

## 1. INTRODUCTION:

A solution is a homogeneous mixture of two or more substances which are chemically nonreacting.

## 2. TYPES OF SOLUTION:

	Solvent	Solute	Examples
1.	Gas	Gas	Mixture of gases, eg. air.
2.	Gas	Liquid	Water vapour in air, mist. $\text{CHCl}_3(\ell) + \text{N}_2(\text{g})$
3.	Gas	Solid	Smoke, camphor (s) + $\text{N}_2(\text{g})$ .
4.	Liquid	Gas	$\text{CO}_2$ gas dissolve in water (aerated drink), soda water.
5.	Liquid	Liquid	Mixture of miscible liquids e.g. alcohol in water.
6.	Liquid	Solid	Salt in water, sugar in water.
7.	Solid	Gas	Hydrogen over palladium.
8.	Solid	Liquid	Mercury in zinc, mercury in gold i.e. all amalgams.
9.	Solid	Solid	Alloys e.g. copper in gold. zinc in copper.

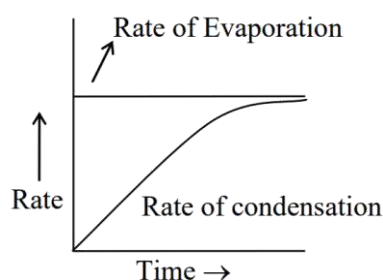
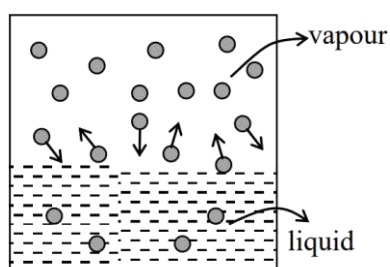
## 3. VAPOUR PRESSURE:

When a liquid is taken in a closed vessel at constant temperature, then there are two process which takes place.

(i) evaporation

(ii) condensation

In the constant evaporation from the surface particles continue to break away from the surface of the liquid. As the gaseous particles bounce around, some of them will hit the surface of the liquid again, and will be trapped there. This is called condensation. The rate of condensation increases with time, but rate of evaporation remain constant. 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.



This pressure at equilibrium is called the **saturated vapour pressure** (also known as **saturation vapour pressure**).

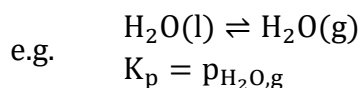
## (Physical Chemistry)

## LIQUID SOLUTION

**Note:** (a) Saturated (Equilibrium) Vapour pressure of water, at a given temperature, is called aqueous tension.

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

At eq. the rate of evaporation = rate of condensation



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

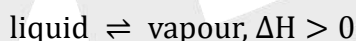
Since vapour pressure is an equilibrium constant. so it's value is dependent only on :

(1) Temperature

(2) Nature of liquid

**Effect of Temperature on vapour pressure**

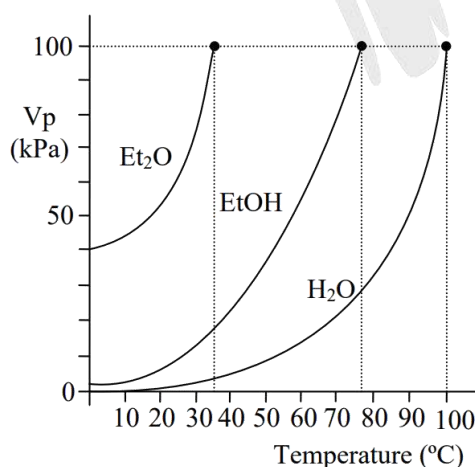
When the space above the liquid is saturated with vapour particles, you have this equilibrium occurring on the surface of the liquid :



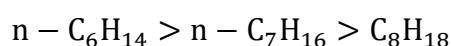
The forward change (liquid to vapour) is endothermic. It needs heat to convert the liquid into the vapour. According to Le Chatelier, increasing the temperature of a system in a dynamic equilibrium favours the endothermic change. That means increasing the temperature increase the amount of vapour present, and so increases the saturated vapour pressure.

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

**equation**  $\ln \left( \frac{p_2}{p_1} \right) = -\frac{\Delta H_v}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$ , where  $\Delta H_v$  = 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  $T_1$ .



Effect of nature:  $V.p \propto \frac{1}{\text{Inter molecular attraction force (I.M.A.F.)}}$



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

**Ex.1** The vapor pressure of water at 80°C is 355 torr. A 100ml vessel contained water saturated oxygen at 80°C, the total gas pressure being 760 torr. The contents of the vessel were pumped into a 50.0ml, 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.**  $P_{O_2} = 810 \text{ mmHg}$ ,  $P_{H_2O} = 355 \text{ mmHg}$ ,  $P_{\text{total}} = 1165 \text{ mmHg}$

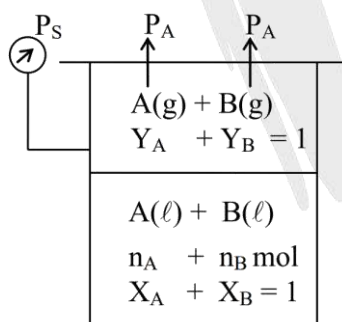
**Sol.** In 100ml vessel which contained water - saturated oxygen, the pressure of  $O_2$  gas =  $760 - 355 = 405$  torr when the contents of this vessel were pumped into 50ml vessel, at the same temperature, the pressure of oxygen gets doubled i.e.  $P_{O_2} = 810$  torr. But pressure of water vapour will remain constant, as some vapour in this 50ml vessel, gets condensed. So  $P_{H_2O} = 355$  torr & Total pressure =  $810 + 355 = 1165$  torr.

#### 4. RAOULT'S LAW:

According to this law, the partial pressure of any volatile constituents of a solution at a constant temperature is equal to the vapour pressure of pure constituents multiplied by the mole fraction of that constituent in the solution.

##### 4.1 FOR LIQUID - LIQUID SOLUTION:

Let a mixture (solution) be prepared by mixing  $n_A$  moles of liquid A and  $n_B$  moles of liquid B. Let  $P_A$  and  $P_B$  be the partial pressures of two constituents A and B in solution and  $P_A^0$  and  $P_B^0$  the vapour pressures in pure state respectively. Thus, according to Raoult's law



$$P_A = \frac{n_A}{n_A + n_B} P_A^0 = X_A P_A^0 \quad \dots (1)$$

and  $P_B = \frac{n_B}{n_A + n_B} P_B^0 = X_B P_B^0 \quad \dots (2)$

If total pressure be  $P_S$ , then

$$P_S = P_A + P_B = \frac{n_A}{n_A + n_B} P_A^0 + \frac{n_B}{n_A + n_B} P_B^0 = X_A P_A^0 + X_B P_B^0$$

$$P_S = X_A P_A^0 + (1 - X_A) P_B^0 [\because X_A + X_B = 1]$$

$$P_S = X_A P_A^0 - X_A P_B^0 + P_B^0$$

$$P_S = X_A [P_A^0 - P_B^0] + P_B^0$$

**4.2 RELATION BETWEEN DALTON'S LAW AND RAOULT'S LAW:**

The composition of the vapour in equilibrium with the solution can be calculated by applying Dalton's law of partial pressures. Let the mole fraction of A and B in vapours be  $Y_A$  and  $Y_B$  respectively.

Let  $P_A$  and  $P_B$  be the partial pressure of vapours A and B respectively and total pressure be  $P$ .

$$P_A = Y_A P_S \quad \dots (1)$$

$$P_B = Y_B P_S \quad \dots (2)$$

$$P_A = X_A P_A^0 \quad \dots (3)$$

$$P_B = X_B P_B^0 \quad \dots (4)$$

Equation eqs.(i) and (ii),

$$Y_A P_S = X_A P_A^0$$

$$\text{or } Y_A = \frac{X_A P_A^0}{P_S} = \frac{P_A}{P_S}$$

$$x_A + x_B = 1 = \frac{Y_A P_S}{P_A^0} + \frac{Y_B P_S}{P_B^0}$$

$$\text{Thus, } \frac{1}{P_S} = \frac{Y_A}{P_A^0} + \frac{Y_B}{P_B^0}$$

Thus, in case of ideal solution the vapour phase is richer with more volatile component, i.e., the one having relatively greater vapour pressure.

**4.3 GRAPHICAL REPRESENTATION OF RAOULT'S LAW:**

$$p_A = x_A P_A^0 \text{ \& } p_B = x_B P_B^0$$

$$P_T = x_A P_A^0 + x_B P_B^0$$

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

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

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

**Note:** If  $P_A^0 > P_B^0$ , A is more volatile than B. B.P. of A < B.P. of B.

**Ex.2** Two liquids, A and B, form an ideal solution. At the specified temperature, the vapour pressure of pure A is 200 mmHg while that of pure B is 75 mmHg. If the vapour over the mixture consists of 50 mol percent A, what is the mole percent A in the liquid ?

**Ans.** 27.3 mole %

$$\text{Sol. } X_A P_A^0 = P_A = Y_A P_T \text{ or } X_A \times 200 = 0.5 P_T = \dots (i)$$

Similarly

$$X_B P_B^0 = P_B = Y_B P_T \text{ or } X_B \times 75 = 0.5 P_T = \dots (ii)$$

Comparing (i) & (ii) we get

$$200X_A = 75X_B = 75(1 - X_A)$$

Solving we get  $X_A = 0.273$

so mol percent of A in liquid = 27.3%

**Ex.3** Two liquids A and B form an ideal solution. At 300 K, the vapour pressure of a solution containing 1 mole of A and 3 moles of B is 550 mm of Hg. At the same temperature, if one mole of B is added to this solution, the vapour pressure of the solution increases by 10 mm of Hg. Determine the vapour pressure of A and B in their pure states.

