Solutions & Colligative Properties

Section (A) : General Introduction & types of solution

1. Introduction :

A solution is a homogeneous mixture of two or more substances which are chemically non-reacting. We come across many types of solutions in our daily life. e.g., solid-liquid, liquid-liquid, gas-gas. In this chapter we will learn several properties of solutions and their applications.

D1 **Solution :** *A homogeneous mixture of two or more substances is known as solution.*

D2 **Solute :** *The substance present in smaller amount in a solution is called solute.*

D3 **Solvent :** *The substance present in larger amount in a solution is called solvent.*

D4 **Binary solutions :** *Those solutions which contain two components are called binary solutions,* e.g., salt solution, benzene and toluene.

D5 **Ternary solutions :** *Those solutions which contain three components are called ternary solutions,* e.g., ethanol + water + acetic acid.

D6 **Aqueous solution :** *When solute is dissolved in water, it is called aqueous solution,* e.g., sugar solution, ethanol in water.

D7 **Non-aqueous solution :** *When solute is dissolved in solvent other than water, it is called non-aqueous solution,* e.g., iodine dissolved in alcohol (Tincture of iodine).

D8 **Miscible liquids :** *Those liquids which mix with each other and form homogeneous mixture are called miscible liquids.*

D9 **Immiscible liquids :** *Those liquids which do not mix with each other are called immiscible liquids.*

D10 **Alloys :** *Solid solutions of the two or more metals are called alloys. One of them can be a non-metal also.*

2. Types of Solutions :

S.No.	Solute	Solvent	Types of Solutions	Examples
Solid Solutions				
1	Solid	Solid	Solid in solid	All alloys like brass, bronze, an alloy of copper and gold, etc.
2	Liquid	Solid	Liquid in solid	Amalgam of mercury with Na, $CuSO_4.5H_2O$. $FeSO_4.7H_2O$
3	Gas	Solid	Gas in solid	Solution of H_2 in Pd, dissolved gases in minerals.
Liquid Solutions				
4	Solid	Liquid	Solid in liquid	Sugar solution, salt solution, I_2 in CCl_4
5	Liquid	Liquid	Liquid in liquid	Benzene in toluene, alcohol in water.
6	Gas	Liquid	Gas in liquid	CO_2 in water, NH_3 in water etc.
Gaseous Solutions				
7	Solid	Gas	Solid in gas	Iodine vapours in air, camphor vapours in N_2.
8	Liquid	Gas	Liquid in gas	Water vapours in air, $CHCl_3$ vapours in N_2.
9	Gas	Gas	Gas in gas	Air (O_2 + N_2)

The concentration of a solution can be expressed by different concentration terms which are described as follows.

Section (B) : Concentration terms (Revision of mole)

3. Concentration Terms :

3.1 % Concentration

D11 **Mass percentage :** *It is the amount of solute in grams dissolved per 100 g of solution.* e.g., 10% solution of sodium chloride means 10 g of solid sodium chloride present in 100 g of solution.

F1 **% w/w** = $\frac{\text{weight of solute(g)}}{\text{weight of solution(g)}} \times 100$

Ex. 10% w/w urea solution = 10 g of urea is present in 100 g of solution.
= 10 g of urea is present in 90 g of water.

D12 **Mass by volume percentage (% w/v) :** *It is defined as mass of solute dissolved per 100 ml of solution.* It is commonly used in medicine and pharmacy.

F2 **% wt/vol. (w/v)**

% w/v = wt. of solute/100 mL of solution

% w/v = $\frac{\text{gram of solutes}}{\text{volume of solution in mL}} \times 100$

Ex. 10% (w/v) urea solution. = 10 g of urea is present in 100 mL of solution.
But not 10 g of urea present in 90 ml of water
for dilute solution : volume solution = volume solvent.

D13 **Volume percentage (% v/v) :** *It is defined as volume of a solute dissolved per 100 ml of solution.*

% v/v = $\frac{\text{volume of solute}}{\text{volume of solution}} \times 100$

3.2 **Strength of solution in g/L**

Weight of solute (in gram) per litre (1000 mL) of solution.

Ex. 10% (w/v) sucrose solution, then specify its concentration in g/L
100 mL .... 10 g
1000 mL .... $\frac{10}{100} \times 1000 = 100$ g/L

Solved Examples

Example-1 : If we have 6% w/w urea solution with density 1.060 g/mL, then calculate its strength in g/L ?

Solution : 6 g urea is present in 100 g solution.

6 g in $\frac{100}{1.060}$ mL

$\frac{100}{1.060}$ mL $\longrightarrow$ 6 g.

$\therefore$ 1000 mL = $\frac{6}{100} \times 1.060 \times 1000 = 10.6 \times 6 = 63.6$

D14 **Molarity (M) :** *It is expressed as the number of moles of solute per litre of solution.*

3.3 **Molarity** = No. of moles of solute per litre of solution.

Let n = No. of moles of solute ; N = No. of moles of solvent ; V = volume of solution

F3 $M = \frac{n}{V \text{ (in L)}} = \left(\frac{W}{M}\right) \times \frac{1000}{V \text{ (in mL)}}$

no. of moles of solute = molarity x volume (in L)
no. of m. moles of solute = molarity x volume (in mL)

Der.1 If V_1 mL of C_1 molarity solution is mixed with V_2 mL of C_2 molarity solution (same substance or solute)
$\therefore$ $C_f (V_1+V_2) = C_1V_1 + C_2V_2$

$C_f = \left[\frac{C_1V_1 + C_2V_2}{V_1 + V_2}\right] = \frac{\text{Total moles}}{\text{Total volume}}$ where C_f = molarity of final solution

D15 **Molality (m) :** *It is defined as number of moles of solute per 1000 g or 1 kg of solvent.*

3.4 **Molality** = No. of moles of solute per kg(1000 g) of solvent.

Let w gram of solute (Molar mass = Mg/mole) is dissolved in 'W' gram of solvent.

F4 $$\text{molality} = \left(\frac{w}{M}\right) \times \frac{1000}{W(g)}$$

$$\text{molality} = \frac{\text{moles} \times 1000}{W(g)\text{ of solvent}}$$

Molality not depends on temperature.

Solved Examples

Example-2 : If 20 ml of 0.5 M Na_2SO_4 is mixed with 50 ml of 0.2 M H_2SO_4 & 30 ml of 0.4 M $Al_2(SO_4)_3$ solution. Calculate $[Na^+]$, $[H^+]$, $[SO_4^{2-}]$, $[Al^{3+}]$. [Assuming 100% dissociation]

Solution : $\text{Molarity} = \frac{\text{moles}}{\text{volume}}$ ⇒ 10 m. moles of Na_2SO_4 ⇒ 20 m. moles of Na^+

(i) $[Na^+] = \frac{20}{100} = 0.2\text{ M}$

(ii) $[H^+] = ?$

10 m. moles H_2SO_4

20 m. moles H^+

$[H^+] = \frac{20}{100} = 0.2\text{ M}$

(iii) $[SO_4^{2-}] = \frac{10+10+36}{100} = \frac{56}{100} = 0.56\text{ M}$

(iv) $[Al^{3+}] = \frac{24}{100} = 0.24\text{ M}$

Example-3 : **(a)** Derive a relationship between molality & molarity of a solution in which w g of solute of molar mass M g/mol is dissolved in W g solvent & density of resulting solution = 'd' g/ml.

(b) Calculate molality of 1.2 M H_2SO_4 solution ? If its $\rho = 1.4$ g/mL

Solution : **(a)** Say 1 L solution taken,

mass of 1 lit solution = (1000 d) g

moles of solute = (molarity)

mass of solute = (molarity) x m

mass of solvent = W = 1000 d – (molarity) × m

$$\text{molality} = \frac{(\text{molarity}) \times 1000}{1000\text{ d} - \text{molarity} \times \text{M.Wt}}$$ [Where no.of moles of solute = molarity]

(b) Molality = $\frac{1.2 \times 1000}{1000 \times 1.4 - 1.2 \times 98}$ **= 0.936**

3.5 D16 Normality : *It is defined as number of gram equivalents of solute dissolved per litre of solution.*

F5 $$\text{No.of equivalents per litre of solution} = \frac{\text{no. of equivalents of solute}}{\text{volume of solution (in L)}}$$

= n-factor × molarity No. of equivalents = normality × volume (in L)

F6 $$\text{Equivalent mass} = \frac{\text{Molar mass}}{\text{n} - \text{factor}}$$

F7 $$\text{No. of equivalent} = \frac{\text{Mass of the species}}{\text{equivalent mass}} = \frac{\text{Mass of the species}}{\frac{\text{Molar mass}}{\text{n} - \text{factor}}}$$

3.6 'n' - factor

(i) For oxidizing/reducing agents : no. of e^- involved in oxidation/reduction half reaction per mole of oxidising agent /reducing agent.

e.g. : $5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + H_2O$ n- factor = 5

(ii) For acid/ base reactions : no. of H^+ ions displaced/ OH^- ions displaced per mole of acid/ base.

e.g. : NaOH n - factor = 1 H_2SO_4 n - factor = 2

(iii) For salt :

$$\left.\begin{array}{l}\text{n = Total charge on cations.}\\ \qquad\text{or}\\ \text{total charge on anions}\end{array}\right\}\text{Simple salts}$$

e.g. : $Al_2(SO_4)_3$ n - factor = charge on the cation = 2 x 3 = 6

3.7 D17 Mole-fraction (x) : *It is the ratio of number of moles of a particular component to the total number of moles of all the components.* e.g., mole-fraction of component A, $x_A = \frac{n_A}{n_A + n_B}$, where n_A is the number of moles of component 'A' and n_B is the number of moles of component 'B'.

For binary mixture.

F8 $$X_{solute} = \frac{\text{moles of solute}}{\text{total moles in solutions}} = \frac{n}{n+N}$$

F9 $$X_{Solvent} = \frac{\text{moles of solvent}}{\text{Total moles in solutions}} = \frac{N}{n+N}$$

F10 $X_{solute} + X_{Solvent} = 1$

3.8 D18 Parts per million (ppm) : *The number of parts of solute present in 1 million parts of solution are called its ppm.* When a solute is present in small quantities (very minute amounts), it is easier to express the concentration in parts per million.

F11 **(a)** $$\text{ppm (w/w)} = \frac{\text{wt. of solute (in g)}}{\text{wt. of solution (in g)}} \times 10^6$$

F12 **(b)** $$\text{ppm (w/v)} = \frac{\text{wt. of solute (in g)}}{\text{vol. of solution (in mL)}} \times 10^6$$

F13 **(c)** $$\text{ppm (moles/moles)} = \frac{\text{moles of solute}}{\text{moles of solution}} \times 10^6$$

Table : 1

Name	Units	Advantage	Disadvantages
Molarity (M)	$\frac{\text{mol solute}}{\text{L solution}}$	Useful in stoichiometry; measure by volume	Temperature-dependent; must know density to find solvent mass
Mole fraction (x)	None	Temperature-independent; useful in special applications	Measure by mass ; must know density to convert to molarity
Mass %	%	Temperature-independent; useful for small amounts	Measure by mass ; must know density to convert to molarity
Molality (m)	$\frac{\text{mol solute}}{\text{kg solvent}}$	Temperature-independent useful in special applications	Measure by mass ; must know density to convert to molarity

Note : All volume related concentration terms are temperature dependent.

Solved Examples

Example-4 : If we have 10 molal urea solution, Calculate mole fraction of urea in this solution & also calculate % w/w of urea (MW = 60).

Solution : 10 moles urea in 1000 g of water

$$X_{urea} = \frac{10}{10 + \frac{1000}{18}} = \frac{10}{65.55} = 0.1526$$

$$\text{\% w/w weight of urea} = \frac{10 \times 60}{10 \times 60 + 1000} \times 100 = 37.5\%$$

*** Note :** For dil. aq. solution molality molarity, as d ≈ 1 g/mL

$$\text{molality} = \frac{\text{molarity} \times 1000}{1000 \times d - \text{molarity} \times m}$$

Example-5 : Calculate molarity of $CaCO_3$(aq.)solution which has concentration of $CaCO_3$=200ppm.

Solution : 200 g of $CaCO_3$ in 10^6 g of water.

$\frac{200}{100} = 2$ moles of $CaCO_3$ in 10^3 liters of water. (density =1g/mL)

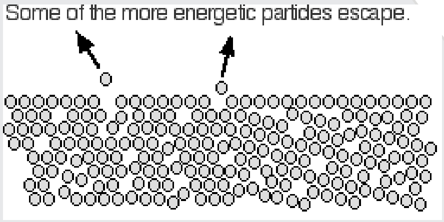
So molarity = $\frac{2}{10^3} = 2 \times 10^{-3}$ M.

Section (C) : Vapour Pressure

4. Vapour Pressure of a pure liquid or pure solid :

4.1 The origin of saturated vapour pressure: The evaporation of a liquid

Some of the more energetic particles on the surface of the liquid move fast enough to escape from the attractive forces holding the liquid together. They evaporate. The diagram shows a small region of a liquid near its surface.

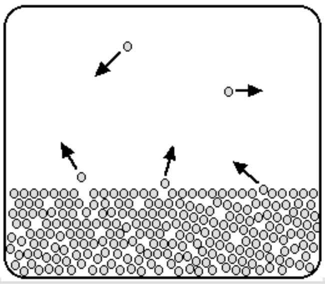


Note: evaporation only takes place on the surface of the liquid. That's quite different from boiling which happens when there is enough energy to disrupt the attractive forces throughout the liquid. That's why, if you look at boiling water, you see bubbles of gas being formed all the way through the liquid.

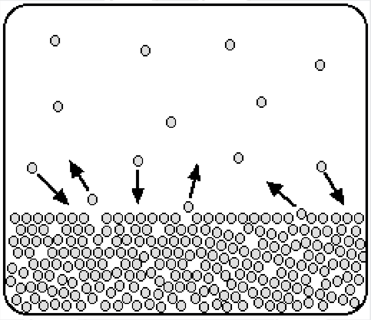
If you look at water which is just evaporating in the sun, you don't see any bubbles. Water molecules are simply breaking away from the surface layer. Eventually, the water will all evaporate in this way.

