value of pressure at this composition?

Solution:

We have $\qquad y_A = \dfrac{x_A P_A^*}{P_B^* + (P_A^* - P_B^*)x_A}$

$$y_A - x_A = \dfrac{x_A P_A^*}{P_B^* + (P_A^* - P_B^*)x_A} - x_A$$

Differentiating w. r. t. x_A we get

$$\dfrac{d}{dx_A}(y_A - x_A) = \dfrac{P_A^*}{P_B^* + (P_A^* - P_B^*)x_A} - \dfrac{x_A P_A^*(P_A^* - P_B^*)}{\{P_B^* + (P_A^* - P_B^*)x_A\}} - 1$$

The value of x_A at which $(y_A - x_A)$ is maximum value can be obtained by setting the above differential equal to zero. Thus, we have.

$$\dfrac{x_A P_A^*}{P_B^* + (P_A^* - P_B^*)x_A} - \dfrac{x_A P_A^*(P_A^* - P_B^*)}{\{P_B^* + (P_A^* - P_B^*)x_A\}} - 1 = 0$$

Solving for x we get

$$x_A = \frac{\sqrt{P_A^* P_B^*} - P_B^*}{P_A^* - P_B^*}$$

The value of P at this composition is

$$P = x_A P_A^* + x_B P_B^* = P_B^* + (P_A^* - P_B^*)x_A = P_B^* + (P_A^* - P_B^*)\left[\frac{\sqrt{P_A^* P_B^*} - P_B^*}{P_A^* - P_B^*}\right] = \sqrt{P_A^* P_B^*}.$$

Example 15

100 g of sucrose (Molar mass = 342) solution in water is cooled to $-0.5°C$. What mass of ice would he separated out at this temperature if the solution starts freezing at $-0.38°C$? K_f for H_2O = 1.86 kg mol^{-1} K.

Solution:

Let 100 g solution contains w g of solute in (100 − w) g at solvent.

$$\Delta T_f = \frac{K_f \times w \times 1000}{(100 - w) \times \text{molar mass of solute}}$$

$$0.38 = \frac{1.86 \times w \times 1000}{(100 - w) \times 342}$$

On solving above equation we get.

w = 6.6 g

Now at $-0.5°C$, some water separates out as ice and solute exists as 6.6 g.

$$0.5 = \frac{1000 \times 1.86 \times 6.6}{W \times 342}$$ Where W is the mass of water left in solution.

W = 71.78 g.

∴ Weight of ice separated out is (93.40 − 71.78) g = 21.62 g.