**Ans.**  $p_A^0 = 400$  mm of Hg,  $p_B^0 = 600$  mm of Hg

**Sol.** In first case,  $X_A = \frac{1}{4}$ ,  $X_B = \frac{3}{4}$  &  $P_T = 550$

According to Raoult's law,

$$X_A P_A^0 + X_B P_B^0 = P_T$$

$$\text{so } \frac{1}{4} P_A^0 + \frac{3}{4} P_B^0 = 550 \text{ or } P_A^0 + 3P_B^0 = 2200$$

In second case

$$X'_A = 1/5, X'_B = 4/5 \text{ \& } P_T = 560$$

$$\frac{1}{5} P_A^0 + \frac{4}{5} P_B^0 = 560 \text{ or } P_A^0 + 4P_B^0 = 2800$$

Subtracting (i) from (ii), we get

$$P_A^0 = 400 \text{ mm}, P_B^0 = 600 \text{ mm of Hg.}$$

**Ex.4** An ideal solution contains two volatile liquids A ( $p^\circ = 100$  torr) and B ( $p^\circ = 200$  torr). If mixture contain 1 mole of A and 4 mole of B then total vapour pressure of the distillate is:

**Sol.**  $P = P_A^0 x_A + P_B^0 x_B$

$$= 100 \times \frac{1}{5} + 200 \times \frac{4}{5} = 180 \text{ torr}$$

$$Y_A \text{ (composition of A in vapour phase)} = \frac{P_A^0 x_A}{P} = \frac{20}{180} \quad Y_B = \frac{8}{9}$$

For condensation  $y_A = x_A^1$ ;  $y_B = x_B^1$

$$P_{\text{total}} = P_A^0 x_A^1 + P_B^0 x_B^1;$$

$$P_{\text{total}} = 100 \times \frac{1}{9} + \frac{8}{9} \times 200 \Rightarrow 188.88 \text{ torr}$$

**Ex.5** Vapour pressure of  $C_6H_6$  and  $C_7H_8$  mixture at  $50^\circ\text{C}$  is given  $P(\text{mmHg}) = 180X_B + 90$ , where  $X_B$  is the mole fraction of  $C_6H_6$ . A solution is prepared by mixing 936gm benzene and 736gm toluene and if vapours over this solution are removed and condensed into liquid and again brought to the temperature  $50^\circ\text{C}$ , what would be mole fraction of  $C_6H_6$  in the vapour state. (At. wt. of C = 12, H = 1)

**Ans.**  $Y_B = 0.932$ .

**Sol.**  $P(\text{mmHg}) = 180X_B + 90$

$$P_B^\circ (\text{Benzene}) = 180 + 90(X_B = 1)$$

$$= 270 \text{ mmHg}$$

$$P_T^\circ (\text{Toluene}) = 90 \text{ mmHg} (X_B = 0)$$

$$\text{moles of } C_6H_6 = 12, X_B = 0.6$$

$$\text{moles of } C_6H_5CH_3 = 8 \quad X_T = 0.4$$

$$\text{Vapour Pressure of solution } P_S = X_B P_B^\circ + X_T P_T^\circ$$

$$P_S = 198 \text{ mmHg}$$

$$\text{mole fraction of Benzene in vapour state } Y_B = \frac{P_B}{P_S}$$

$$Y_B = \frac{X_B P_B^\circ}{P_S} = \frac{0.6 \times 270}{198} = 0.82$$

Mole fraction of Toluene in vapour state

$$Y_T = 0.18$$

Now this vapour when condensed

$$\begin{aligned} P_S &= Y_T P_T^\circ + Y_B P_B^\circ \\ &= 0.18 \times 90 + 0.82 \times 270 = 237.6 \text{ mmHg.} \end{aligned}$$

Now mole fraction of benzene in vapour state is

$$Y'_B = \frac{Y_B P_B^\circ}{P_S} = \frac{0.82 \times 270}{237.6} \quad \text{Ans. } Y'_B = 0.932$$

#### 4.4 FOR SOLID - LIQUID SOLUTION:

Let us assume A = non volatile solid & B = volatile liquid

According to Raoult's law -

$$\therefore P_S = X_A P_A^0 + X_B P_B^0$$

$$\text{For A, } P_A^0 = 0$$

$$\therefore P_S = X_B P_B^0 \quad \dots (5)$$

Let  $P_B^0 = P^0$  = Vapour pressure of pure state of solvent.

here  $X_B$  is mole fraction of solvent

$$P_S = \frac{n_B}{n_A + n_B} P^0 \quad \dots (6)$$

$$P_S \propto \frac{n_B}{n_A + n_B} \text{ i.e. vapour pressure of solution } \propto \text{mole fraction of solvent}$$

$$\Rightarrow P_S = X_B P_B^0 \Rightarrow P_S = (1 - X_A) P_B^0 \Rightarrow P_S = P_B^0 - X_A P_B^0 \Rightarrow \frac{P_B^0 - P_S}{P_B^0} = X_A$$

$$\text{or } \frac{P^0 - P_S}{P^0} = X_A \quad \dots (7)$$

$$\frac{P^0 - P_S}{P^0} = \frac{n_A}{n_A + n_B} \quad \dots (8)$$

$$\text{or } \frac{P^0}{P^0 - P_S} = \frac{n_A + n_B}{n_A} \text{ or } \frac{P^0}{P^0 - P_S} = 1 + \frac{n_B}{n_A} \text{ or } \frac{P^0}{P^0 - P_S} - 1 = \frac{n_B}{n_A}$$

$$\frac{P_S}{P^0 - P_S} = \frac{n_B}{n_A}$$

$$\frac{P^0 - P_S}{P_S} = \frac{n_A}{n_B} = \frac{w_A \cdot m_B}{m_A \cdot w_B} \quad \dots (9)$$

(Physical Chemistry)

# LIQUID SOLUTION

**Ex.6** Twenty grams of a solute are added to 100 g of water at 25°C. The vapour pressure of pure water is 23.76mmHg; the vapour pressure of the solution is 22.41 Torr.

(a) Calculate the molar mass of the solute.

(b) What mass of this solute is required in 100 g of water to reduce the vapour pressure to one-half the value for pure water?

**Ans.** (a) 60 g/mol, (b) 333.6 g

**Sol.** (a) Relative lowering of vapour pressure = mole fraction of solute

$$\frac{23.76-22.41}{23.76} = \frac{20/M}{20/M+100/18} = 0.0568$$

so M = 60 g/mol

(b) Let w be the mass of solute reqd.

$$\& P = \frac{P^\circ}{2}$$

$$\text{so } \frac{P^\circ - P}{P^\circ} = \frac{w/60}{w/60+100/18} \text{ or } \frac{P^\circ - P^\circ/2}{P^\circ} = \frac{w/60}{w/60+5.56}$$

w = 333.6gm

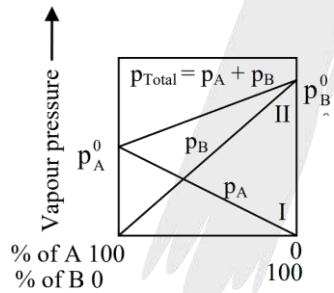
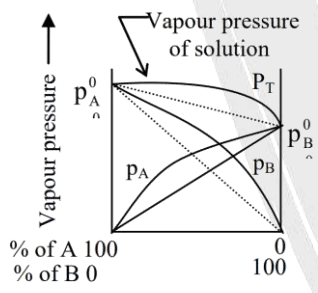
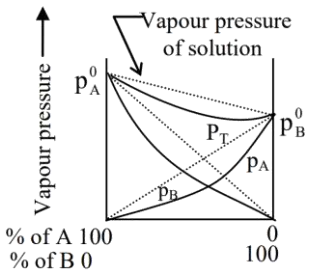
## 5. IDEAL AND NON IDEAL SOLUTIONS

**Table: Comparison between Ideal and Non-ideal solutions**

Ideal solutions		Non-ideal solutions	
		+ve deviation from Raoult's law	-deviation from Raoult's law
1.	Obeys Raoult's law at every concentrations.	Do not obey Raoult's law.	Do not obey Raoult's law.
2.	$\Delta H_{\text{mix}} = 0$ ; Neither heat is evolved nor absorbed during dissolution.	$\Delta H_{\text{mix}} > 0$ . Endothermic dissolution; heat is absorbed.	$\Delta H_{\text{mix}} < 0$ ; exothermic dissolution heat is evolved.
3.	$\Delta V_{\text{mix}} = 0$ ; total volume of solution is equal to sum of volumes of the components.	$\Delta V_{\text{mix}} > 0$ . Volume is increased after dissolution.	$\Delta V_{\text{mix}} < 0$ ; volume is decreased during dissolution.
4.	$P = p_A + p_B = p_A^0 X_A + p_B^0 X_B$ i.e., $p_A = p_A^0 X_A$ ; $p_B = p_B^0 X_B$	$p_A > p_A^0 X_A$ ; $p_B > p_B^0 X_B$ $\therefore p_A + p_B > p_A^0 X_A + p_B^0 X_B$	$p_A < p_A^0 X_A$ ; $p_B < p_B^0 X_B$ $\therefore p_A + p_B < p_A^0 X_A + p_B^0 X_B$
5.	A – A, A – B, B – B Interactions should be same, i.e., 'A' and 'B' are	A – B, attraction force should be weaker than A – A and B – B attractive forces. 'A' and 'B'	A – B, attraction force should be greater than A – A and B – B attractive forces. 'A' and 'B'