The evaporation of a liquid in a closed container: Evaporation and Condensation

Now imagine what happens if the liquid is in a closed container. Common sense tells that water in a sealed bottle doesn't disappear over time. But, there is still constant evaporation from the surface. Particles continue to break away from the surface of the liquid - but this time they are trapped in the space above the liquid.



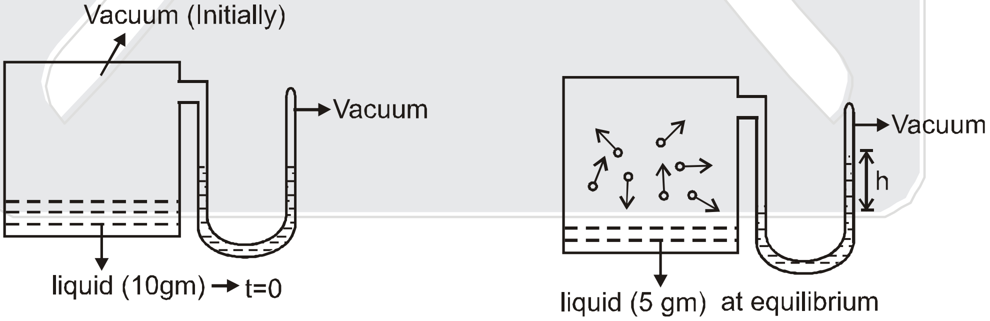
As the gaseous particles bounce around, some of them will hit the surface of the liquid again, and be trapped there. This is called as condensation. There will rapidly be an equilibrium set up in which the number of particles leaving the surface is exactly balanced by the number rejoining it. **At equilibrium, rate of evaporation becomes equal to the rate of condensation.**



In this equilibrium, there will be a fixed number of the gaseous particles in the space above the liquid. When these particles hit the walls of the container, they exert a pressure. This pressure is called the **saturated vapour pressure** (or just **vapour pressure**) of the liquid.

Suppose,we take 10 gram liquid in a chamber. Initially, there are no molecules in the gaseous phase. Thus, no pressure is exerted on the mercury and the level of mercury in both columns is equal. Suppose, after vapourization of 5 gram of the liquid vapour-liquid equillibrium is established. Now, molecules in the gaseous phase exert pressure on the mercury and level of mercury in the column attached to the chamber decreases.

Note: From the figure, we can see that, Vapour Pressure of the liquid = h mm Hg.



(Imagine no liquid molecule exist in vapour phase)

Note: Volatile solids (like Iodine) also evaporate and have a vapour pressure at any given temperature, just like liquids.

4.2 Important Points related to vapour pressure :

D19 **Vapour pressure of a pure liquid :** *The pressure exerted by the vapours over the liquid surface at equilibrium is called vapour pressure.* It increases with the increase in temperature.

D20 **Vapour pressure of solution :** *The pressure exerted by the vapours of solvent 'A' and solute 'B' in equilibrium with the liquid phase is called the vapour pressure of solution.*

D21 **Partial vapour pressure :** *The pressure of vapours of a component ‘A’ over a solution of ‘A’ and ‘B’ is called partial vapour pressure of component A.* It is denoted by p_A.

(1) **Definition of vapour pressure :** The partial pressure of vapours in equilibrium with pure solid or pure liquid at a given temperature.

At eq. the rate of evaporation = rate of condensation

e.g. $H_2O(l) \rightleftharpoons H_2O(g)$

$K_p = p^{eq}_{H_2O,g}$

Hence V.P is equilibrium constant (K_P) of the reaction, liquid $\rightleftharpoons$ vapours.

(2) Since vapour pressure is an equilibrium constant. so it's value is dependent only on temperature.

(a) **Nature of liquid :** The value of a liquid's vapour pressure depends on the magnitude of the intermolecular forces in the liquid. The smaller the intermolecular forces, higher the vapour pressure becuause loosely held molecules escape more easily into vapour phase.

(b) **Temperature of the given liquid :** At higher temperature, more molecules from the liquid have enough KE to escape from the surface of the liquid. That will increase the saturated vapour pressure.

$$\text{liquid} \rightleftharpoons \text{vapour} \qquad \Delta H \text{ is } +\text{ve}$$

Vapourization (liquid to vapour) is always endothermic. It needs heat to convert the liquid into the vapour.

According to Le Chatelier, increasing the temperature of a system in a dynamic equilibrium favours the endothermic change. That means that increasing the temperature increases the amount of vapour present, and so increases the saturated vapour pressure.

The dependence of vapour pressure with temperature is given by **Clausius-Clapeyron equation**

F14 $\ln\left(\frac{p_2}{p_1}\right) = -\frac{\Delta Hv}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$, where ΔH_v = molar enthalpy of vapourisation of the given liquid,

p_2 = vapour pressure of the liquid at T_2 and p_1 = vapour pressure of the liquid at T_1.

(3) Vapour pressure of a liquid does not depend on :

(i) the amount of liquid taken

(ii) surface area of the liquid

(iii) volume or shape of the container

(4) **Partial pressure of vapours**: If vapours of a liquid are present in a gaseous mixture then,

Partial pressure of vapours of the liquid = $\dfrac{\text{Pressure of vapours}}{\text{Total pressure}}$

Saturation: A gas or gaseous mixture is said to be saturated with the vapours of a liquid if the partial pressure of the liquid vapours is equal to its (saturated) vapour pressure.

(5) (a) Saturated (Equillibrium) Vapour pressure of water, at a given temprature, is called aqueous tension. The value of aqueous tension is different at different temprature.

F15 (b) Relative Humidity (R.H.) = $\dfrac{\text{Partial pressure of water vapour at given temperature}}{\text{Vapour pressure of water at the same temperature}} \times 100\%$

(6) **Saturated vapour pressure and boiling point:**

A liquid boils when its saturated vapour pressure becomes equal to the external pressure on the liquid. When that happens, it enables bubbles of vapour to form throughout the liquid. If the external pressure is higher than the saturated vapour pressure, these bubbles are prevented from forming, and we just get evaporation at the surface of the liquid.

* $P_{ext} > P_{sat} \Rightarrow$ evaporation

* $P_{ext} = P_{sat} \Rightarrow$ Boiling

If the liquid is in an open container and exposed to normal atmospheric pressure, the liquid boils when its saturated vapour pressure becomes equal to 1 atmosphere. This happens with water when the temperature reaches 100°C. But at different pressures, water will boil at different temperatures. For example, at the top of Mount Everest the pressure is so low that water will boil at about 70°C.

(a) Boiling point : The boiling point is the temperature at which the vapour pressure of a liquid is equal to the external pressure.

(b) At boiling temperature, vapour pressure of the pure liquid i.e. $P^o = P_{ext}$

(c) At normal boiling point, vapour pressure of the pure liquid i.e. $P^o = 1\text{atm}$

(7) **Saturated vapour pressure and solids: Sublimation**

Solids can also loose particles from their surface to form a vapour, except that in this case we call the effect sublimation rather than evaporation. Sublimation is the direct change from solid to vapour without going through the liquid stage.

The forces of attraction in many solids are too high to allow much loss of particles from the surface. However, there are some solids which easily form vapours.

Naphthalene (used in "moth balls") has quite a strong smell. Molecules must be breaking away from the surface as a vapour, because otherwise we wouldn't be able to smell it.

Solid carbon dioxide never forms a liquid at atmospheric pressure and always converts directly from solid to vapour. That's why it is known as dry ice.

(8) If partial pressure of vapours of a liquid is increased beyond the saturated (equillibrium) vapour pressure value (P^o), its vapours begin to condense till their partial pressure becomes equal to the saturated vapur pressure.

(9) If the partial pressure of vapour is less than v.p. of liquid, the liquid (if present) will vaporize till
(a) its v.p. is attained or (b) the liquid completely gets vaporized

(10) If a volatile solid/ liquid is brought in contact with a gas (or vaccuum), vapours of that solid/ liquid occupy the gas phase till the gas phase becomes saturated with that solid /liquid vapours.

Solved Examples

Example-6 : The vapor pressure of water at 80º C is 355 torr. A 100 ml vessel contained water–saturated oxygen at 80º C, the total gas pressure being 760 torr. The contents of the vessel were pumped into a 50.0 ml, vessel at the same temperature. What were the partial pressures of oxygen and of water vapor, what was the total pressure in the final equilibrated state ? Neglect the volume of any water which might condense.

Ans. P_{O_2} **= 810 mm Hg,** P_{H_2O} **= 355 mm Hg , P_{total} = 1165 mm Hg**

Solution : In 100 ml vessel which contained water - saturated oxygen, the pressure of O_2 gas = 760 – 355 = 405 torr when the contents of this vessel were pumped into 50 ml vessel, at the same temperature, the pressure of oxygen gets doubled i.e. P_{O_2} = 810 torr.

But pressure of water vapour will remain constant, as some vapour in this 50 ml vessel, gets condensed.

So, P_{H_2O} = 355 torr & Total pressure = 810 + 355 = 1165 torr.

Section (D) : Solutions of Solid and Gases in Liquids

5. D22 **Saturated solution :** *A solution in which no more solute can be dissolved at the same temperature is called saturated solution.*

D23 **Unsaturated solution :** *It is a solution in which more amount of solute can be dissolved at the same temperature.*

D24 **Supersaturated solution :** *It is a solution which contains more mass of the dissolved solute than the saturated solution at the same temperature and pressure.* It should be prepared in a dust-free vessel and at a higher temperature. It is metastable. Mechanical stress, such as shaking or addition of solute, causes deposition of solute.

D25 **Solubility :** Solubility of a substance is its maximum amount that can be dissolved in a specified amount of solvent (generally 100 g of solvent) at a specified temperature to form a saturated solution.

Solubility of one substance into another depends on
(i) nature of the solute and solvent. (ii) Temprature (iii) Pressure

5.1 Solubility of a solid in a liquid :

Like dissolves like: Polar solutes dissolve in polar solvents and non polar solutes in non-polar solvents.

Sodium chloride and sugar dissolve readily in water, naphthalene and anthracene do not. On the other hand, naphthalene and anthracene dissolve readily in benzene but sodium chloride and sugar do not.

Dissolution : When a solid solute is added to the solvent, some solute dissolves and its concentration increases in solution. This process is known as dissolution.

Crystallisation : Some solute particles in solution collide with the solid solute particles and get separated out of solution. This process is known as crystallisation.

At equilibrium, rate of dissolution is equal to rate of crystallisation. At this stage the concentration of solute in solution will remain constant under the given conditions, i.e., temperature and pressure. Such a solution is said to be saturated with the given solute.

$$\text{Solute + Solvent} \rightleftharpoons \text{Solution}$$

5.2 Effect of temperature on solubility of a solid in a liquid

Consider the equilibrium: Solute + Solvent $\rightleftharpoons$ Solution. By Le Chatelier's Principle:

If above process is exothermic i.e. $\Delta H < 0$, then as T increases, solubility decreases.

If above process is endothermic i.e. $\Delta H > 0$, then as T increases, solubility increases.

5.3 Effect of pressure on solubility of a solid in a liquid (no effect)

Pressure does not have any significant effect on solubility of solids in liquids. It is so because solids and liquids are highly incompressible and practically remain unaffected by changes in pressure.

6. Solubility of gases in liquids :

6.1 Factors Affecting Solubility of Gas In Liquid :

(i) Nature of gas (ii) Nature of liquid (iii) Temperature (iv) Pressure

6.2 Henry's Law (effect of pressure on solubility of gases in liquids) :

Statement : The solubility of a gas in a liquid at a given temperature is directly proportional to its partial pressure at which it is dissolved.

Der.2 Let x = Mole fraction of unreacted gas in solution at a given temperature as a measure of its solubility.

p = Partial pressure of gas in equilibrium with the solution.

By Henry's law: $x \propto p$ or $p \propto x$

That is; **F16** $p = K_Hx$ or $x = \frac{p}{K_H}$, where K_H = Henry's law constant.

6.3 Characteristics of Henry's Law constant (K_H).

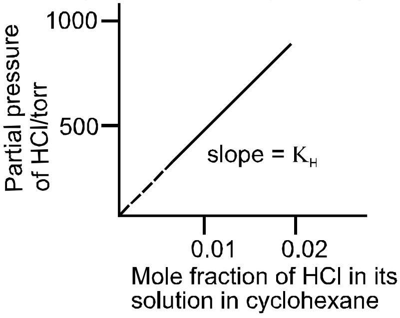
(i) Unit same as those of pressure: torr or bar.

(ii) Different gases have different value of K_H for the same solvent.

(iii) The K_H value of a gas is different in different solvents and it increase with the increase in temperature.

(iv) Higher the value of K_H of a gas, lower will be its solubility. Since, $x = \frac{p}{K_H}$.

Plot of p Vs x is a straight line passing through the origin with slope equal to K_H.



Plot of p Vs x for solution of HCl in cyclohexane.

Note : If a mixture of gases is brought in contact with solvent each constituent gas dissolves in proportion to its partial pressure. It means Henry's law applies to each gas independent of the pressure of other gas.

Solved Examples

Example-7 : Henry's law constant for O_2 dissolved in water is 4.34×10^4 atm at 25°C. If the partial pressure of oxygen in air is 0.4 atm. Calculate the concentration (M) of dissolved oxygen in water in equilibrium with air at 25°C :

Solution : Given $K_H = 4.34 \times 10^4$ atm

$p_{O_2} = 0.4$ atm

acc. to Henry's Law

$p = K_H X$

$$X_{O_2} = \frac{0.4}{4.34 \times 10^4} = 9.2 \times 10^{-6}$$

Moles of water $(n_{H_2O}) = \frac{1000}{18} = 55.8$ mol

$$X_{O_2} = \frac{n_{O_2}}{n_{O_2} + n_{H_2O}}$$

Since n_{O_2} is very small in comparison to n_{H_2O}

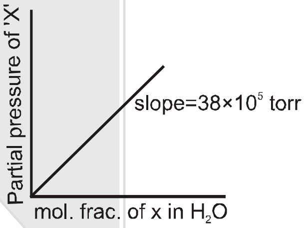
$$X_{O_2} = \frac{n_{O_2}}{n_{H_2O}}$$

or $X_{O_2} \times n_{H_2O} = n_{O_2}$

So $n_{O_2} = 9.2 \times 10^{-6} \times 55.55 = 5.11 \times 10^{-4}$ mol

So $M = 5.11 \times 10^{-4}$

Example-8 : A gas 'X' is present with saturated water vapour over water liquid at total pressure of 1.5 atm. Vapour pressure of H_2O at same temperature is 0.5 atm. What is the solubility of gas 'X' in terms of moles in 10 moles $H_2O(\ell)$.