## (Physical Chemistry)

## LIQUID SOLUTION

	identical in shape, size and character.	have different shape, size and character.	' have different shape, size and character.
6.	<p>Escaping tendency of 'A' and 'B' should be same in pure liquids and in the solution.</p> <p>Example:</p> <p>dilute solutions;</p> <p>benzene + toluene;</p> <p>n-hexane + n-heptane</p> <p>chlorobenzene +</p> <p>bromobenzene;</p> <p>ethyl bromide + ethyl iodide;</p> <p>n-butyl chloride + n-butyl bromide</p> <p><math>\text{CCl}_4 + \text{SiCl}_4</math>;</p> <p><math>\text{C}_2\text{H}_4\text{Br}_2 + \text{C}_2\text{H}_4\text{Cl}_2</math></p> <p><math>\text{C}_2\text{H}_5\text{Br} + \text{C}_2\text{H}_5\text{Cl}</math></p> 	<p>'A' and 'B' escape easily showing high vapour pressure than the expected value.</p> <p>Example:</p> <p>acetone + ethanol;</p> <p>acetone + <math>\text{CS}_2</math>;</p> <p>water + methanol</p> <p>water + ethanol;</p> <p><math>\text{CCl}_4 + \text{CHCl}_3</math>;</p> <p><math>\text{CCl}_4 + \text{toluene}</math>;</p> <p>acetone + benzene</p> <p><math>\text{CCl}_4 + \text{CH}_3\text{OH}</math>;</p> <p>Cyclohexane + ethanol</p> 	<p>Escaping tendency of both components A and B is lowered showing lower vapour pressure than expected ideally.</p> <p>Example:</p> <p>acetone + aniline ;</p> <p>acetone + chloroform ;</p> <p><math>\text{CH}_3\text{OH} + \text{CH}_3\text{COOH}</math>;</p> <p><math>\text{H}_2\text{O} + \text{HNO}_3</math>;</p> <p>chloroform + diethyl ether;</p> <p>water + <math>\text{HCl}</math>;</p> <p>acetic acid + pyridine</p> <p>chloroform + benzene</p> <p><math>\text{HNO}_3 + \text{CHCl}_3</math></p> 

## DO YOURSELF-1

- The vapour pressure of a pure liquid A is 40mm Hg at 310 K. The vapour pressure of this liquid in a solution with liquid B is 32mmHg. Mole fraction of A in the solution, if it obeys Raoult's law is:  
 (A) 0.8 (B) 0.5 (C) 0.2 (D) 0.4
- Mixture of volatile components A and B has total vapour pressure (in Torr)  $p = 254 - 119x_A$ , where  $x_A$  is mole fraction of A in mixture. Hence  $p_A^0$  and  $p_B^0$  are (in Torr)  
 (A) 254,119 (B) 119,254 (C) 135,254 (D) 119,373

3. Two liquids 'A' and 'B' are mixed in the molar ratio of 1:2 and the vapour pressure of the solution is 24 torr. When the two liquids are mixed in the reverse ratio, the vapour pressure of the solution increases by a fraction of  $\frac{1}{4}$ . The vapour pressures of pure 'A' and 'B' are respectively.
- (A) 20 torr, 40 torr (B) 40 torr, 20 torr (C) 36 torr, 18 torr (D) 18 torr, 36 torr
4. For an ideal binary solution with  $P_A^0/P_B^0$  which relation between  $X_A$  (mole fraction of A in liquid phase) and  $Y_A$  (mole fraction of A in vapour phase) is correct,  $X_B$  and  $Y_B$  are mole fraction of B in liquid and vapour phase respectively : (Given :  $P_A^0 > P_B^0$ )
- (A)  $X_A = Y_A$  (B)  $X_A > Y_A$   
 (C)  $\frac{X_A}{X_B} < \frac{Y_A}{Y_B}$  (D)  $X_A, Y_A, X_B$  and  $Y_B$  cannot be correlate
5. Which of the following liquid pairs shows a positive deviation from Raoult's law ?
- (A) Acetone – chloroform (B) Benzene - methanol  
 (C) Water - nitric acid (D) Water - hydrochloric acid
6. Which is/are true about ideal solutions ?
- (A) The volume of mixing is zero (B) The enthalpy of mixing is zero  
 (C) The entropy of mixing is zero (D) The enthalpy of mixing is negative

## 6. APPLICATION OF RAOULT'S LAW:

### 6.1 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 Raoult's Law.

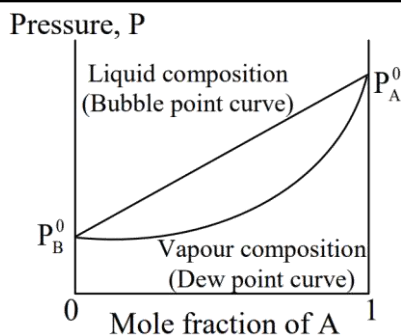
$$\frac{1}{P_T} = \frac{y_A}{P_A^0} + \frac{y_B}{P_B^0} = \frac{y_A}{P_A^0} + \frac{1-y_A}{P_B^0}$$

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

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:  $P_T = (P_A^0 - P_B^0)x_A + P_B^0$

(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.

**Ex.7** Benzene and toluene form nearly ideal solutions. At 300 K,

$$P_{\text{toluene}}^0 = 30 \text{ mmHg and } P_{\text{benzene}}^0 = 100 \text{ mmHg.}$$

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?

## (Physical Chemistry)

## LIQUID SOLUTION

Ans. (a) 58 mm Hg (b)  $Y_B = 20/29$  (c) 250/6 mm Hg (d)  $X_B = 1/6$

(b) Composition of the first trace of vapour formed

$$Y_{\text{benzene}} = \frac{X_B P_B^0}{P_{\text{total}}} = \frac{2}{5} \times \frac{100}{58} = \frac{20}{29} \quad \& \quad Y_{\text{toluene}} = 1 - \frac{20}{29} = \frac{9}{29}$$

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

$$\frac{1}{p} = \frac{Y_A}{P_A^0} + \frac{Y_B}{P_B^0}$$

$$\frac{1}{p} = \frac{3}{5 \times 30} + \frac{2}{5 \times 100} \quad \text{or} \quad p = \frac{250}{6} \text{ mmHg}$$

(d) The composition of the last trace of liquid

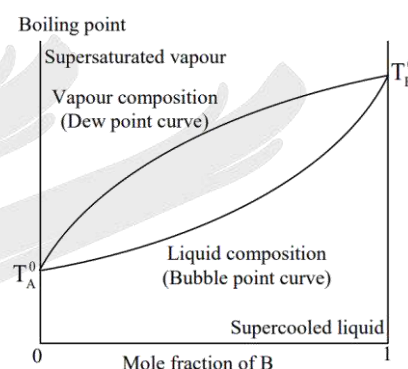
$$X'_{\text{benzene}} = \frac{Y_{\text{benzene}} P_{\text{Total}}}{P_B^0} = \frac{\frac{2}{5} \times \frac{250}{6}}{100} = \frac{1}{6}$$

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

## 6.2 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 temperature



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.

## 6.3 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.

**Ex.8** 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  $P_T = 200 + 400X_{ben}$ .

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

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

**Sol.** (a)  $P_{Benzene}^0 = 600 \text{ mm of Hg}$ ;  $P_{Toluene}^0 = 200 \text{ mm of Hg}$

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

$$P_{benz} = x_{ben} P_{ben}^0 = y_{ben} P_T.$$

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

$$(b) \quad P_T = \frac{3}{4} \times 600 + \frac{1}{4} \times 200 = 500 \text{ mm of Hg} \quad y_{ben} = \frac{3/4 \times 600}{500} = 0.9 = 90\%$$

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

## 7. 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.

### 7.1 Immiscible Liquids:

When two liquids are mixed in such a way that they do not mix at all then both liquids constitute two different phases. Hence, mole fraction of each liquid is one in its own phase.

$$(i) \quad P_T = P_A + P_B$$

$$(ii) \quad P_A = P_A^0 x_A \quad \text{But, } x_A = 1. \text{ Thus, } P_A = P_A^0$$

$$(iii) \quad P_B = P_B^0 x_B \quad \text{But, } x_B = 1. \text{ Thus, } P_B = P_B^0$$

$$(iv) \quad P_T = P_A^0 + P_B^0$$

$$(v) \quad \frac{P_A^0}{P_B^0} = \frac{n_A}{n_B}$$

$$(vi) \quad \frac{P_A^0}{P_B^0} = \frac{W_A M_B}{M_A W_B}$$

$$(vii) \quad P_A^0 = \frac{n_A RT}{V}; P_B^0 = \frac{n_B RT}{V}$$

where  $n_A$  and  $n_B$  are the numbers of moles of each component present in the vapor phase.

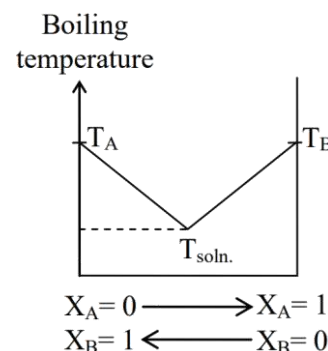
(viii) To express the ratio of A to B in the vapor in terms of the actual weights  $w_A$  and  $w_B$ , the numbers of moles must be multiplied by the respective molecular weights  $M_A$  and  $M_B$ ; hence,

**7.2 Steam Distillation of Immiscible liquids:** 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.

(i) A system of two immiscible liquids will boil when the total vapor pressure  $P$  is equal to the atmospheric 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. 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.



**Ex.9** Boiling point of a mixture of water and nitrobenzene is  $99^\circ\text{C}$ , the vapour pressure of water is 733 mm of Hg and the atmospheric pressure is 760 mm of Hg. The molecular weight of nitrobenzene is 123. Find the ratio of weights of the components of the distillate.

**Ans.**  $\frac{W_W}{W_N} = 3.973$

**Sol.**  $\frac{n_W}{n_N} = \frac{W_W}{18} = \frac{123}{W_N} = \frac{733}{27} \Rightarrow \frac{W_W}{W_N} = \frac{18 \times 733}{27 \times 123} = 3.973$  **Ans.**

**Colligative property  $\propto$  No. of particles/molecules/ions**

**or**

**Colligative property  $\propto$  No. of moles of solute**

**or**

**Colligative property  $\propto$  Mole fraction of solute**

**or**

**Colligative property  $\propto$  1/mol. wt. of solute**

### 8.1 Relative lowering in vapour pressure :

When a non-volatile solute 'A' is dissolved in a pure solvent 'B', the vapour pressure of the solvent is lowered i.e. the vapour pressure of a solution is always lower than that of pure solvent, because the escaping tendency of solvent molecules decreases.

If at a certain temperature  $P^\circ$  is the vapour pressure of pure solvent, and  $P_s$  is the vapour pressure of solution then

$$\text{Lowering of vapour pressure} = P^\circ - P_s$$

$$\text{Relative lowering of vapour pressure} = \frac{P^\circ - P_s}{P^\circ}$$

from equation (8)

$$\frac{P^\circ - P_s}{P^\circ} = \frac{\Delta P}{P^\circ} = \frac{n_A}{n_A + n_B} = X_A$$

for a more dilute solution  $n_A \ll n_B$

$$\text{So } \frac{P^\circ - P_s}{P^\circ} = \frac{n_A}{n_B} = \frac{w_A}{m_A} \times \frac{m_B}{w_B} \quad [\text{Only for v.dilution solutions}]$$

**Ex.10** Calculate wt of urea which must be dissolved in 400gm of water so final solutions has V.P 2% less than V.P. of pure water :

**Sol.** Let V.P be V. of water

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

$$P_s = 0.98 V$$

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

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

**Ex.11** 10gm of a solute is dissolved in 80gm of acctone V.P. of this sol = 271 mmofHg. If V.P. of pure acctone is 283 mm of Hg. Calculate molar mass of solute.

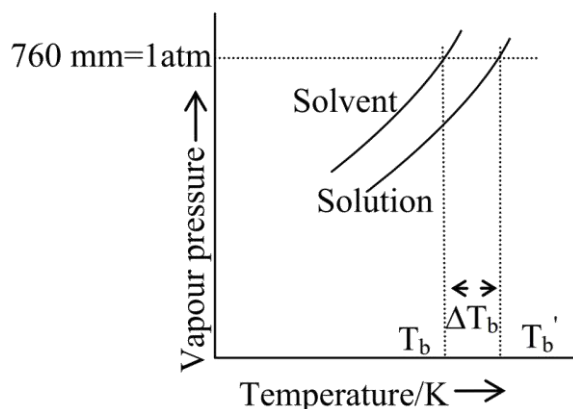
**Sol.** 
$$\frac{P^\circ - P_s}{P_s} = \frac{w}{m} \times \frac{M}{W}$$

$$\frac{283 - 271}{271} = \frac{10}{m} \times \frac{58}{80}$$

$$m = 163 \text{ gm/mol.}$$

### 8.2 Elevation in boiling point (Ebullioscopy) :

The normal boiling point of a liquid is that temperature at which its vapour pressure becomes equal to the atmospheric pressure. i.e. 760 mm of Hg.



The vapour pressure curve for solution lies below the curve for pure solvent.  $\Delta T$  denotes the elevation of boiling point of a solution.

- $K_b$  is defined as the elevation in boiling point produced when 1 mole of solute is dissolved in 1000 g of the solvent.

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

The elevation in boiling point of solution of non-electrolyte is proportional to its molality and equimolal solution of all the substances in the same solvent will show equal elevation in boiling points. These are known as Raoult's laws of elevation of boiling point.

Molal elevation constant is characteristic of a particular solvent and can be calculated from the thermodynamical relationship.

$$K_b = \frac{RT_b^2}{1000L_v}$$

where,  $R$  is molar gas constant = 2 cal/mol – K

$T_b$  is the boiling point of the solvent (in K) and  $L_v$  the latent heat of vaporisation of pure solvent in calories per gram =  $\Delta H_{\text{vap}} (\text{Cal/mol}) / M_{\text{solvent}} (\text{g/mol})$

$$\text{For water } K_b = \frac{2 \times (373)^2}{1000 \times 540} = 0.515 \text{ K – kg/mol}$$

The molal elevation constant for some common solvents are given in the following table

Solvent	B.P. (°C)	Molal elevation constant
Water	100.0	0.52
Acetone	56.0	1.70
Chloroform	61.2	3.63
Carbon tetra chloride	76.8	5.03
Benzene	80.0	2.53
Ethyl alcohol	78.4	1.20

**Ex.12** 1.22 g of a monobasic acid is dissolved in 100 g of benzene. Boiling point of solution increases by  $0.13^\circ\text{C}$  with respect to pure benzene. Find the molecular mass of acid in benzene solvent (in u). Report your answer after dividing it by 100 and Round it off to nearest integer. ( $K_b$  of benzene =  $2.6 \text{ K kg mol}^{-1}$ ).

**Ans.** 2

**Sol.**  $\Delta T_b = K_b \times m$

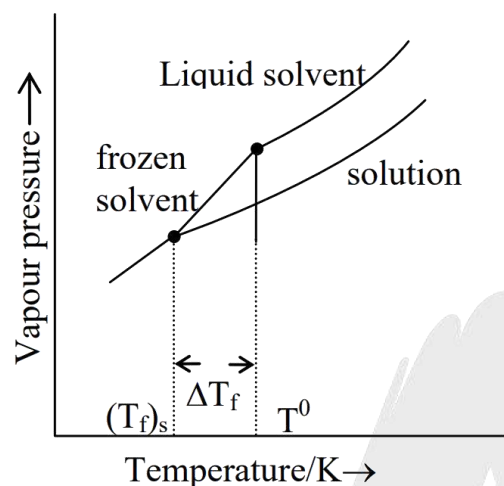
$$0.13 = 2.6 \times \frac{1.22/M}{0.1}$$

$$\therefore M = 244\text{u}$$

## 8.3 Depression in freezing point (Cryoscopy) :

The freezing point of a liquid is that temperature at which the liquid and its solid state exist in equilibrium with each other.

It may be defined as the temperature at which the liquid and solid states of a substance have the same vapour pressure.



- $K_f$  is defined as the depression of freezing point produced when 1 mole of solute is dissolved in 1000 g of the solvent.

$$\text{or } \Delta T_f = \frac{1000 K_f \times w_A}{m_A \times w_B} \quad \text{or} \quad \boxed{\Delta T_f = \text{molality} \times K_f}$$

$K_f$  is characteristic of a particular solvent and can be calculated from the thermodynamical relationship

$$\boxed{K_f = \frac{RT_f^2}{1000 L} = \frac{0.002 T_f^2}{L_f}}$$

Where,  $T_f$  is the freezing point of solvent in absolute scale and  $L_f$  the latent heat of fusion in calories per gram of the solvent. For water,

$$K_f = \frac{0.002 \times (273)^2}{80} = 1.86 \text{ K} - \text{kg/mol}$$

the molal depression constant for some common solvents are given in the following table

Solvent	F.P. (°C)	Molal depression solvents
Water	0.0	1.86
Ethyl alcohol	-114.6	1.99
Chloroform	-63.5	4.79
Carbon tetra chloride	-22.8	31.8
Benzene	5.5	5.12
Camphor	179.0	39.70

**Ex.13** A solution of  $x$  moles of sucrose in 100 grams of water freezes at  $-0.2^\circ\text{C}$ . As ice separates the freezing point goes down to  $0.25^\circ\text{C}$ . How many grams of ice would have separated?

- (A) 18 grams      (B) 20 grams      (C) 25 grams      (D) 23 grams

**Sol.** (i)  $\Delta T_f = m \times K_f$

$$0.2 = \frac{X \times 1000}{100} \times 1.86$$

$$X = \frac{0.2}{10 \times 1.86}$$

after freezing

$$\Delta T_f = m \times K_f$$

$$\Delta T_f = \frac{X \times 1000}{(100 - y)} \times 1.86 \quad \Delta T_f = 0.25$$

On solving, Amount of ice  $y = 20$  g ice

**Ex.14** Calculate the freezing point of a solution of a non-volatile solute in a unknown solvent of molar mass 30 g/ mole having mole fraction of solvent equal to 0.8 . Given that latent heat of fusion of solid solvent =  $2.7\text{kcal mol}^{-1}$ , freezing point of solvent =  $27^\circ\text{C}$  and  $R = 2\text{cal mol}^{-1}\text{K}^{-1}$ .