Solution : $P_T = P_x + P_{H2O}$

$P_x = 1.5 - 0.5 = 1$ atm

slope of graph $= K_H = 5 \times 10^3$

$$P_x = K_H \frac{n_x}{n_{H_2O}}$$

$$1 = 5 \times 10^3 \times \frac{n_x}{10}$$

$$n_x = \frac{1}{500} = 2 \times 10^{-3}$$

6.4 Effect of temperature : Solubility of gases in liquids decreases with rise in temperature.

Explanation: When dissolved, the gas molecules are present in liquid phase and the process of dissolution can be considered similar to condensation and heat is evolved in this process. We have learnt that dissolution process involves dynamic equilibrium and thus must follow Le Chatelier's principle. As dissolution of gases in liquids is an exothermic process, the solubility should decrease with increase of temperature.

Note : K_H values for both N_2 and O_2 increase with increase of temperature indicating that the solubility of gases increases with decrease of temperature. It is due to this reason that aquatic spcies are more comfortable in cold water rather than warm water.

6.5 Applications of Henry's law :

It has several applications in biological and industrial phenomena.

(i) To increase the solubility of CO_2 in soft drinks and soda water the bottle is sealed under high pressure.

(ii) Scuba divers must cope with high concentrations of dissolved gases while breathing air at high pressure underwater. Increased pressure increases the solubility of atmosphere gases in blood. When the divers come towards surface, the pressure is gradually decreased. This releases the dissolved gases and leads to the formation of bubbles of nitrogen in the blood. This blocks capillaries and creates a medical condition known as **bends**, which are painful and dangerous to life. To avoid bends, as well as, the toxic effects of high concentrations of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).

(iii) At high altitudes the partial pressure of oxygen is less than that at the ground level. This leads to low concentrations of oxygen in the blood and tissues of people living at high altitudes or climbers. Low blood oxygen causes climbers to become weak and unable to think clearly, symptoms of a condition known as **anoxia**.

6.6 Limitation of Henry's law :

Henry's law is valid only under following condition.

(i) The pressure of gas is not too high. **(ii)** The temperature is not too low.

(iii) The gas should not undergo any chemical reaction with the solvent.

(iv) The gas should not undergo dissociation in solution.

Section (E) : Immiscible Liquids

7. Vapour Pressure of liquid-liquid solution: volatile solute + volatile solvent

7.1 Completely Immiscible Liquids and Steam Distillation

For mixture of two completely immiscible liquids, each liquid exerts its own vapor pressure, independent of the other, and the total vapor pressure is the sum of the separate vapour pressures of the two components in the pure state at the given temperature.

Thus, $p_A = P_A^0$ & $p_B = P_B^0$

F17 $$P_T = P_A^0 + P_B^0 \; ; \; \frac{P_A^0}{P_B^0} = \frac{n_A}{n_B}$$

where n_A and n_B are the numbers of moles of each component present in the vapor phase, which on condensing form distillate.

The ratio of A to B in the vapor in terms of the actual weights w_A and w_B is

F18 $$\frac{w_A}{w_B} = \frac{n_A M_A}{n_B M_B} = \frac{p_A^0 M_A}{p_B^0 M_B}$$

(i) A system of two immiscible liquids will boil when the total vapor pressure P is equal to the atmospheric pressure or the given external pressure. The boiling point of the mixture is thus lower than that of either constituent.

(ii) Further, since the total vapor pressure is independent of the relative amounts of the two liquids, the boiling point, and hence the composition of the vapor and distillate, will remain constant as long as the two layers are present. e.g. Water and Benzene has boiling point = 68.9ºC.

But boiling point = H_2O (pure) C_6H_6 (pure)
100ºC 80.2ºC

Steam Distillation: The boiling point of a solution of two immiscible liquids is less than the individual boiling points of both the liquids. This concept is used in steam distillation.

A liquid (generally organic) that is immiscible with water, and that has a higher boiling point than water can be boiled (distilled) at a much lower temperature by passing steam through it. In this way, the organic liquid can be purified from impurities using steam distillation.

Section (F) : Completely miscible liquids : Raoult's law

7.2 Statement of Raoult's law (for volatile liq. mixture) : In solution of volatile liquids, the partial vapour pressure of each component is directly proportional to its mole fraction.

$$p_A \propto x_A$$

F19 $p_A = x_A P_A^o$

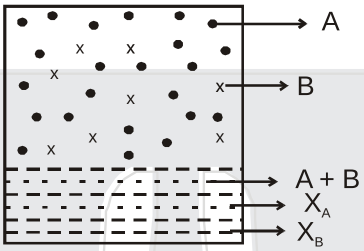
p_A = Partial vapour pressure of component A

x_A = Mole fraction of component 'A' in solution.

P_A^o = Vapour pressure of pure component 'A' at given temperature

Der.3 **Derivation of total pressure over solution using Raoult's law and Dalton's law:**

Let A, B be to two volatile liquids in a closed container as shown.



$p_A = x_A P_A^o$

Similarly, for liquid B we have,

$p_B = x_B P_B^o$

Total pressure over the solution P_T , according to Dalton's law is

F20 $P_T = p_A + p_B = x_A P_A^0 + x_B P_B^0$

Determining composition of vapour phase:

Let, y_A = mole fraction of A in vapour phase above the solution and

y_B = mole fraction of B in vapour phase above the solution

Now, we have, $p_A = y_A P_T$ .....Dalton's law of partial pressure for a gaseous mixture

$p_A = x_A P_A^\circ$ ....Raoult's law

Thus, $p_A = y_A P_T = x_A P_A^o$

Also, $p_B = y_B P_T = x_B P_B^o$

$$x_A + x_B = 1 = \frac{y_A P_T}{P_A^0} + \frac{y_b P_T}{P_B^0}$$

F21 Thus, $$\frac{1}{P_T} = \frac{y_A}{P_A^0} + \frac{y_B}{P_B^0}$$

Graphical Representation of Raoult's Law:

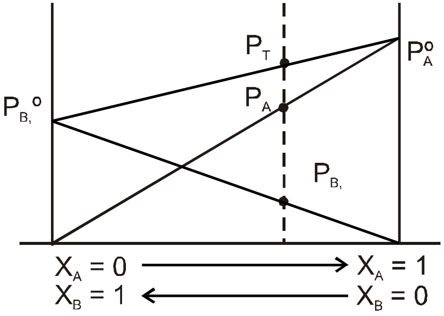
$p_A = x_A P_A^o$ & $p_B = x_B P_B^o$

$P_T = x_A P_A^o + x_B P_B^o$

$P_T = (P_A^o - P_B^o)\, x_A + P_B^0$

$P_T = (P_B^o - P_A^o)\, x_B + P_A^0$

This represents equation of straight line. P_T v.s x



Note: If $P_A^\circ > P_B^\circ$, A is more volatile than B. B.P. of A < B.P. of B.

7.3 Application of Raoult's Law:

(1) Phase Diagrams of Two-Component Ideal Solutions: Bubble and Dew Points

The compositions of the liquid and vapour that are in mutual equilibrium are not necessarily the same. Common sense suggests that the vapour should be richer in the more volatile component. This can be easily derived from Raouls's Law.

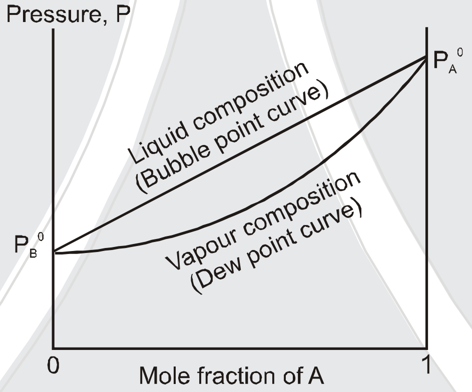
$$\frac{1}{P_T} = \frac{y_A}{P_A^0} + \frac{y_B}{P_B^0} = \frac{y_A}{P_A^0} + \frac{1-y_A}{P_B^0}$$

$$P_T = \frac{P_A^0 P_B^0}{P_A^0 + (P_B^0 - P_A^0) y_A}$$

From the above equation, the plot of P_T with respect to y is a curve instead of a straight line. We can superimpose this curve on the diagram for graphical representation of Raoult's Law to get following phase diagrams.

(A) Pressure versus Composition Phase Diagram (At constant T): P vs. x and y

In this kind of phase diagram the temperature has a fixed value. The mole fraction of one component is plotted on the horizontal axis and the pressure is plotted on the vertical axis. If A is more volatile than B, then we get following diagram.



Explanation :

(i) On horizontal-axis we have plotted both x and y that is both liquid composition and vapour composition.

(ii) The lower curve (Dew Point Curve) represents the total pressure as a function of the composition i.e. mole fraction in the vapor phase at equilibrium with the liquid phase. It is plotted using P_T vs. y_A equation:

$$P_T = \frac{P_A^0 P_B^0}{P_A^0 + (P_B^0 - P_A^0) y_A}$$

(iii) The upper curve i.e. Bubble Point Curve (a straight line in the case of an ideal solution) represents the total pressure as a function of composition i.e. mole fraction in the liquid. It is plotted using P_T vs. x_A equation: $P_T = (P_A^o - P_B^o)\, x_A + P_B^0$

(iv) The area between these two curves is vapour-liquid equilibrium region. Vapours cannot exist above the bubble point curve and liquid can not exist below the dew point curve.

(v) Suppose, initially the pressure over the solution is very high so that no vapour exist above the liquid. As we gradually decrease the pressure, a point (Bubble point) comes when we cross the Bubble-Point curve and first bubble of vapour starts forming. Hence, the name bubble point curve. Now we have entered the vapour-liquid equilibrium region. On further decreasing the pressure, a point (Dew Point) comes when we cross the Dew-Point curve when almost all the liquid has evaporated into vapour i.e. only the last drop of liquid (Dew) remains. Beyond this point no liquid exists in the system.

Solved Examples

Example-9 : Benzene and toluene form nearly ideal solutions. At 300 K, $P^o_{toluene}$ = 30 mm Hg and $P^o_{benzene}$ = 100 mm Hg.
A liquid mixture is composed of 3 mol of toluene and 2 mol of benzene.
(a) If the pressure over the mixture at 300 K is reduced. At what pressure does the first vapour form?
(b) What is the composition of the first trace of vapour formed ?
(c) If the pressure is reduced further, at what pressure does the last trace of liquid disappear?
(d) What is the composition of the last trace of liquid?

Ans. (a) 58 mm Hg (b) y_b = 20/29 (c) 250/6 mm Hg (d) x_b = 1/6

Solution : (a) $P = X_AP^0_A + X_BP^0_B = \frac{3}{5} \times 30 + \frac{2}{5} \times 100 = 58$ mm Hg

(b) Composition of the first trace of vapour formed

$$Y_{benzene} = \frac{X_bP^0_b}{P_{Total}} = \frac{2}{5} \times \frac{100}{58} = \frac{20}{29} \qquad \& \qquad Y_{toluene} = 1 - \frac{20}{29} = \frac{9}{29}$$

(c) The last trace of liquid disappear at $\begin{matrix} Y_A = 3/5 \\ Y_B = 2/5 \end{matrix}$

$$\frac{1}{p} = \frac{Y_A}{P^0_A} + \frac{Y_B}{P^0_B}$$

$$\frac{1}{p} = \frac{3}{5\times30} + \frac{2}{5\times100} \qquad \text{or} \qquad p = \frac{250}{6} \text{ mm Hg}$$

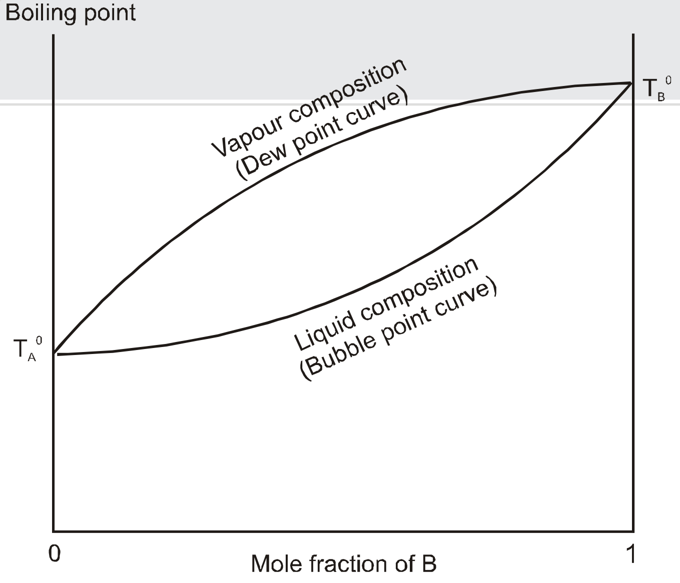
(d) The composition of the last trace of liquid

$$X'_{benzene} = \frac{Y_{benzene}P_{Total}}{P_b{}^o} = \frac{\frac{2}{5}\times\frac{250}{6}}{100} = \frac{1}{6}$$

so $X'_{toluene} = \frac{5}{6}$.

(B) Temperature versus Composition Phase Diagrams i.e. T vs x and y diagram

(i) In this type of phase diagram the pressure is held fixed. The mole fraction of one component is plotted on the horizontal axis and the boiling temperature is plotted on the vertical axis.



(ii) The upper curve (Dew-Point curve) gives the boiling temperature at the given pressure as a function of the mole fraction in the vapor phase, and the lower curve (Bubble-Point curve) gives the boiling tempera ture at the given pressure as a function of the mole fraction in the liquid phase.

Note: If a liquid has a high vapour pressure at a particular temperature, it means that its molecules can escape easily from the surface. The liquid with the higher vapour pressure at a particular temperature is the one with the lower boiling point. If A is more volatile than B, then we get following diagram.

(2) Distillation:

(i) The compositions of the liquid and vapour that are in mutual equilibrium are not necessarily the same. Common sense suggests that the vapour should be richer in the more volatile component.