**Ans.**  $10.33^\circ\text{C}$

**Sol.**  $K_f = \frac{MRT_f^2}{1000\Delta H_f} = \frac{2 \times 300 \times 300 \times 30}{1000 \times 2700} = 2.00 \text{ K kg mol}^{-1}$

mole fraction of water = 0.8

mole fraction of solute = 0.2

$$0.2 = \frac{n}{n+N} \quad \text{and} \quad 0.8 = \frac{N}{n+N}$$

$$\frac{n}{N} = \frac{0.2}{0.8} = \frac{1}{4} = \frac{wM}{mW} \quad \therefore \frac{w}{mW} = \frac{1}{4 \times 30}$$

$$\frac{1}{4} = \frac{w \times 30}{mW} \quad \therefore \frac{1000 \times 2.0}{4 \times 30} = 16.67$$

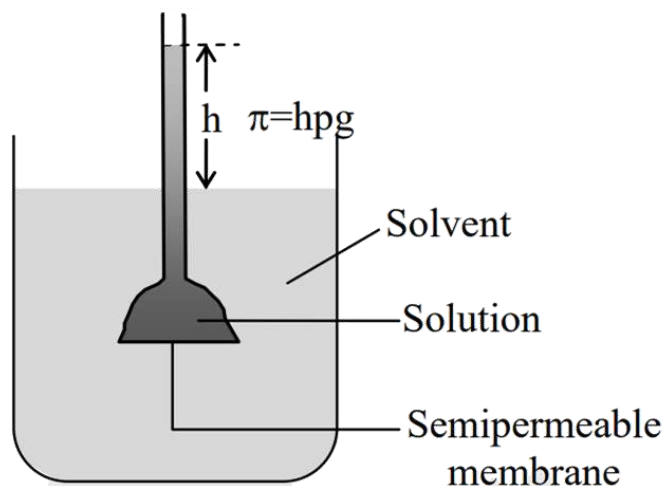
$$\Delta T_f = \frac{1000 \times W \times K_f}{m \times W} = \frac{1000 \times 2.0}{4 \times 30} = 16.67$$

$$\Delta T_f = \frac{1000 \times w \times K_f}{m \times W} = 10.3^\circ\text{C}.$$

## 8.4 Osmosis and osmotic pressure :

### 8.4.1 Osmosis :

Osmosis is defined as the spontaneous flow of solvent molecules through semipermeable membrane from a its high concentration to its low concentration.



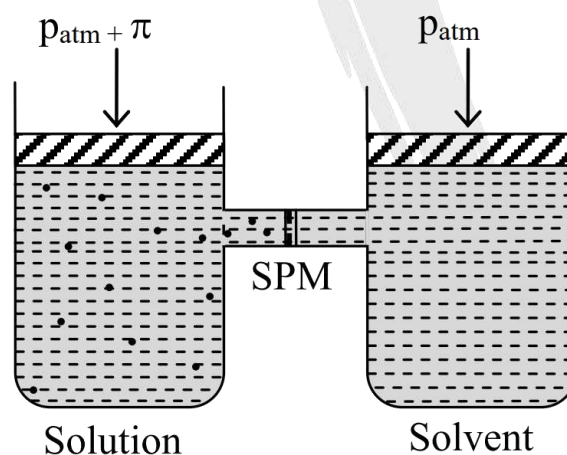
Level of solution rises in the funnel due to osmosis of solvent

### 8.4.2 Osmotic pressure ( $\pi$ ) :

The hydrostatic pressure developed as a result of osmosis is a measure of osmotic pressure of the solution.

or

The hydrostatic pressure built up on the solution which just stops the osmosis. osmotic pressure = hydrostatic pressure



$$\pi = h\rho g$$

$h$  = increase in level in the tube of unit cross section.

$d$  = density of solution,

$g$  = acceleration due to gravity

**8.4.3 Van't Hoff law for dilute solutions :**

The osmotic pressure (  $P$  or  $p$  ) of a solution is directly proportional to its concentration( $C$ ) when the temperature is kept constant. The concentration of the solution containing in one gram mole in  $V$  litres is equal to  $1/V$ .

thus  $P \propto C$  (when temperature is constant)

$$\text{Or } P \propto \frac{1}{V}$$

$$\text{Or } \boxed{\pi V = \text{constant} = nST}$$

**8.4.4 Isotonic or iso-osmotic solution:**

Solution which have the same osmotic pressure are termed isotonic or iso-osmotic solutions

$$\pi_1 = \pi_2$$

$$\text{i.e. } C_1ST = C_2ST$$

$$C_1 = C_2$$

**8.4.5 Hypertonic solution**

A solution having higher osmotic pressure than some other solution is said to be called hypertonic solution

**8.4.6 Hypotonic solution**

A solution having a lower osmotic pressure relative to some other solution is called hypotonic solution.

When isotonic solution are separated by semipermeable membrane no osmosis occurs between them. For example, the osmotic pressure associated with the fluid inside the blood cell is equivalent to that of 0.9% (mass/volume) sodium chloride solution, called normal saline solution and it is safe to inject intravenously. On the other hand, if place the cells in a solution containing more than 0.9% (mass/volume) sodium chloride, water will flow out of the cells and they would shrink. Such a solution is called hypertonic. If the salt concentration is less than 0.9% (mass/volume), the solution is said to be hypotonic. In this case, water will flow into the cells if placed in this solution and they would swell.

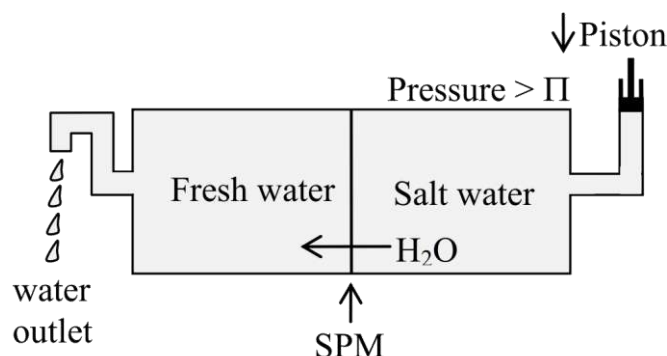
**8.4.7 Semipermeable Membrane**

A membrane which allows the passage of solvent molecules but not that of solute. Eg. Copper ferrocyanide  $Cu_2[Fe(CN)_6]$ .

**8.4.8 Reverse Osmosis :**

If External pressure greater than osmotic pressure is applied, the flow of solvent molecules can be made to proceed from solution towards pure solvent, i.e., in reverse direction of the ordinary osmosis. Reverse osmosis is used for the desalination of sea water for getting fresh drinking

osmosis. Reverse osmosis is used for the desalination of sea water for getting fresh drinking water



Reverse osmosis occurs when a pressure larger than the osmotic pressure is applied to the solution.

**Ex.15** Calculate osmotic pressure of 0.1 M urea aqueous solution at 300 K,

**Sol.**  $R = 0.082 \text{ lit atm } K^{-1}$

$$p = CRT$$

$$p = 0.1 \times 0.082 \times 300$$

$$p = 2.46 \text{ atm.}$$

**Ex.16** If 10 gm of an unknown substance (not-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?

$$\text{Sol. } 1.23 = \frac{10 \times 1000}{M \times 500} \times 0.082 \times 300$$

$$M = \frac{20}{1.23} \times \frac{0.082}{100} \times 300 = 400 \text{ gm/mol}$$

**Ex.17** If 6 gm of urea, 18 gm glucose & 34.2 gm sucrose is dissolved to make 500 mL of a solution at 300 K calculate osmotic pressure ?

**Sol.** molecular weight of urea = 60 gm, Glucose = 180gm, Sucrose = 342 gm

$$p = C \times 0.082 \times 300$$

$$p = \frac{0.3 \times 1000 \times 0.082 \times 300}{500}$$

$$= 14.76 \text{ atm}$$

**Ex.18** Insulin ( $C_2H_{10}O_5$ )<sub>n</sub> is dissolved in a suitable solvent and the osmotic pressure  $p$  of the solution of various concentration (in kg/m<sup>3</sup>) is measured at 20°C. The slope of a plot of  $p$  against  $c$  is found to be  $8.134 \times 10^{-3}$  (SI units) The molecular weight of the insulin (in kg/mol) is :

(1)  $4.8 \times 10^5$

(2)  $9 \times 10^5$

(3)  $293 \times 10^3$

(4)  $8.314 \times 10^5$

**Sol.**  $p = CRT$

$$p = \frac{c}{M} RT \quad C = \text{moles/liter, } c = \text{kg/m}^3$$

$$\frac{\pi}{c} = \frac{RT}{M}$$

$$M = \frac{RT}{\pi/c} [p/c = 8.314 \times 10^{-3}]$$

$$M = \frac{8.314 \times 293}{8.314 \times 10^{-3}} = 293 \times 10^3$$

**Ex.19**  $\frac{0.1M \text{ urea}}{(A)}, \frac{0.1MNaCl}{(B)}, \frac{0.1MBaCl_2}{(C)}$

<b>Sol.</b>	order of p	$C > B > A.$
	order of R.L.V.P	$C > B > A.$
	order of V.P	$A > B > C.$
	order of $\Delta T_b$	$C > B > A.$
	order of $T_b$ of solution	$C > B > A.$
	order of $\Delta T_f$	$C > B > A.$
	order of $T_b$ of solution	$A > B > C.$