(ii) In a simple distillation, the vapour over a boiling mixture is withdrawn and condensed in a separate container. The liquid collected in the new container is called condensate or distillate and the liquid remaining in the original container is called residue. The condensate has higher mole fraction of the more volatile component than the original mixture. The residue has higher mole fraction of the less volatile component than the original mixture. This is the principle of distillation and is used to separate a more volatile liquid from a less volatile liquid.

(iii) In fractional distillation, the boiling and condensation cycle is repeated successively to get a distillate which gets richer in the more volatile component after each cycle.

Solved Examples

Example-10 : An equimolar mixture of benzene & toluene is prepared. The total vapour pressure of this mixture as a function of mole fraction of benzene is found to be $P_T = 200 + 400\ X_{ben}$.

(a) Calculate composition of vapours of this mixture [Assume that the number of moles going into vapour phase is negligible in comparsion to number of moles present in liquid phase].

(b) If the vapour above liquid in part (a) are collected and condensed into a new liqiuid, calculate composition of vapours of this new liquid.

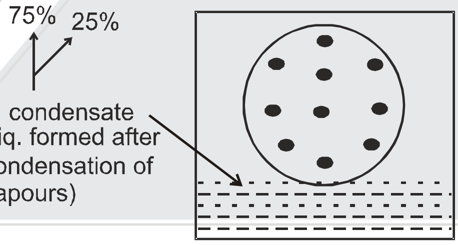
Solution : (a) $P^0_{Beazene}$= 600 mm of Hg ; $P^0_{Toloune}$ = 200 mm of Hg

$$P_T = \frac{1}{2} \times 600 + \frac{1}{2} \times 200 = 400 \text{ mm of Hg}$$

$$P_{benz} = x_{ben}\ '\ P^o_{ben} \qquad = y_{ben}P_T.$$

$$y_{benzene} = \frac{1/2 \times 600}{400} = \frac{3}{4} = 75\% \ ; \qquad y_{Toloune} = \frac{1}{4} = 25\%$$

(b)



$$P_T = \frac{3}{4} \times 600 + \frac{1}{4} \times 200 = 500 \quad \Rightarrow \quad y_{ben} = \frac{3/4 \times 600}{500} = 0.9 = 90\%$$

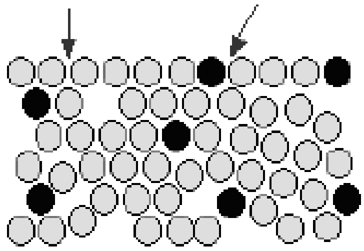
$$y_{Toluene} = 0.1 = 10\%$$

7.4 Limitations of Raoult’s Law: Raoult's Law only works for ideal solutions. Very dilute solutions obey Raoult's Law to a reasonable approximation.

(1) Ideal Solutions : Those solutions which obey Raoult's law over the entire range of conc. are called ideal solutions. When the forces of attraction between A—A, B—B is similar to A—B, then A and B will form ideal solution.

In an ideal solution, the forces between the solvent molecules

.... are exactly the same as those between solvent and solvent and solute.



Thatmeans that it takes the same amount of energy for solvent molecules to break away from the surface in either case.

Properties of ideal solution :

(i) Raoult's law is obeyed

(ii) $\Delta H_{mix} = 0$, i.e., there should not be enthalpy change when components of ideal solutions are mixed.

(iii) $\Delta V_{mix} = 0$, (1L + 1L = 2L) i.e., there should not be change in volume on mixing. e.g.; n-hexane and n-heptane; ethyl bromide and ethyl iodide; benzene and toluene; chlorobenzene and bromobenzene form ideal solutions.

Section (G) : Non-ideal Solutions

(2) Non-Ideal Solutions :

Those solutions which do not obey Raoult's over the entire range of concentration are called non-ideal solutions.

When the forces of attraction between A—A, B—B is different from A—B then 'A' and 'B' form non-ideal solutions. For these solutions :

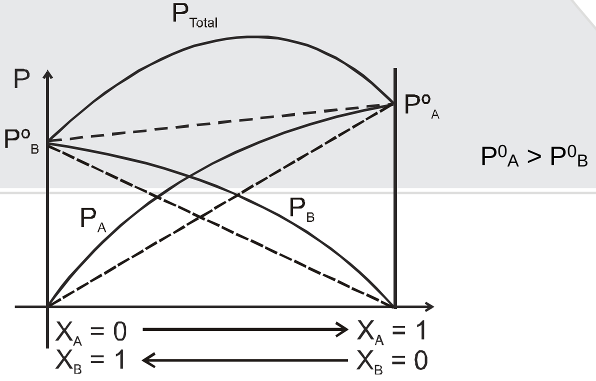
(i) Raoult's law is not obeyed. (ii) $\Delta H_{mix} \neq 0$; (iii) $\Delta V_{mix} \neq 0$.

Types of Non-Ideal Solutions:

(A) Non-Ideal Solutions Showing Positive Deviation From Raoult's Law :

(i) In this case, partial pressure of each component A and B is higher than that calculated from Raoult's law, and hence total pressure over the solution is also higher than if the solution were ideal, as shown in figure.

(ii) Boiling point of such a solution is relatively lower than the boiling points of both A and B.



Note: Dashed lines represent vapour pressures and total pressure corresponding to ideal solution

Examples: water and ethanol, chloroform and water, ethanol and CCl_4, methanol and chloroform, benzene and methanol, acetic acid and toluene, acetone and ethanol, methanol and H_2O, C_2H_5OH + cyclohexane.

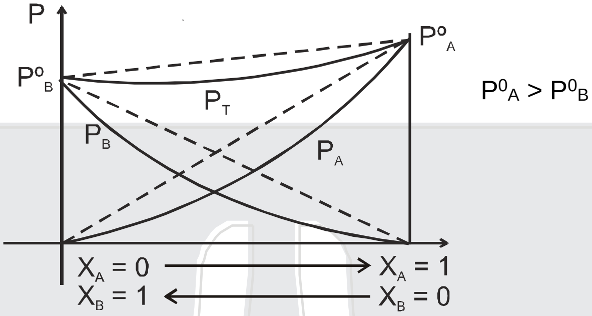
Explanation: The fact that the vapour pressure is higher than ideal in these mixtures means that molecules are breaking away more easily than they do in the pure liquids. That is because the intermolecular forces between molecules of A and B are less than they are in the pure liquids.

You can see this when you mix the liquids. Less heat is evolved when the new attractions are set up than was absorbed to break the original ones. Heat will therefore be absorbed when the liquids mix. The enthalpy change of mixing is endothermic.

(B) **Non-Ideal Solutions Showing Negative Deviation From Raoult's Law :**

(i) In this case, partial pressure of each component A and B is lower than that calculated from Raoult's law, and hence total pressure over the solution is also lower than if the solution were ideal, as shown in figure.

(ii) Boiling point of such a solution is relatively higher than the boiling points of both A and B.



Note: Dashed lines represent vapour pressures and total pressure corresponding to ideal solution.

Examples: chloroform and acetone, chloroform and methyl acetate, H_2O and HCl, H_2O and HNO_3, acetic acid and pyridine, Phenol & Aniline.

Explanation: These are cases where the molecules break away from the mixture less easily than they do from the pure liquids. New stronger forces must exist in the mixture than in the original liquids.

You can recognise this happening because heat is evolved when you mix the liquids-more heat is given out when the new stronger bonds are made than was used in breaking the original weaker ones.

	Positive deviation solution		**Negative deviation solution**
(i)	$P_T > (X_A P_A^0 + X_B P_B^0)$	(i)	$P_T < X_A P_A^0 + X_B P_B^0$
(ii)	The inter molecular interaction is weaker as interaction found in any one of the pure components.	(ii)	The inter molecular interaction is more than the interaction found in any of the pure components
	A............A B............B molecular interaction is Stronger than A............B		A............B molecular interaction is more than A............A B............B
(iii)	There is increase in volume on mixing and absorption of heat.	(iii)	There is decrease in volume on mixing and evolution of heat takes place on mixing
	ΔV_{mix} = positive ΔH_{mix} = positive		$\Delta V_{mix} = -ve$ $\Delta H_{mix} = -ive$
	$\Delta S_{mix} = +ive$ $\Delta G_{mix} = -ive$		$\Delta S_{mix} = +ive$ $\Delta G_{mix} = -ive$
Ex.	$H_2O + CH_3OH$, C_2H_5OH + Hexane C_2H_5OH + Cyclohexane, $CHCl_3 + CCl_4$	Ex.	$H_2O + HCOOH$, $H_2O + CH_3COOH$ $H_2O + HNO_3$, $CHCl_3 + CH_3OCH_3$

7.5 **Azeotropic Mixtures :** Very large deviations from ideality lead to a special class of mixtures known as azeotropes, azeotropic mixtures, or constant-boiling mixtures.

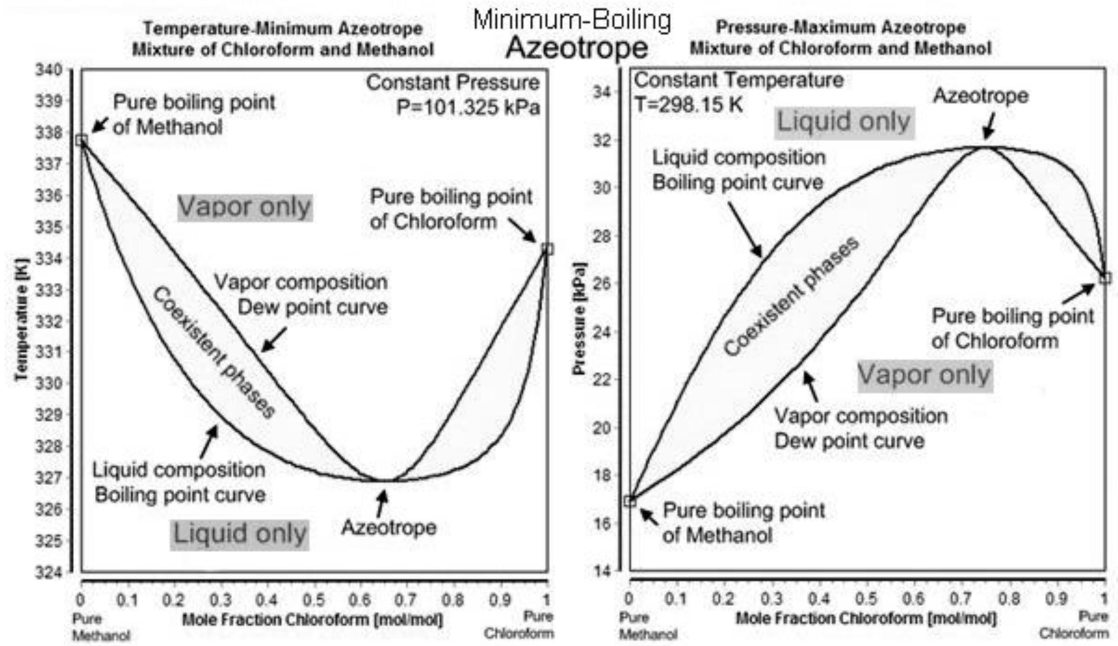
D26 **Azeotropes :** Liquid mixtures which distill over without changes in composition are called constant boiling mixtures or Azeotropes or Azeotropic mixtures.

A boiling liquid mixture at the azeotropic composition produces a vapour of exactly the same composition, and the liquid does not change its composition as it evaporates. Two types of azeotropes are known.

(1) D27 Minimum Boiling Azeotropes : *Non-ideal solutions showing large positive deviation from Raoult's law form minimum boiling azeotropes which boil at temperature lower than boiling point of its components 'A' and 'B',* e.g., water and benzene, chloroform and methanol.

The figures below show the Temprature vs. composition (at constant pressure) phase diagram on the left side and Pressure vs. composition (at constant temprature) phase diagram for a minimum-boiling azeotropic mixture chloroform and methanol.

Note: The detailed values in the diagram are not important. Only the qualitative shape of the diagram is important.

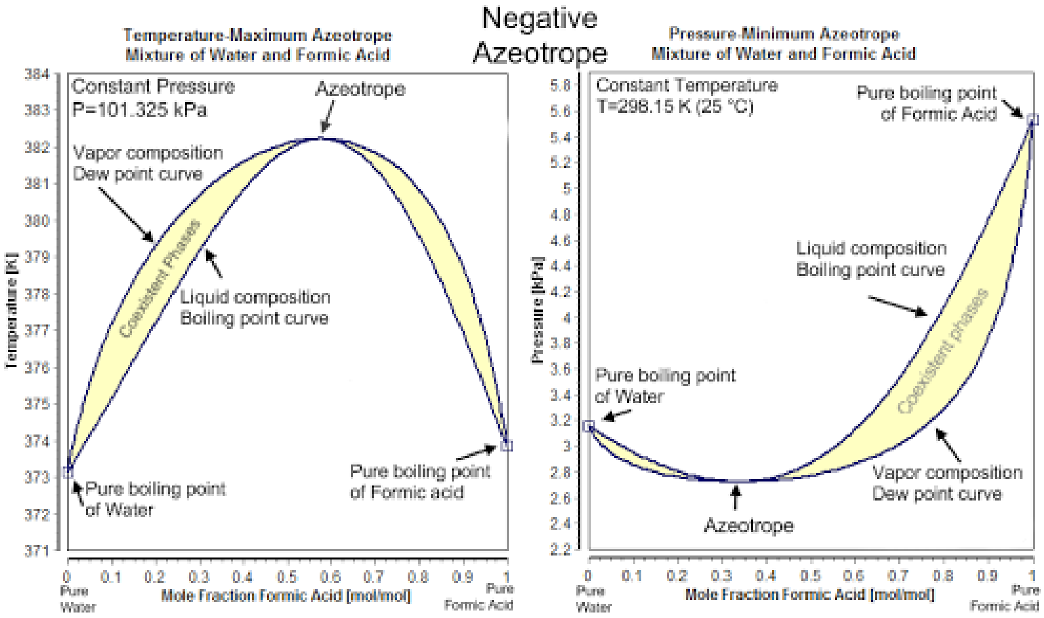


At the lowest point in the temperature vs. composition phase diagram, the concentration in the vapour phase is the same as the concentration in the liquid phase (y = x). This concentration is known as the azeotropic composition. At this point, the mixture boils at a constant temperature and without change in composition.

(2) D28 Maximum Boiling Azeotropes : *Non-ideal solutions showing large negative deviation from Raoult's law form maximum boiling azeotropes which boil at temperature higher than the boiling point of its components A and B respectively,* e.g., a mixture of HCl and H_2O containing 20.2% HCl by weight boils at 108.5ºC higher than either pure HCI (– 85°C) or water (100°C).

The figures below show the Temprature vs. composition (at constant pressure) phase diagram on the left side and Pressure vs. composition (at constant temprature) phase diagram for a maximum-boiling azeotropic mixture water and formic acid.

Note: The detailed values in the diagram are not important. Only the qualitative shape of the diagram is important.



(3) **Separation of Azeotropic Mixtures**

When the azeotropic composition has been reached, the condensate has the same composition as the azeotropic liquid. The vapour phase is not richer in any component than the liquid phase. Thus, azeotropic mixtures can't be separated beyond the azeotropic composition using distillation.

Section (H) : Degree of Ionisation/Dissociation for Weak Electrolytes

8. Colligative properties & constitutional properties :

D29 ● **Constitutional Properties :**

Properties which are dependent on nature of particles are constitutional properties like electrical conductance.

D30 ● **Colligative properties :**

The properties of the solution which are dependent only on the total no. of particles relative to solvent/solution or total concentration of particles in the solution and are not dependent on the nature of particle i.e. shape, size, neutral /charge etc. of the particles.

There are 4 colligative properties of solution.

1. Relative lowering in vapour pressere $\left(\frac{\Delta P}{P}\right)$

2. Elevation in boiling point (ΔT_b)

3. Depression in freezing pt. (ΔT_f)

4. Osmotic pressure (π)

8.1 Abnormal Colligative Properties :

Vant–Hoff correction :

- For electrolytic solutes the number of particles would be different from the number of particles actually added, due to dissociation or association of solute.
- The actual extent of dissociation/association can be expressed with a correction factor known as vant Haff factor (i).

F22 **Vant–Hoff factor :** $i = \frac{\text{moles of particles in solution after dissociation/association}}{\text{moles of solute dissolved}}$

D31 ● If solute gets associated or dissociated in solution then experimental / observed / actual value of colligative property will be different from theoretically predicted value so it is also known as **abnormal colligative property.**

- This abnormality can be calculated in terms of Vant-Hoff factor.

$i = \frac{\text{exp/observed/actual/abnormal value of colligative property}}{\text{Theoretical value of colligative property}}$

$$= \frac{\text{exp./observed no. of particles or concentration}}{\text{Theoretical no. of particles or concentration}} = \frac{\text{(Theoretical molar mass of substance)}}{\text{(Experimental molar mass of the substance)}}$$

$i > 1$ dissociation

$i < 1$ association

Der.4 **Case - I : Electrolyte dissociates**

Relation between i & α (degree of dissociation) :

Let the electrolyte be A_xB_y

$$A_xB_y\ (aq.) \longrightarrow xA^{y+} + yB^{x-}$$

t = 0	C	0	0
t_{eq}	$C(1-\alpha)$	$xC\alpha$	$yC\alpha$

Net concentration = $C - C\alpha + xC\alpha + yC\alpha = C\,[1 + (x+y-1)\,\alpha] = C\,[1 + (n-1)\,\alpha]$.

$n = x + y$

= no. of particles in which 1 molecule of electrolyte dissociates

$$i = \frac{C\ [1+(n-1)\alpha]}{C}$$

F23 $$i = 1 + (n-1)\,\alpha$$

e.g. NaCl (100% ionised), i = 2. ; $BaCl_2$ (100% ionised), i = 3. ; $K_4[Fe(CN)_6]$ (75% ionised), i = 4.

Der.4 **Case - II : Electrolyte associates**

Relation between degree of association β & i.

$$nA \longrightarrow A_n.$$

t = 0	C	0
t_{eq}	$C\,(1-\beta)$	$\frac{C\beta}{n}$

Net concentration = $C - C\beta + \frac{C\beta}{n}$

$$= C\,[\,1 + \left(\frac{1}{n} - 1\right)\beta\,]$$

F24 $$i = 1 + \left(\frac{1}{n} - 1\right)\beta$$

if dimerise n = 2 ; trimerise n = 3 ; tetramerise n = 4.

e.g. CH_3COOH 100% dimerise in benzene, $i = \frac{1}{2}$; C_6H_5COOH 100% dimerise in benzene, $i = \frac{1}{2}$

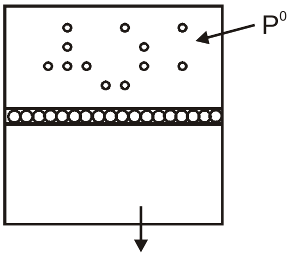
Section (I) : Relative lowering of vapour pressure

8.2 Relative lowering in vapour pressure (RLVP) :

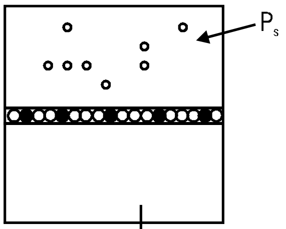
Vapour Pressure of a solution of non-volatile solute in a volatile solvent

Vapour Pressure of a solution of a non volatile solute (solid solute) is always found to be less than the vapour pressure of pure solvent.

Reason : Some of the solute molecules will occupy some surface area of the solutions so tendency of the solvent particles to go into the vapour phase is slightly decreased hence $P^o > P_S$, where P^o is vapour pressure of pure solvent and P_S is vapour pressure of the solution.



Pure solvent



solution of non-volatile solute in volatile solvent

Lowering in VP = $P^o - P_S = \Delta P$

and Relative lowering in Vapour Pressure = $\frac{\Delta P}{P^0}$

Raoult's law (For non–volatile solutes): The vapour pressure of a solution of a non-volatile solute is equal to the vapour pressure of the pure solvent at that temperature multiplied by its mole fraction.
OR Relative Lowering in Vapour Pressure = mole fraction of the non volatile solute in solution.

Der.6 $P_S = x_{solvent}P^0 = (1 - x_{solute})P^0$

F25 $\text{RLVP} = \frac{P^0\text{-}P_s}{P^0} = x_{Solute} = \frac{n}{n+N}$

where n = number of moles of non-volatile solute and N = number of moles of solvent in the solution.

$$\frac{P^0}{P^0\text{-}P_s} = \frac{n+N}{n} = 1 + \frac{N}{n}$$

$$\frac{N}{n} = \frac{P^0\text{-}P_s}{P^0} - 1 = \frac{P_s}{P^0\text{-}P_s}$$

$$\frac{P^0\text{-}P_s}{P_s} = \frac{n}{N}$$

$$\frac{P^0\text{-}P_s}{P_s} = \frac{w}{m} \times \frac{M}{W} = \frac{w}{m} \times \frac{M}{W} \times \frac{1000}{1000} = \frac{w}{m} \times \frac{1000}{W} \times \frac{M}{1000}$$

F26 $\frac{P^0\text{-}P_s}{P_s}$ **= (molality) ×** $\frac{M}{1000}$

where w and W = mass of non-volatile solute and volatile solvent respectively
m and M = molar mass of non-volatile solute and volatile solvent respectively

If solute gets associated or dissociated ; $\frac{P^0\text{-}P_s}{P_s} = \frac{i.n}{N}$ that is $\frac{P^0\text{-}P_s}{P_s} = i \times (\text{molality}) \times \frac{M}{1000}$

Solved Examples

Example-11 : Calculate weight of urea which must be dissolved in 400 g of water so final solutions has vapour pressure 2% less than vapour pressure of pure water :

Solution : Let vapour pressure be P^o of water

$P^0 - P_s = .02\ V$

$P_s = 0.98\ V$

$\Rightarrow \quad \frac{0.02}{0.98} = \frac{w}{60} \times \frac{18}{400}$; where w = weight of urea.

$w = \frac{2 \times 60 \times 400}{18 \times 98}$ g = 27.2 g.

Example-12 : 10 g of a solute is dissolved in 80 g of acetone. Vapour pressure of this sol = 271 mm of Hg. If vapour pressure of pure acetone is 283 mm of H

$\frac{P^0\text{-}P_s}{P_s} = \frac{w}{m} \times \frac{M}{W} \quad \Rightarrow \quad \frac{283\text{-}271}{271} = \frac{10}{m} \times \frac{58}{80}$

m = 163 g/mol.

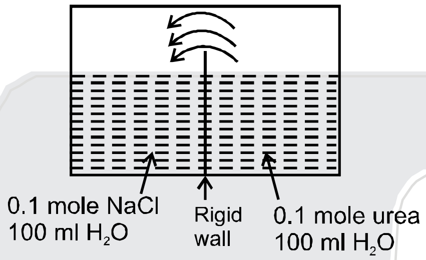
Example-13 : Vapour pressure of solute containing 6 g of non volatile solute in 180 g of water is 20 Torr. If 1 mole of water is further added into it, vapour pressure increases by 0.02 torr. Calculate vapour pressure of pure water and molecular weight of non-volatile solute.

Solution : $\frac{P^0\text{-}P_s}{P_s} = \frac{w}{m} \times \frac{M}{W} \Rightarrow \frac{P^o\text{-}20}{20} = \frac{6}{m} \times \frac{18}{180}$

$\frac{P^o\text{-}20.02}{20.02} = \frac{6}{m} \times \frac{18}{198} \Rightarrow P^o = 20.22$ Torr.

m = 54 g/mol.

Example-14 :



What is the final volume of both container.

Solution : $i_1C_1 = i_2C_2$

$\frac{0.1 \times 2}{100 + x} = \frac{0.1 \times 1}{100 - x}$.

200 – 2x = 100 + x.

x = 33.3 ml.

So, final volume of container containing NaCl = 133.3 ml.

Example-15 : If 0.1 M solutions of $K_4[Fe(CN)_6]$ is prepared at 300 K then its density = 1.2 g/mL. If solute is 50% dissociated calculate ΔP of solution if P of pure water = 25 mm of Hg. (K = 39, Fe = 56)

Solution : $i = 1 + (5 - 1) \times \frac{1}{2} = 3.$

$m = \frac{0.1 \times 1000}{1000 \times 1.2 - 1.2 \times 368}$

$\frac{P^0\text{-}P_s}{P_s} = \frac{im \times M}{1000} = \left(\frac{3 \times 0.1 \times 1000}{1000 \times 1.2 - 1.2 \times 368}\right) \times \frac{18}{1000}$

$\frac{P^0}{P_s} = 1 + 7.12 \times 10^{-3}$

$P_s = 24.82$ mm of Hg

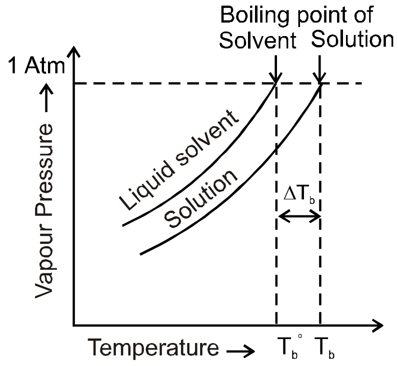
$\Delta p = 25 - 24.82 = 0.18$ mm of Hg

Section (J) : Elevation of Boiling Point & Depression of Freezing Point

8.4 Elevation in Boiling point of a solution of non-volatile solute in volatile solvent (ΔT_b)

D32 **Boiling point:** The temperature at which vapour pressure of a liquid becomes equal to the external pressure present at the surface of the liquid is called b.p of liquid at that pressure.

D33 **Normal Boiling Point:** The boiling temperature when P_{ext} = 1 atm = 760 mm of Hg is called normal boiling point of the liquid (T_b).



The vapour pressure curve for solution lies below the curve for pure water. The diagram shows that ΔT_B denotes the elevation of boiling point of a solution in comparison to solvent.

Elevation of Boiling point of any solution :
Since vapour pressure of solution is smaller than vapour pressure of pure solvent at any temperature hence to make it equal to $P_{ext.}$ we have to increase the temperature of solution by greater amount in comparison to pure solvent.

Der.7 $\Delta T_b = T_b - T_b^o$

$\Delta T_b \propto m$

m = Molality

F27 $\Delta T_b = K_b m$

Note: (i) If solute gets associated/dissociated then $\Delta T_b = i \times K_b \times$ molality

(ii) **Units of K_b:** $\dfrac{\Delta T_b}{\text{molality}} = \dfrac{K}{\text{mol/kg}}$. Thus units of K_b = K kg mol^{-1}

(iii) K_b is dependent on property of solvent and known as ebullioscopic constant of solvent

D34 *It is equal to elevation in boiling point of 1molal solution.* It is also called molal elevation constant. The units of K_b, is K/m or °C/m or K kg mol^{-1}.

F28 $K_b = \dfrac{RT_b^{\,2}\;M}{1000 \times \Delta H_{vap}} = \dfrac{RT_b^{\,2}}{1000 \times L_{vap}}$

where, ΔH_{vap} is molar enthalpy of vaporisation (cal/mol or J/mol)
L_{Vap} is Latent Heat of Vapourisation in cal/g or J/g
M is molar mass of the solvent in gram
R = 2 cal mol^{-1} K^{-1} or 8.314 J/mol-K
T_b = Boiling point of pure liquid solvent (in kelvin)

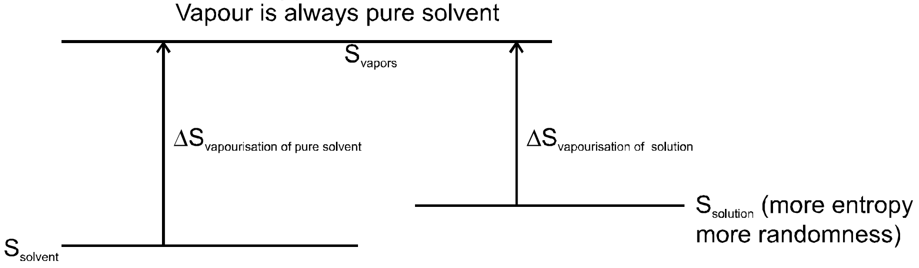
F29 $L_{vap} = \left(\dfrac{\Delta H_{vap}}{M}\right)$

(iv) Elevation in boiling point is proportional to the lowering of vapoure pressure i.e. $\Delta T_b \propto \Delta P$

For water L_{vap} = 540 Cal/g, T_b = 100ºC

$\Rightarrow \quad K_b = \dfrac{2 \times 373 \times 373}{1000 \times 540}$ = K kg mol^{-1} = 0.52 K k/g

Extra Information (Not for Boards)
As only solvent particles are going into vapours,
We have: $\Delta H_{\text{vapourisation of solvent}} = \Delta H_{\text{vapourisation of solution}}$
S means "entropy".