### DO YOURSELF-3

- Vapour pressure of  $CCl_4$  at  $25^\circ C$  is 143mmHg. 0.5 g of a non-volatile solute (molar mass =  $65 \text{ mol}^{-1}$ ) is dissolved in 100 mL of  $CCl_4$  (density =  $1.538 \text{ g mL}^{-1}$ ). Vapour pressure of solution is  
 (A) 141.9mmHg (B) 94.4mmHg  
 (C) 99.3mmHg (D) 144.1mmHg
- The elevation in boiling point of a solution containing 13.44 g of  $CuCl_2$  in 1 kg of water is :  
 ( $K_b = 0.52 \text{ K kg mol}^{-1}$ )  
 (A) 0.05 (B) 0.10 (C) 0.16 (D) 0.21
- How many moles of sucrose should be dissolved in 500gms of water so as to get a solution which has a difference of  $104^\circ C$  between boiling point and freezing point. ( $K_f = 1.86 \text{ KKgmol}^{-1}$ ,  $K_b = 0.52 \text{ KKgmol}^{-1}$ )  
 (A) 1.68 (B) 3.36 (C) 8.40 (D) 0.840
- If 200 mL of 0.1M urea solution is mixed with 300 mL of 0.2M glucose solution at 300 K, Calculate osmotic pressure?
- Osmotic pressure of a 2%w/v solution of glucose is same as 5%w/v solution of a nonvolatile non-electrolyte solute. The molar mass of the solute is :  
 (A) 180 (B) 450 (C) 72 (D) 45

### 9. ABNORMAL COLLIGATIVE PROPERTIES :

It has been observed that difference in the observed and calculated molecular masses of solute is due to association or dissociation of solute molecules in solution. It results in a change in the number of particles in solution.

**9.1 Association of solute particles :**

The formation of a bigger molecule by the union of two, three or more solute molecules is called association.

Let '  $n$  ' simple molecules combine to give an associated molecule as :



( $n$  single molecules)  $\rightarrow$  (one bigger molecule) [ $n > 1$ ]

As a result, the total number of particles in solution becomes less than the number of molecules initially dissolved in the solution and hence the colligative properties will have lower value. As the molar mass of solute is inversely proportional to the colligative properties, so the molar mass of solute will be greater than theoretical value.

**9.2 Dissociation of solute molecules :**

Molecules of electrolytes undergo ionization or dissociation in ionizing solvents to give more particles in solution. For example, one AB molecule ionizes in solution to give two particles.



This dissociation results in an increase in the total number of particles, and therefore the value of colligative properties of such solutions will be higher. As the colligative properties are inversely related to molecular weight, so the molecular weight of ionizable solute will be less than the theoretical value.

**VAN'T HOFF FACTOR ( $i$ ) :**

In order to express the extent of association or dissociation with certain solutes are expected to undergo in solution.

Van't Hoff in 1886, introduced a factor, called Van't Hoff factor ( $i$ ). The factor  $i$  is defined as

$$i = \frac{\text{observed colligative property}}{\text{Calculated colligative property}} = \frac{\text{Normal molecular weight}}{\text{observed molecular mass}}$$

In case of association of solute particles in solution, the observed molecular weight of solute being more than the normal, the value of factor ' $i$ ' is less than unity (i.e.  $i < 1$ ), while for dissociation the value of  $i$  is greater than unity (i.e.  $i > 1$ ), because the observed molecular weight has lesser value than normal molecular weight.

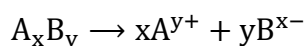
**10.1 Van't Hoff factor and degree of dissociation :**

The fraction of the total number of molecules which dissociates in the solution into simple ions or molecules is called the degree of dissociation.

$$i = \frac{\text{number of particles after dissociation}}{\text{Number of particles initially taken.}}$$

Calculation of 'i' :

Let, solute be  $A_xB_y$

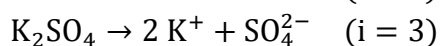
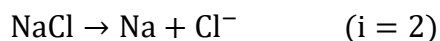


Initial mol                      1              0              0

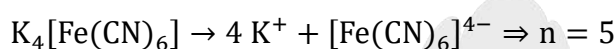
after dissociation             $1 - \alpha$      $x\alpha$          $y\alpha$

Total no. of solute particles =  $1 - \alpha + x\alpha + y\alpha = 1 - \alpha + \alpha(x + y)$  or  $i = 1 - \alpha + n\alpha$  [where

$x + y = n$  (total ions.)) for strong electrolytes :  $\alpha = 1$  or 100% so  $i = n$  (total no. of ions)



for complex compound



S.no.	Solute type	Example	Ionisation	No. of particles in the solution from 1 mole solute (n)	van't Hoff factor ('i')	Abnormal molecular mass
1.	Non-electrolyte	Urea, sucrose, glucose, fructose	-	1	1	$m_{\text{normal}}$
2.	Binary electrolyte AB type	NaCl, KCl, HCl CH <sub>3</sub> COOH NH <sub>4</sub> OH, NaOH etc.	$AB$ $\rightleftharpoons A^+ + B^-$ 1 $-\alpha \quad \alpha \quad \alpha$	2	$1 + \alpha$	$\frac{m_{\text{normal}}}{1 + \alpha}$
3.	Ternary electrolyte AB <sub>2</sub> type or A <sub>2</sub> B type	CaCl <sub>2</sub> , BaCl <sub>2</sub> H <sub>2</sub> SO <sub>4</sub> , K <sub>2</sub> [PtCl <sub>6</sub> ]	$AB_2$ $\rightleftharpoons A^{2+} + 2 B^-$ 1 $-\alpha \quad \alpha \quad 2\alpha$ $A_2 B$ $\rightleftharpoons 2 A^+ + B^-$ 1 $-\alpha \quad 2\alpha \quad \alpha$	3 3	$1 + 2\alpha$ $1 + 2\alpha$	$\frac{m_{\text{normal}}}{1 + 2\alpha}$ $\frac{m_{\text{normal}}}{1 + 2\alpha}$

(Physical Chemistry)

# LIQUID SOLUTION

4.	Quaternary electrolyte $AB_3$ or $A_3B$ type	$AlCl_3, K_3[Fe(CN)_6]$	$AB_3$ $\rightleftharpoons A^{3+}$ $+ 3B^{-}$	$4$ $4$	$1 + 3\alpha$ $1 + 3\alpha$	$\frac{m_{normal}}{1 + 3\alpha}$ $\frac{m_{normal}}{1 + 3\alpha}$
5.	General electrolyte $AB_{n-1}$	One mole of solute giving 'n' ions in the solution	$AB_{n-1}$ $\rightleftharpoons A^{+(n-1)}$ $+ (n - 1)B^{-}$ $1 - \alpha \quad \alpha (n - 1)\alpha$	n	$1 + (n - 1)\alpha$	$\frac{m_{normal}}{[1 + (n - 1)\alpha]}$

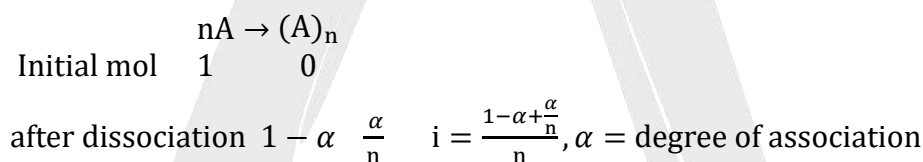
## 10.2 Van't Hoff factor and degree of association :

The fraction of the total number of molecules of the substance which is present as associated molecules is known as the degree of association.

$$i = \frac{\text{Number of particles association}}{\text{Number of particles before association}}$$

### Calculation of 'i' :

Let, solute be A



$$i = 1 - \alpha + \alpha/n$$

$$m_{Abnormal} = \frac{m_{Normal}}{\left[1 - \left(1 - \frac{1}{n}\right)\alpha\right]}$$

**Ex.20** In which of the following pairs of solutions will the values of the vant Hoff factor be the same?

- (A) 0.05MK<sub>4</sub>[Fe(CN)<sub>6</sub>] and 0.10MFeSO<sub>4</sub>
- (B) 0.10MK<sub>4</sub>[Fe(CN)<sub>6</sub>] and 0.05MFeSO<sub>4</sub>(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> · 6H<sub>2</sub>O
- (C) 0.20MNaCl and 0.10MBaCl<sub>2</sub>
- (D) 0.05MFeSO<sub>4</sub>(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> · 6H<sub>2</sub>O and 0.02MKCl · MgCl<sub>2</sub> · 6H<sub>2</sub>O

**Sol.** Number of particles from K<sub>4</sub>[Fe(CN)<sub>6</sub>] = 5

number of particles from FeSO<sub>4</sub>(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> · 6H<sub>2</sub>O = 5

number of particles from KCl · MgCl<sub>2</sub> · 8H<sub>2</sub>O = 5

**Ex.21** Relative decrease in vapour pressure of an aqueous solution containing 2 moles  $[\text{Cu}(\text{NH}_3)_3\text{Cl}]\text{Cl}$  in 3 moles  $\text{H}_2\text{O}$  is 0.50. On reaction with  $\text{AgNO}_3$ , this solution will form (assuming no change in degree of ionisation of substance on adding  $\text{AgNO}_3$ )