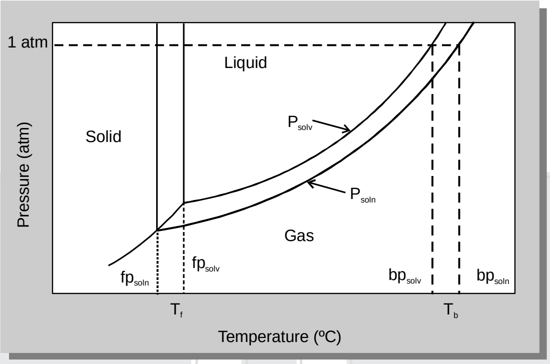
$\Delta S_{\text{vapourisation}} = \dfrac{\Delta H_{\text{vapourisation}}}{T_{b,\text{solvent}}}$

$\Delta S_{\text{vapourisation of pure solvent}} = \dfrac{\Delta H}{T_{b,\text{solvent}}}$

$\Delta S_{\text{vapourisation of solution}} = \dfrac{\Delta H}{T_{b,\text{ solution}}}$

Since, $\Delta S_{\text{vapourisation of pure solvent}} > \Delta S_{\text{vapourisation of solution}}$; So, $T_{b,\text{ solvent}} < \Delta T_{b,\text{ solution.}}$

Due to presence of solute, it is difficult to vapourise the solution, i.e it is difficult to boil the solution. So, there is elevation in boiling point with respect to pure solvent.



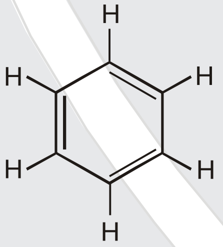
Phase diagram for a pure solvent and a solution of a nonvolatile solute. Because the vapour pressure of the solution is lower than that of the pure solvent at a given temperature, the temperature at which the vapour pressure reaches atmospheric pressure is higher for the solution than for the solvent. Thus, the boiling point of the solution is higher by an amount ΔT_b.

Solved Examples

Example-16 : A solution of 122 g of benzoic acid in 1000 g of benzene shows a boiling point elevation of 1.4º. Assuming that solute is dimerized to the extent of 80 percent, calculate normal boiling point of benzene. Given molar enthalpy of vapourization of benzene = 7.8 Kcal/mole.

Solution :

$$T_b - T_i = \frac{122 \times 1000}{122 \times 1000} \times K_b \left(1 + \left(\frac{1}{2} - 1\right)\right) \quad 0.8$$



$$T_b - T_i = K_b \times 0.4$$

$$K_b = \frac{RT_b^{\,2}}{1000 \times L_{vap.}}$$

$$K_b = \frac{2 \times T_b^{\,2} \times 78}{1000 \times 7.8 \times 1000}$$

$$1.4 = \frac{0.4 \times 2}{10^5} T_b^{\,2}$$

$$T_b = 418.33 \text{ K}$$

Example-17 : 1 Lit. of aq. solution of urea having density = 1.060 g/mL is found to have ΔT_b = 0.5ºC. If temperature of this solution increase to 101.5ºC, then calculate amount of water which must have gone in vapour state upto this pt. given K_b = 0.5 K kg mol^{-1} for water

Solution : mass of solution = 1.060×10^3 = 1060 g

$0.5 = 0.5\ m \quad \Rightarrow \quad m = 1$; if moles of urea = x

$$1 = \frac{x}{1060 - 60x} \; ; \; x = 1$$

mass of water = 1060 – 60 = 1000 g

$1.5 = \Delta T_b = (\text{molality})_f \times K_b$

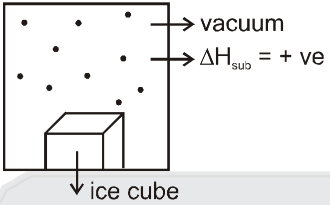
$$(\text{Molality})_f = 3 \quad \Rightarrow \quad 3 = 1 \times \frac{1000}{W_{water}}$$

$$W_{water} = \frac{1000}{3} \text{ g.}$$

$$\text{mass of water vaporised} = 1000 - \frac{1000}{3} = \frac{2000}{3} \text{ g} = 666.67 \text{ g}$$

8.5 Depression in freezing point of a solution of non-volatile solute in volatile solvent (ΔT_b)

D35 **Freezing point :** Temperature at which vapour pressure of solid becomes equal to vapour pressure of liquid is called freezing point of liquid or melting point of solid.



$\Delta H_{sub} > \Delta H_{vap.}$

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

$H_2O(s) \rightleftharpoons H_2O\ (g)$

$K_p = /_{eq.}\ P_{H_2O}(g)$

$= $ vapour pressure of solid

Reason for Depression In Freezing Point :

At the freezing point, the vapour pressure of solid and liquid is equal. When non-volatile solute is dissolved in the solvent, the vapour pressure of solvent in the solution decreases. It means vapour pressure of solid and liquid solvent will become equal at lower temperature, i.e., freezing point of solvent in solution is lower than that of pure solvent.

D36 **Depression In Freezing Point :**

The difference between freezing point of pure solvent T_f^o and freezing point of solution T is called depression in freezing point (ΔT_f) as shown in figure.

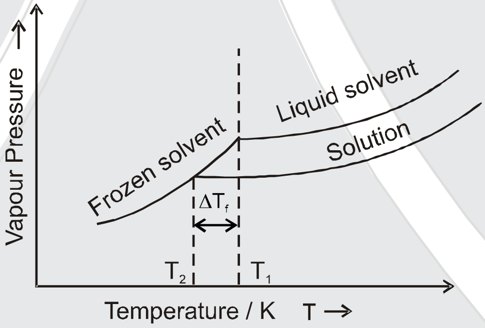


Diagram showing ΔT_f depression of the freezing point of a solvent in a solution.

Der.8 $\Delta T_f = T_f^o - T_f$

$\Delta T_f \propto m$

m = Molality

F30 $\Delta T_f = K_f m$

F31 Cryoscopic constant K_f = molal depression constant = $\dfrac{RT_f^2}{1000 \times L_{fusion}} = \dfrac{RT_f^2\ \ M}{1000 \times \Delta H_{fusion}}$

where, ΔH_{fusion} is molar enthalpy of fusion (cal/mol ; J/mol)

L_{fusion} is Latent Heat of fusion in cal/g or J/g

M is molar mass of the solvent in gram

T_f = freezing point of solvent

F32 $L_{fusion} = \left(\dfrac{\Delta H_{fusion}}{M}\right)$

D37 **K_f, Freezing point Depression Constant (Molal Depression Constant) :**

It is equal to depression in freezing point of 1 molal solution. It is also called cryoscopic constant. The units of K_f is K/m or °C/m or K kg mol^{-1}.

For water T_f = 273 K & L_{Fusion} = 80 cal/g. Thus, $K_f = \dfrac{2 \times 273 \times 273}{1000 \times 80} = 1.86\ K\ kg\ mol^{-1}$

Note: (i) Depression in freezing point is proportional to the lowering of vapoure pressure i.e. $\Delta T_f \propto \Delta P$

(ii) If solute gets associated/dissociated then $\Delta T_f = i \times K_f \times$ molality

(iii) **Units of** K_f **:** $\frac{\Delta T_f}{\text{molality}} = \frac{K}{\text{mol/kg}}$. Thus units of K_f = K kg mol^{-1}

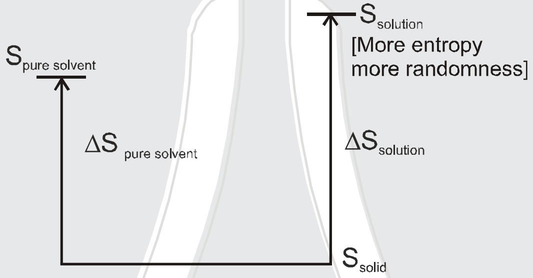
(iv) At freezing point or below it, only solvent molecules will freeze not solute molecules (solid will be of pure solvent)

(v) K_f = depression in freezing point of 1 molal solution.

(vi) $\Delta S_{Fusion}\ \frac{\Delta H_{fusion}}{T_{f.p.}} =$ or $T_{f.p.} = \frac{\Delta H_{fusion}}{\Delta S_{fusion}}$

ΔH_{Fusion} for solvent and solution is same.

But for entropy, we can see following diagram.



Only pure solvent.

$\therefore \Delta S_{Solution} > \Delta S_{solvent}$ So, freezing point of solution < freezing point of solvent

Solved Examples

Example-18 : Van't Hoff factors of aqueous solutions of X, Y, Z are 1.8, 0.8 and 2.5. Hence, their (assume equal concentrations in all three cases)

(A) b.p. : X < Y < Z (B) f. p. Z < X < Y

(C) osmotic pressure : X = Y = Z (D) v. p. : Y < X < Z

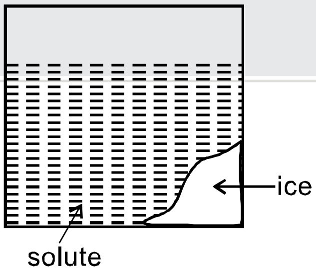
Solution : As van't Hoff factor increases RLVP increases i.e., V.P. decreases y > x > z

Elevation in b.p. increases i.e., b.p. increases y < x < z

Depresion in f.p increases i.e., f.p decreases y > x > z

Osmotic pressure increases so y < x < z. **Ans. (B)**

Example-19 : 1000 g H_2O have 0.1 mole urea and its freezing point is – 0.2ºC and now it is freezed upto – 2ºC then how much amount of ice will form.



Solution : It is assumed that solute do not freeze and do not vapourise

$\Delta T_F = 0.2 = K_f\ \frac{0.1}{1000} \times 1000$ ....(i)

$\Delta T_F = 2 = K_f\ \frac{0.1}{\text{wt. of solvent}} \times 1000$ ....(ii) on dividing $= \frac{\text{wt. of solvent}}{1000} \cdot \frac{0.2}{2}$

Weight of remaining H_2O is 100 g and weight of ice is 900 g.

Example-20 : If boiling point of an aqueous solution is 100.1ºC. What is its freezing point? Given latent heat of fusion and vaporization of water are 80 cal g^{-1} and 540 cal g^{-1} respectively.

Solution : For a given aqueous solution

$$\Delta T_b = K_b' \times \text{molality}$$

$$\Delta T_f = K_f' \times \text{molality}$$

$$\therefore \quad \frac{\Delta T_b}{\Delta T_f} = \frac{K_b'}{K_f'} = \frac{RT_b^2}{1000\ l_v} \times \frac{1000\ l_f}{RT_f^2}\ .$$

$$\frac{\Delta T_b}{\Delta T_f} = \frac{T_b^2 \times l_f}{T_f^2 \times l_v}$$

$T_b = 100 + 273 = 373$ K.

$T_f = 0 + 273 = 273$ K.

$l_f = 80$ cal g^{-1}.

$l_v = 540$ cal g^{-1}.

$$\therefore \quad \frac{0.1}{\Delta T_f} = \frac{373 \times 373 \times 80}{273 \times 273 \times 540}\ .$$

$$\therefore \quad \Delta T_f = 0.362.$$

$$\therefore \quad T_f = 0.0 - 0.362 = \mathbf{-\ 0.362ºC.}$$

Example-21 : A 0.001 molal solution of a complex reprsented as $Pt(NH_3)_4Cl_4$ in water had a freezing point depression of 0.0054ºC. Given K_f for H_2O = 1.86 molality^{-1}. Assuming 100% ionisation of the complex, write the ionisation nature and formula of complex.

Solution : Let n atoms of Cl be the acting as ligand. Then formula of complex and its ionisation is :

$$\begin{array}{lll} [Pt(NH_3)_4Cl_n]Cl_{(4-n)} \longrightarrow & [Pt(NH_3)_4Cl_n]^{+(4-n)} + & (4-n)\ Cl^- \\ 1 & 0 & 0 \\ 0 & 1 & (4-n) \end{array}$$

Thus particles after dissocation = 4 – n + 1 = 5 – n

and therefore, van't Hoff factor (i) = 5 – n

Now $\Delta T_f = K'_f \times$ molality × van't Hoff factor

$0.0054 = 1.86 \times 0.001 \times (5 - n)$

$\therefore$ $n = 2.1 \approx 2$ (integer value)

Thus complex and its ionisation is :

$$[Pt(NH_3)_4Cl_2]Cl_2 \longrightarrow [Pt(NH_3)_4Cl_2]^{2+} + 2Cl^-$$

Example-22 : Depression of freezing point of 0.01 molal aq. CH_3COOH solution is 0.02046°. 1 molal urea solution freezes at – 1.86°C. Assuming molality equal to molarity, pH of CH_3COOH solution is :

(A) 2 (B) 3 (C) 3.2 (D) 4.2

Solution : For urea

$$\Delta T_f = k_f \times m \quad \text{or} \quad k_f = \frac{\Delta T_f}{m} = \frac{1.86}{1} = 1.86$$

Now for CH_3COOH

$$\Delta T_f = i\ k_f\ m$$

so $i = \dfrac{0.02046}{1.86 \times 0.01} = 1.1$

Now $i = 1 + \alpha$

so $\alpha = 1.1 - 1 = 0.1$

$$\begin{array}{lllll} \text{Now} & CH_3COOH \rightleftharpoons & CH_3COO^- & + & H^+ \\ & C & 0 & & 0 \\ & C - C\alpha & C\alpha & & C\alpha \end{array}$$

$[H^+] = C\alpha = 0.01 \times 0.1 = 0.001$

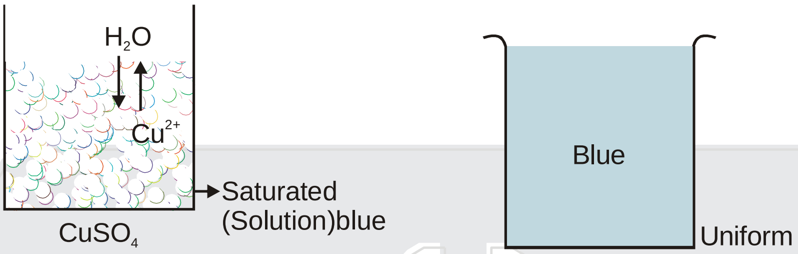
so pH = 3. **Ans. (B)**

Section (K) : Osmotic Pressure

8.6 Osmosis & Osmotic pressure :

D38 **Diffusion :** Spontaneous flow of particles from high concentration region to lower concentration region is known as diffusion.

Ex.



Figure

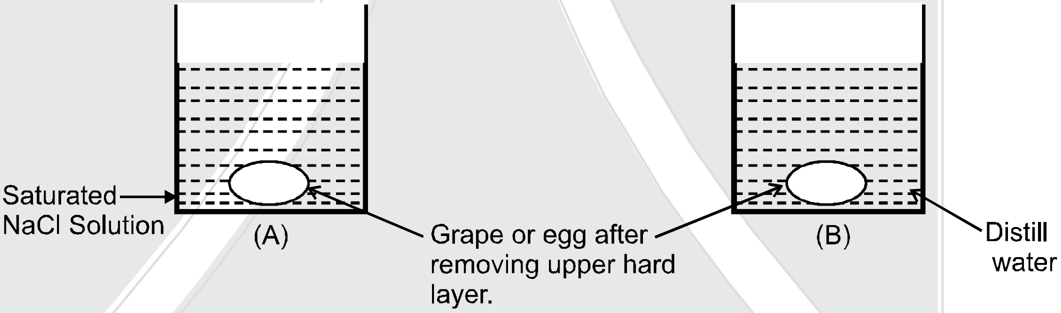
D39 **Osmosis :**
The spontaneous flow of solvent particles from solvent side to solution side or from solution of low concentration side to solution of high concentration side through a semipermeable membrane (SPM) is known as osmosis.

D40 **Semipermeable Membrane (SPM):** A membrane which allows only solvent particles to move across it.

(a) Natural : Semi permeable membrane
Animal/plant cell membrane formed just below the outer skins.

(b) Artificial membranes also : A copper ferrocyanide.
$Cu_2[Fe(CN)_6]$ & Silicate of Ni, Fe, Co can act as SPM.

Ex.



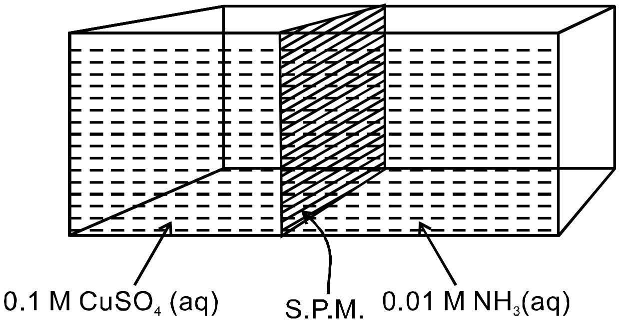
Figure

Conclusion : After some time in (A) grape or egg will shrink and in (B) grape or egg will swell.

e.g. (i) A raw mango placed in concentrated salt solution loses water & shrivel into pickle.
(ii) People taking lot of salt, experience water retention in tissue cells. This results in puffiness or swelling called edema.

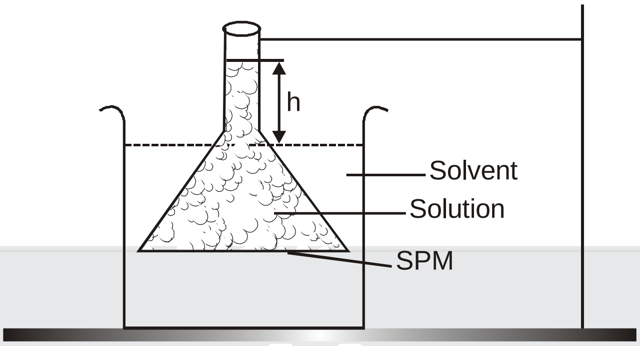
Solved Examples

Example-23 : In which soluton side complex $[Cu(NH_3)_4]^{2+}$ will form and deep blue colour will obtain.



Solution : In neither of side colour complex will form. No solute particle passes through SPM.

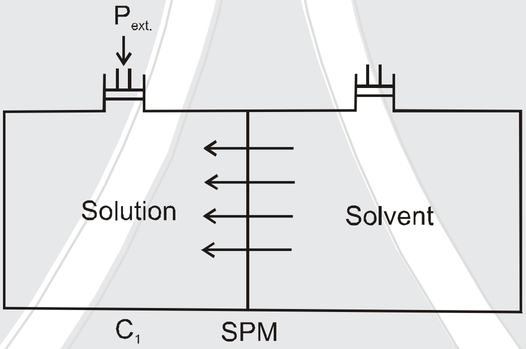
Osmotic Pressure :



Figure

The equilibrium hydrostatic pressure developed by solution column when it is seperated from solvent by semipermeable membrane is called osmotic pressure of the solution.

$\pi = \rho gh$; ρ = density of solution
g = acceleration due to gravity ; h = eq. height
1 atm = 1.013×10^5 N/m^2



Figure

D41 **Osmotic Pressure :** The external pressure which must be applied on solution side to stop the process of osmosis is called osmotic pressure of the solution.

If two solutions of concentration C_1 and C_2 are kept separated by SPM, and $C_1 > C_2$ then particle movement take place from lower to higher concentration. So, extra pressure is applied on higher concentration side to stop osmosis.

And $P_{ext.} = (\pi_1 - \pi_2)$

D42 **Reverse Osmosis :**

If the pressure applied on the solution side is more than osmotic pressure of the solution then the solvent particles will move from solution to solvent side. This process is known as reverse osmosis.

Berkely : Hartely device/method uses the above pressure to measure osmotic pressure.

e.g. used in desalination of sea-water.

Vant – Hoff Formula (For calculation of osmotic pressure)

- $\pi \propto$ concentration (molarity)
  $\propto T$
  $\pi = CST$
  S = ideal solution constant π = atm.
  = 8.314 J mol^{-1} K^{-1} (exp value)
  = R (ideal gas) constant

$$\left\{\begin{array}{l} C - \text{mol/lit.} \\ R - 0.082\ \text{lit.atm. mol}^{-1}\text{K}^{-1} \\ T - \text{kelvin} \end{array}\right.$$

F33 $\pi = CRT = \frac{n}{V}RT$ (just like ideal gas equation)

- In ideal solution solute particles can be assumed to be moving randomly without any interactions.

C = total concentration of all types of particles.

$$= C_1 + C_2 + C_3 + s\ldots\ldots\ldots\ldots = \frac{(n_1 + n_2 + n_3 + \ldots\ldots\ldots)}{V}$$

Solved Examples

Example-24 : If V_1 mL of C_1 solution + V_2 mL of C_2 solution are mixed together then calculate final concentration of solution and final osmotic pressure. If initial osmotic pressure of two solutions are π_1 and π_2 respectively ?

Solution : $C_f = \dfrac{C_1V_1 + C_2V_2}{V_1 + V_2}$

$$\pi_1 = C_1RT,\ \ C_1 = \left(\frac{\pi_1}{RT}\right)\ ;\ \pi_2 = C_2RT,\ \ C_2 = \left(\frac{\pi_2}{RT}\right)$$

$$\pi = \left(\frac{C_1V_1 + C_2V_2}{V_1 + V_2}\right)RT$$

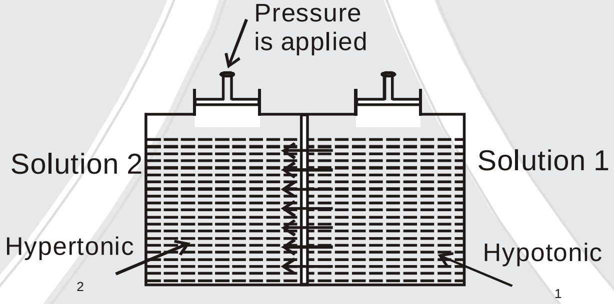
$$\pi = \left(\frac{\pi_1V_1 + \pi_2V_2}{V_1 + V_2}\right)$$

Type of solutions :

D43 **(a) Isotonic solution :** Two solutions having same osmotic pressure are consider as isotonic solution.

$\pi_1 = \pi_2$ (at same temperature)

D44 **(b) Hypotonic & Hypertonic solutions :** If two solutions 1 and 2 are such that $\pi_2 > \pi_1$, then 2 is called hypertonic solution and 1 is called hypotonic solution.



Figure

Conclusion :

Pressure is applied on the hypertonic solution to stop the flow of solvent partices, this pressure become equal to ($\pi_2 - \pi_1$) and if hypotonic solution is replaced by pure solvent then pressure becomes equal to π_2.

Note : **Osmotic pressure of very dilute solutions is also quite significant. So, its measurement in lab is very easy.**

D45 **Plasmolysis :** *When the cell is placed in solution having osmotic pressure greater than that of the cell sap, water passes out of the cell due to osmosis. Consequently, cell material shrinks gradually. The gradual shrinking of the cell material is called plasmolysis.*

Solved Examples

Example-25 : Calculate osmotic pressure of 0.1 M urea aqueous solution at 300 K ,

Solution : R = 0.082 lit atm K^{-1}

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

Example-26 : If 10 g of an unknown substance (non-electrolytic) is dissolved to make 500 mL of solution,then osmotic pressure at 300 K is observed to be 1.23 atm find molecular weight?

Solution : $1.23 = \frac{10 \times 1000}{M \times 500}$ x 0.082 x 300

$M = \frac{20}{1.23} x \frac{0.082}{100}$ x 300 $\approx$ 400 g/mol

Example-27 : If 6 g of urea, 18 g glucose & 34.2 g sucrose is dissolved to make 500 mL of a solution at 300 K calculate osmotic pressure ?

Solution : molecular weight of urea = 60 g, Glucose = 180 g , Sucrose = 342 g

π = C x 0.082 x 300

$\pi = \frac{0.3 \times 1000 \times 0.082 \times 300}{500}$ $\Rightarrow$ 14.76 atm

Example-28 : If 200 mL of 0.1 M urea solution is mixed with 300 mL of 0.2 M glucose solution at 300 K. Calculate osmotic pressure?

Solution : 0.02 moles urea

0.06 moles glucose $\Rightarrow \pi = \frac{0.08}{0.5} \times 0.082 \times 300 = 3.94$ atm.

Example-29 : If urea (aq) solution at 500K has O.P. = 2.05 atm. & glucose solution at 300 K has OP = 1.23 atm. If 200 ml of Ist solution & 400 ml of 2nd solution are mixed at 400 K then calculate O.P. of resulting solution at 400 K (assume molarity is not dependent on temp.)

Solution : $C_{urea} = \frac{2.05}{R \times 500} = 0.05 \Rightarrow$ V_{urea} = 200 mL

$C_{glucose} = \frac{1.23}{R \times 300} = 0.05 \Rightarrow$ $V_{glucose}$ = 400 mL

$C_{total} = \frac{C_1V_1 + C_2V_2}{V_1 + V_2} = \frac{0.05 \times 200 + 0.05 \times 400}{600} = 0.05$

$\pi = CRT = 0.05 \times 0.082 \times 400$

π = 1.64 atm

Example-30 $\frac{0.1\,M\ \text{urea}}{(A)}, \frac{0.1\,M\ \text{NaCl}}{(B)}, \frac{0.1\,M\ \text{BaCl}_2}{(C)}$

Solution :

Order of π	C > B > A.
Order of R.L.V.P	C > B > A.
Order of V.P	A > B > C.
Order of ΔT_B	C > B > A.
Order of T_B of solution	C > B > A.
Order of ΔT_F	C > B > A.
Order of T_F of solution	A > B > C.

(Calculating osmotic pressure when reaction is not taking place)

Example-31 : Calculate osmotic pressure of a solutions having 0.1 M NaCl & 0.2 M Na_2SO_4 and 0.5 MHA. (Given : Weak acid is 20% dissociated at 300 K).

Soluiton : $\pi = \pi_{NaCl} + \pi_{Na2SO4} + \pi_{HA}$

= 0.1 RT × 2 + 0.2 RT × 3 + 0.5 RT × 1.2

= 0.0821 × 300 (0.2 + 0.6 + 0.6) = 34.482 atm.

Example-32 : If 0.04 M Na_2SO_4 solutions at 300 K is found to be isotonic with 0.05 M NaCl (100 % disscociation) solutions. Calculate degree of disscociation of sodium sulphate ?

Soluiton : $i_1 C_1 RT = i_2 C_2 RT$

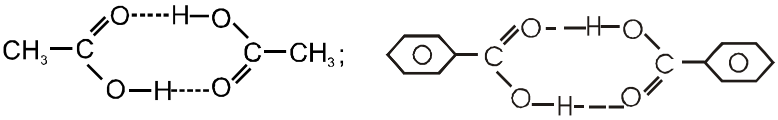
$i_1 C_1 = i_2 C_2$

$0.04 (1 + 2\alpha) = 0.05 \times 2$

α = 0.75 = 75%.

Example-33 : If 6 g of CH_3 COOH is dissolved in benzene to make 1 litre at 300 K. Osmotic pressure of solution is found to be 1.64 atm. If it is known that CH_3COOH in benzene forms a dimer. Calculate degree of association of acetic acid in benzene ?

Soluiton :



$$i = 1 + \left(\frac{1}{n} - 1\right)\beta.$$

$$1.64 = 0.0821 \times 300 \times \left[\, 1 + \left(\frac{1}{n} - 1\right) \beta \,\right] \times 0.1$$

$$\Rightarrow \qquad 1.64 = 0.0821 \times 300 \ \left[1 - \frac{\beta}{2}\right] 0.1$$

$$\frac{1.64}{0.0821 \times 30} = \frac{2\text{-}\beta}{2}$$

$$\frac{1.64}{2.46} = \frac{2\text{-}\beta}{2} \qquad 4 = 6 - 3\beta$$

$$3\beta = 2$$

$$\beta = 2/3$$

(Calculating osmotic pressure when reaction is taking place)

Example-34 : If 200 ml of 0.2 M $BaCl_2$ solution is mixed with 500 ml of 0.1 M Na_2SO_4 solution. Calculate osmotic pressure of resulting solutions ?