- (A) 1 mol  $\text{AgCl}$  (B) 0.25 mol  $\text{AgCl}$   
(C) 0.5 mol  $\text{AgCl}$  (D) 0.40 mol  $\text{AgCl}$

**Sol.**  $\frac{\Delta P}{P} = \frac{ni}{ni+N}$

$$0.5 = \frac{2i}{2i+3}$$

$$i + 1.5 = 2i$$

$$i = 1.5$$

$$i = 1 + (y - 1)a$$

$$1.5 = 1 + (2 - 1)a$$

$$a = 0.5$$

**Ex.22**  $\text{PtCl}_4 \cdot 6\text{H}_2\text{O}$  can exist as a hydrated complex 1 molal aq. solution has depression in freezing point of  $3.72^\circ$ . Assume 100% ionisation and  $K_f(\text{H}_2\text{O}) = 1.86^\circ \text{mol}^{-1} \text{kg}$ , then complex is -

- (A)  $[\text{Pt}(\text{H}_2\text{O})_6]\text{Cl}_4$  (B)  $[\text{Pt}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$   
(C)  $[\text{Pt}(\text{H}_2\text{O})_3\text{Cl}_3]\text{Cl} \cdot 3\text{H}_2\text{O}$  (D)  $[\text{Pt}(\text{H}_2\text{O})_2\text{Cl}_4] \cdot 4\text{H}_2\text{O}$

**Sol.**  $\Delta T_f = i \times m \times k_f$

$$i = \frac{3.72}{1.86 \times 1} = 2$$

So salt is  $(\text{Pt}(\text{H}_2\text{O})_3\text{Cl}_3)\text{Cl} \cdot 3\text{H}_2\text{O}$ .

**Ex.23** The freezing point of aqueous solution that contains 3% urea, 7.45%  $\text{KCl}$  and 9% of glucose is (given  $K_f$  of water = 1.86 and assume molarity = molality).

- (A) 290 K (B) 285.5 K (C) 267.42 K (D) 250 K

**Sol.**  $\Delta T_f = i \cdot m \cdot K_f$

$$\Delta T_f = i_1 m_1 K_f + i_2 m_2 K_f + i_3 m_3 K_f = (m_1 + 2 m_2 + m_3) K_f$$

$$\Delta T_f = \frac{3 + \frac{7.45 \times 2}{60} + \frac{9}{180}}{100} \times 1000 \times 1.86$$

$$\Delta T_f = 3 \times 1.86 = 5.58$$

$$T_f \text{ of solution} = 273 - 5.58 = 267.42 \text{ K Ans.}$$

**Ex.24** If 0.04M  $\text{Na}_2\text{SO}_4$  solutions at 300 K is found to be isotonic with 0.05M  $\text{NaCl}$  (100% dissociation) solutions. Calculate degree of dissociation of sodium sulphate ?

**Sol.**  $i_1 C_1 RT = i_2 C_2 RT$

$$i_1 C_1 = i_2 C_2$$

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

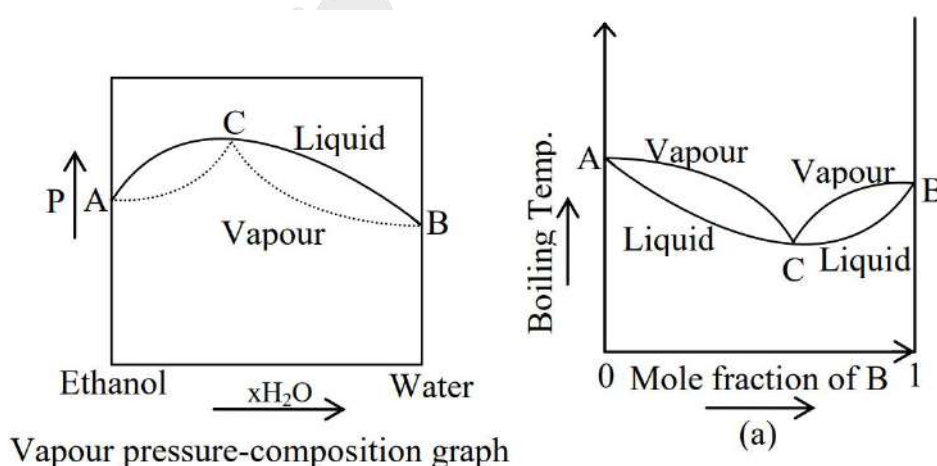
$$\alpha = 0.75 = 75\%.$$

## 11.1 AZEOTROPIC MIXTURES

Binary mixtures that have same composition in liquid and vapour phase and boil at a constant temperature and can be distilled unchanged in composition are known as azeotropic mixture or simply azeotropes. Thus azeotropes behave as pure liquid. There are two types of azeotropes called as minimum boiling azeotropes and maximum boiling azeotropes respectively.

## (i) Minimum boiling Azeotropic mixtures

The non-ideal binary solution which shows positive deviation from Raoult's law form minimum boiling azeotropes at a constant composition. As we can see from vapour-pressure-composition graph.

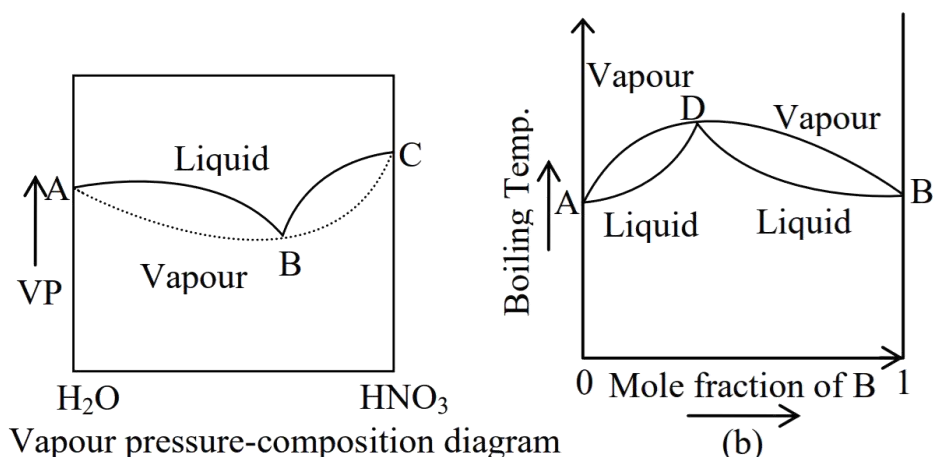


## Minimum boiling point Azeotropic

Mixture	% Composition of azeotrope	Boiling point (pressure = 1 atm)
1. Water-Ethanol	96 Ethanol	78.15°C
2. Pyridine-Water	57.00 Pyridine	92.60°C
3. Ethanol-Benzene	32.4 Ethanol	67.80°C
4. Acetic acid-Toluene	28.0 Acetic acid	105.40°C

## (ii) Maximum boiling azeotropic mixtures

The non-ideal solution which shows negative deviation Raoult's law form maximum boiling azeotropes. From the vapour-pressure-composition diagram, we can see that the solution has a minimum vapour pressure at a particular composition.



Maximum boiling point Azeotropic

Mixture	% Composition of azeotrope	Boiling point (pressure = 1 atm)
1. Nitric acid-Water	68% Nitric acid	125.5°C
2. Acetic acid-Pyridine	65% Pyridine	139.0°C
3. Chloroform-Acetone	80% Chloroform	65.0°C
4. Hydrogen chloride-Water	79.8 Water	108.6°C

## 12. SOLUBILITY :

Maximum amount of solute which can be dissolved in a specified amount of solvent at constant temperature is solubility. Solubility is effected by

1. nature of solute and solvent
2. temperature and
3. pressure

### 12.1 Solubility of Solid in a Liquid :

Polar solutes are soluble in polar solvent and non polar solutes are soluble in non polar solvent due to similar intermolecular forces. When solid solutes are dissolved in solvent then following equilibrium exists.



Such a solution in which no more solute can be dissolved at the same temperature and pressure is called a saturated solution. An unsaturated solution is one in which more solute can be dissolved at the same temperature. The solution which is in dynamic equilibrium with undissolved solute is the saturated solution and contains the maximum amount of solute dissolved in a given amount of solvent.

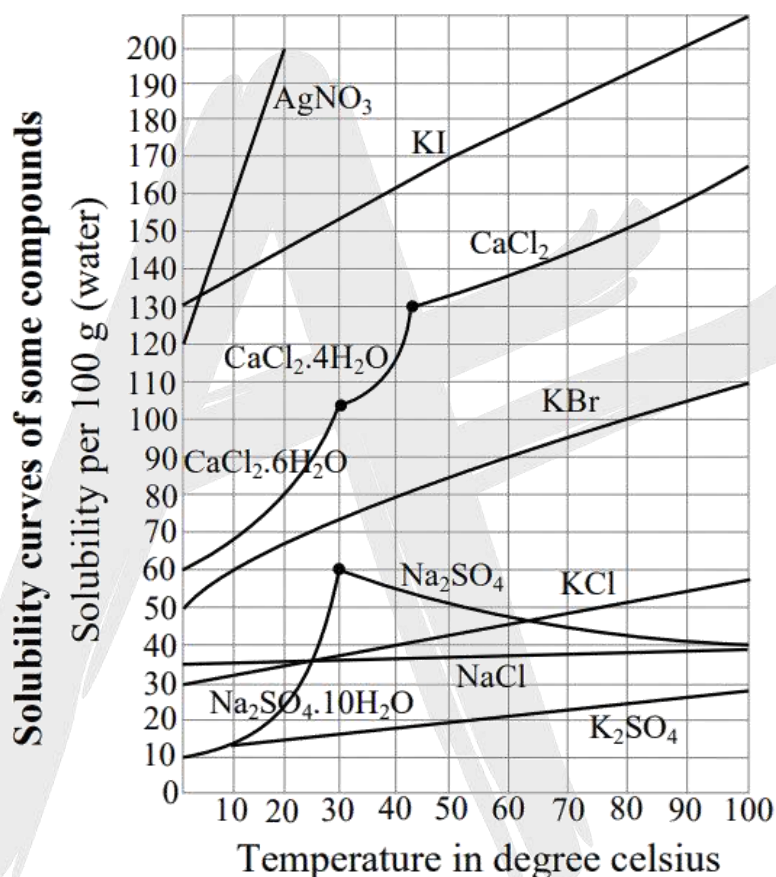
## 12.1.1 Effect of temperature :

The solubility of a solid in a liquid is significantly affected by temperature changes. Consider the following equilibrium



This, being dynamic equilibrium, must follow Le Chateliers

Principle. In general, if in a nearly saturated solution, the dissolution process is endothermic ( $\Delta_{\text{sol}} H > 0$ ), the solubility should increase with rise in temperature and if it is exothermic ( $\Delta_{\text{sol}} H < 0$ ) the solubility should decrease. These trends are also observed experimentally.

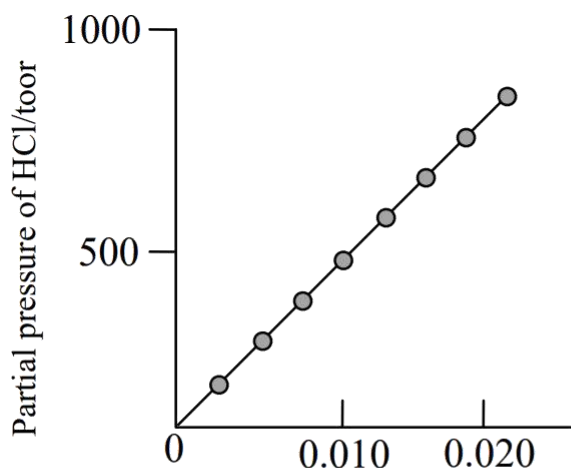


## 12.1.2 Effect of pressure :

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.

## 12.2 Solubility of Gases in Liquid :

Certain gases are highly soluble in water like NH<sub>3</sub>, HCl etc. and certain gases are less soluble in water like O<sub>2</sub>, N<sub>2</sub>, He etc. Solubility of gases is highly effected by pressure and temperature. Increasing pressure increases solubility increase in temperature decreases solubility since dissolution of any gas in any liquid is exothermic in nature.



Mole fraction of HCl in its solution in cyclohexane

Experimental result for the solubility of HCl gas in cyclohexane at 293 K. The slope of the line is the Henry's Law constant  $K_H$

### 12.2.1 Henry' Law :

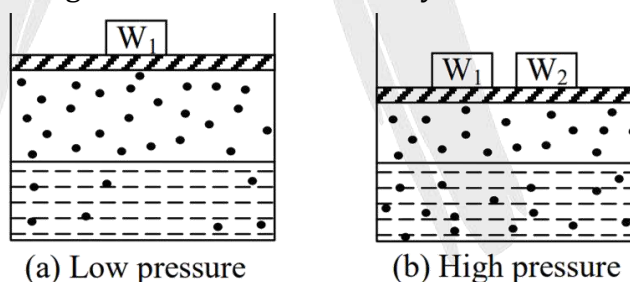
Mole fraction of gas in the solution is proportional to the partial pressure of the gas over the solution.

Or

The partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution.

$$P = K_H X \quad K_H = \text{Henry's Constant}$$

Henry's Constant depends on nature of gas and temperature.  $K_H$  increases with increases in temperature therefore high  $K_H$  means low solubility.



Effect of pressure on the solubility of a gas. The concentration of dissolved gas is proportional to the pressure on the gas above the solution.

The solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution.

### Effect of Temperature

Solubility of gases in liquids decreases with rise in temperature. 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. Dissolution process involves dynamic equilibrium and thus must follow Le Chatelier's Principle. As dissolution is an exothermic process, the solubility should decrease with increase of temperature

## 12.2.2 Henry' Law application :

- (1) To increase the solubility of  $\text{CO}_2$  in soft drinks and soda water, the bottle is sealed under high pressure.
- (2) Scuba divers must cope with high concentrations of dissolved gases while breathing air at high pressure underwater. Increased pressure increases the solubility of atmospheric gases in blood. When the divers come towards surface, the pressure gradually decreases. 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).
- (3) 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.

## Values of Henry's Law Constant for Some Selected Gases in Water

Gas	Temperature/K	$K_H/\text{kbar}$
He	293	144.97
$\text{H}_2$	293	69.16
$\text{N}_2$	293	76.48
$\text{N}_2$	303	88.84
$\text{O}_2$	293	34.86
$\text{O}_2$	303	46.82
Argon	298	40.3
$\text{CO}_2$	298	1.67
Formaldehyde	298	$1.83 \times 10^{-5}$
Methane	298	0.413
Vinyl chloride	298	0.611

**Ex.25** The partial pressure of ethane over a solution containing  $6.56 \times 10^{-3}$  g of ethane is 1 bar. If the solution contains  $5.00 \times 10^{-2}$  g of ethane, then what shall be the partial pressure of the gas ?

**Ans.** 7.62 bar

**Sol.**  $\frac{6.56 \times 10^{-3}}{5 \times 10^{-2}} = \frac{1}{P}$

$\Rightarrow P = 7.62 \text{ bar.}$

**Ex.26** If  $N_2$  gas is bubbled through water at 293 K, how many millimoles of  $N_2$  gas would dissolve in 1 litre of water, if  $N_2$  exerts a partial pressure of 0.987 bar. Given that Henry's law constant for  $N_2$  at 293 K is 76.48 kbar.

**Ans.** 0.716 mmol.

**Sol.** The solubility of gas is related to the mole fraction in aqueous solution. The mole fraction of the gas in the solution is calculated by applying Henry's law. Thus :

$$x(\text{Nitrogen}) = \frac{p(\text{nitrogen})}{K_H} = \frac{0.987 \text{ bar}}{76,480 \text{ bar}} = 1.29 \times 10^{-5}.$$

As 1 litre of water contains 55.5 mol of it, therefore if  $n$  represents number of moles of  $N_2$  in solution,

$$x(\text{Nitrogen}) = \frac{n \text{ mol}}{n \text{ mol} + 55.5 \text{ mol}} = \frac{n}{55.5} = 1.29 \times 10^{-5}.$$

( $n$  in denominator is neglected as it is  $\ll 55.5$ )

Thus  $n = 1.29 \times 10^{-5} \times 55.5 \text{ mol} = 7.16 \times 10^{-4} \text{ mol}$ .

$$= \frac{7.16 \times 10^{-4} \text{ mol} \times 1000 \text{ mol}}{1 \text{ mol}} = 0.716 \text{ mmol}.$$

#### DO YOURSELF-4

- The boiling point of an azeotropic mixture of water and ethyl alcohol is less than that of theoretical value of water and alcohol mixture. Hence, the mixture shows :  
 (A) That solution is highly saturated (B) Positive deviation from Raoult's law  
 (C) Negative deviation from Raoult's law (D) Nothing can be said
  - A complex of iron and cyanide ions is 100% ionised at 1 m (molal). If its elevation in b.p. is 2.08. Then the complex is ( $K_b = 0.52^\circ \text{mol}^{-1} \text{ kg}$ ) :  
 (A)  $K_3[Fe(CN)_6]$  (B)  $Fe(CN)_2$   
 (C)  $K_4[Fe(CN)_6]$  (D)  $Fe(CN)_4$
  - The boiling point of an azeotropic mixture of water and ethyl alcohol is less than that of theoretical value of water and alcohol mixture. Hence, the mixture shows :  
 (A) That solution is highly saturated (B) Positive deviation from Raoult's law  
 (C) Negative deviation from Raoult's law (D) Nothing can be said
  - Match the Column
- | Column I                 | Column II                                  |
|--------------------------|--|
| (A) $0.1 M Al_2(SO_4)_3$ | (p) Solution with highest boiling point.   |
| (B) $0.1 M AlPO_4$       | (q) Van't Hoff factor is greater than 1.   |
| (C) $0.1 M \text{urea}$  | (r) Solution with lowest osmotic pressure. |
| (D) $0.1 M MgCl_2$       | (s) Solution with lowest freezing point.   |
- Select correct statements :  
 (A) Gases which have high value of van der Waals constant '  $a$  ' are easily liquefied  
 (B) Easily liquefiable gases are water soluble  
 (C) Ions forming gases in a solvent are soluble in that solvent  
 (D) Under same conditions,  $NH_3$  has low solubility than that of  $CO_2$ .