Solution :

$BaCl_2$ +	Na_2SO_4 $\rightarrow$	$BaSO_4$ +	2 NaCl
0.04 moles	0.05	0	0
0	0.01	No effect	0.08
	$\frac{0.01}{0.7}$	No effect	$\frac{0.08}{0.7}$

$$\pi = (i_1C_1 + i_2C_2)\ RT.$$

$$= \left(3 \times \frac{0.01}{0.7} + 2 \times \frac{0.08}{0.7}\right) 0.082 \times 300. = \mathbf{6.685\ atm.}$$

Example-35 : If 200 ml of 0.2 M $HgCl_2$ solution is added to 800 ml of 0.5 M KI (100% dissociated) solution. Assuming that the following complex formation taken place to 100% extent.

$$Hg^{2+} + 4I^- \longrightarrow [HgI_4]^{2-}$$

0.04 0.4

Calculate osmotic pressure of resulting initially solution at 300K ?

Solution :

$HgCl_2$ +	4KI $\longrightarrow$	$K_2[HgI_4]$ +	2KCl.
40	400	0	0
0	400 –160	40	80
	$\frac{240}{1000}$	$\frac{40}{1000}$	$\frac{80}{1000}$

$$\pi = (i_1C_1 + i_2C_2 + i_3C_3)\ RT.$$

$$= (0.24 \times 2 + 3 \times 0.04 + 0.08 \times 2)\ 0.082 \times 300. = \mathbf{18.69\ atm.}$$

Example-36 : (**Note:** Attempt this problem after you have studied co-ordination compounds)
Ba^{2+} ions, CN^- & Co^{2+} ions form a water soluble complex with Ba^{2+} ions as free cations. For a 0.01 M solution of this complex, osmotic pressure = 0.984 atm & degree of dissociation = 75%. Then find coordination number of Co^{2+} ion in this complex (T=300 K, R=0.082 L atm. mol^{-1} k^{-1})

Solution : Say C.N. = x

$0.984 = i\,CRT$

$0.984 = i\ 0.01 \times 0.082 \times 300 = i \times 0.246$

$i = 4 = 1 + (n - 1)\ \alpha$

$\Rightarrow$ $n = 5$

Charge on co-ordination sphere = charge on Cobalt ion - charge on x cyanide ions = – (x – 2)
i.e. co-ordination sphere is $[Co(CN)_x]^{-(x-2)}$
Charge on Barium ion is +2
Thus, formula of the complex will be $Ba_{(x-2)}\,[Co(CN)_x]_2$ by charge balance.

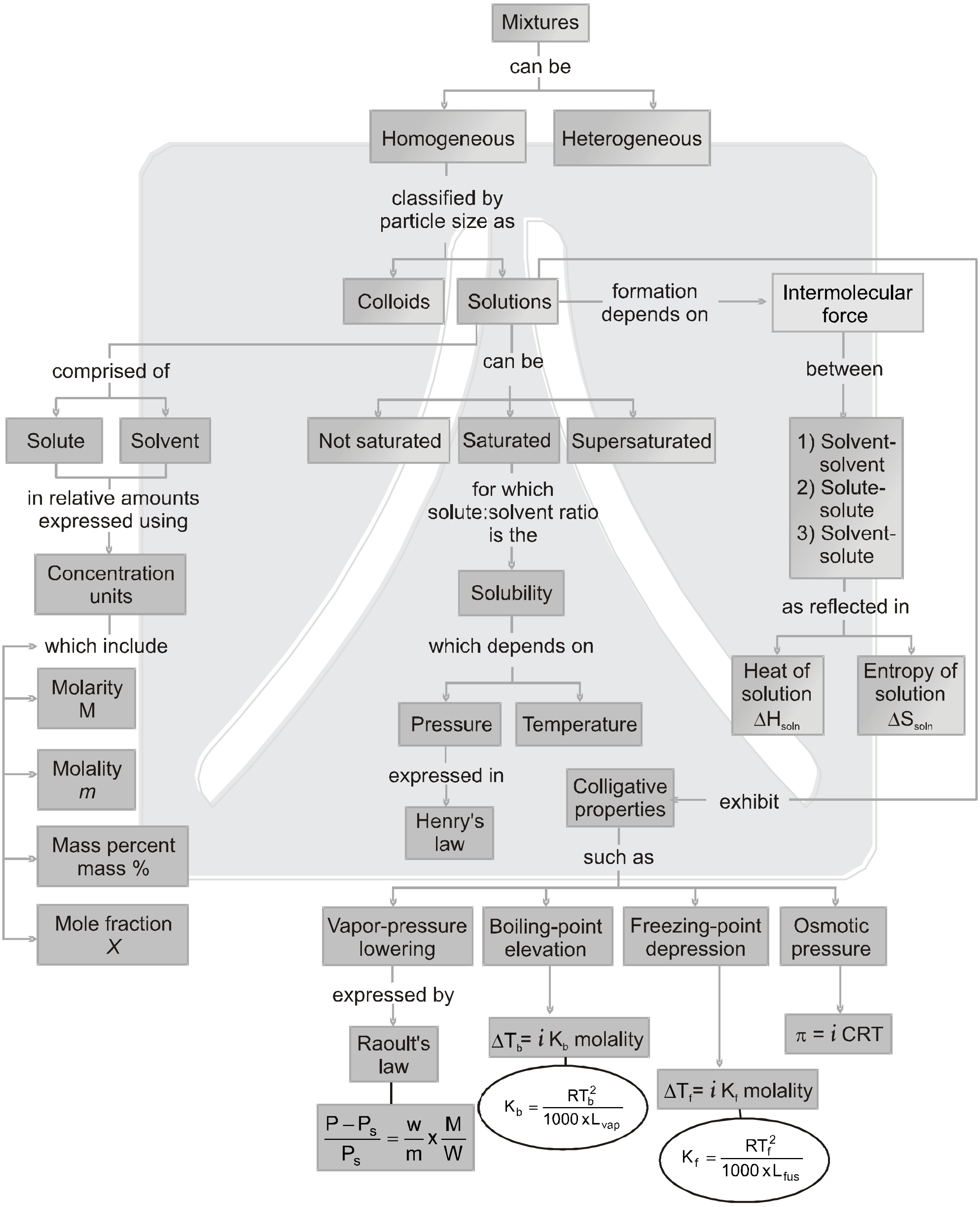
$x - 2 + 2 = 5$

$x = 5$

$\therefore$ CN = 5

$\therefore$ Formula is $Ba_3[Co(CN)_5]_2$..

Summary


Mixtures
can be
Homogeneous
Heterogeneous
classified by particle size as
Colloids
Solutions
formation depends on
Intermolecular force
between
1) Solvent-solvent
2) Solute-solute
3) Solvent-solute
as reflected in
Heat of solution ΔH_{soln}
Entropy of solution ΔS_{soln}
comprised of
Solute
Solvent
in relative amounts expressed using
Concentration units
which include
Molarity M
Molality m
Mass percent mass %
Mole fraction X
can be
Not saturated
Saturated
Supersaturated
for which solute:solvent ratio is the
Solubility
which depends on
Pressure
Temperature
expressed in
Henry's law
exhibit
Colligative properties
such as
Vapor-pressure lowering
Boiling-point elevation
Freezing-point depression
Osmotic pressure
expressed by
Raoult's law
$\frac{P-P_s}{P_s} = \frac{w}{m} \times \frac{M}{W}$
$\Delta T_b = i\,K_b$ molality
$K_b = \frac{RT_b^2}{1000 \times L_{vap}}$
$\Delta T_f = i\,K_f$ molality
$K_f = \frac{RT_f^2}{1000 \times L_{fus}}$
$\pi = i\,CRT$

MISCELLANEOUS SOLVED PROBLEMS (MSPs)

1. A 6.90 M solution of KOH in water has 30% by weight of KOH. Calculate density of solution.

Sol. Let V = 1 lt , then moles of solute = 6.9

wt of solute = 6.9 × 56 gm

$\% = \frac{M_{solute}}{M_{solution}} \times 100$ So, $= \frac{6.9 \times 56}{d \times 1000} \times 100 = 30$; d = 1.288 gm/litre

2. 10 ml of sulphuric acid solution (sp. gr. = 1.84) contains 98% by weight of pure acid. Calculate the volume of 2.5 M NaOH solution required to just neutralise the acid.

Sol. Wt of solute = $10 \times 1.84 \times \frac{98}{100}$ g

So moles of solute = $\frac{18.4}{98} \times \frac{98}{100} = 0.184$

$n_{H^+} = 2 \times 0.184$

$2 \times 0.184 = \frac{2.5 \times V}{1000}$ V = **147.2**

3. A sample of H_2SO_4 (density 1.8 g mL^{-1}) is labelled as 74.66% by weight. What is molarity of acid ? (Give answer in rounded digits)

Sol. Let V = 1lt = 1000 ml

So mass of solution = 1800 gm

So mass of solute = $1800 \times \frac{74.66}{100}$ g

So molarity = moles of solute in 1lt = $\frac{18 \times 74.66}{98}$ = 13.71 M **Ans**.

4. The density of 3M solution of $Na_2S_2O_3$ is 1.25 g mL^{-1}. Calculate.

(a) the % by weight of $Na_2S_2O_3$ (b) mole fraction of $Na_2S_2O_3$

Ans. (a) 37.92 (b) 0.065

Sol. (a) $m_{solution} = 1000 \times 1.25 = 1250$ gm

Mass of $Na_2S_2O_3$ = 3 × 158 = **474**

% (w/w) = $\frac{474}{1250} \times 100 = 37.92$

(b) $X_{Na_2S_2O_3} = \frac{3}{3 + 43.11}$ = **0.065.**

5. Calculate Molality of aqueous urea solution which has $X_{urea} = 0.2$

Sol. Molality = $\frac{1000X_1}{(1 - X_1)m_2} = \frac{1000 \times 0.2}{0.8 \times 18} = 13.88$.

6. If 200 mL of 0.1 M urea solution is mixed with 300 mL of 0.2 M Glucose solutions at 300 K calculate osmotic pressure.

Ans. 3.94 atm

Sol. $C_{net} = \frac{C_1V_1 + C_2V_2}{V_1 + V_2}$

Now $\pi = C_{net}$ RT

p = (0.04 + 0.12) × 0.0821 × 300 = 3.94 atm.

7. A 500 gm liquid consist of 15 gm ethane at any temp. T, at a pressure = 2 atm. Find Pressure of gas required to dissolve 30 gm gas in 300 gm liquid.

Ans. P_2 = 6.66 atm.

Sol. $\frac{15/500}{30/300} = \frac{2}{P} \Rightarrow \frac{3}{10} = \frac{2}{P} \Rightarrow P = 6.66$ atm.

Check List

Definitions (D)

D1	Solution	☐
D2	Solute	☐
D3	Solvent	☐
D4	Binary solutions	☐
D5	Ternary solutions	☐
D6	Aqueous solution	☐
D7	Non-aqueous solution	☐
D8	Miscible liquids	☐
D9	Immiscible liquids	☐
D10	Alloys	☐
D11	Mass percentage	☐
D12	Mass by volume percentage	☐
D13	Volume percentage	☐
D14	Molarity (M)	☐
D15	Molality (m)	☐
D16	Normality	☐
D17	Mole-fraction (x)	☐
D18	Parts per million (ppm)	☐
D19	Vapour pressure of a pure liquid	☐
D20	Vapour pressure of solution	☐
D21	Partial vapour pressure	☐
D22	Saturated solution	☐
D23	Unsaturated solution	☐
D24	Supersaturated solution	☐
D25	Solubility	☐
D26	Azeotropes	☐
D27	Minimum Boiling Azeotropes	☐
D28	Maximum Boiling Azeotropes	☐
D29	Constitutional Properties	☐
D30	Colligative properties	☐
D31	Abnormal colligative property	☐
D32	Boiling Point	☐
D33	Normal Boiling Point	☐
D34	Elevation Of Boiling Point	☐
D35	Freezing Point	☐
D36	Depression In Freezing Point	☐
D37	K_f, Freezing point Depression Constant	☐
	(Molal Depression Constant)	☐
D38	Diffusion	☐
D39	Osmosis	☐
D40	Semi-permeable Membrane	☐
D41	Osmotic Pressure	☐
D42	Reverse Osmosis	☐
D43	Isotonic solution	☐
D44	Hypotonic & Hypertonic solutions	☐
D45	Plasmolysis	☐

Formule (F)

F1	% w/w	☐
F2	% wt/vol. (w/v)	☐
F3	molarity	☐
F4	molality	☐
F5	No. of equivalents per litre of solution	☐
F6	Equivalent mass	☐
F7	No. of equivalent	☐
F8	X_{solute}	☐
F9	$X_{Solvent}$	☐
F10	$X_{solute} + X_{Solvent} = 1$	☐
F11	ppm (w/w)	☐
F12	ppm (w/v)	☐
F13	ppm (moles/moles)	☐
F14	Clausius-Clapeyron equation	☐
F15	Relative Humidity (R.H.)	☐
F16	Henry's Law	☐
F17	Distillation of Immiscible liquids	☐
F18	Composition of distillate obtained from distillation of Immiscible liquids	☐
F19	Raoult's Law	
F20	Total pressure of vapour in ideal solutions of two miscible liquids	☐
F21	relation between total pressure and vapour composition over an ideal solution of two miscible liquids	☐
F22	Vant–Hoff factor	☐
F23	Relation of i with α	☐
F24	Relation of i with β	☐
F25	RLVP	☐
F26	Relation of ΔP with molality	☐
F27	ΔT_b	☐
F28	K_b	☐
F29	L_{vap}	☐
F30	Formula for Depression of freezing point	☐
F31	Cryoscopic constant K_f	☐
F32	L_{fusion}	☐
F33	Osmotic Pressure	☐

Derivations (Der.)

Der1	Molarity of mixture of two solutions of known molarity and volume of same solute	☐
Der2	Henry's Law	☐
Der3	Total pressure over solution using Raoult's law and Dalton's law	☐
Der4	Relation of i with α	☐
Der5	Relation of i with β	☐
Der6	RLVP	☐
Der7	ΔT_b	☐
Der8	ΔT_f	☐